Synthesis and Reactivity of [closo-1-CB\(_9\)H\(_8\)-1-N\(_2\)]: Functional Group Interconversion at the Carbon Vertex of the {closo-1-CB\(_8\)} Cluster

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The dinitrogen derivative [closo-1-CB\(_9\)H\(_8\)-1-N\(_2\)] (1) was prepared from amine [closo-1-CB\(_8\)H\(_9\)-1-NH\(_3\)] (2) and reacted with three types of nucleophiles: activated arenes (phenolate and aniline), divalent sulfur compounds (Me\(_2\)S and Me\(_2\)NCHS), and pyridine, giving products of substitution at C\(_\text{cage}\). The reaction of 1 with pyridine gave all four isomers 11a–11d, indicating the Gomberg–Bachmann mechanism, which involves radical anion [closo-1-CB\(_9\)H\(_8\)]\(^{−}\) (26). The radical and also closed-shell electrophilic aromatic substitution mechanisms were probed with the aid of DFT and MP2 computational methods and compared to those of phenylation of pyridine. Overall, experimental results supported by computational analysis suggest two mechanisms for the substitution of the N\(_2\) group in 1: (i) thermal heterolytic cleavage of the C\(_\text{cage}\)–N bond and the formation of electrophilic carbonium ylide [closo-1-CB\(_9\)H\(_8\)] (19) and (ii) electron-transfer-induced homolytic cleavage of the C\(_\text{cage}\)–N bond and the formation of 26. Decomposition of 1 in MeCN is believed to proceed by the nonradical mechanism involving formation of the ylide 19 as the rate-determining step with experimental activation parameters \(\Delta H^\# = 38.4 \pm 0.8\) kcal mol\(^{-1}\) and \(\Delta S^\# = 44.5 \pm 2.5\) cal mol\(^{-1}\) K\(^{-1}\). The electron-transfer-induced formation of 26 is consistent with the relatively high reduction potential of 1 (\(E^\text{pc} = -0.54\) V), which is more cathodic than that of PhN\(_2\)\(^{−}\) by 0.38 V. Transformations of the phenol 8a and the Me\(_2\)NCHS adduct 10 were demonstrated by O-methylation of the former and hydrolysis of 10 followed by S-alkylative cyclization. Direct products and their derivatives were investigated by UV–vis spectroscopy and analyzed with the ZINDO computational method.

Introduction

Dinitrogen derivatives of the [closo-B\(_{10}\)H\(_{10}\)]\(^{2−}\) cluster are isolable stable\(^{1–6}\) and important intermediates in the preparation of a variety of nitrogen,\(^{3,4,6,8,9}\) sulfur,\(^{4,10}\) oxygen,\(^{4,10}\) and even carbon\(^{4}\) derivatives. Our calculations showed that the moderate stability and hence synthetic usefulness of these intermediates originate from the electronic interaction between the cluster and the N\(_2\) group, which appears to be general for the apical position of 10-vertex closo-boranes.\(^{11}\) Indeed, scant indirect evidence suggests that [closo-1-CB\(_8\)H\(_9\)-1-NH\(_3\)] (1), formed by diazotization of amine [closo-1-CB\(_8\)H\(_9\)-1-NH\(_3\)] (2), is also reasonably stable and was implied as an intermediate in a reaction with Me\(_2\)S.\(^{11}\) Therefore, in analogy to the dinitrogen derivatives of [closo-B\(_{10}\)H\(_{10}\)]\(^{2−}\), compound 1 and its derivatives have the potential of becoming synthetically valuable intermediates in the introduction of substituents at the C\(_\text{cage}\) position of the [closo-1-CB\(_8\)] cage.

Our interest\(^{12,13,15}\) in highly polar and ionic molecular materials, including liquid crystals, focused our attention on dinitrogen derivatives 1, 10-substituted derivatives of 1, as potential intermediates in the synthesis of zwitterionic and anionic azo compounds of the general structures II and III, respectively (Figure 1). In this context, we recently developed\(^{16}\) synthetic access to isomerically pure [closo-1-CB\(_8\)H\(_8\)-1-NH\(_2\)-10-I]\(^{−}\) as the

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key starting material for the preparation of II and III. In this precursor, the amino group is expected to serve as a synthetic handle for the introduction of a sulfonium fragment, a pyridin-1-yl group, and an azo group through the dinitrogen derivative I. Therefore, we desired to gain an understanding of the properties and reactivity of I as a model for II and a step toward the development of synthetic access to II and III.

Here, we report a reliable method for the preparation of amine 2, which upon diazotization gives \([\text{closo-1-CB}_9\text{H}_9\text{N}_2](1)\). Then, we describe the thermal stability and reactivity of dinitrogen derivative I with several nucleophilic reagents. In particular, we explored reactions that lead to derivatives with the protected mercapto functionality, diazocoupling to aromatic compounds, and reactions with pyridine. The mechanism of the reaction of I with pyridine was investigated experimentally and analyzed with the aid of DFT and MP2 computational methods. The dinitrogen derivative I and several products derived from it were investigated with \(\nu\)-vis spectroscopic methods, and the experimental results were compared to the ZINDO computational data. Finally, the transmission of the \(C\) cage substituent electronic effects through the \(\text{closo-1-CB}_9\) cage was briefly investigated and compared to that of \(\text{closo-1-CB}_{11}\) and the benzene ring.

**Results**

**Synthesis of \(\text{closo-1-CB}_9\text{H}_9\text{N}_2\) (I).** The preparation of \(\text{closo-1-CB}_9\text{H}_9\text{N}_2\) (1) was accomplished by diazotization of \(\text{closo-1-CB}_9\text{H}_9\text{N}_2\) (2) in a 50% aqueous \(\text{AcOH}\) with 1.1 equiv of \(\text{NaNO}_2\) (Scheme 1). The dinitrogen derivative I was formed as a white precipitate and conveniently isolated by filtration in yields >80%. Diazotization of contaminated amine 2, for example, with carboxylic acid 3, also was satisfactory, albeit with lower yields of I, since the ionic impurity tends to stay in solution. The ratio and amounts of \(\text{AcOH}\) and \(\text{H}_2\text{O}\) were optimized to maximize the material recovery.

The dinitrogen derivative I is a white microcrystalline substance easily soluble in common organic solvents, except for alkanes. It is stable in the solid state at 0 °C for at least 18 months without traces of decomposition. When heated, solid I rapidly decomposes at 87 °C. Its solutions in \(\text{MeCN}\) are stable for 24 h at ambient temperature in the dark with little (about 10%) decomposition (vide infra). In contrast, dinitrogen 1 completely decomposes in \(\text{CH}_2\text{Cl}_2\) and benzene solutions into a mostly intractable mixture of presumably polymeric and degradation products after 24 h in the dark at ambient temperatures. NMR spectra of I display a significant solvent dependence. Thus, the signals of \(^{11}\text{B}(10)\) and \(^1\text{H}(10)\) nuclei are shifted by about 6 and 1.2 ppm, respectively, downfield in benzene-\(d_6\) relative to those measured in \(\text{CD}_3\text{CN}\) solutions.

Although amine 2 has been reported in the literature, its previous preparation was complicated by the formation of the closely related \([\text{closo-1-CB}_9\text{H}_9\text{N}_2\text{H}_2\text{N}_2\text{N}_2]\) as a byproduct. Also, this method does not allow for introduction of a substituent at the B(10) position. Therefore, we decided to develop reliable access to 2 starting from the readily accessible carboxylic acid 3. Our initial attempts at direct conversion of carboxylic acid 3 to amine 2 using several methods such as the classical Schmidt and Curtius reactions, azidotrimethylsilane, azidotrimethylsilane and \(\text{NaNO}_2\), diphenylphosphoryl azide, and hydroxyamine sulfonic acid were unsatisfactory and plagued by poor yields, irreproducibility, low reactivity with acid 3[\(\text{NET}_4\)], and numerous unidentified side products, as evident from \(^{11}\text{B}\) NMR. Eventually, we focused on the Curtius reaction and carbamate 4 as the isolable intermediate, which could be purified and serve as a convenient storage for amine 2. Conditions for each synthetic step were optimized, and the reactions were followed by monitoring the chemical shifts of the B(10) nucleus in \(^{11}\text{B}\) NMR spectra and the IR vibrations of the carbonyl group (see the Supporting Information).

Thus, the required carbamate 4a[\(\text{NET}_4\)] was prepared in four steps and about 50% overall yield based on carboxylic acid 3[\(\text{NET}_4\)] using a modified Curtius rearrangement (Scheme 2).

The first step of the preparation of carbamate 4a[\(\text{NET}_4\)] was the typically quantitative transformation of carboxylic solution. The ratio and amounts of \(\text{AcOH}\) and \(\text{H}_2\text{O}\) were optimized to maximize the material recovery.

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acid 3[NEt₄] to carbonyl chloride 5[NEt₄] using (COCl)₂.
The crude chloride 5[NEt₄] was then converted to acyl azide 6[NEt₄] using Me₂SiN₃ in the presence of ZnCl₂ according to a general literature procedure.²³ ¹¹B NMR spectra typically showed 85% conversion to the azide 6[NEt₄], with the remaining chloride 5[NEt₄] being hydrolyzed back to acid 3[NEt₄]. A minor peak at 25.1 ppm in ¹¹B NMR spectra of the crude reaction mixture was also present, which was later attributed to isocyanate 7[NEt₄]. The premature rearrangement of azide 6[NEt₄] to 7[NEt₄] was most likely promoted by the Lewis acid catalyst rather than thermal induction.²⁴

Attempts at improving this process through manipulation with reaction times, catalyst loading, and thorough drying of the catalyst were unsuccessful. The IR spectrum of azide 6[NEt₄] revealed vibrations characteristic for the azido and carbonyl groups and is similar to that reported for benzoyl azide.²⁵

Crude azide 6[NEt₄] was rearranged to isocyanate 7[NEt₄] by refluxing in anhydrous CH₃CN. The completeness of the transformation was evident from ¹¹B NMR spectra in which the B(10) chemical shift of the former at 36.4 ppm was replaced with a peak at 25.1 ppm in the isocyanate. The product also showed an intense peak at 2262 cm⁻¹ in the IR spectrum, which is consistent with the νNCO vibration reported for phenyl isocyanate in the solid state (2255 cm⁻¹).²⁶ On the basis of the ¹¹B NMR spectrum, the purity of the crude isocyanate 7[NEt₄] was estimated as about 90%.

Initially, we envisioned conversion of isocyanate 7[NEt₄] directly to amine 2, but this approach was not fruitful. Isocyanate 7[NEt₄] was insoluble in aqueous HCl even at elevated temperatures. Attempted hydrolysis of 7[NEt₄] in a 1:1 mixture of 18% HCl and CH₂OH at 80 °C gave a mixture of amine 2 and methyl carbamate 4b[H₃O] upon extraction from acidified aqueous solutions, according to ¹¹B NMR analysis. The carbamate 4b[H₃O] was cleanly converted to amine 2 under basic conditions, which prompted us to investigate the carboxamates as possible intermediates that could easily be purified and converted to amine 2 in high yields. However, attempts to separate the methyl carbamate 4b[H₃O] from carboxylic acid 3[NEt₄] by chromatography proved difficult due to its low solubility and also an insufficient difference in mobility on silica gel. Therefore, we focused on t-Bu carbamate 4a[NEt₄], which could be converted to the amine under mildly acidic conditions.

A reaction of isocyanate 7[NEt₄] with anhydrous t-butanol gave carbamate 4a[NEt₄] in high yield. Initial attempts at chromatographic separation on a SiO₂ column using CH₃CN/CH₂Cl₂ (1:4) as the eluent showed that pure carbamate 4a[NEt₄] could be isolated in low yields (~20%). Mass balance was achieved with more polar fractions, which contained mostly amine 2, apparently arising from deprotection of the BOC group on the SiO₂ support. The decomposition of 4a[NEt₄] was minimized by buffering the solvent system with 1% NEt₃. The yield of carbamate 4a[NEt₄] rose to about 50%, but

The azophenol $8a\text{NMe}_4^+$ was easily methylated under basic conditions to give the methoxy derivative $13\text{NMe}_4^+$ in 95% yield (Scheme 5).

Dinitrogen derivative 1 was completely reacted with neat Me$_2$S at ambient temperature over a period of 24 h, giving adduct 9a, which was isolated in 40% yield. $^{11}$B NMR analysis of the crude reaction mixture revealed four signals: three doublets of product 9a and an unrelated singlet at 20.1 ppm. The singlet appears to be associated with the film of white material, presumably boric acid, which was poorly soluble in CD$_3$CN and well-soluble in CD$_2$OD (18.8 ppm). Previously, 9a was prepared in 68% yield based on amine 2 without isolation of the intermediate 1.

A 24 h reaction of 1 with N,N-dimethyldithioformamidine at ambient temperature gave 80% yield of crude 10 after washing with toluene. $^{11}$B NMR analysis of the crude product revealed the presence of about 10% of the parent anion [closo-1-CB$_9$H$_{10}$] (14), and also a low intensity singlet at 20.1 ppm. Attempts to purify the zwitterion 10 further were unsuccessful due to its partial decomposition observed during recrystallization from CH$_3$CN/toluene mixtures or 1,2-dichloroethane. Purification on silica gel was avoided, since 10 appeared to be hydrolytically unstable. Alkylation of crude 10 with 1,5-dibromopentane in the presence of a base followed by chromatographic separation and recrystallization gave pure 9b in 50% yield based on 1 (Scheme 6). This represents a slightly higher yield than that for a single-step preparation of 9a directly from 1.

Reactions of 1 with pyridine were most interesting. When 1 was reacted in neat pyridine at ambient temperature for several hours, $^{11}$B NMR analysis revealed a complex mixture of at least four products exhibiting characteristic doublets in the region of 25–40 ppm (Table 1). Surprisingly, the major component of the reaction mixture, about 50%, was identified as the 2-isomer 11b[PyH]. A doublet at δ 29.6 ppm with 20% intensity was assigned to the parent anion 14 on the basis of a comparison with literature data.

This was further supported by a comparison with an authentic sample of 14 with pyridinium as the counterion (14[PyH]) to maintain consistency with the reaction conditions.

The crude mixture was separated on silica gel giving the 2-isomer 11b[PyH] in 40% isolated yield as the first fraction. The doublet at δ 35.7 ppm observed in the crude mixture and originally assigned to the B(10) nucleus of 11b was shifted downfield by about 2 ppm in the isolated sample. This shift presumably results from transformation of the pyridinium salt of 11b[Py] to the zwitterionic structure 11b[PyH] of the isolated product. Such downfield shifts were observed for the other two isomers 11c and 11d, but they were less significant. The more polar fraction contained a mixture of two isomers, 11c[H] and 11d[H], which were identified on the basis of 1D $^1$H and 2D $^1$H–$^1$H correlation spectroscopy (COSY) NMR analysis.

The addition of hot pyridine to the dinitrogen derivative 1 had a different outcome. $^{11}$B NMR analysis of the crude reaction mixture revealed four products [δ B(10): 35.0, 33.1, 31.9, 29.6]. Chromatographic separation gave 11a in 17% isolated yield as the least polar fraction. The more polar fraction contained the remaining three isomers and also the parent anion 14 in about a 4:4:2:1 ratio (Table 1).

To provide more information about the possible mechanism for the formation of these products, reactions of 1 were run in dilute solutions of pyridine at ambient temperature for 18 h. Thus, a reaction of 1 with a 4% solution of pyridine in CH$_2$Cl$_2$ gave [closo-1-CB$_9$H$_7$-1-Cl] (15)$^{22}$ as the major product along with 11a, 11b, and 14 in an approximate ratio of 8:3:1:3, respectively, according to the $^{11}$B NMR analysis of the crude reaction mixture (Table 1). A similar reaction of 1 with a 4% solution of pyridine in benzene gave [closo-1-CB$_9$H$_7$-1-Ph]$^{20}$ as the major product. Isomers 11a and 11b were formed as minor products, in 13% and 17% yields, respectively, and no signals belonging to 11e or 11d were found in the $^{11}$B NMR spectrum of the crude mixture (Table 1). For comparison, decomposition of 1 in pure benzene-d$_6$ at ambient temperature gave a number of products, among which 16$\text{d}$$_6$ was identified by MS. A solution of 1 in CD$_2$Cl$_2$ gave only a broad featureless absorption band in a range −10 to −40 ppm and a broad band around 20 ppm in $^{11}$B NMR after 24 h at ambient temperature, which suggests complete destruction of the [closo-1-CB$_9$] cluster. Dinitrogen derivative 1 in a 4% solution of pyridine in CD$_3$CN was stable at 0°C for 3 h, whereas at 45°C, 45% of 1 reacted in 75 min, giving about 30% 17 (Scheme 7) and 4% 11a in addition to unidentified signals at 16.7, 25.3, and 10.0 ppm (in decreasing intensity order) in the $^1$H-decoupled spectrum.

**Reaction with MeCN and Kinetic Data for 1.** Decomposition of dinitrogen derivative 1 in dried CH$_3$CN at elevated temperatures (~50°C) gave a mixture of zwitterion 17 and acetamide 18 in about a 1:1 ratio as the only products (Scheme 7). $^1$H NMR revealed two partially overlapping quartets centered at 5.91 and 5.52 ppm attributed to 17 and 18, respectively. Adduct 17 appears to be the primary product, which partially undergoes hydration to the acetamide 18 with residual H$_2$O in the reaction mixture.

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(28) For details, see the Supporting Information.
About 75% of total mass recovery after separation on SiO2. B(10)-\[H\] (15) constituted 56% of the mixture. Ratio of low field signals for the crude reaction mixture. [closo-i-C6H5-i-Ph] (16) constituted 65% of the crude reaction mixture. Chemical shifts of the isolated products or mixtures.

**Table 1. Product Distributions in Reaction of I with Pyridine**

<table>
<thead>
<tr>
<th>Condition/products</th>
<th>11a</th>
<th>11b[H]</th>
<th>11c[H]</th>
<th>11d[H]</th>
<th>14</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat Pyridine</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25 °C</td>
<td>traces</td>
<td>40%b</td>
<td>17%c</td>
<td>10%f</td>
<td>6%f</td>
</tr>
<tr>
<td>90 °C</td>
<td>17%b</td>
<td>20%c</td>
<td>18%c</td>
<td>9%c</td>
<td>5%f</td>
</tr>
<tr>
<td>Solutions of Pyridine</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4% in CH2Cl2(^d)</td>
<td>17%e</td>
<td>7%e</td>
<td>0%e</td>
<td>0%e</td>
<td>20%e</td>
</tr>
<tr>
<td>4% in benzene(^f)</td>
<td>13%e</td>
<td>17%e</td>
<td>0%e</td>
<td>0%e</td>
<td>5%e</td>
</tr>
<tr>
<td>(^{11})B NMR for B(10), δ(^f)</td>
<td>33.1 ppm</td>
<td>37.2 ppm</td>
<td>33.9 ppm</td>
<td>35.9 ppm</td>
<td>29.6 ppm</td>
</tr>
</tbody>
</table>

a About 75% of total mass recovery after separation on SiO2. b Yield of isolated product. c Yield based on \(^{11}\)B NMR of the mixture corrected for its mass. d [closo-i-C6H5-i-Ph] (15) constituted 56% of the mixture. e Ratio of low field signals for the crude reaction mixture. f [closo-i-C6H5-i-Ph] (16) constituted 65% of the crude reaction mixture. g Chemical shifts of the isolated products or mixtures.

**Scheme 7**

The kinetics of decomposition of the dinitrogen derivative I were investigated in dried CD3CN as a function of the temperature and were followed by \(^1\)H NMR spectroscopy. Intensities of the disappearing B(10)-H signal at 7.21 ppm, belonging to the pseudo quintet (partially overlapping quartets of 17-\(d_3\) and 18-\(d_3\), were used to calculate the ratio of I to the sum of products 17-\(d_3\) and 18-\(d_3\). Standard kinetic analysis using the Eyring equation found Δ\(H^\ddagger\) = 38.4 ± 0.8 kcal mol\(^{-1}\), Δ\(S^\ddagger\) = 44.5 ± 2.5 cal mol\(^{-1}\) K\(^{-1}\), and Δ\(G^\ddagger\) = 25.1 ± 0.8 kcal mol\(^{-1}\) at 298 K. \(^{28}\)

**Mechanistic Studies. Computational Analysis.** To shed more light on properties of I and its reactions with nucleophiles, we conducted quantum-mechanical calculations initially at the B3LYP/6-31G(d,p) level of theory to establish conformational minima and to obtain thermodynamic corrections. The resulting structures were used to calculate the self-consistent field (SCF) energies at the MP2/6-31G(d,p) level of theory. Since I and other molecules involved are highly polar or ionic, the SCF solvation model was used to compute their SCF energies at the MP2/6-31G(d,p) or MP2/6-31+G(d,p) level of theory in an appropriate dielectric medium (pyridine or MeCN). Computational results are shown in Figures 2–6 and Tables 2–7, and full numerical data are provided in the Supporting Information. \(^{28}\)

**Generation and Structure of the Carbonium Ylide 19.** The dinitrogen derivative I undergoes a heterolytic cleavage of the C-N bond, and the process is calculated to be endothermic by 33.2 kcal/mol in the gas phase at the MP2//DFT level of theory with the 6-31G(d,p) basis set. This value is practically the same as that obtained using the MP2//MP2 method with the same basis set (Table 2). Since the resulting carbonium ylide 19 (\(\mu = 4.0\) D) is less polar than 1 (\(\mu = 6.1\) D), the endotherm increases to 35.4 kcal/mol in pyridine (\(\varepsilon = 13.3\)) and to 36.4 kcal/mol in the MeCN (\(\varepsilon = 36.6\)) dielectric medium. The MP2//DFT and MP2//MP2 calculations using diffuse functions do not change the results significantly, although they give lower Δ\(H^\ddagger\) values up to 2 kcal/mol for the latter method. In contrast to the MP2 results, the enthalpy change in the reaction calculated by the DFT method was smaller by about 10 kcal/mol. This difference is related to the inadequate treatment of electron correlation by the DFT methods and demonstrates the importance of dispersive forces in the stabilization of I.

A transition state search with the DFT method for the loss of N2 by I located a transition structure, I-TS, in...
which the Ccage–N bond is elongated by about 0.8 Å (dc–N = 2.13 Å). The DFT calculated activation parameters, \( \Delta H^* = 25.4 \text{ kcal/mol} \) and \( \Delta S^* = 12.5 \text{ cal/(mol K)} \), fall short of the experimental data (vide supra). Single-point calculations for 1-TS at the MP2//DFT level of theory gave \( \Delta H^* = 30.4 \text{ kcal/mol} \) in the pyridine dielectric medium, which is lower by 6 kcal/mol than the enthalpy change for the complete reaction. In addition, the calculations closely approximated an energy plateau between \( \Delta H^* = 25.4 \text{ kcal/mol} \) and \( \Delta H^* = 12.5 \text{ kcal/mol} \) for the complete reaction is 37.8 kcal/mol.

MP2-level calculations demonstrated that the carbonium ylide 19, a member of a hypercloso family, is a zwitterionic species. The carbon exocyclic (radial) orbital is practically a pure p orbital and partially populated (−0.34 e) at the expense of the boron atoms in the lower belt (Table 3). The lowest unoccupied molecular orbital (LUMO) of 19 is primarily localized on the Ccage atom with a contribution from the lower belt of boron atoms (Figure 2). The loss of electron density from the carbon exocyclic orbital markedly affects the geometry of the \{closo-1-CB_{11}\} cage (Table 3). Thus, the departure of N2 from 1 results in a less pyramidalized apical carbon atom, contraction of the Ccage–B interatomic distances, and significant expansion of the interbelt B–B bonds in the ylide 19 as compared to 1.

Electronic and geometrical features of 19 are similar to those found for its recently reported and extensively discussed 12-vertex \( \text{B}_{11} \text{Me}_{11} \) analogue, the \{closo-1-CB_{11}\} ylide. 31

**Reaction of Ylide 19 with Nucleophiles.** The resulting electron-deficient intermediate, carbonium ylide 19, is a highly reactive electrophile. In the simplest case, it reacts with Lewis bases in a two-electron process, giving C-substitution products such as 9, 11a, and 20. The overall two-step nucleophilic substitution reactions (S_{N}2) of 1 are highly exothermic, with the enthalpy change exceeding −30 kcal/mol and typically about −60 kcal/mol in a vacuum (Table 4).

**Figure 3.** Electrophilic substitution of pyridine. Energy change relative to ylide 19 and pyridine (MP2/6-31G(d,p)//B3LYP/6-31G(d,p), \( \varepsilon = 13.3 \)). For the reaction with radical ion 26, the intermediates 28 are analogous to 21 with the delocalized unpaired spin instead of the positive charge.

**Figure 4.** Structures of the edge adducts of 19 to pyridine.

than the C(2) isomer 11b[-] and more stable by 1.7 kcal/mol than 11c[-].

**Formation of Pyridine Derivatives 11.** The formation of four regioisomeric products, 11a–11d, may involve either a two-electron or a one-electron process. Initially, we focused on the former and considered electrocyclic reactions of the carbonium ylide 19 with pyridine.

The formation of the N(1) isomer (11a) can be envisioned as a simple one-step collapse of a Lewis acid (ylide 19) and a Lewis base (pyridine) to form the Ccage 19 with pyridine.

Instead of a Wheland-type adduct, in which the {1-closo-CB\(_9\)} cluster is connected to the arenium fragment by a C–N bond (Figure 3), our attempts to locate the transition state for the reaction using the DFT method were unsuccessful. The computational result favors the C(3) isomer 21c consistent with the established regioselectivity of electrophilic substitution in pyridine\(^{22}\) but is not consistent with the experimental observation of formation of the C(2) regioisomer 11b as the major product.

Full structure optimizations at the MP2/6-31G(d,p) level of theory gave a different geometry for the intermediate complex of ylide 19 with pyridine (Figure 4). Instead of a Wheland-type adduct, in which the [1-closo-CB\(_9\)] cluster is connected to the arenium fragment by a single bond about 1.60 Å long (21, Figure 3), the MP2-optimized geometry shows addition to an edge (C=\(\equiv\)C bond) of the aromatic ring forming a three-center, two-electron bond in 22bc and 22cd (Figure 4). Attempts at


**Table 2.** Enthalpy Change in Heterolytic Dissociation of 1\(^a\)

<table>
<thead>
<tr>
<th>method</th>
<th>(\Delta H), kcal/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>B3LYP/6-31G(d,p)</td>
<td>24.6</td>
</tr>
<tr>
<td>MP2/6-31G(d,p)</td>
<td>33.2</td>
</tr>
<tr>
<td>MP2/6-31G(d,p)</td>
<td>33.3</td>
</tr>
<tr>
<td>ICPM model ((\varepsilon = 36.6))</td>
<td>34.4</td>
</tr>
</tbody>
</table>

\(^a\)B3LYP/6-31G(d,p) thermodynamic corrections. \(\Delta S = +43.6\) cal/molK.

**Table 3.** Calculated Structural Parameters for Selected Derivatives of \{1-closo-1-CB\(_9\}\}

<table>
<thead>
<tr>
<th>X</th>
<th>Geometry(^ab)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>C(1)–B(2)/Å 1.602 1.624 1.585 1.532</td>
</tr>
<tr>
<td></td>
<td>B(2)–B(3)/Å 1.836 1.885 1.849 1.928</td>
</tr>
<tr>
<td></td>
<td>B(3)–B(6)/Å 1.802 1.785 1.809 1.829</td>
</tr>
<tr>
<td></td>
<td>B(6)–B(10)/Å 1.700 1.711 1.698 1.678</td>
</tr>
<tr>
<td></td>
<td>B–C–B/deg 108.3 110.2 111.2 125.8</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>X</th>
<th>Natural Atomic Charge(^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>C(1)</td>
</tr>
<tr>
<td></td>
<td>B(2)</td>
</tr>
<tr>
<td></td>
<td>B(6)</td>
</tr>
<tr>
<td></td>
<td>B(10)</td>
</tr>
</tbody>
</table>

\(^ab\)Optimized at the MP2/6-31G(d,p) level of theory at the C\(_p\) point group symmetry. \(^c\)C\(_\text{cage}\)–N distance, 1.337 Å; N–N distance, 1.149 Å. NBO analysis. Exocyclic orbital occupancy in parentheses.

renders the process irreversible. The computational result favoring the C(3) isomer 21c is consistent with the established regioselectivity of electrophilic substitution in pyridine\(^{22}\) but is not consistent with the experimental observation of formation of the C(2) regioisomer 11b as the major product.

Full structure optimizations at the MP2/6-31G(d,p) level of theory gave a different geometry for the intermediate complex of ylide 19 with pyridine (Figure 4). Instead of a Wheland-type adduct, in which the [1-closo-CB\(_9\)] cluster is connected to the arenium fragment by a single bond about 1.60 Å long (21, Figure 3), the MP2-optimized geometry shows addition to an edge (C=\(\equiv\)C bond) of the aromatic ring forming a three-center, two-electron bond in 22bc and 22cd (Figure 4). Attempts at

An alternative mechanism for the formation of 11b–11d may involve a radical process initiated by the addition of pyridine to the electrophilic dinitrogen group of 1. Indeed, both DFT- and MP2-level calculations located the pyridine adduct 23 on the potential energy surface (PES). The formation of the highly polar azene 23 (μ = 23.2 D) was found to be endothermic by 14.3 kcal/mol or endoergic by 24.8 kcal/mol at the MP2/DFT level of theory in the pyridine dielectric medium (ε = 13.3).

According to this mechanism, azene 23 undergoes fragmentation with a homolytic cleavage of the N–pyridine bond, leading to the radical ion pair 24 and 25 (Figure 5). The process is highly endothermic in the gas phase (ΔH = 133.0 kcal/mol), but it becomes more favorable in the pyridine dielectric medium (ΔG_298 = +44.5 kcal/mol). The diazenyl radical 24 easily loses molecular nitrogen (ΔG_298 = −24.8 kcal/mol) and forms radical ion 26. The dissociation of the Ccage--N bond and the direct formation of radical anion 26 is also possible, although the second ion, the pyridinediazene radical (27), was not located on the potential energy surface with the DFT method. The calculated overall enthalpy change for the formation of the ion pair and N₂ from 1 is +145.9 kcal/mol in the gas phase, but in pyridine (ε = 13.3), this energy is lowered to ΔH = 56.4 kcal/mol or ΔG_298 = 44.4 kcal/mol (Figure 5).

NBO analysis indicates that the apical carbon atom in radical ion 26 has a significant negative charge density (−0.36) and the radical is expected to be moderately nucleophilic (Table 3). Therefore, it may react with a molecule of neutral pyridine (solvent), which leads to regiosomeric radical anion adducts 28 (analogous to zwitterions 21 in Figure 3). Results show that, in the gas phase, the C(2) intermediate 28b, which leads to the experimentally observed major product 11b, is least favored, and its regioisomers are more stable by about 3–4 kcal/mol (stability order: 28c > 28a, 28d > 28b, Table 6). The IPCM calculations demonstrated diminished exotherms of the adduct formation in the dielectric medium, with the heat of formation for the C(2) adduct 28b being least affected. Consequently, the order of stability of the intermediates is changed in pyridine; the N(1) adduct 28a, leading to the unobserved 11a, becomes the least favored, whereas 28b is less stable than 28c by only 1.4 kcal/mol (order of stability: 28c > 28b > 28d > 28a, Table 6). The resulting adducts 28b–28d undergo a highly exothermic (about 115 kcal/mol) process, leading to products 11b[1]−11d[1] and involving either a hydrogen atom transfer or a sequence of electrons followed by proton transfer with pyridinium radical 25. A reaction of radical anion 26 with pyridine radical cation 25 is predicted to be highly exothermic and lead directly to 11a.

Our initial attempts to locate transition state structures for either type of adduct, radicals 28 or zwitterions 21, were unsuccessful and, due to computational intensity, were not pursued further.

Phenylation of Pyridine. To provide a better support for the proposed radical process of formation of 11, we also analyzed an analogous reaction between the benzene-diazonium ion and pyridine (Figure 6 and Table 6). According to the accepted mechanism, the formation of...

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**Table 4. Enthalpy Change in Substitution Reactions of 1**

<table>
<thead>
<tr>
<th>reagent</th>
<th>product</th>
<th>X</th>
<th>ΔH/kcal mol⁻¹</th>
<th>dipole/D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me₂S</td>
<td>9a</td>
<td>Me₂S⁺</td>
<td>45.5</td>
<td>14.0</td>
</tr>
<tr>
<td>pyridine</td>
<td>11a</td>
<td>-H</td>
<td>30.7</td>
<td>14.0</td>
</tr>
<tr>
<td>11b-[H]</td>
<td>2-C₅H₄NH⁺</td>
<td>-H</td>
<td>30.7</td>
<td>14.0</td>
</tr>
<tr>
<td>11c-[H]</td>
<td>3-C₅H₄NH⁺</td>
<td>-H</td>
<td>30.7</td>
<td>14.0</td>
</tr>
<tr>
<td>11d-[H]</td>
<td>4-C₅H₄NH⁺</td>
<td>-H</td>
<td>30.7</td>
<td>14.0</td>
</tr>
<tr>
<td>MeCN</td>
<td>17</td>
<td>MeCN⁺</td>
<td>30.7</td>
<td>14.0</td>
</tr>
<tr>
<td>NM₃</td>
<td>20</td>
<td>NM₃⁺</td>
<td>30.7</td>
<td>14.0</td>
</tr>
</tbody>
</table>

*a* MP2/6-31G(d,p)//B3LYP/6-31G(d,p) level with DFT thermodynamic corrections. *b* Vacuum calculations. *c* IPCM solvation model.

---

**Table 5. Calculated Free Energy Change in Deprotonation Reactions of 1**

<table>
<thead>
<tr>
<th></th>
<th>ΔG_298 kcal mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>b</td>
<td>−5.9</td>
</tr>
<tr>
<td>c</td>
<td>+0.5</td>
</tr>
<tr>
<td>d</td>
<td>−7.3</td>
</tr>
</tbody>
</table>

*a* MP2/6-31G(d,p)//B3LYP/6-31G(d,p) calculations with DFT thermodynamic corrections. IPCM solvation model ε = 13.3.
N-phenylazopyridinium (29) is the first step in the free radical phenylation of pyridine, which leads to three regioisomeric C-phenylpyridines (30). DFT calculations located the N-diazene 29 on the potential energy surface, and subsequent MP2/DFT calculations revealed that its formation is more endothermic ($\Delta H = +2.9 \text{ kcal/mol}$, $\Delta G_{298} = +14.5 \text{ kcal/mol}$) in the pyridine dielectric medium (Figure 6). Homolytic cleavage of the N-N bond leading to the formation of phenyldiazenyl radical (31) and radical cation 25 is significantly endothermic ($\Delta G_{298} = +51.7 \text{ kcal/mol}$). This is partially compensated by the favorable decomposition of the diazenyl radical 31 and the formation of phenyl radical (32) and $N_2$ ($\Delta H = -11.6 \text{ kcal/mol}$, $\Delta G_{298} = -21.5 \text{ kcal/mol}$). Nevertheless, the overall process of formation of the phenyl radical is exothermic (Figure 6).

The addition of the resulting phenyl radical (32) to pyridine and the formation of the intermediates 33 is moderately exothermic with the highest exotherm calculated for the N-adduct 33a (stability order: $33a > 33c > 33b > 33d$) in the gas phase (Table 6). The same calculations in the dielectric medium decrease the reaction exotherm for 33a and 33b and increase the exotherm for 33c and 33d. Consequently, the order of thermodynamic stability of the four intermediates is altered, giving the preference for the C(3) isomer 33c (stability order: $33c > 33d > 33a > 33b$) in pyridine. Subsequent H• transfer from 33 to 25 is highly exothermic ($\Delta H \approx -110 \text{ kcal/mol}$) and gives the isomeric pyridines 30. The calculated order of their thermodynamic stability (30b > 30d > 30c) is consistent with experimentally established trends in heats of formation.37

Finally, we assessed the accuracy of the IPCM method in predicting the formation of ion pairs, such as 25 and 26, by computing the energy change for dissociation of azosulfone 34 and the formation of ion pair $\text{PhN}_2^+$ and $\text{PhSO}_2^-$ in a dielectric medium. The experimentally established association constant $k_{assoc} \approx 1.44 \times 10^7 \text{ L/mol}$ for the ion pair $\text{PhN}_2^+$ and $\text{PhSO}_2^-$ in MeOH at 29 °C allows for the calculation of $\Delta G_{302} = +7.1 \text{ kcal/mol}$

Table 6. Calculated Enthalpy Change for Reactions with Pyridine

<table>
<thead>
<tr>
<th>reaction intermediate</th>
<th>N(1)</th>
<th>C(2)</th>
<th>C(3)</th>
<th>C(4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R* + PhN2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PhN2 + N2</td>
<td>7h</td>
<td>-92.5</td>
<td>-32.0</td>
<td>-36.4</td>
</tr>
<tr>
<td></td>
<td>13.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PhN2 + N2</td>
<td>7h</td>
<td>-28.0</td>
<td>-24.9</td>
<td>-29.2</td>
</tr>
<tr>
<td></td>
<td>13.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PhN2 + N2</td>
<td>7h</td>
<td>-28.4</td>
<td>-26.0</td>
<td>-27.6</td>
</tr>
<tr>
<td></td>
<td>13.3</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 7. Energy Change in Dissociation of 34 in MeOH

<table>
<thead>
<tr>
<th>$\epsilon$</th>
<th>$\Delta H$/kcal mol$^{-1}$</th>
<th>$\Delta G_{302}$/kcal mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1b</td>
<td>67.9</td>
<td>56.1</td>
</tr>
<tr>
<td>30.9$c,d$</td>
<td>24.5</td>
<td>12.6</td>
</tr>
</tbody>
</table>

$^a$ MP2/6-31G(d,p)//B3LYP/6-31G(d,p) level with DFT thermodynamic corrections. $^b$ Vacuum calculations. $^c$ IPCM solvation model.

for the dissociation of $\text{34}$. Our MP2//DFT calculations in the gas phase demonstrated a high endotherm ($\Delta H = +67.9 \text{ kcal/mol}$) for the dissociation process of $\text{34}$ (Table 7). In the dielectric medium, however, the dissociation process of $\text{34}$ becomes significantly more favorable, reaching a value of $\Delta G = +12.6 \text{ kcal/mol}$ in MeOH. This represents a fairly good agreement between the theory and experimental results and indicates that MP2//DFT calculations underestimated the solvation of the ions by 5.5 kcal/mol. Consequently, the stability of other ions in a dielectric medium is most likely underestimated, and their formation is more favorable than calculated.

Electronic Absorption Spectroscopy. Spectroscopic analysis of four derivatives, $\text{1, 8, 9a, 11a}$, and trimethylamine zwitterion $\text{20}$ provides a convenient means to study electronic interactions between the $\{\text{closo-1-CB}_9\}$ cage and the substituent at the C(1) position.

Among the five substituents, NMe$_3$ in $\text{20}$ is the simplest and does not possess easily available electrons or accessible orbitals. Therefore, the electronic absorption spectrum of $\text{20}$ closely resembles that of the parent $\{\text{closo-1-CB}_9\}^-$ anion ($\text{14}$) with the absorption tailing to about 250 nm and the maximum below 200 nm (Figure 7a). The presence of an electron pair in the SM$_2$ substituent of $\text{9a}$ resulted in the increased intensity of the band at about 200, the appearance of a shoulder band at about 225 nm, and also a broad low-intensity band at 272 nm.

These spectral features are consistent with the transitions observed at about 230 and 200 nm for trialkylsulfonium salts. It was also noted that the UV spectra of sulfonium salts are affected by the presence of molecular oxygen, which gives rise to the appearance of charge-transfer (CT) bands.

The dinitrogen, N$_2$, and pyridine groups are $\pi$ substituents, and their orbitals can interact with the electronic manifold of the $\{\text{closo-1-CB}_9\}$ cage. Thus, the dinitrogen derivative $\text{1}$ exhibits a single absorption band at 250 nm (Figure 7a). ZINDO//MP2 calculations revealed that $\text{1}$ exhibits two $\pi \rightarrow \pi^*$ transitions, at 280 nm ($f = 0.49$) and a weaker one at 242 nm ($f = 0.12$) in a vacuum. The former involves the double-degenerated highest occupied molecular orbital (HOMO), localized mostly on the cage, and the LUMO, localized primarily on the N$_2$ group (Figure 8). The higher energy transition is due to intracage excitations (HOMO $\rightarrow$ LUMO + 1). The same calculations conducted for $\text{1}$ in the dielectric medium of the solvent ($\varepsilon = 36.6$) revealed a substantial negative solvatochromic effect of the cage-to-substituent excitation and practically no solvent effect of the intracage excitation. As a consequence, the two transitions merge into one, which is calculated at 247 nm ($f = 0.56$) and observed at 250 nm.

Figure 7. Electronic absorption spectra for selected compounds recorded in CH$_3$CN.

Figure 8. DFT-generated MO contours for 1. For clarity, only one part of each degenerated MO is shown.

Figure 9. DFT-generated HOMO and LUMO contours for 11a.

Figure 10. ZINDO-generated HOMO and LUMO + 1 contours for 8b.

Pyridine is the most complex substituent among the five groups; it has both the low-lying LUMO and also its own π→π* transitions in the UV region. Consequently, the pyridine derivative 11a is expected to exhibit three types of electronic transitions: cage-ring, intraring, and intracage. The first two types apparently overlap and form a complex structure in the range of 240–300 nm (Figure 7a). The maximum of the broad, intense underlying band is estimated at 269 nm and attributed to the cage-to-ring CT transition. The upper fine structure has two maxima at 268 and 274 nm and represents the π→π* transition at 445 nm (Figure 7b), while the forbidden transition at 425 nm in CH3CN.42 In 4-aminoazobenzene, both absorption bands overlap to form a broad band43 with a maximum at 382 nm in CH3CN.44

Electronic spectra of the azo derivatives 8a and 8b exhibit absorption bands typical for azobenzenes.41 The intense band of the π→π* transition in azophenol 8a appears at 318 nm (log ε = 4.30) and in azoaniline 8b at 348 nm (Figure 7b), while the forbidden π→π* transition is located at about 400 nm in both derivatives.

ZINDO//DFT calculations in the MeCN dielectric medium (ε = 36.6) demonstrated a low-intensity transition at 445 nm (f < 0.001), which involves excitation from HOMO→2 and HOMO→4, localized on the nitrogen atom lone pairs and the cage, to the σ symmetry orbitals LUMO + 1 and LUMO + 4, which are delocalized over the molecule with the main component from the {closo-1-CB9} cage. The more intense transition is calculated at 329 nm (f = 0.82), which involves the excitation from the HOMO, localized on the organic fragment, mainly to the LUMO + 1 and also to the LUMO + 4 localized on the CB9H0−N=N fragment (Figure 10).

In comparison to the azobenzene analogs, the electronic transitions of the {closo-1-CB9} derivatives 8a and 8b are blue-shifted by 24–34 nm. For instance, absorption bands of 4-hydroxyazobenzene are recorded at 344 and 425 nm in CH3CN.42 In 4-aminoazobenzene, both absorption bands overlap to form a broad band43 with a maximum at 382 nm in CH3CN.44

NMR Studies. The availability of several diverse derivatives of the [closo-1-CB9]H10− cluster provided an opportunity to analyze the transmission of the substituent effect through the cage and compare the results to those for analogous benzene and [closo-1-CB11H13] derivatives. Thus, the relative NMR chemical shifts (Δδ) for the antipodal B(10)-H were plotted versus the substituent σp values,45 and the results are shown in Figure 11.

A Hammett plot of δ versus Hammett σp for 1H NMR B(10)-H chemical shifts showed a good linear fit for several substituents (Figure 11a). The correlation factor r² is 0.94 for all substituents, and it increases to 0.99 if the two outlying data points (X = NH3 and X = CI) are removed. This change has little effect on the slope (ρ) of the linear fit, which slightly increases from 0.70 ± 0.05 to 0.73 ± 0.02 for the smaller data set. Interestingly, the slope for the B(10)-H chemical shift is practically the same as that obtained for the C(4)-H chemical shift in monosubstituted benzene derivatives (ρ = 0.70 ± 0.09) after correction for anisotropic shielding.28,46

The Hammett plot of B(10) and B(12)11B NMR chemical shifts for {closo-1-CB9} and {closo-1-CB11},

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respective, showed that \( \{\text{closo-1-CB}_9\} (\rho = 12.7 \pm 1.8) \) appears to be significantly more sensitive than \( \{\text{closo-1-CB}_{11}\} (\rho = 5.3 \pm 1.3) \) to the nature of the C(1) substituent (Figure 11b).

Discussion

Experiments demonstrated that the dinitrogen derivative 1 is stable in the solid state but decomposes in solutions. In MeCN, the process is slow, and the estimated half-life of 1 is \( t_{1/2} = 91 \) h at 25 °C and \( t_{1/2} = 2 \) s at 90 °C. The consistency of the measured high enthalpy of activation \( \Delta H^\ddagger \) of 38.4 ± 0.8 kcal/mol with the calculated enthalpy change, \( \Delta H \), and the formation of a single product (17) support the heterolytic mechanism for the decomposition of 1 and the formation of the reactive intermediate 19 in MeCN. In addition, the unusually high experimental entropy of activation, \( \Delta S^\ddagger \) (44.5 ± 2.5 cal/mol K), is similar to the calculated \( \Delta S \) value of 43.6 cal/mol K. This suggests that the dissociation process involves stretching the \( \text{C}_\text{cage} = \text{N} \) bond to the edge of the van der Waals contact between the atoms. Alternatively, solvent molecules are involved in the transition state, and the high value of \( \Delta S^\ddagger \) reflects differential solvation of the ground and transition states. The proposed heterolytic unimolecular decomposition reaction of 1 is similar to that described for PhN= in polar aprotic solvents.48 Interestingly, \( \Delta G^\ddagger \) and \( \Delta S^\ddagger \) for 1 is higher by about 1.5 kcal/mol than that reported for PhN= in neat pyridine.49 Also, the heterolysis of 1 has a significantly higher \( \Delta S^\ddagger \) than that measured for PhN= in MeCN (18.3 cal/mol K) or in MeNO2 (30.9 cal/mol K).48

A change of solvent significantly accelerates the transformation of 1, which is then usually fully consumed in less than 20 h at ambient temperature. The observed increase of the reaction rate can be due to the lower activation energy for the decomposition of 1 in less polar solvents. Calculations showed that the activation energy for the formation of ylide 19 is lower by 1 kcal/mol in the pyridine dielectric medium and 3.2 kcal/mol in a vacuum relative to that in MeCN (Table 2) due to a greater dielectric stabilization of 1 than the products. Consequently, heterolysis of 1 can be nearly 20 times faster in pyridine and nearly 50 times faster in a vacuum than in MeCN, assuming the same \( \Delta S^\ddagger \) and that the difference in \( \Delta H \) of the reaction reflects the difference in \( \Delta H^\ddagger \). Often, however, \( \Delta S^\ddagger \) changes with the solvent (cf. \( \Delta S^\ddagger \) for PhN=). Thus, for heterolysis of 1 in less polar solvents, the entropy of activation may be smaller, which will partially compensate the change in \( \Delta H^\ddagger \), and consequently less impact on the reaction rate will be observed. Alternatively, a change of mechanism can be responsible for the significantly different reaction rate.

The reaction of ylide 19 with pyridine is expected to give the N(1) adduct 11a directly as the only or dominant product, since the process is favored kinetically (anticipated low activation barrier) and has a large exotherm (\( \Delta H = -102.6 \) kcal/mol). Support for this expectation is provided by the reported smooth transformations of similar dinitrogen derivatives of the \{closo-B(10)H(10)\} cluster with pyridine,7-4,6-8 and also the isolation of \{closo-1-CB(1)Me(1)-1-C(3)H(2)N\} as the only product of a reaction of the \{hypercloso-1-CB(1)Me(1)\} ylide with pyridine.35 Instead, the observed distribution of products in the reaction of 1 with pyridine suggests a radical pathway, which is similar to the known Gomberg–Bachmann free-radical arylation reaction.49 In both reactions, all C-substituted pyridine isomers are formed with the dominant proportions of the C(2) isomer.34,50 The radical mechanism for the formation of 11 is supported also by computational results, which demonstrate that the formation of radical ion 26 from 1 is as feasible as the generation of Ph N= (32) from PhN=, considering the difference in the treatment of ion pairs and nonionic molecules by the IPCM model.

From the mechanistic point of view, reaction of 1 in neat pyridine can proceed by either a heterolytic or homolytic pathway (Figure 12). The first and also rate-determining step in the former mechanism is a unimolecular first-order reaction, whereas the rate-limiting step in the radical pathway is pseudo-first-order formation of diazenyl radical 24, since [pyridine] \( \approx \) const \( > \) [1]. At ambient temperature, the radical process appears to be significantly faster \( (k_c \approx k_c k_e) \), and the resulting radical anion 26 attacks the dominant neutral pyridine (solvent) following pseudo-first-order kinetics. This reaction is faster than the energetically more favorable (Table 4) ion recombination reaction of 26 and the pyridinium radical 25 (a second-order process), which, presumably, leads directly to the N(1) adduct 11a. The attack of 26 on pyridine is calculated to be moderately exoeergic (\( \Delta G^\ddagger \) between \(-11.3 \) kcal/mol for 28a and \(-13.7 \) kcal/mol for 28c), and with a sufficiently low activation barrier, the process may be reversible, leading to the thermodynamic intermediate 28. The subsequent electron transfer (ET) from 28a and hydrogen transfer (HT) from 28b–28d to 252 and the formation of 11a and 11b [–11d], respectively, are highly exothermic (\( \Delta H > 100 \) kcal/mol in the dielectric medium) and considered irreversible. Therefore, the formation of 11b as the major component of the mixture may arise either from the kinetic preference for the formation of intermediate 28b (if the barrier is sufficiently high and the HT

(51) From the steady-state approximation considering that the rate of decomposition of adduct 23 is much slower than the reverse reaction.
(52) Since [26] \( \approx [25] \), radical anion 26 competes with 25 for the hydrogen from 28, which may explain the observed low yield formation of 14.
process is fast) or from the thermodynamic stability of \(28b\) (if the barrier is sufficiently low and the HT process is slow). The latter implies that the calculations underestimated the stability of \(28b\) by about 2 kcal/mol relative to \(28c\), which is not unreasonable. In fact, all \(C\)-substituted intermediates have comparable calculated energies within 2 kcal/mol in the pyridine dielectric medium. It needs to be remembered that the dielectric medium significantly destabilizes \(28c\) and has the least effect on the energy of formation of \(28b\) (Table 6). Also, \(28a\) is the thermodynamically least favorable intermediate, which is in agreement with its practical absence among the reaction products. A similar discrepancy between the calculated thermodynamic stability of the radical intermediates 33 and the distribution of the products 30 is found for the phenylation of pyridine (Table 6). Again, this may indicate that product formation is governed by kinetics (irreversible processes), or the relative energies are calculated with an error of \(\pm 2\) kcal/mol.

At higher temperatures, the rate of formation of the ylide 19 becomes competitive with that of generation of the radical anion 26 (\(k_2 \sim k_{1c2}\)), and consequently, the \(N(1)\) isomer 11a is formed in substantial amounts along with its \(C\)-isomers (Table 1).

In dilute solutions of pyridine in benzene, both mechanisms, the heterolytic and the homolytic decomposition of 1, may operate at the same time, as is indicated by the formation of \(N(1)\) and \(C(2)\) isomers (11a and 11b, respectively) in comparable amounts (Table 1). The lower dielectric permittivity of benzene may increase the rate of the formation of 19, while the lower concentration of pyridine in solution could decrease the rate of formation of radical anion 26. Consequently, both intermediates, 19 and 26, can be formed at similar rates. The radical anion is expected to react easily with both pyridine and benzene, leading to 11b and [\(\text{closo-1-CB}_{11}\text{H}_{11-1-\text{Ph}}\)] (16), respectively. Calculations support this expectation and demonstrate that both addition reactions of 26 to benzene and pyridine at the \(C(2)\) position have comparable exotherms \(\Delta H^o\) of \(-24.9\) and \(-23.4\) kcal/mol, respectively, in the pyridine dielectric medium. The ylide 19 is expected to attack pyridine’s N atom, leading to 11a and benzene to form 16. The formation of the latter presumably follows the mechanism proposed for the electrophilic substitution of aromatic hydrocarbons with the \(\text{[hypercloso-1-CB}_{11}\text{Me}_{11}]\) ylide and involves an three-center, two-electron bond intermediate analogous to 22 (Figure 4).

In methylene chloride solutions, the situation is similar, and transformation of 1 may follow both mechanistic pathways involving both reactive intermediates. The radical anion 26 is expected to react with pyridine, giving 11b, and to abstract hydrogen from the solvent, giving the observed parent cluster 14. It may also transfer a Cl atom to form the chloride [\(\text{closo-1-CB}_{11}\text{H}_{11-1-\text{Cl}}\)] (15).

Results of reactions of 1 in dilute solutions of pyridine in MeCN are also consistent with the dual mechanism and involvement of the two reactive intermediates. In addition to 17 and 11a, products expected for trapping of the ylide 19, the reaction mixture contained several unidentified signals, which are presumably related to reactions of radical ion 26 with the solvent and pyridine. Interestingly, the rate of decomposition of 1 in the MeCN/pyridine solution is approximately the same as the rate in pure MeCN.

The mechanism of pyridine-induced radical reactions of 1 is similar to the accepted mechanism of free-radical arylation of pyridine with benzenediazonium salts.\(^{34–36,54}\) In both cases, a stable adduct of pyridine to the \(N_2\) group was located on the PES (compounds 23 and 29). The relatively high energy of adducts 23 and 29 suggests that they are transient species formed at low concentrations, which give rise to the radical ion pairs. Further studies of reactions of arenediazonium salts indicated that the radical/cationic pathway correlates with the nucleophilicity of the solvent\(^{56,54}\) and does not necessarily involve a stable transient adduct but rather involves an intermolecular electron transfer (outer-sphere ET).\(^{56}\) Thus, pyridine has one of the highest nucleophilicity parameters, whereas acetonitrile has one of the lowest nucleophilicity parameters.\(^{54,55}\) Therefore, the former may induce radical generation, while the latter will favor cationic processes. This is indeed observed experimentally for the decomposition of both 1 (present work) and benzenediazonium salts\(^{56–60}\) for which the corresponding aceticamides are the main products in MeCN solutions (see Scheme 7).

The propensity of a nucleophile to induce radical reactions of 1 and \(\text{PhN}_2^+\) can be assessed from the energetics of ET between the diazonium and the donor calculated from ionization potential (\(I_0\)) and electron affinity (\(E_a\)) for a gas-phase reaction, or from oxidation (\(E^{\text{ox}}_\text{red}\)) and reduction (\(E^{\text{red}}_\text{red}\)) potentials in solutions (Table 8). Calculations demonstrate that, while the \(E_0\) for the two electrophiles, 1 and \(\text{PhN}_2^+\), are different in the gas phase by over 3.5 eV, they are practically the same in MeCN solutions. The dielectric medium stabilizes charged molecules, and consequently, the addition of an electron to 1 becomes more favorable, while the reduction of \(\text{PhN}_2^+\) is less exothermic in MeCN.

The calculated \(I_0\) values for the five reagents compare well with the experimental data\(^{61}\) with a systematic underestimation by about 0.3 eV. In the MeCN dielectric medium, the calculated \(I_0\) values are lowered by 2–3 eV relative to the gas phase. A comparison of the calculated ionization values to the experimental electrochemical data (Table 8) can be made only at a qualitative level, since all investigated processes as the counterion in the crystal structure of the isolated chloride.\(^{15,55}\)

Thus, this mechanism is probably the one that operates in the reaction of \(\text{PhN}_2^+\) with pyridine in MeCN.


(61) NIST Standard Reference Database Number 69 (http://webbook.nist.govchemistry/) and references therein.
are irreversibly in solution and the observed current peak potentials do not represent thermodynamic processes. The calculated ionization potentials $I_a$ generally follow the trend in experimental anodic peak potentials $E_{pa,ox}$ for all reagents, with the exception of Me$_2$S (Table 8). In agreement with calculations, the lowest oxidation potential is observed for the thioformamide and the highest for MeCN. The experimental $E_{pa,ox}$ for Me$_2$S is higher by over 0.5 V than predicted, presumably due to complex chemical behavior of the radical cation.

A comparison of calculated electron affinities with the electrochemical data shows that the reduction of 1 is more cathodic by 0.39 V than that of PhN$_2^+$.

The discrepancy between calculated solution $E_a$ values and observed $E_{pa,ox}$ values (Table 8) is presumably due to the difference in ion solvation (cation vs anion) and solvent reorganization energy.

Calculation data in Table 9 demonstrate that ET between pyridine and PhN$_2^+$ (outer-sphere process) and the formation of a radical ion pair are endothermic in pyridine ($\Delta G_{298} = 66.3$ kcal/mol) and practically the same in MeCN solution (Table 9), which corresponds to the difference in the measured current peak potentials of $\Delta E_p \approx 1.7$ V (Table 8). The same analysis for 1 and pyridine gives a similar value for the ET process in MeCN ($\Delta G_{298} = 65.3$ kcal/mol) but a larger experimental electrochemical potential ($\Delta E_p \approx 2.0$ V).

Calculations suggest that the ET process between 1 and Me$_2$S and also Me$_2$NCHS is more favorable, and it should be faster than that with pyridine (Table 9). Both sulfur reagents have markedly lower $I_a$ values relative to pyridine, and consequently $\Delta G_{298}$ values for electron transfer to 1 are lower.

*(MP2/6-31G(d,p)//B3LYP/6-31G(d,p) level with DFT enthalpic corrections. $^b$ Peak potential recorded in MeCN (0.05 M Bu$_4$NPF$_6$) vs SCE. $^c$ Vacuum calculations. $^d$ IPCM solvation model. $^e$ Lit. $^f$ Lit.$^2$ +1.71 V vs SCE. $^g$ Recorded in neat pyridine. $^h$ Solvent electrochemical limit; ref 65.

**Table 8. Calculated Adiabatic Electron Affinity ($E_a$) and Ionization Potential ($I_a$) and Experimental Electrochemical Reduction/Oxidation Potentials for Selected Compounds**

<table>
<thead>
<tr>
<th>compound</th>
<th>$\epsilon = 1$</th>
<th>$\epsilon = 13.3^d$</th>
<th>$\epsilon = 36.6^d$</th>
<th>$E_{pa,ox}$/V</th>
<th>$E_{pe,red}$/V</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeCN</td>
<td>12.10</td>
<td>9.28</td>
<td>9.42</td>
<td>-0.54</td>
<td></td>
</tr>
<tr>
<td>C$_6$H$_5$N$_2^+$</td>
<td>2.11</td>
<td>3.69</td>
<td>3.76</td>
<td>-0.16</td>
<td></td>
</tr>
<tr>
<td>C$_6$H$_5$N$_2^+$</td>
<td>5.84</td>
<td>3.86</td>
<td>3.76</td>
<td>-0.16</td>
<td></td>
</tr>
<tr>
<td>Me$_2$S</td>
<td>8.29</td>
<td>5.91</td>
<td>5.77</td>
<td>1.78</td>
<td></td>
</tr>
<tr>
<td>Me$_2$NCHS</td>
<td>7.94</td>
<td>5.93</td>
<td>5.83</td>
<td>1.25</td>
<td></td>
</tr>
<tr>
<td>pyridine</td>
<td>8.95</td>
<td>6.82</td>
<td>6.72</td>
<td>lit. $&lt; 1.5^b$</td>
<td></td>
</tr>
<tr>
<td>CH$_2$Cl$_2$</td>
<td>10.93</td>
<td>8.40</td>
<td>8.27</td>
<td>$&lt; 1.8^f$</td>
<td></td>
</tr>
<tr>
<td>MeCN</td>
<td>12.10</td>
<td>9.28</td>
<td>9.42</td>
<td>$&lt; 2.4^f$</td>
<td></td>
</tr>
</tbody>
</table>

**Table 9. Calculated Free Energy Change $\Delta G_{298}$ for the Electron Transfer Process between 1 and Selected Solvents**

<table>
<thead>
<tr>
<th>R</th>
<th>$\epsilon = 1^b$</th>
<th>$\epsilon = 13.3^d$</th>
<th>$\epsilon = 36.6^d$</th>
<th>$\epsilon = 1^b$</th>
<th>$\epsilon = 13.3^d$</th>
<th>$\epsilon = 36.6^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me$_2$S</td>
<td>138.8</td>
<td>47.4</td>
<td>43.0</td>
<td>53.7</td>
<td>44.4</td>
<td>43.9</td>
</tr>
<tr>
<td>Me$_2$NCHS</td>
<td>132.3</td>
<td>49.6</td>
<td>45.8</td>
<td>47.2</td>
<td>46.6</td>
<td>46.7</td>
</tr>
<tr>
<td>pyridine</td>
<td>154.7</td>
<td>69.2</td>
<td>65.3</td>
<td>69.6</td>
<td>66.3</td>
<td>66.2</td>
</tr>
<tr>
<td>CH$_2$Cl$_2$</td>
<td>200.9</td>
<td>106.0</td>
<td>101.4</td>
<td>115.8</td>
<td>103.0</td>
<td>102.3</td>
</tr>
<tr>
<td>MeCN</td>
<td>227.3</td>
<td>125.7</td>
<td>127.5</td>
<td>142.2</td>
<td>122.8</td>
<td>128.4</td>
</tr>
</tbody>
</table>

$^b$ MP2/6-31G(d,p)//B3LYP/6-31G(d,p) level with DFT thermodynamic corrections. Energies in kcal/mol. $^c$ IPCM solvation model. $^d$ by 20 kcal/mol, or 1/3, than those for pyridine (Table 9). This is consistent with a smaller $\Delta E_p$ of 1.79 V (Table 8) for the reaction of 1 and Me$_2$NCHS and indicates that the formation of 10 and possibly also 9a may involve a radical process, which begins with outer-sphere ET (intermolecular) and formation of the radical ion pair. According to the proposed radical mechanism of reaction of 1 with Me$_2$S, the radical ion pair collapses to form the product 9a (Figure 13). Since the concentration of the ions is small and the rate of this bimolecular process is low, other processes take place, such as a loss of proton and presumably an abstraction of H. Consequently, the adduct 9a is isolated only in 40% yield, with the rest of the precursor forming polymeric/decomposition products. It is expected that the reaction of 19 with Me$_2$S would give the adduct 9a in a much higher yield.

The reaction with Me$_2$NCHS is much more efficient. The thionocarboxyls are known to react smoothly with C-centered radicals, often in a chain process, in which the weak S=C bond is eliminated. Thus, it can be postulated that radical ion 26 preferentially attacks the sulfur atom, giving rise to the C-centered transient radical 35 stabilized by both the N and S atoms (Figure 14). Subsequent ET to the Me$_2$NCHS radical cation gives product 10. Overall, the preparation of dialkylsulfonium derivatives such as 9 is most efficiently done in a two-step process using 10 as the intermediate.

The intermediacy of ylide 19 in the formation of 9a or 10 cannot be excluded, and clearly more detailed studies are necessary for a better understanding of the mechanism and intermediates involved in transformations of 1.

Solvents with high $I_a$ ($> 10$ eV) and $E_{pa,ox}$ such as MeCN and CH$_2$Cl$_2$ are not expected to transfer an electron to 1 and induce its radical transformations. Therefore, decomposition of 1 in these solvents is likely to involve ylide 19, as postulated for thermolysis in MeCN. The products of reactions of 1 in CH$_2$Cl$_2$ and also benzene are largely intractable, which may be a result of their extensive decomposition caused by an unsolvated counterion, either +CH$_2$Cl (in reaction with CH$_2$Cl$_2$) or H$^+$ (in reaction with benzene). The yields of 15 and 16 may be improved by using a non-nucleophilic base with a high $I_a$ in the reaction medium.

Overall, slow decomposition of 1 through ylide 19 can be expected in solvents such as MeNO$_2$ with a high $I_a$, for which


*(66) No stable adduct of Me$_2$S to 1 nor to PhN$_2^+$ was located on the PES with the DFT method.
adducts to 19 are relatively stable zwitterions (do not produce aggressive electrophiles), and have been demonstrated to promote the heterolytic unimolecular decomposition of PhN₂⁻. 68 On the other hand, reagents with a high nucleophilicity and low Ip, such as amines and sulfur compounds, are likely to induce radical transformations of 1.

Analysis of electronic absorption spectra and chemical shifts revealed significant similarities between the [closo-1-CB₉H₁₀]⁻ and benzene. Thus, electronic absorption spectra demonstrated substantial electronic communication between the [closo-1-CB₉]⁻ cage and π substituents. This is consistent with our previous experimental and theoretical studies for the derivatives of [B₁₀H₁₀]⁻ and C₂B₈H₁₀. 6,8,11,68,70 In the absence of π substituents, the compounds are practically UV-transparent. Since the cage is negatively charged, the electronic excitations of zwitterionic derivatives such as 1 and 11a involve the cage-to-substituent transitions, which exhibit strong solvatochromism 5,8 and may find applications as NLO chromophores.

The Hammett analysis of NMR chemical shifts demonstrated a similar ability to transmit electronic effects through the [closo-1-CB₉H₁₀]⁻ cage and benzene ring, which is significantly higher than that found for the [closo-1-CB₁₁H₁₂]⁻ derivatives. The stronger antipodal effect 6,72 observed in the [closo-1-CB₉] cluster relative to the [closo-1-CB₁₁] may be related to the smaller size and higher electron density for the former as compared to the latter. The only other Hammett correlation previously reported for boron clusters was for ¹³C NMR chemical shifts of C-arylated p-carborane derivatives. 73 A comparison 28 of the slope (ρ values) reported for 1-aryl-p-carboranes with that for ¹³C NMR chemical shifts of 4-substituted biphenyls demonstrates that the transmission of a substituent effect through the 12-vertex carborane cage is about 70% as effective as through the benzene ring. 28 This finding is consistent with results presented in Figure 11.

Figure 13. Proposed mechanism for the formation of 9a.

Summary and Conclusions

The present studies describe an alternative and reliable method for the preparation of amine 2 and dinitrogen derivative 1 and provide good understanding of the properties of the latter and its usefulness as a synthetic intermediate in the preparation of more complex derivatives, including liquid crystals. The method for the formation of amino functionality through the COOH group permits the introduction of an antipodal substituent at the stage of [closo-2-CB₃H₅-2-COOH]⁻. 16 Such compounds are being currently investigated in our laboratory.

In many respects, dinitrogen derivative 1 displays behavior similar to that of benzzenediazonium salt; it has similar stability, undergoes diazo coupling, reacts with sulfur nucleophiles, with pyridine gives C-substituted products, and undergoes heterolysis in MeCN, forming N-substituted acetamide. A detailed analysis of the experimental data and computational results revealed two possible mechanisms for the transformations of 1: the closed-shell zwitterionic pathway through ylide 19 and an open-shell radical pathway involving radical anion 26. The latter is analogous to the nucleophile-induced decomposition of PhN₂⁻ and operates for reagents and solvents, which are good nucleophiles and electron donors (low Ip and low E₁/²(ox)). In the absence of electron donors (reagents with high Ip and E₁/²(ox)) , dinitrogen 1 undergoes heterolytic cleavage of N₂, and the resulting ylide 19 gives products of electrophilic addition. The properties and reactivity, such as the preferential formation of the N-adduct with pyridine, of 19 are very similar to those observed before for the [hypercloso-1-CB₉Me₁₁] ylide. Clearly, more kinetic experiments need to be done for a better understanding of the reactivity of 1 and to provide more evidence for the involvement of ylide 19 and radical anion 26 in transformations of 1.

Experimental results demonstrated that 1 serves as a convenient precursor for the preparation of dialkylsulfonium derivatives such as 9b; the two-step process through 10, a masked thiol generated in situ, is more efficient due to a higher yield of the first step. Also, the diazocoupling of 1, leading to azophenols such as 8, is an efficient process, which has already been exploited for the preparation of ionic liquid crystals. 15 In contrast, the preparation of N-substituted pyridine 11a, which is of interest for the investigation of molecular materials, is a low-yield process of little synthetic value at present.

Spectroscopic investigation indicates significant electronic interactions between the [closo-1-CB₉]⁻ cage and π substituents, which indicates a possibility of control of photophysical properties in specifically designed molecular materials.
Overall, results demonstrate that dinitrogen 1 is an attractive compound for further mechanistic investigation and synthetic applications.

Computational Details

Quantum-mechanical calculations were carried out with the B3LYP74,75 and MP2(fc)76 methods with the 6-31G(d,p) basis set using the Gaussian 98 computational package.77 Geometry optimizations were undertaken using appropriate symmetry constraints and tight convergence limits. Vibrational frequencies were obtained with the B3LYP/6-31G(d,p) method and were used to characterize the nature of the stationary points and to obtain thermodynamic parameters.

Zero-point energy corrections were scaled by 0.9806.78 A population analysis for single-point calculations (MP2//DFT) was performed using the Density keyword. For MP2-level calculations of open-shell species, the spin-projected energies were used for comparative studies.

Experimental Details

Reagents and solvents were obtained commercially. Solvents were dried and deoxygenated before use, and reagents were used as supplied. ZnCl2 was dried by heating at ~100 °C under a vacuum. Reactions were carried out under dry Ar and subsequent manipulations conducted in the air. NMR spectra were obtained at 128.4 MHz (1H), 100.6 MHz (13C), and 400.1 MHz (1H) in CD2Cl2 unless otherwise specified.1H NMR and 13C NMR spectra were referenced to the solvent.

11B chemical shifts are relative to the resonance of the solvent.

11BNMR: δ 0.61, J(1H) 130 Hz, 1H); 5.00 (s, 1H), 4.03 (s, 1H), 2.51 (q, J(1H) 158 Hz, 4H), 1.38 (s, 6H), 1.33 (s, 6H).13CNMR: δ 31.8 (4B), 29.5 (1B), 31.3 (1B), 31.0 (1B), 15.4 (1B), 15.2 (1B). IR: 1772 (C=O), 1662 (C=C) cm−1. 

Preparation of [closo-1-CB9H9-1-N=O](4a)

A suspension of [closo-1-CB9H9-1-COOH]+NEt4+ (3[NEt4]H) (1.14 g, 3.88 mmol) in 

Preparation of [closo-1-CB9H9-1-NH=O](4b)

A suspension of [closo-1-CB9H9-1-COOH]+NEt4+ (3[NEt4]H) (1.14 g, 3.88 mmol) in

Preparation of [closo-1-CB9H9-1-NH=O](4b)

A suspension of [closo-1-CB9H9-1-COOH]+NEt4+ (3[NEt4]H) (1.14 g, 3.88 mmol) in
yellow solid. $^{11}$B$^1$H NMR: $\delta$ -26.1 (4B), -16.0 (4B), 25.1 (1B). IR: 2262 (N=C=O).

A solution of anhydrous tert-butanol (15 mL), anhydrous CH$_3$CN (5 mL), and crude [closo-1-CB$_9$H$_9$-1-NCO]$^-$NEt$_4^+$ (7[NEt$_4$], 1.04 g, 3.58 mmol) was stirred at 90 °C for 2 h, after which solvents were removed, leaving 1.20 g of crude [closo-1-CB$_9$H$_9$-1-NHBoc]$^-$NEt$_4^+$ (4a[NEt$_4$]) as a yellow solid. The crude solid was dissolved in CH$_2$Cl$_2$ and passed through a silica gel plug buffered with 1% NEt$_3$ in CH$_2$Cl$_2$. Elution with a buffered CH$_3$CN/CH$_2$Cl$_2$ solution (1% NEt$_3$, 20% CH$_3$CN, 79% CH$_2$Cl$_2$) afforded 0.68 g (48% yield based on starting acid 3[NEt$_4$]) of pure [closo-1-CB$_9$H$_9$-1-NHBoc]$^-$NEt$_4^+$ (4a[NEt$_4$]) as a light yellow solid: mp 140 °C. $^1$H NMR: $\delta$ 0.45 (q, $J$ = 143 Hz, 4H), 1.19 (t, $J$ = 7.3 Hz, 12H), 1.49 (s, 9H), 1.67 (q, $J$ = 156 Hz, 4H), 3.14 (q, $J$ = 7.3 Hz, 8H), 5.07 (q, $J$ = 151 Hz, 1H), 7.12 (s, 1H), $^{13}$C NMR: $\delta$ 7.7 (N=CH$_2$CH$_3$), 28.6 (C(CH$_3$)$_3$), 47.3 (C(CH$_3$)$_2$), 53.0 (N=CH$_2$CH$_3$), 156.0 (C=O). Carbon associated with the {closo-1-CB$_9$} cluster was not observed. Minor signals at 9.0 and 53.5 ppm were attributed to excess NEt$_4^+$Br$^-$. $^{11}$B NMR: $\delta$ -26.2 (d, $J$ = 135 Hz, 4B), -17.2 (d, $J$ = 152 Hz, 4B), 23.8 (d, $J$ = 158 Hz, 1B). IR: 3505 (N=H), 1737 (C=O) cm$^{-1}$. Anal. Caled for C$_{14}$H$_{39}$B$_9$N$_2$O$_2$: C, 46.10; H, 10.78; N, 7.38. Found: C, 46.26; H, 10.76; N, 7.53.

Subsequent fractions produced 0.56 g of a 30:70 mixture of [closo-1-CB$_9$H$_9$-1-COOH]$^-$NEt$_4^+$ (3[NEt$_4$]) and [closo-1-CB$_9$H$_9$-1-NH$_2$]$^-$NEt$_4^+$ (2[NEt$_4$]). $^1$H NMR: $\delta$ 1.23 (t, $J$ = 7.2 Hz, 12H), 3.19 (q, $J$ = 8.0 Hz, 8H), 7.31 (s, 2H). $^{11}$B $^1$H NMR: $\delta$ -26.1 (4B), -17.1 (4B), 24.1 (1B), [lit.$^{11}$ data for (2[NHEt$_3$]): $^1$H NMR: $\delta$ 0.91 (4H), 1.69 (4H), 5.40 (1H), 8.52 (2H). $^{11}$B NMR: $\delta$ -25.8 (4B), -17.2 (4B), 26.0 (1B)]

Acknowledgment. Financial support for this work was received from the National Science Foundation (DMR-0111657 and DMR-0606317). We thank Mr. Andrzej Balinski for his technical assistance with the isolation of 11b[H].

Supporting Information Available: Experimental procedures for the reactions of 1 and analytical data for products, COSY spectra for 11c[H] and 11d[H], kinetic data for the decomposition of 1, Hammett correlation data, and details of computational results. This material is available free of charge via the Internet at http://pubs.acs.org.