Diazotization of the Amino Acid \([\textit{closo}-1-\text{CB}_9\text{H}_8^{-1}-\text{COOH}-6-\text{NH}_3]\) and Reactivity of the \([\textit{closo}-1-\text{CB}_9\text{H}_8^{-1}-\text{COO}-6-\text{N}_2]^-\) Anion

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Supporting Information

ABSTRACT: A comparative study of the reactivity of dinitrogen acids \([\textit{closo}-1-\text{CB}_9\text{H}_8^{-1}-\text{COOH}-10-\text{N}_2]\) (3[10]) and \([\textit{closo}-1-\text{CB}_9\text{H}_8^{-1}-\text{COOH}-6-\text{N}_2]\) (3[6]) was conducted by diazotization of a mixture of amino acids \([\textit{closo}-1-\text{CB}_9\text{H}_8^{-1}-\text{COOH}-6-\text{NH}_3]\) (1[6]) and \([\textit{closo}-1-\text{CB}_9\text{H}_8^{-1}-\text{COOH}-10-\text{NH}_3]\) (1[10]) with \(\text{NO}_2^+\text{BF}_4^-\) in the presence of a heterocyclic base (pyridine, 4-methoxy pyridine, 2-picoline, or quinoline). The 10-amino acid 1[10] formed an isolable stable 10-dinitrogen acid 3[10], while the 6-dinitrogen carboxylate 3[6] reacted in situ, giving products of N-substitution at the B6 position with the heterocyclic solvent (4[6]). The molecular and crystal structures for pyridinium acid 4[6]a were determined by X-ray crystallography. The electronic structures and reactivity of the 6-dinitrogen derivatives of the \{1-\text{CB}_9\} cluster were assessed computationally at the B3LYP/6-31G(d,p) and MP2/6-31G(d,p) levels of theory and compared to those of the 10-dinitrogen, 2-dinitrogen, and 1-dinitrogen analogues.

INTRODUCTION

Apical dinitrogen derivatives of the \([\textit{closo}-\text{B}_{10}\text{H}_{10}]^{-2}\) and \([\textit{closo}-1-\text{CB}_9\text{H}_8]^-\) clusters have been shown to be isolable and stable.1–8 Intermediates used in the preparation of a variety of nitrogen,1–6,8 sulfur,3,5,9–11 oxygen,12 and even carbon3 derivatives, which include liquid crystals.10,13–16 The robustness of such dinitrogen derivatives originates from the electronic interaction between the cluster and the N2 group, which appears to be apical for the apical positions (1 and 10) of the 10-vertex \(\textit{closo}\)-boranes.17 However, to the best of our knowledge, derivatives of 10-vertex \(\textit{closo}\)-boranes with the dinitrogen group at the equatorial position have not been investigated either experimentally or computationally. One obstacle to experimental studies of such derivatives of the \{1-\text{CB}_9\} cluster is the lack of appropriate amino derivatives.

Recently, we demonstrated6 the preparation of an amino acid \([\textit{closo}-1-\text{CB}_9\text{H}_8^{-1}-\text{COOH}-10-\text{NH}_3]\) (1[10]) by palladium-catalyzed amination of iodo acid \([\textit{closo}-1-\text{CB}_9\text{H}_8^{-1}-\text{COOH}-10-\text{I}]^-\) (2[10]), which was separated from isomeric iodo acid 2[6]. Our preliminary results indicated that the amination procedure is effective for a mixture of iodo acids 2[10] and 2[6], and a mixture of amino acids \([\textit{closo}-1-\text{CB}_9\text{H}_8^{-1}-\text{COOH}-6-\text{NH}_3]\) (1[6]) and 1[10] could be obtained.6 Diazotization of this mixture of amino acids would provide an opportunity to study the generation and reactivity of \([\textit{closo}-1-\text{CB}_9\text{H}_8^{-1}-\text{COOH}-6-\text{N}_2]\) (3[6]), the first example of an equatorial dinitrogen derivative of a 10-vertex \(\textit{closo}\)-borane.

Here, we report comparative studies of diazotizations of a mixture of amino acids 1[6] and 1[10] in solutions of heteroaromatic bases (pyridine, \(p\)-methoxy pyridine, 2-picoline, and quinoline), the formation of dinitrogen acids 3[6] and 3[10], and their reactivity. The heterocycles were chosen in such a way as to vary their basicity and steric effects. The structure of one of the reaction products was confirmed by single-crystal X-ray analysis. The experimental results are augmented with computational analysis of the electronic structures and thermo dynamic stability of selected B6 derivatives and a comparison to their isomeric B10, B2, and C1 analogues.

RESULTS AND DISCUSSION

Synthesis. A 4:1 mixture of iodo acids 2[6] and 2[10] was aminated with \(\text{LiN(SiMe}_3\text{)}_2\) in the presence of \(\text{Pd}(0)\) using conditions previously described for the pure 2[10] derivative (Scheme 1).6 The amino acids 1[6] and 1[10] were obtained in about a 5:1 ratio and 37% yield. In another experiment, the ratio of isolated amino acids increased to 12:1 with a yield of 47%.19 The mixture was contaminated with up to 7% of the parent acid \([\textit{closo}-1-\text{CB}_9\text{H}_8^{-1}-\text{COOH}]^-\) and used in subsequent studies without further separation.

We previously demonstrated that, for successful diazotization of 1[10] and the formation of dinitrogen acid 3[10], the reaction mixture must contain a base such as pyridine.6 Diazotization of a mixture of amino acids under these conditions (MeCN containing pyridine) gave 3[10], the 6-pyridinium derivative \([\textit{closo}-1-\text{CB}_9\text{H}_8^{-1}-\text{COOH}-6-C_2\text{H}_5\text{N}]^-\) (4[6]a), and another \{1-\text{CB}_9\} product derived presumably from MeCN. To eliminate side
reactions with MeCN, diazotization reactions were conducted in neat pyridine. A reaction of enriched 6-amino acid 1[6] (∼90% pure) with NO\(^{−}\)BF\(_4^{−}\) in pyridine at −20 °C gave 6-pyridinium acid 4[6]a as the sole product isolated in 58% yield (entry 1, Table 1), with only traces of 10-dinitrogen acid 3[10] observed by \(^{11}\)B NMR (Scheme 2). As in experiments with pure 10-amino acid 1[10], no 10-pyridinium acid 4[10]a was detected under these conditions.

A similar reaction of a 5:1 mixture of the amino acids in neat 4-methoxypyridine gave full conversion of the reactants to 6-aminium acid 4[6]b and 10-dinitrogen acid 3[10] as the only products observed in \(^{11}\)B NMR. The former was isolated by chromatography in 73% yield corrected for the content of amino acid 4[6]. The latter was observed in the crude reaction mixture. Of amino acid 1[6] by \(^{11}\)B NMR. Aromatic diazotization separation and calculation based on the content of amino acid 1[6] in the mixture. Dinitrogen acid 3[10] was observed in the crude reaction mixture. Dinitrogen acid 3[10] was not observed in the crude reaction mixture.

Mechanistic Analysis. The reaction of 6-amino acid 1[6] and the formation of pyridinium adduct 4[6] appear to be similar to that of the 10-amino acid 1[10] and presumably involve deprotonation of the ammonium group, diazotization of the resulting amino group, and decomposition of the apparently unstable dinitrogen derivative 3[6]. The resulting boronium ylide 5[6] is trapped with nucleophilic pyridine (Scheme 3). Formation of the N-regioisomer 4[6] as the only observable product supports heterolytic cleavage of the B−N bond in 3[6] and formation of the ylide 5[6] and is consistent with that of the 10-isomer 3[10]. In contrast, the C1 dinitrogen derivative [closo-1-CB₉H₈-6-CN\(^{-}\)] (6[1]) undergoes nucleophile-assisted homolytic cleavage of the C−N bond and yields C-substituted pyridine. For a better understanding of the experimental results for 1[6] and 1[10], we conducted theoretical analyses for a series of four isomeric derivatives of 1-CB₃, which for simplicity were lacking the COOH group.

MP2/6-31G(d,p) level calculations demonstrated that the parent [closo-1-CB₃H₄-6-NH₂]\(^−\) is highly basic. Using Scheme 4 and the experimental pK\(_a\) value \(^{24}\) for [closo-1-CB₃H₄-10-NH₃], its pK\(_a\) was estimated at 18.1, which is lower by 3.7 than pK\(_a\) for the 10-amino analogue [closo-1-CB₃H₄-10-NH₂]\(^−\) in aqueous EtOH (Table 2). This suggests that the equilibrium in Scheme 3 is shifted further to the right for [closo-1-CB₃H₄-10-NH₂] than for the 10-isomer 1[10] and the higher concentration of free amine [closo-1-CB₃H₄-6-COO-6-NH₂]\(^2−\) in solution results in faster diazotization of 6-amino than the 10-amino isomer. This is consistent with the experimental results, which show that quinoline, which is less basic than pyridine, conversion of 1[6] is much faster than that of its 10-isomer 1[10]. A comparison of the four isomeric amines [closo-1-CB₃H₄-6-NH₂] demonstrates that the closer the substituent is to the C1 position, the less basic the amine is (Table 2).

The parent 6-dinitrogen derivative [closo-1-CB₃H₄-6-N₂] (6[6]) is the least stable among the four regioisomers 6. The calculated free energy \(\Delta G_{298} = 18.1\) kcal/mol for heterolysis of the B−N bond in 6[6] is lower by nearly 13 kcal/mol than that

<table>
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<th>yield of 4[10] (%)c</th>
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<tbody>
<tr>
<td>1</td>
<td>pyridine</td>
<td>100</td>
<td>a, 58c</td>
</tr>
<tr>
<td>2</td>
<td>4-methoxypyridine</td>
<td>100</td>
<td>b, 73c</td>
</tr>
<tr>
<td>3</td>
<td>2-picoline</td>
<td>50</td>
<td>c, 24c</td>
</tr>
<tr>
<td>4</td>
<td>quinoline</td>
<td>30</td>
<td>d, 3c</td>
</tr>
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</table>

\(^{a}\) Reaction conditions: 3 equiv of NO\(^{−}\)BF\(_4^{−}\) added to a solution of 0.5 mmol of 1 in ∼3 mL of solvent at −20 °C (entries 1−3) or 0 °C (entry 4); reaction time 3 h. The ratio of 1[6]/1[10] in entry 1 is 12:1, and that in entries 3 and 4 is 5:1. \(^{b}\) Percent of reacted amino acid 1[6] by \(^{11}\)B NMR. \(^{c}\) After chromatographic separation and calculation based on the content of amino acid 1[6] in the mixture. \(^{d}\) Dinitrogen acid 3[10] was observed in the crude reaction mixture. \(^{e}\) Dinitrogen acid 3[10] was not observed in the crude reaction mixture.

Table 1. Results for Diazotization of Mixtures of 1[6] and 1[10]a

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dx.doi.org/10.1021/ic102557s | Inorg. Chem. 2011, 50, 2654–2660
for the 10-dinitrogen isomer $6[10]$ and by about 5 kcal/mol than those for $6[1]$ and $6[2].$ The order of stability, $6[10] > 6[1] > 6[6]$, is consistent with experimental observations showing that the dinitrogen acid $3[10]$ is stable to storage, and in solutions at ambient temperature, $6[1]$ is stable in the solid state but slowly decomposes in solutions at ambient temperature, while the $3[6]$ derivative easily undergoes dissociation even at low temperatures. Computational results demonstrate that the 2-dinitrogen derivative $6[2]$ has a stability comparable to that of $6[1]$, which suggests the possibility of its isolation.

The difference in the stability of the dinitrogen group in $6$ originates in the efficiency of the molecular orbital (MO) overlap between the N$_2$ fragment and the $\{1$-CB$_9\}$ cage and also the electron density at the point of attachment to the cage. In the apical isomers $6[10]$ and $6[1]$, the double-degenerate $\pi$-symmetry MO of the cage provides electronic communication with the N$_2$ $\pi$ system, which is more effective than that between the nondegenerate $\pi$-symmetry MO of the $\{1$-CB$_9\}$ cage and N$_2$ in the equatorial isomers $6[6]$ and $6[2]$ (Figure 2). Analysis of the bonding in the three B isomers shows that the B–N distance increases from 1.459 Å in the 10-isomer $6[10]$ to 1.491 Å in $6[6]$ to 1.499 Å in the 2-isomer $6[2]$ (Table 3). At the same time, the N–N distance decreases from 1.138 to 1.135 Å in the same order. This trend is paralleled by Wiberg bond index (WBI) values, which indicate a progressively weaker B–N bond and increasing triple-bond character between the N atoms in the series $6[10]$, $6[6]$, and $6[2]$ (Table 3). This is consistent with the lower enthalpy of decomposition of the two equatorial dinitrogen derivatives $6[6]$ and $6[2]$ than the axial analogue $6[10]$ by 13.1 and 8.0 kcal/mol, respectively. The 2-dinitrogen derivative $6[2]$ has a higher endotherm of decomposition than is expected from the WBI trend because of the significantly lower electron density of the B$_2$ atom than the B$_6$ atom measured by the atomic charge $q_B$ of $+0.13$ versus $-0.08$ (Table 3).

Analysis of the data for 1-dinitrogen $6[1]$ demonstrates that it has higher bond order between the cage and N$_2$ fragment and significantly less triple-bond character between the N atoms than was observed in the B isomers (Table 3). It is, however, less thermodynamically stable than might be expected from the trend in WBI because of higher negative atomic charge of the C atom ($q_C = -0.52$) and, consequently, a lower tendency to retain the N$_2$ fragment.

This analysis is consistent with the results for benzenediazonium ions, in which substituents that increase the electron density at the C1 atom stabilize the transition state and, hence, destabilize the diazonium ion, while electron-withdrawing substituents stabilize the cation against heterolysis. Overall, the N$_2$ fragment is the least strongly held by the $\{1$-CB$_9\}$ cage in the 6 position, and the B$_6$–N bond most easily undergoes heterolysis, forming ylide $7[6]$. 

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**Figure 1.** Thermal ellipsoid diagram representations of $4[6]a$ and drawn at 50% probability. Selected interatomic distances (Å) and angles (deg): B6–N1, 1.5470(18); C1–B (av), 1.6089; C1–C2, 1.4835(18); C1–B10, 3.543; C2–C1–B (av), 125.7; N1–B6–B10, 121.59(11); O1–C2–O2, 123.54(12); C3–N1–B6–B10, 6.09(19); C3–N1–B6–B2, 139.18(12); O1–C2–C1–B2, –6.6(2).
derivatives, the 10- and 6-isomers have comparable stability, while the B2 analogues are generally less thermodynamically stable. In contrast, the 6-boronium ylide \(7\{6\}\) appears to be more stable than the 10-isomer \(7\{10\}\) by 12.1 kcal/mol, according to MP2/6-31G(d,p) level calculations in the gas phase.

The process for transformation of the dinitrogen carboxylate anions \(3\), which exist in pyridine solutions (Figure 4), to pyridinium derivatives is similar to that of the parent dinitrogen compounds. Heterolysis of the B–N bond is more favorable for the 6-isomer \(3\{6\}\) than for the 10-isomer \(3\{10\}\) by nearly 14 kcal/mol. The calculated \(\Delta G_{298}\) of 17.2 kcal/mol for the former is sufficiently low for the process to take place in situ at low temperature, while \(\Delta G_{298}\) of 31.3 kcal/mol for the 10-isomer \(3\{10\}\) is high enough for the compound to be stable under these conditions.

**Electronic Spectroscopy.** The UV absorption spectrum of \(4\{6\}\) in MeCN showed a moderately strong absorption band with a maximum at 264 nm and vibronic splitting of about 810 cm\(^{-1}\) (Figure 5). This is essentially the same wavelength as that recorded\(^{25}\) for the 10-vertex pyridinium acid \(4\{10\}\). ZINDO//MP2/6-31G(d,p) level calculations for global minima of \(4\{10\}\) and \(4\{6\}\) revealed that their lowest energy transitions occur at 351 and 352 nm, respectively, and involves excitation from the highest occupied MO, localized mainly on the cage, to the LUMO, localized on the pyridine ring. Both transitions exhibit a significant hypsochromic shift, and in a MeCN dielectric medium, the transitions are calculated at 303 nm for \(4\{10\}\) and 317 nm for \(4\{6\}\).\(^{27}\)

Excitation of \(4\{10\}\) at 263 nm results in a weak fluorescence with a maximum at 426 nm. No emission was observed for the 6-pyridinium analogue \(4\{6\}\).

### SUMMARY AND CONCLUSIONS

The results demonstrate that 6-iodo acid \(2\{6\}\) can be effectively aminated using LiN(SiMe\(_3\))\(_2\) in the presence of Pd(0). Diazotization of the resulting 6-amino acid \(1\{6\}\) in solutions of aromatic amines leads to the replacement of the NH\(_2\) group with a solvent molecule. The mechanism involves the initial formation of the unstable 6-dinitrogen derivative \(3\{6\}\), which in situ undergoes heterolysis of the B–N bond. The resulting electrophilic boronium ylide \(5\{6\}\) is trapped by a nucleophilic solvent. The reaction appears to be efficient and synthetically useful for basic and sterically unhindered heteroaromatic bases such as pyridine and 4-methoxypyridine.

The results of theoretical analysis of the two dinitrogen carboxylate anions \(3\{6\}\) and \(3\{10\}\) and a series of regioisomeric amino and dinitrogen derivatives of \{closo-1-CB\(_9\)\} are consistent with experimental data. Analysis of a series of isomeric amines demonstrates that their basicity increases with an increase in the distance from the C1 position. A comparison of the electronic structures and stabilities of the parent dinitrogen derivatives 6 shows significant differences between C–N and B–N bonding in the series and the importance of the electron density at the substitution site for their stability. Computational results suggest that the stability of the dinitrogen derivatives can be increased by using electron-withdrawing substituents on the cage, which decrease the electron density of the atom substituted with the N\(_2\) fragment.

The presented findings open up the possibility for conversion of other B-amino compounds, whose \(pK_a\) is not greater than that of \(1\{10\}\), to pyridinium derivatives. Computational results...
indicate that amino derivatives of the \{closo-1-CB_{11}\} cluster are suitable substrates for such a diazotization/substitution reaction, while amino derivatives of \{closo-B_{12}\} and \{closo-B_{10}\} clusters are too basic for the process to be efficient. The introduction of other substituents using this diazotization method still poses a challenge because of the solubility of the amino acid and compatibility of the solvent/nucleophile with the nitrosonium cation.

## COMPUTATIONAL DETAILS

Quantum mechanical calculations were carried out with the B3LYP\textsuperscript{28,29} and MP2(fc)\textsuperscript{30} methods with a 6-31G(d,p) basis set using the Gaussian 09 package.\textsuperscript{31} Geometry optimizations were undertaken using the appropriate symmetry constraints and tight convergence limits. Vibrational frequencies were used to characterize the nature of the stationary points and to obtain thermodynamic parameters. Zero-point-energy corrections were scaled by 0.9806.\textsuperscript{32} Hybridization parameters, WBI matrices, and natural charges were obtained using the natural bond order (NBO) algorithm supplied in the Gaussian 09 package.\textsuperscript{32} Population analysis of the MP2 wave function (MP2//MP2) was performed using the DENSITY(MP2) keyword. The isodensity polarizable continuum solvation model (IPCM)\textsuperscript{34} was used with default parameters and $\varepsilon = 52.5$ for EtOH/H$_2$O (1:1, v/v) at 25 °C, which was interpolated from the reported values for EtOH/H$_2$O mixtures.\textsuperscript{35}

### Figure 2. MP2/6-31G(d,p)-derived contours and energies for the relevant MOs of dinitrogen derivatives 6. For 6[10] and 6[1], only one of the two degenerate MOs is shown.

### Table 3. Bonding Properties of the Isomeric Dinitrogen Derivatives\textsuperscript{a}

<table>
<thead>
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<tr>
<td>$d_{X-N}$/Å</td>
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<td>1.491</td>
<td>1.499</td>
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<tr>
<td>$d_{N-N}$/Å</td>
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<td>2.51</td>
<td>2.33</td>
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<td>X</td>
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<td>sp$^{5.2}$</td>
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<td>sp$^{0.8}$</td>
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<tr>
<td>$q_N$</td>
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<td>+0.13</td>
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<td>+0.21</td>
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</table>

\textsuperscript{a}NBO analysis of the MP2/6-31G(d,p) wave function. X = B for 6[10], 6[6], and 6[2]. X = C for 6[1].

### Table 4. Relative Thermodynamic Stability for Selected Pairs of Isomers\textsuperscript{a}

<table>
<thead>
<tr>
<th></th>
<th>$\Delta H = H_{[1]} - H_{[10]}$ (kcal/mol)</th>
<th>$\Delta H = H_{[1]} - H_{[6]}$ (kcal/mol)</th>
<th>$\Delta H = H_{[1]} - H_{[2]}$ (kcal/mol)</th>
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<td>N$_2$</td>
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<td>+,b</td>
<td>+44.5</td>
<td>+56.6</td>
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</tr>
<tr>
<td>pyridinium</td>
<td>+38.9</td>
<td>+38.1</td>
<td>+31.0</td>
</tr>
</tbody>
</table>

\textsuperscript{a}The MP2/6-31G(d,p) level with density functional theory thermodynamic corrections. The difference in the enthalpy of formation between the [1] and [X] isomers. \textsuperscript{b}Vacant orbital in the ylide.

dx.doi.org/10.1021/ic102557s | Inorg. Chem. 2011, 50, 2654–2660

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Excitation energies for 6-pyridinium acid 4[6]a were obtained at its MP2-determined geometry using the INDO/2 algorithm (ZINDO)\(^{36}\) as supplied in Cerius2 suite of programs and including all electrons and orbitals in the configuration interaction. ZINDO calculations with the solvation model (self-consistent reaction field, SCRF) in the MeCN medium (\(\epsilon = 36.64, n = 1.3441\)) used cavity radii (5.02 Å for 4[10]a and 5.10 Å for 4[6]a) derived from the MP2 calculations with the VOLUME and DENSITY(MP2) keywords.

**Experimental Section**

Reagents and solvents were obtained commercially. Pyridine, 4-methoxypyridine, 2-picoline, and quinoline were distilled from CaH\(_2\), stored under argon, and cooled to \(-78^\circ\text{C}\). Amino Acids 1[6] and 1[10].

General Procedure for Diazotization of a Mixture of Amino Acids 1[6] and 1[10]. Under argon, a mixture of amino acids 1[6] and 1[10] (0.5 mmol) was dissolved in neat amine (~3 mL) and cooled to \(-20^\circ\text{C}\) (reactions in quinoline were run at 0 °C). To the resulting light-yellow solution was added NO\(^+\)BF\(_4\)^– (3 equiv), and the reaction mixture was stirred for 3 h at the same temperature. The reaction mixture was diluted with 10% HCl (30 mL), and the products were extracted into Et\(_2\)O (3 × 10 mL). The combined Et\(_2\)O layers were washed with 10% HCl (30 mL) and dried (Na\(_2\)SO\(_4\)), and the solvents were evaporated to dryness. The crude product was passed through a short silica gel plug (CH\(_3\)OH/CH\(_2\)Cl\(_2\), 1:19) and washed with boiling isooctane followed by hot water, and analytical samples of 4[6]a–4[6]c were obtained by recrystallization from aqueous solution. Compound 4[6]d was purified only by column chromatography. Yields are calculated on the content of amino acid 1[6] in the mixture.

**Figure 4.** Enthalpy, \(\Delta H\) (kcal/mol), of reaction of dinitrogen carboxylates in a pyridine dielectric medium. MP2/6-31G(d,p)/MP2/6-31G(d,p) level with density functional theory thermodynamic corrections (PCM).

**Figure 5.** Electronic absorption spectra for pyridinium acids 4[6]a and 4[10]a recorded in CH\(_3\)CN.
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Amination of a Mixture of [closo-1-C₆B₉H₆-1-COOH-6-NH₃] (2) and [closo-1-C₆B₉H₆-1-COOH-10-NH₃] (2). Following the literature procedure, a 4:1 mixture of keto acids 2 and 2 (2.0 g, 5.5 mmol) was transformed into 0.370 g of product containing 90% amino acid 1 [6], 15% amino acid 1 [10], 7% of [closo-1-C₆B₉H₆-1-COOH-9] (B10 (CD₂CN) δ 34.4 ppm), and 4% of an unknown [closo-1-C₆B₉] cluster derivative (B10 (CD₂CN) δ 40.1 ppm), according to 1B NMR. A second attempt starting from another 4:1 mixture of keto acids 2 and 2 (1.34 g, 3.69 mmol) gave 0.311 g of product containing 90% amino acid 1 [6], 7% amino acid 1 [10], and about 3% of [closo-1-C₆B₉H₆-1-COOH] [8].

Major signals attributed to [closo-1-C₆B₉H₆-1-COOH-6-NH₃] (1) [6], 1B NMR (CD₂CN, 400 MHz): δ 0.8–2.8 (m, 8H), 4.87 (t, J = 46 Hz, 3H), 5.6 (q, J = 156 Hz, 1H), 9.53 (s, 1H). 1B NMR (CD₂CN, 128 MHz): δ = 26.3 (d, J = 144 Hz, 1B), –20.6 (d, J = 144 Hz, 1B), –0.6 (d, J = 156 Hz, 2B), –16.7 (d, J = 156 Hz, 2B), –12.3 (s, 1B), –11.7 (d, J = 141 Hz, 2B), 30.0 (d, J = 154 Hz, 1B).

**ASSOCIATED CONTENT**

**Supporting Information.** Table with calculated reaction energies, full crystal data collection information for 4[a], archive files of MEP equilibrium geometries for selected molecules. This material is available free of charge via the Internet at http://pubs.acs.org.

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**ACKNOWLEDGMENT**

This project was supported by NSF Grant DMR-0907542.

**REFERENCES**

(19) The yield and proportions of the two amino acids vary from run to run presumably because of the quality of LiN(TMS), and the workup details.
(23) Crystal data for 4[a] (CCDC no. 804225): C₁₂H₁₀B₁₂N₂O₂, monoclinic, P2₁/n, a = 6.5604(7), β = 18.4803(18), c = 10.8552(11), V = 198.3(1), Z = 4, T = 123(2) K, λ = 0.71073 Å, R(F²) = 0.0387 or Rw(F²) = 0.0999 [for 2252 reflections with I > 2σ(I)]. For details, see the Supporting Information.
(25) For details, see the Supporting Information.
(27) The calculated excitation energy depends on the radius of the cavity used in the SCRF calculations. For the two acids, higher energies are obtained for smaller cavities.