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Transmission of Electronic Effects through the {*closo*-1-CB_9} and {*closo*-1-CB_{11}} Cages: Apparent Dissociation Constants for Series of [*closo*-1-CB_9H_8-1-COOH-10-X] and [*closo*-1-$CB_{11}H_{10}$-1-COOH-12-X] Acids

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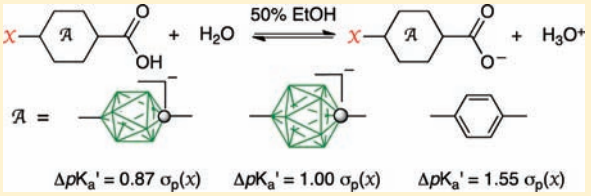
Supporting Information

ABSTRACT: The apparent ionization constants pK_a' for series of carboxylic acids [*closo*-1-CB_9H_8-1-COOH-10-X]$^-$ (**1**) and [*closo*-1-$CB_{11}H_{10}$-1-COOH-12-X]$^-$ (**2**), where X = H, I, *n*-C_6H_{13}, $^+NMe_3$, $^+N_2$, $^+SMe_2$, OC_5H_{11}, were measured in EtOH/H_2O (1/1, v/v) at 24 °C. Correlation analysis of the pK_a' values using Hammett substituent constants σ_p(X) gave the reaction constant ρ = 0.87 ± 0.04 for series **1** and ρ = 1.00 ± 0.09 for series **2**. These values are higher than for derivatives of PhCH═CHCOOH (ρ = 0.70 ± 0.09 in 55% EtOH) and correspond to 56% and 65% efficiencies in transmission of electronic effects by [*closo*-1-CB_9H_{10}]$^-$ (**E**) and [*closo*-1-$CB_{11}H_{12}$]$^-$ (**F**), respectively, as compared to benzene (**A**). Experimental results were supported with DFT calculations of relative acidity for series of acids derived from **A**, **E**, and **F** in aqueous medium.



INTRODUCTION

The rational design of functional molecules for electronic and photonic applications requires rigid and linear structural elements[1] for which the ability to transmit electronic effects is known.[2] Some elements must be weakly interacting (electronically insulating), while others are expected to be efficient conduits for electronic effects and also for charge and energy transport. Therefore, the degree of electronic coupling between various structural elements in designing functional molecules is of particular interest.

Benzene (**A**, Figure 1) is the classical structural element of efficient electronic conjugation with π substituents and is generally considered one of the most effective conduits of electronic effects by both resonance and inductive mechanisms. On the other hand, only inductive and field effects are transmitted through the aliphatic bicyclo[2.2.2]octane (BCO, **B**) ring.[3,4] Other structural elements that may serve as potential conduits for electronic effects include the 10- and 12-vertex *closo*-boranes, such as carboranes **C** and **D**, which are considered to be σ aromatic,[5,6] possess the ability to interact with π substituents,[7−10] and exhibit a strong "antipodal" effect (or the A effect).[11,12] The strength of these interactions appears to follow the order **A** > **C** > **D** ≫ **B**.[8,9]

The first studies of the transmission of electronic effects through boron clusters focused on donor−acceptor derivatives of carborane **D**. Investigations by spectroscopic[13] and subsequently dipole moment additivity methods[10] concluded that the 12-vertex *p*-carborane (**D**) does indeed transmit electronic effects, although it is a significantly weaker conduit than benzene (**A**). Recent cyclic voltammetry studies of

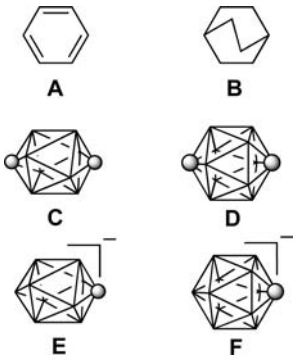


Figure 1. Structures of benzene (**A**), bicyclo[2.2.2]octane (BCO, **B**), 1,10-dicarba-*closo*-decaborane (10-vertex *p*-carborane, **C**), 1,12-dicarba-*closo*-dodecaborane (12-vertex *p*-carborane, **D**), 1-carba-*closo*-decaborate (**E**), and 1-carba-*closo*-dodecaborate (**F**). In **C**−**F** each vertex corresponds to a BH fragment and the sphere represents a carbon atom.

dimetallic derivatives of *p*-carboranes **C** and **D** demonstrated a substantial separation of 1-electron oxidation potentials for the 10-vertex carborane derivatives compared to the 12-vertex analogues.[14,15] A similar separation of anodic potentials was found in a cobalt derivative of **D** (ΔE^o_{ox} = 0.105 V) that was comparable to that found in the benzene analogue (ΔE^o_{ox} =

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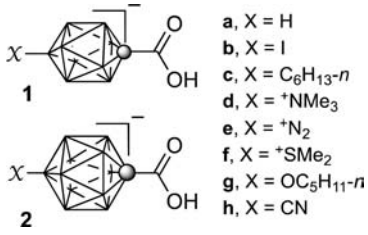
0.110 V).[16] Both results demonstrate significant electronic communication through the carborane cages.

The classic method for studying the degree of transmission of electronic effects through a structural element involves comparing the reactivity of a series of derivatives as a function of a substituent.[17] Most conveniently, an evaluation of ionization constants for a series of substituted carboxylic acids using Hammett's substituent constants[18] $\sigma_p(X)$ provides direct quantitative comparison to benzene as a conduit for electronic effects. Surprisingly, no such systematic investigations for boron clusters have been reported to date,[19] in part due to the lack of appropriate derivatives, especially of monocarbaborates **E** and **F**.

Our recent advances[20−24] in the chemistry of the [*closo*-1-$CB_9H_{10}]^-$ (**E**) and [*closo*-1-$CB_{11}H_{12}]^-$ (**F**) clusters and the availability of several substituted 1-carboxylic acids derived from these clusters provided an opportunity to determine the extent of transmission of the substituent effect through the cages (Figure 1) by Hammett-type correlation analysis. Here we report ionization constant studies of two series of compounds, [*closo*-1-CB_9H_8-1-COOH-10-X]$^-$ (**1**) and [*closo*-1-$CB_{11}H_{10}$-1-COOH-12-X]$^-$ (**2**), which are derived from the parent carboxylic acids [*closo*-1-CB_9H_9-1-COOH]$^-$ (**1a**) and [*closo*-1-$CB_{11}H_{11}$-1-COOH]$^-$ (**2a**), respectively, by substitution in the antipodal position. The apparent dissociation constants pK_a' obtained in EtOH/H_2O (1/1 v/v) were analyzed using substituent constants $\sigma_p(X)$, and the results were compared to those reported for the corresponding 4-substituted benzoic,[25] *trans*-cinnamic,[26] and bicyclo[2.2.2]octane-1-carboxylic acids[3] in the same solvent. Analysis of experimental data is augmented with DFT results of realtive acidity in each series calculated in aqueous medium.



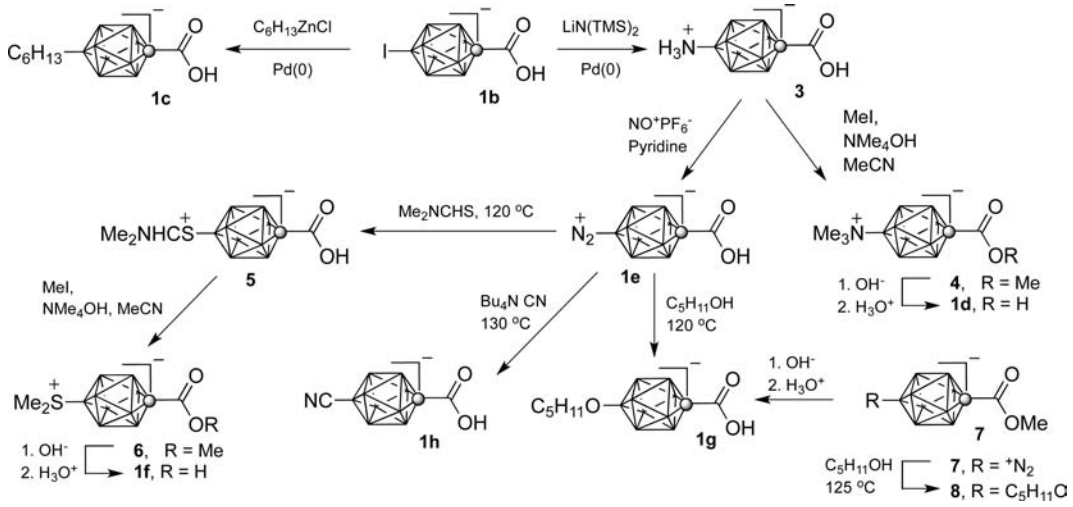
RESULTS AND DISCUSSION

Synthesis. Iodo acid[20,27] **1b** was a convenient precursor to the remaining acids **1** substituted at the B(10) position (Scheme 1). Thus, the reaction of **1b** with hexylzinc chloride under Negishi conditions gave the 10-hexyl acid **1c**.[22] Pd-catalyzed amination of **1b** with $LiN(TMS)_2$ as an ammonia equivalent gave the 10-amino acid **3**.[23,27] Methylation of **3** with MeI resulted in methyl ester **4**, which was hydrolyzed in alcoholic KOH, forming the 10-trimethylammonium acid **1d**. Dinitrogen acid **1e** was obtained by diazotization of amino acid **3** in the presence of pyridine.[23,27] Thermolysis of **1e** in Me_2NCHS gave the masked mercaptan **5**,[23,27] which was methylated with MeI. The resulting methyl ester **6** was hydrolyzed, giving dimethylsulfonium acid **1f**. Thermolysis of dinitrogen acid **1e** in 1-pentanol resulted in the formation of the 10-pentyloxy acid **1g**. Alternatively, acid **1g** was obtained by thermolysis of the dinitrogen acid methyl ester **7**[23] in 1-pentanol followed by hydrolysis of the resulting methyl ester **8** (Scheme 1).

The preparation of 10-cyano acid **1h** was plagued by low yields and difficulties with isolation of pure product. Thus, cyanation of iodo acid **1b** with CuCN in NMP at 160 °C gave mostly insoluble materials, while no reaction occurred at lower temperatures. Pd-catalyzed cyanation of **1b** with $Zn(CN)_2$, according to an analogous general procedure[28] and employing the catalyst previously used in Negishi alkylation of **1b**,[23] resulted in recovery of the starting material. A last attempt involved thermolysis of dinitrogen acid **1e** in dry and molten $[NBu_4]^+CN^-$ at 130 °C. The product obtained as an acid extract from Et_2O and constituting about 16% yield is believed to be the desired acid **1h**, according to MS and IR methods.[29] The majority of the product was presumably a mixture of zwitterions resulting from insertion of the transient boronium ylide[23] into the C−H bond in one of the butyl chains in the $[NBu_4]^+$ cation. This is evident from the significantly downfield chemical shift (~50 ppm in ^{11}B NMR), which is consistent with 10-alkyl derivatives of the [*closo*-1-$CB_9H_{10}]^-$ anion such as **1c**. Attempts to isolate a pure sample of **1h** as a salt were unsuccessful, and the acid was not pursued further.

The parent acid **1a** was isolated as the deiodinated byproduct in the amination reaction of **1b**.[23,27] The dinitrogen acid methyl ester **7** was prepared using a mixture of isomeric iodo acids

Scheme 1



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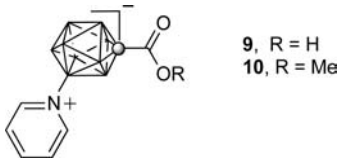
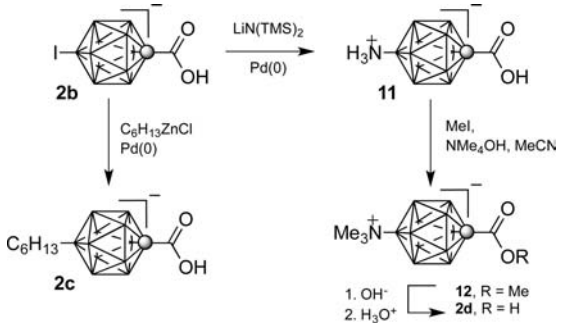
remaining after separation of pure **1b**.[23,27] Thus, a 4/5 mixture of 10-iodo acid **1b** and its 6-iodo analogue was aminated under the usual conditions[27] to give a mixture of amino acids 10-amino **3** and the corresponding 6-isomer. Diazotization of this mixture in pyridine solutions gave both acid **1e** and the 6-pyridinium acid **9**,[30] which was treated with CH_2N_2. The resulting methyl esters **7** and **10** were conveniently separated using chromatography, giving products in 13% and 10% overall yields, respectively.[29]



Access to carboxylic acids **2** derived from the 12-vertex monocarbaborate **F** is limited by the lack of a stable dinitrogen derivative **2e** and relies solely on limited transformations of iodo acid **2b**.[21,31] Thus, iodo acid **2b** was alkylated to form the 12-hexyl acid **2c**[21] and aminated to give the 12-amino acid **11**,[24] as described for the {*closo*-1-CB_9} derivatives (Scheme 2).

Scheme 2

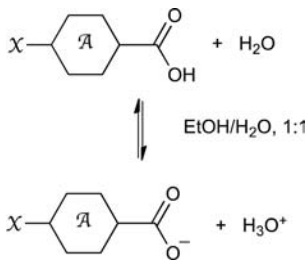


Methylation of **11** with MeI gave 12-trimethylammonium ester **12**, which was hydrolyzed, giving acid **2d** in 79% yield. The parent acid **2a** was prepared by lithiation of monocarbaborate [*closo*-1-$CB_{11}H_{12}$]$^-$ (**F**) followed by carboxylation with CO_2.[31]

Protonation and Deprotonation of Acids 1 and 2. Deprotonation of the carboxyl group with $[NMe_4]^+OH^-$ resulted in upfield shifts of the resonance of the antipodal boron atom: −5 ± 1 ppm for the B(10) nucleus in series **1** and −3 ± 2 ppm for the B(12) nucleus in series **2**.[29] In series **1**, the largest difference was observed for **1c** (−7.0 ppm) and the smallest for **1e** (−3.7 ppm). Replacing the $[NR_4]^+$ counterion in nonzwitterionic acids with hydronium, H_3O^+, by extraction of the ion pair from acidic solutions to Et_2O, resulted in minor deshielding of B(10) in **1** and B(12) in **2** by less than +0.5 ppm in all acids, except for the pentyloxy derivative **1g**. In the latter case, B(10) was shielded by −5.2 ppm, presumably due to protonation of the alkoxy group oxygen atom in **1g** and the formation of a zwitterionic structure. This result is consistent with our findings for amino acid **3** and its methyl ester, which demonstrated high basicity of the nitrogen atom and its preferential protonation, resulting in −10 ppm shielding of the B(10) nucleus.[23] Consequently, the diazotization of **3** and formation of **1e** requires basic conditions, such as the presence of pyridine (Scheme 1).

Dissociation Constant Measurements. Acidity of acids in series **1** and **2** was investigated by potentiometric titration in aqueous EtOH (1/1, v/v), which was previously used as a solvent for the study of substituted benzoic and bicyclo[2.2.2]-octane-1-carboxylic acids. Results are shown in Table 1 and presented in Figure 2.

Table 1. Apparent Ionization Constants pK_a' for Selected Derivatives of [*closo*-1-CB_9H_8-1-COOH-10-X] (1) and [*closo*-1-$CB_{11}H_{10}$-1-COOH-12-X] (2) in 50% EtOH (v/v) at 24 °C



	X \ A	1	2
a	H	6.53±0.02 [a]	6.17±0.02 [a]
b	I	6.38±0.02 [b]	5.86±0.02 [a]
c	*n*-C_6H_{13}	6.87±0.03 [b]	6.36±003 [a]
d	$^+NMe_3$	5.83±0.02	5.38±0.04
e	$^+N_2$	4.93±0.03	–
f	$^+SMe_2$	5.68±0.02	–
g	*n*-$C_5H_{11}O$	6.90±0.03 [a]	–

[a]The $[NEt_4]^+$ counterion. [b]The $[NMe_4]^+$ counterion.

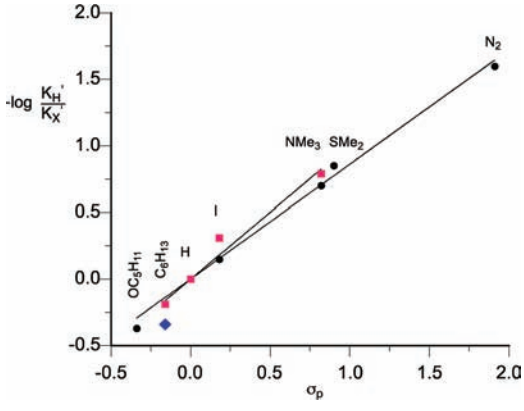


Figure 2. Hammett plot of $\Delta pK_a'$ values for derivatives of [*closo*-1-CB_9H_8-1-COOH-10-X]$^-$ (**1**; black dots, ρ = 0.87 ± 0.04, r^2 = 0.99) and [*closo*-1-$CB_{11}H_{10}$-1-COOH-12-X]$^-$ (**2**; red squares, ρ = 1.00 ± 0.09, r^2 = 0.97) in 50% EtOH (v/v) at 24 °C. The blue diamond represents the data point for **1c**.

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Results in Table 1 show that carboxylic acids derived from [*closo*-1-$CB_{11}H_{12}$]$^-$ (**F**) are generally more acidic than those derived from the 10-vertex analogue **E**. For four parent acids the acidity decreases in the following order: PhCOOH (pK_a' = 5.66) > **2a** (pK_a' = 6.17) > **1a** (pK_a' = 6.53) > BCO−COOH (pK_a' = 6.74)[3] in 50% EtOH.

A plot of $\Delta pK_a' = pK_H' - pK_X'$ values for series **1** against standard $\sigma_p(X)$ parameters[18] demonstrated good correlation, and regression analysis of the data gave the reaction constant ρ = 0.87 ± 0.04 (r^2 = 0.98). When the most outlying data point for hexyl acid **1c** was removed, the correlation improved (ρ = 0.86 ± 0.02, r^2 = 0.99). The pK_a' value for **1c** may be higher than expected due to aggregation of the hydrophobic hexyl chains in the aqueous medium, which affects the ionization constant. Essentially the same value of ρ was obtained for series **1** without including the data points for **1c**,**g**. The slope (reaction constant ρ) depends heavily on the far right data point for dinitrogen acid **1e**. When this data point was removed from the correlation, the value of ρ increased to 0.93 ± 0.07, but with a larger error (r^2 = 0.97). Overall, the values of ρ for full or partial sets of acids **1** are within 1 standard deviation. The same analysis for the series of 12-vertex carboxylic acids **2** shows a reaction constant, ρ = 1.00 ± 0.09 (r^2 = 0.97), slightly higher than that obtained for the 10-vertex series **1** (either full or comparable data sets).

The reaction constants, ρ, obtained for series **1** and **2** are smaller than those obtained in correlations of $\Delta pK_a'$ values for *p*-substituted benzoic acids at 25 °C with the same set of $\sigma_p(X)$ parameters[18] (ρ = 1.55 ± 0.04, r^2 = 0.99).[25] Similar analysis for five para-substituted *trans*-cinnamic acids (55% EtOH, v/v, 25 °C) gave a ρ value that is about half of those for benzoic acids (ρ = 0.70 ± 0.09, r^2 = 0.94).[26] Thus, the results indicate that the effectiveness of the transmission of electronic effects follows the order benzene (**A**) > [*closo*-1-$CB_{11}H_{12}$]$^-$ (**F**) > [*closo*-1-CB_9H_{10}]$^-$ (**E**) > PhCH=CH_2.

A better comparison of the ρ values can be made after normalization for the distance between the carboxyl group and the substituent. According to Hammett, the reaction constant depends on the distance *d* from the substituent X to the reacting group, temperature *T*, and reaction type and medium *C* (eq 1).[32]

$$\rho = \frac{1}{d^2 T} C \qquad (1)$$

Since the only variable in the considered set of reactions is *d*, the experimental ρ values were normalized (eq 2) by using the

$$\rho' = \rho \times d^2 \qquad (2)$$

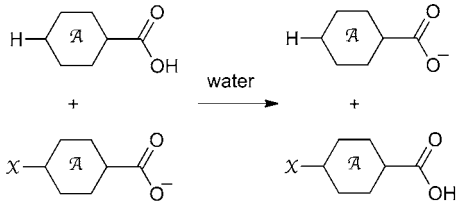
H···C(O) distance that was obtained for each parent acid at the DFT level of theory. Results show that the normalized ρ' values for the boron clusters are similar (ρ' = 33.4 ± 1.5 for **E** and ρ' = 35.3 ± 3.2 for **F**) and significantly lower than those obtained for benzene (44.6 ± 1.2) and styrene (41.9 ± 5.4). This further demonstrates that both clusters, [*closo*-1-CB_9H_{10}]$^-$ and [*closo*-1-$CB_{11}H_{12}$]$^-$, are less efficient conduits for transmission of electronic effects in comparison to classical π systems.

Correlation of $\Delta pK_a'$ values for series **1** and **2** with Swain−Lupton inductive/field parameters[18] *F*(X) was also investigated. In the case of series **1**, fitting to the function $\Delta pK_a' = \rho F(X)$ had a poor correlation factor (ρ = 0.89 ± 0.15, r^2 = 0.82), and the best-fit linear function $\Delta pK_a' = \rho F(X) + \beta$ had an intecept of −0.32 (ρ = 1.18 ± 0.15, r^2 = 0.92). Removing the most outlying data point for the pentyloxy derivative **1g** improved the correlation (ρ = 1.11 ± 0.10, β = −0.21, r^2 = 0.97). This data point is diagnostic for the type of interactions between the substituents and the cage ($\sigma_p(OC_5H_{11})$ = −0.34, $F(OC_5H_{11})$ = +0.29), and the lack of corrrelation with the *F*(X) scale indicates the significance of a resonance-type mechanism in the transmission of electronic effects. For comparison, the available pK_a' data for derivatives of bicyclo[2.2.2]octane-1-carboxylic acid[3,33] correlate well with the parameters *F*(X) (ρ = 1.50 ± 0.10, r^2 = 0.96) but poorly with parameters $\sigma_p(X)$. This clearly demonstrates that the transmission of electronic effects through the {*closo*-1-CB_9} cage involves both a type of resonance and inductive/field mechanisms related to the "antipodal" effect observed in boron clusters.

Analysis of the relatively short series of acids **2** demonstrated a correlation with the field/inductive paramaters *F*(X) better than that found for the 10-vertex derivatives **1**. Thus, correlation of $\Delta pK_a'$ values for the four acids **2a**−**d** with the *F*(X) parameters gave a comparable ρ and smaller intercept (ρ = 1.02 ± 0.13, β = −0.10, r^2 = 0.97) than for the same set of 10-vertex analogues **1a**−**d** (ρ = 0.99 ± 0.25, β = −0.19, r^2 = 0.89). This might suggest that the field/inductive mechanism is more important for transmission of electronic effects in 12-vertex cluster **F**, whereas the resonance mechanism is more significant in the 10-vertex cluster, as is the case for benzene. This conclusion is consistent with results of computational analysis for the 10- and 12-vertex clusters, which demonstrated greater electronic interaction of π substituents with the 10-vertex clusters compared to 12-vertex analogues.[8]

To confirm the experimental results, the free energy change, ΔG_{298}, for the isodesmic reaction shown in Scheme 3 was

Scheme 3



a, X = H; **e**, X = N_2^+; **h**, X = CN; **i**, X = CCH; **j**, X = F; **k**, X = Cl; **l**, X = CH_3; **m**, X = CH_2CH_3; **n**, X = NH_3^+; **o**, X = OH; **p**, X = O^-

calculated using the B3LYP/6-31G(d,p) method and the PCM solvation model for each series of acids. Substituents used in the isodesmic reaction were simple, typically second-row elements, to avoid complications of conformational potential energy surface (Scheme 3).[29]

Results for benzoic acid derivatives show that the calculated ΔG_{298} values generally follow the trend of the Hammett parameters $\sigma_p(X)$, and the correlation is satisfactory (ρ = 6.05 ± 0.24, intercept =0.42 ± 0.16, r^2 = 0.99), after removing data points for **n** (X = $^+NH_3$) and **p** (X = O^-). The isodesmic reaction for the former is excessively exothermic, due to high basicity of the dianion, while the value for the latter reaction is higher than expected by about 2 kcal/mol. To avoid systematic errors, free energy changes in isodesmic reactions for series **1** and **2** were compared directly to those of benzoic acid derivatives, and the results are shown in Figure 3.

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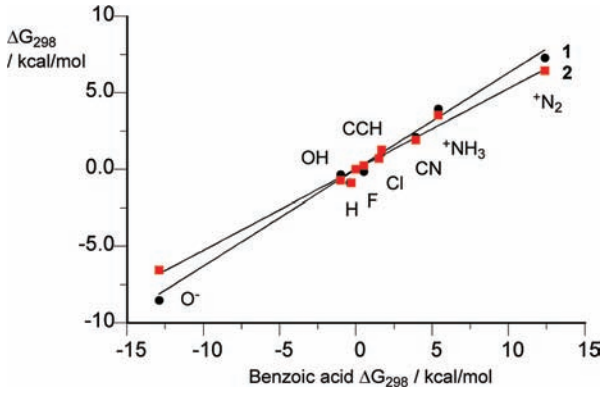

Figure 3. Plot of ΔG_{298} for the isodesmic reaction in Scheme 3 for series **1** (black dots, $m = 0.63 \pm 0.02$, $r^2 = 0.99$) and **2** (red squares, $m = 0.53 \pm 0.02$, $r^2 = 0.99$) versus ΔG_{298} values for benzoic acid derivatives. Data points for **l** and **m** are excluded.

Both series of monocarbaborate acids show good correlation with the analogous values for benzoic acid derivatives. In general, substituents in both series **1** and **2** have a smaller effect on the acidity of the parent acid than in the benzoic acid series. This is reflected in the slopes of the best-fit functions that are smaller than unity, $m = 0.63$ in series **1** and $m = 0.53$ for series **2**, and is consistent with the experimentally observed approximately 60% efficiency of transmission of electronic effects in benzoic acid derivatives. Intertestingly, the computational results predict a higher exotherm for the isodesmic reaction involving the alkyl derivatives of monocarbaborates (**l** and **m**) than for the corresponding OH derivatives **1n** and **2n**, while calculations for benzoic acid derivatives are consistent with the order of $\sigma_p(X)$ values ($\sigma_p(Me) = -0.17$, $\sigma_p(OH) = -0.37$). The computational results for the monocarbaborate acids are consistent with the experimental findings of lower than expected acidity of 10-hexyl acid **1c** and suggest a stereoelectronic origin of the effect rather than aggregation in solutions (see above).

CONCLUSIONS

Analysis of experimental results demonstrated that apparent dissociation constants pK_a' measured for series **1** and **2** correlate well with $\sigma_p(X)$ substituent parameters and poorly with inductive/field paramaters $F(X)$. This suggests that both resonance and inductive mechanisms are important in transmitting electronic effects through the $[closo\text{-}1\text{-}CB_9H_{10}]^-$ and $[closo\text{-}1\text{-}CB_{11}H_{12}]^-$ clusters. The resulting reaction constants ρ indicate that the monocarbaborate cages **E** and **F** are good conduits for the transmission of substituent effects, and their effectivenes is about 60% relative to that of benzene, or about 75% considering the normalized constant ρ'. Additional data points are necessary for a more accurate determination of the reaction constants ρ.

Computational analysis of relative acidity in each series of acids is consistent with experimental results and demonstrates similar effectiveness of transmission of electronic effects through the monocarbaborate cages **E** and **F**, 63% and 53%, respectively, relative to that of benzene. The calculations also showed lower than expected acidity of alkyl monocarbaborate carboxylic acids, which is consistent with experimental observations in series **1**. Further light into the nature of the transmission mechanism might be shed by detailed computational analysis of the data in the context of the "antipodal" effect.

The iodo acid $[closo\text{-}1\text{-}CB_9H_8\text{-}1\text{-}COOH\text{-}10\text{-}I]^-$ (**1b**) and dinitrogen acid **1e** proved to be convenient and versatile precursors to several derivatives of the parent acid **1a**. The preparation of a larger number of derivatives of carboxylic acid **2a** requires further developments in the chemistry of the iodo acid $[closo\text{-}1\text{-}CB_{11}H_{10}\text{-}1\text{-}COOH\text{-}12\text{-}I]^-$ (**2b**).

COMPUTATIONAL DETAILS

Quantum-mechanical calculations were carried out with the B3LYP[34,35] method and 6-31G(d,p) basis set using the Gaussian 09 package.[36] Geometry optimizations were undertaken using appropriate symmetry constraints and default convergence limits. Vibrational frequencies were used to characterize the nature of the stationary points and to obtain thermodynamic parameters at 25 °C. Zero-point energy (ZPE) corrections were scaled by 0.9806.[37] Geometry optimizations and vibrational frequency calculations were conducted using the PCM solvation model[38] in conjuction with the keyword SOLVENT=WATER.

EXPERIMENTAL SECTION

Melting points are not corrected. NMR spectra were obtained at 128.4 MHz (^{11}B) and 400.1 MHz (^1H) in CD_3CN unless specified otherwise. ^1H NMR spectra were referenced to the solvent, and ^{11}B NMR chemical shifts were referenced to an external boric acid sample in CH_3OH that was set to 18.1 ppm.

The preparation of acids **1b**,**c**,**g**, **3**, and **5**, and ester **7** and the isolation of acid **1a** were described before.[23,27] Syntheses of iodo acid **2b**,[21,31] hexyl acid **2c**,[21] and amino acid **11**[24] are described elsewhere.

pK_a' Measurements. Apparent acidity constants (pK_a') were determined by potentiometric titration at 24 ± 0.1 °C. The pK_a' for each compound was calculated as an average of pK_a' values determined at individual points using the Henderson–Hasselbach equation in a range of ±0.25 pH unit from the half neutralization point[39] for at least three titrations. Selected compounds were dissolved in EtOH/H_2O (4.00 mL, 1/1 v/v, ~0.01 M) and covered with Parafilm to minimize evaporation of the solvent. Neutralization was achieved under moderate stirring with 0.02 M NaOH in EtOH/H_2O (1/1, v/v), which was added in 50 μL increments using a digital pipet. After addition of NaOH, the pH was recorded upon stabilization (~30 s). The pH electrode was calibrated in aqueous buffer (pH = 4.0, 7.0, and 10.0) followed by conditioning in EtOH/H_2O (1/1 v/v) for several hours until the pH reading stabilized. The pH of a 3.1 mM solution of PhCOOH in EtOH/H_2O (1/1 v/v) half-neutralized with NaOH showed a value of 5.75 ± 0.02 after several hours, in accordance with the literature.[33,40]

Corrections were not made for free hydrogen or hydroxyl ions or the ionic strength of the medium.

All pK_a' values in the region of ±0.25 pH from the half neutralization point were analyzed statistically, and the results are shown in Table 1. Using this protocol, the pK_a' value for benzoic acid (0.01 M solution) was obtained as 5.66 ± 0.01, while the standarized value in 50% EtOH at 25 °C is 5.72.[25]

Preparation of $[closo\text{-}1\text{-}CB_9H_8\text{-}1\text{-}COOH\text{-}10\text{-}NMe_3]$ (1d). A suspension of the amino acid[23,27] $[closo\text{-}1\text{-}CB_9H_8\text{-}1\text{-}COOH\text{-}10\text{-}NH_3]$ (**3**; 0.100 g, 0.56 mmol), $[NMe_4]^+OH^-\cdot 5H_2O$ (0.506 g, 2.79 mmol), and CH_3I (0.35 mL, 5.6 mmol) in CH_3CN (10 mL) was stirred overnight at room temperature. The mixture was filtered and the solvent removed in vacuo. The crude mixture was passed through a short silica gel plug (CH_2Cl_2), and the resulting residue was washed with hot hexane, giving 0.130 g of crude methyl ester **4**: mp 120–125 °C; ^1H NMR (CD_3CN) δ 1.16 (br q, J = 142 Hz, 4H), 1.75 (br q, J = 158 Hz, 4H), 3.46 (s, 9H), 3.93 (s, 3H); ^{11}B NMR (CD_3CN) δ −22.7 (d, J = 149 Hz, 4B), −17.0 (d, J = 153 Hz, 4B), 44.8 (s, 1B).

Methyl ester **4** was hydrolyzed for 3 h at 50 °C in CH_3OH (4 mL) containing KOH (0.100 g, 1.78 mmol). Water was added (2 mL) and CH_3OH removed. HCl (10%, 10 mL) was added, and the mixture was

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extracted with Et_2O (3 × 5 mL). The organic layers were combined, dried (Na_2SO_4), and evaporated, giving 0.110 g (89% yield) of the acid [*closo*-1-CB_9H_8-1-COOH-10-NMe_3] (**1d**) as a light yellow solid. The product was dissolved in CH_2Cl_2, the solution was filtered through a cotton plug (to remove insoluble particulates), the solvent was removed, and the resulting acid **1d** was further purified by repeated recrystallization from aqueous CH_3OH: mp >260 °C; ^{1}H NMR (CD_3CN) δ 1.16 (br q, J = 143 Hz, 4H), 1.75 (br q, J = 157 Hz, 4H), 3.46 (s, 9H), 9.62 (br s, 1H); ^{11}B NMR (CD_3CN) δ −22.6 (d, J = 145 Hz, 4B), −16.9 (d, J = 161 Hz, 4B), 44.6 (s, 1B). Anal. Calcd for $C_5H_{18}B_9NO_2$: C, 27.11; H, 8.19; N, 6.32. Found: C, 27.38; H, 8.19; N, 6.25.

Preparation of [*closo*-1-CB_9H_8-1-COOH-10-SMe_2] (1f). A suspension of protected mercaptan [*closo*-1-CB_9H_8-1-COOH-10-$SCHNMe_2$] (**5**; 0.100 g, 0.40 mmol),[23,27] $[NMe_4]^+OH^-\cdot 5H_2O$ (0.290 g, 1.59 mmol), and CH_3I (0.25 mL, 4 mmol) in CH_3CN (10 mL) was stirred overnight at room temperature. The mixture was filtered, and the solvent was removed in vacuo. The crude residue was passed through a short silica gel plug (CH_2Cl_2), the solvent was evaporated, and the residue was washed with hot hexane, giving 84 mg of crude methyl ester **6**: mp 115−118 °C; ^{1}H NMR (CD_3CN) δ 1.24 (br q, J = 145 Hz, 4H), 1.88 (br q, J = 159 Hz, 4H), 3.01 (s, 6H), 3.94 (s, 3H); ^{11}B {^{1}H} NMR (CD_3CN) δ −20.2 (4B), −14.8 (4B), 33.7 (1B).

Methyl ester **6** was hydrolyzed at 50 °C in CH_3OH (4 mL) containing KOH (0.100 g, 1.78 mmol) for 3 h. Water was added (2 mL) ,and CH_3OH was removed. HCl (10%, 10 mL) was added, and the mixture was extracted with Et_2O (3 × 5 mL). The organic layers were combined, dried (Na_2SO_4), and evaporated, giving 0.075 g (84% yield) of the acid [*closo*-1-CB_9H_8-1-COOH-10-SMe_2] (**1f**) as a light yellow solid. The product was dissolved in CH_2Cl_2, the solution was filtered through a cotton plug (to remove insoluble particulates), the solvent was removed, and the resulting acid was recrystallized from aqueous CH_3OH and then toluene containing a few drops of acetonitrile: mp 217−220 °C; ^{1}H NMR (CD_3CN) δ 1.23 (br q, J = 142 Hz, 4H), 1.89 (br q, J = 158 Hz, 4H), 3.01 (s, 6H), 9.67 (s, 1H); ^{11}B NMR (CD_3CN) δ −20.2 (d, J = 147 Hz, 4B), −14.8 (d, J = 160 Hz, 4B), 33.6 (s, 1B). Anal. Calcd for $C_4H_{15}B_9O_2S$: C, 21.40; H, 6.73. Found: C, 21.67; H, 6.79.

Preparation of [*closo*-1-CB_9H_8-1-COOH-10-OC_5H_{11}]$^-$[NEt_4]$^+$ (1g[NEt_4]). *Method A.* A solution of the dinitrogen acid [*closo*-1-CB_9H_8-1-COOH-10-N_2] (**1e**; 0.080 g, 0.42 mmol)[23,27] and freshly distilled 1-pentanol (3 mL) was heated at 120 °C for 1 h. As the reaction progressed, bubbling of N_2 was observed. The reaction mixture was cooled to room temperature, and excess 1-pentanol was removed by short-path distillation (90 °C, 1 mmHg), leaving the crude product as a brown solid. The crude material was heated at 50 °C in CH_3OH (5 mL) containing KOH (0.050 g, 1.25 mmol) for 3 h to hydrolyze small amounts of ester that were formed during the thermolysis. Water was added (2 mL), and CH_3OH was removed. HCl (10%, 10 mL) was added, and the mixture was extracted with Et_2O (3 × 5 mL). Half of the Et_2O was evaporated, and water (2 mL) was added. The remaining Et_2O was evaporated, and the aqueous layer was filtered to remove insoluble material. $[NEt_4]^+Br^-$ (0.088 g, 0.42 mmol) was added to the filtrate, resulting in the formation of a precipitate, which was isolated by extraction into CH_2Cl_2 (3 × 5 mL). The CH_2Cl_2 layers were combined, dried ($MgSO_4$), and evaporated, giving 0.094 g (86% yield) of [*closo*-1-CB_9H_8-1-COOH-10-OC_5H_{11}]$^-$[NEt_4]$^+$ (**1g**[NEt_4]) as a light brown solid residue. The product was further purified by passage through a cotton plug (CH_2Cl_2) to remove insoluble particulates, followed by recrystallization from toluene containing a few drops of CH_3CN: mp 177−179 °C; ^{1}H NMR (CD_3CN) δ 0.00−2.00 (br m, 8H), 0.94 (t, J = 7.2 Hz, 3H), 1.20 (tt, J_1= 7.3 Hz, J_2 = 1.9 Hz, 12H), 1.35−1.52 (m, 4H), 1.80 (quint, J = 7.1 Hz, 2H), 3.15 (q, J = 7.3 Hz, 8H), 4.07 (t, J = 6.7 Hz, 2H), 9.18 (br s, 1H); ^{11}B NMR (CD_3CN) δ −28.7 (d, J = 138 Hz, 4B), −20.6 (d, J = 156 Hz, 4B), 52.3 (s, 1B). Anal. Calcd for $C_{15}H_{40}B_9NO_3$: C, 47.44; H, 10.62; N, 3.69. Found: C, 47.59; H, 10.73; N, 3.71.

Method B. A solution of methyl ester **7** (0.100 g, 0.489 mmol) and freshly distilled 1-pentanol (4 mL) was heated at 125 °C for 1 h. Excess 1-pentanol was removed in vacuo, the resulting crude ester **8** was dissolved in CH_3OH (5 mL) containing KOH (0.014 g, 2.45 mmol), and the resulting mixture was heated at 50 °C for 5 h. Water was added (3 mL), and CH_3OH was removed. HCl (10%, 10 mL) was added, and the mixture was extracted with Et_2O (4 × 5 mL). About half of the Et_2O was evaporated, and water (3 mL) was added. The remaining Et_2O was evaporated, and the aqueous layer was filtered to remove insoluble material. $[NEt_4]^+Br^-$ (0.103 g, 0.489 mmol) was added to the filtrate, resulting in the formation of a precipitate, which was isolated by extraction into CH_2Cl_2 (3 × 5 mL). The CH_2Cl_2 layers were combined, dried ($MgSO_4$), and evaporated, giving 0.154 g (83% yield) of [*closo*-1-CB_9H_8-1-COOH-10-OC_5H_{11}]$^-$[NEt_4]$^+$ as a light yellow solid. The product was purified as described in method A.

Preparation of [*closo*-1-$CB_{11}H_{10}$-1-COOH-12-NMe_3] (2d). The amino acid[24] [*closo*-1-$CB_{11}H_{10}$-1-COOH-12-NH_3] (**11**; 0.100 g, 0.493 mmol) was methylated as described for the amino acid **3** to give 0.101 g of methyl ester **12**: mp 232−233 °C; ^{1}H NMR (CD_3CN) δ 1.20−2.60 (br m, 10H), 2.76 (s, 9H), 3.57 (s, 3H); ^{11}B {^{1}H} NMR (CD_3CN) δ −14.7 (d, J = 160 Hz, 10B), 8.3 (1B).

The methyl ester **12** was hydrolyzed as described for methyl ester **4**, and the acid **2d** was isolated in 79% yield as a white crystalline solid: mp >260 °C; ^{1}H NMR (CD_3CN) δ 1.20−2.60 (br m, 10H), 2.76 (s, 9H), 9.2 (br s, 1H); ^{11}B NMR (CD_3CN) δ −14.2 (d, J = 121 Hz, 10B), 8.8 (s, 1B). Anal. Calcd for $C_5H_{20}B_{11}NO_2$: C, 24.50; H, 8.22; N, 5.71. Found: C, 24.85; H, 8.22; N, 5.67.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Text and tables giving synthetic details and characterization data for compounds **1h**, **7**, and **10**, ^{11}B NMR chemical shifts for acid extracts and carboxylate anions, and DFT computational results for benzoic acids and series **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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