

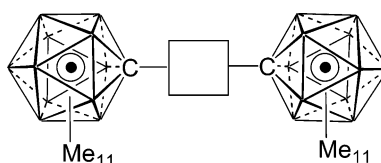
Synthesis of the Isolable Biradicals $\cdot(\text{CH}_3\text{B})_{11}\text{C}-\text{C}\equiv\text{C}-\text{C}(\text{BCH}_3)_{11}\cdot$ and *trans*- $\cdot(\text{CH}_3\text{B})_{11}\text{C}-\text{CH}=\text{CH}-\text{C}(\text{BCH}_3)_{11}\cdot$

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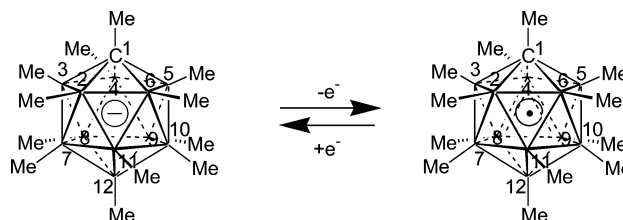
A synthesis of ethene and ethyne derivatives carrying the anionic $-\text{C}(\text{BCH}_3)_{11}^-$ substituent on one or both carbon atoms is described. Two-electron oxidation of the dianions yielded the stable and isolable electroneutral title biradicals.

Introduction

We have developed an interest in transition metal-free stable anion/radical redox pairs as potentially interesting structural elements for the preparation of new tunable redox active polymers. Few anions offer this opportunity because the corresponding radicals usually decompose, dimerize, or are otherwise too reactive. In this regard, the reversibly interconvertible redox pair, the anion¹ $\text{CB}_{11}(\text{CH}_3)_{12}^-$ and the stable radical² $\text{CB}_{11}(\text{CH}_3)_{12}\cdot$, offers a unique promise (Chart 1). The radical is protected by a sheath of methyl groups and shows no inclination toward dimerization. The methyl substituents also make the radical and even the salts of the anion³ highly lipophilic and soluble in solvents of low polarity, and this could be useful.

The redox potential of this couple, 1.16 V above the ferrocene/ferrocenium couple in liquid SO_2 , responds strongly to changes in the number and location of the methyl substituents on the carborane cage and provides opportunities for structural tuning.⁴ It appears that most, if not all, of those derivatives that do not have adjacent unsubstituted boron vertices in positions 7–12 form stable radicals. Interestingly, the methyl groups on

CHART 1. The Carborate Anion/Radical Redox System



the carbon (position 1) and in its antipodal position 12 have little effect on the redox behavior, and these positions appear ideal for the attachment of functional substituents that could allow more complex structures to be constructed. The simplest such construct would be a linear rod containing a series of $-\text{CB}_{11}\text{Me}_{10}^-$ units concatenated through their positions 1 and 12 (Chart 2). The steric demands of the methyl groups prevent the carborane units from attaching directly to each other, and suitable connectors need to be interposed.

For some purposes, it would be useful if charge would travel rapidly along such a chain, and this calls for electronic coupling through the connectors. Little is known at present about conjugative interactions between carborane cages and other structural modules, but π -electron systems, such as vinylene, ethynylene, phenylene, and the like, offer good prospects. The cylindrical symmetry of ethynylene makes it particularly appealing.

The HOMO of the anion is degenerate, and the Jahn–Teller distortion in the radical⁵ may cause the reorganization energy

(5) McKee, M. *J. Am. Chem. Soc.* **1997**, *119*, 4220.

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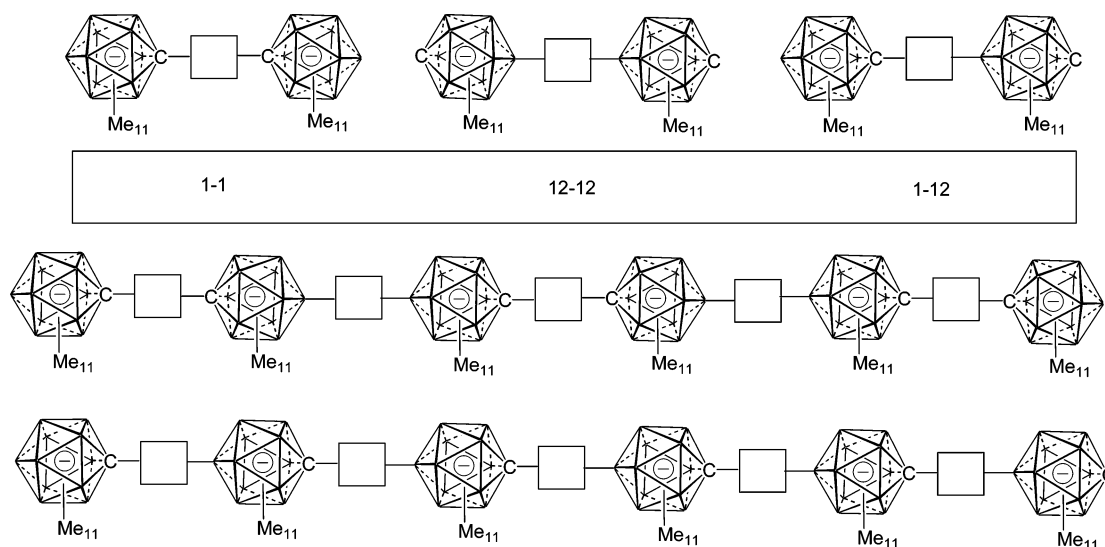
(1) King, B. T.; Janoušek, Z.; Grüner, B.; Trammel, M.; Noll, B. C.; Michl, J. *J. Am. Chem. Soc.* **1996**, *118*, 3313.

(2) King, B. T.; Noll, B. C.; McKinley, A. J.; Michl, J. *J. Am. Chem. Soc.* **1996**, *118*, 10902.

(3) Pospíšil, L.; King, B. T.; Michl, J. *Electrochim. Acta* **1998**, *44*, 103.

(4) King, B. T.; Körbe, S.; Schreiber, P. J.; Clayton, J.; Havlas, Z.; Vyakaranam, K.; Fete, M. G.; Zharov, I.; Ceremuga, J.; Michl, J. Submitted for publication.

CHART 2. Concatenation of Carborate Anions



for electron transfer to be high, leading to slow charge transfer. If it were not for this distortion, elementary molecular orbital considerations would actually predict ferromagnetic coupling of adjacent radicals, and the resulting materials might have not only interesting electrical properties but also interesting magnetic properties. It is not clear to what degree these properties will be suppressed by the Jahn–Teller effect.

A good starting point for the exploration of these various possibilities would be an examination of the properties of dimeric anions and biradicals. Chart 2 shows the three connection modes through positions 1 and 12: the symmetrical coupling of carbon to carbon (1–1) or boron to boron (12–12), and the unsymmetrical coupling of carbon to boron (1–12). These motifs could then be combined into a polymeric chain in numerous ways.

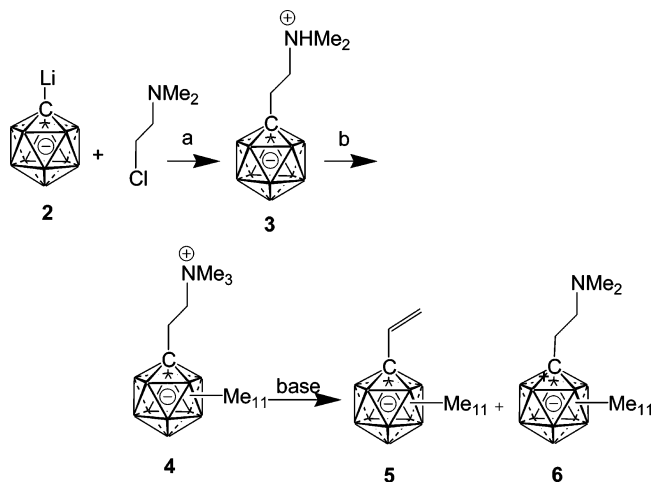
Presently, we report an improved synthesis of the known⁶ 1-vinyl-substituted and otherwise permethylated anion and the synthesis of the 1-ethynyl-substituted otherwise permethylated anion, and their use for the construction of the 1–1 vinylene and ethynylene coupled dianions. The dianions have been characterized by cyclic voltammetry and reversibly oxidized to stable biradicals in bulk by chemical means. A detailed investigation of the physical properties of these compounds will be reported separately. The synthesis of the permethylated 1-phenyl and other 1-aryl derivatives has also been achieved.⁷

Results and Discussion

Synthesis of the Dianions. Since our ultimate goal is to have all three dimers available, 1–1, 12–12, and 1–12, and to couple them to longer units by processes such as Li^+ -induced nucleophilic substitution,⁸ it appeared useful to start by synthesizing the 1-vinyl and 1-ethynyl derivatives of the permethylated CB_{11} cage. This cannot be done by introducing the unsaturated substituent first and then methylating since the multiple bond is susceptible to electrophilic attack by methyl triflate, which is used in the undecamethylation step. In previous work,⁶ the

difficulty was avoided by alkylating position 1 prior to the undecamethylation step with an alkyl that contained the multiple bond in a masked form. The most obvious choice for a masked vinyl group, 1-(2-bromoethyl)- $\text{C}(\text{BH})_{11}^-$, was however found to undergo Grob fragmentation under the influence of methyl triflate. The obstacle was overcome by a three-step synthesis of the 1-(2-Bn $\text{Me}_2\text{N}^+-\text{CH}_2\text{CH}_2$)- $\text{C}(\text{BH})_{11}^-$ ammonium zwitterion (**1**, Bn = benzyl), which was then permethylated without fragmentation.

SCHEME 1. Synthetic Scheme for the Preparation of **5**^a



^a Conditions: (a) DME, 0 °C; (b) MeOTf, CaH_2 , sulfolane.

We now find that this route can be considerably shortened by a direct attachment of the *N,N*-dimethyl-2-aminoethyl group at the carbon atom of $\text{LiC}(\text{BH})_{11}^- \text{Cs}^+$ (**2**). Upon acidic workup, the ammonium zwitterion **3** is isolated and can be subsequently permethylated to **4** without difficulty (Scheme 1). However, another difficulty emerged when we attempted to perform a Hofmann elimination to obtain the desired vinyl-substituted anion **5**. The previously reported Hofmann elimination of **1** was achieved with methylolithium, but the analogous Me_3N elimination reaction on **4** with this reagent failed. Only 20% of **4** was converted to **5**, whereas the remainder reacted in a $\text{S}_{\text{N}}2$ -type manner to give the demethylated amine **6** (Scheme 1).

(6) Vyakaranam, K.; Körbe, S.; Divišová, H.; Michl, J. *J. Am. Chem. Soc.* **2004**, *126*, 15795.

(7) Vyakaranam, K.; Michl, J. Submitted for publication.

(8) Janoušek, Z.; Lehmann, U.; Častulík, J.; Čisářová, I.; Michl, J. *J. Am. Chem. Soc.* **2004**, *126*, 4060.

TABLE 1. Hofmann Elimination Attempts on the Trimethylammonium Salt 4

entry	base	solvent	temp (°C)	yield ^a of 5 (%)	yield of 6 (%)
1	MeLi	THF	-58	<10	>90
2	MeLi	THF	-20	~20	~80
3	MeLi	THF	25	~20	~80
4	MeLi	EtOEt	-20	~20	~80
5	LiH	DME	25	multiple prod	
6	LiH	DME	reflux	multiple prod	
7	LiOH	DME	reflux	multiple prod	
8	KOH	MeOH	reflux	multiple prod	
9	<i>t</i> -BuLi	THF	-58	< 5	>95
10	LDA	THF	-58	~10	~90
11	LiOH/LiTMP	THF	25	~50	~50
12	LiTMP	THF	40	>95	<5

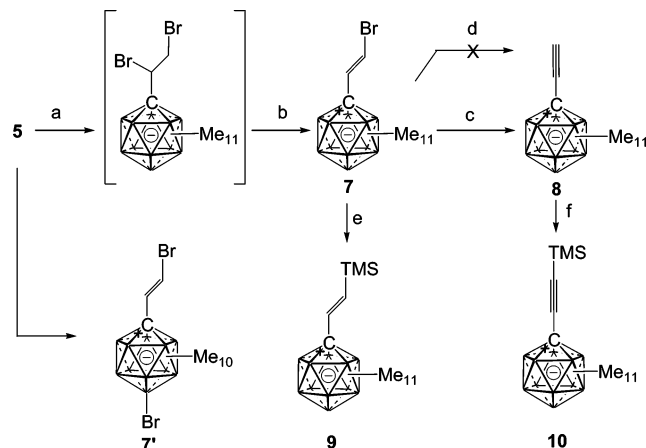
^a Determined by ¹H NMR.

As shown in Table 1 (entries 1–4), attempting the elimination with MeLi at different temperatures had no large impact on the outcome of the reaction. The use of lithium hydride in DME as well as Li/K hydroxide in MeOH or DME gave a complex mixture of numerous products (entries 5–8). We then tried to avoid the nucleophilic displacement reaction on **4** through the use of bulkier bases such as *t*-BuLi and LDA. By the use of the lithium salt of freshly distilled 2,2,6,6-tetramethylpiperidine (LiTMP), we obtained a 95% conversion of the desired **5**.

The conversion of the vinyl anion **5** into the 2-bromovinyl anion **7** and the ethynyl anion **8** ran into additional complications. When bromine is added to the vinyl group of **5**, evolution of HBr occurs spontaneously. Monitoring the course of the reaction by mass spectrometry (ESI) revealed that this acid then attacks the anion in a fashion known for hydrogen fluoride² and replaces a methyl group with a bromine atom (electrophile-induced nucleophilic substitution⁹). At ambient temperature, approximately 60% of **5** is lost to bromination already after 30 min (Scheme 2), most likely by conversion to the 12-brominated **7'**, which we however did not attempt to isolate and characterize. Even at -78 °C, the occurrence of bromination could be detected by ESI before **5** was completely consumed. The losses were avoided by the addition of a non-nucleophilic proton scavenging base, DBU, and **7** was then isolated in 71% yield.

A common dehydrohalogenating system used for the generation of alkynes is sodium amide in refluxing ammonia.¹⁰ This reagent proved inefficient for the formation of **8**. The first base to give full conversion of **7** to **8** via a *syn*-elimination was once again LiTMP in THF at ambient temperature. At 25 °C, the half-life of LiTMP in THF has been reported to be 12 h.¹¹ However, in our hands, the lithiation of THF appears substantially faster. Lithiation of TMP in other solvents such as toluene and *tert*-butylmethyl ether resulted in precipitation of LiTMP, most likely in the form of a tetramer,¹² and this slowed down the reaction very much. The choice of solvents is limited by the solubility of **7**. In the end, we had to use a 30-fold excess of the base in THF to achieve complete elimination.

The syntheses of the 1-(*trans*-2-trimethylsilylvinyl)-C(BMe)₁₁⁻ (**9**) and 1-(2-trimethylsilylethynyl)-C(BMe)₁₁⁻ (**10**) derivatives were straightforward. The transmetalation reaction of **7** using

SCHEME 2. Synthetic Scheme for the Preparation of **8**, **9**, and **10**^a

^a Conditions: (a) Br₂, DBU, THF; (b) -HBr; (c) LiTMP, THF; (d) NaNH₂, NH₃; (e) *t*-BuLi, -78 °C, TMSCl; (f) *n*-BuLi, 0 °C, TMSCl.

t-BuLi at -78 °C followed by quenching with TMSCl at 0 °C produced **9** in almost quantitative yield. Similar lithiation of **8** with *n*-BuLi at 0 °C followed by the reaction with TMSCl gave the anion **10**.

The final task on the way to the dimeric anions is the attachment of a carbon of a second methylated carborane cage on the free side of the multiple bond in **5** and **8**. For the usual nucleophile form of the carborane unit, in which its carbon vertex is activated in the form of a carbanion, this represents a considerable challenge. In its unmethylated form, LiC(BH)₁₁⁻, it could probably be attached by Pd-catalyzed coupling, but subsequent exhaustive methylation would most likely occur on the multiple bond, too. All previous attempts to perform Pd-catalyzed coupling reactions on metal-C(BMe)₁₁⁻, the sterically hindered methylated form, failed.

Fortunately, the undecamethylated form of the carborane cage has recently also become available as an electrophile in the form of the reactive intermediate C(BMe)₁₁,^{6,7} and this is perfectly suited for the present needs. Indeed, the dimers **11** (63% yield) and **12** (60% yield) were obtained from **5** and **8**, respectively, by reaction with C(BMe)₁₁ produced by solvolysis of the permethylated 1-(2-bromoethyl)carborate anion in (CF₃)₂CHOH (Scheme 3). The dimer **11** was assigned a *trans* structure because of its 15.8 Hz *J*_{HH} coupling constant across the double bond, derived from the ¹³C satellites in ¹H NMR. The structure is not a surprise, given the steric bulk of the carboranyl substituents. Unreacted **5** and **8** were recovered, and the remainder of C(BMe)₁₁ ended up as the trapping product with the solvent, (CF₃)₂CHOC(BMe)₁₁⁻ (**13**), which can be reused as a source of C(BMe)₁₁.⁷ This electrophilic version of the C(BMe)₁₁⁻ residue is thus beginning to emerge as a very valuable synthetic tool, and it will be worthwhile to make it more accessible and available in a wider variety of solvents. It is likely that its reaction with ethylene, vinyltrimethylsilane, acetylene, or trimethylsilylacetylene will ultimately offer the best approach to **5** and **8**.

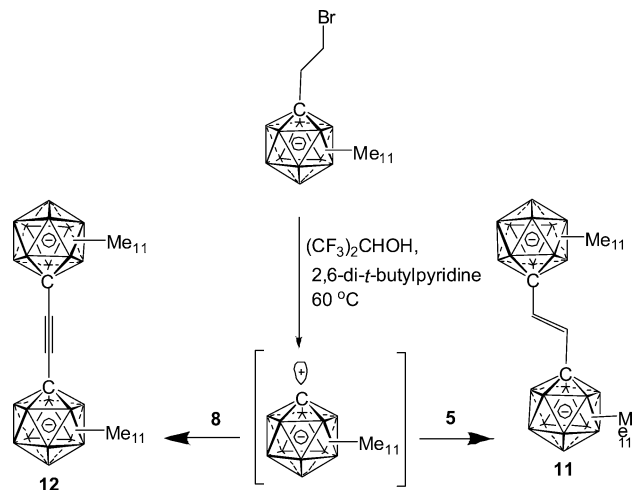
In summary, the ethenes and ethynes carrying one and two C(BMe)₁₁⁻ residues are now available for an examination of physical properties, and should these turn out to be interesting, there are good prospects for a further future simplification of the synthesis.

(9) Körbe, S.; Schreiber, P. J.; Michl, J. *Chem. Rev.* **2006**, *106*, 5208.

(10) Vaughn, T. H. *J. Am. Chem. Soc.* **1934**, *56*, 2064.

(11) Kopka, I. E.; Fataftah, Z. A.; Rathke, M. W. *J. Org. Chem.* **1987**, *52*, 448.

(12) Lappert, M. F.; Slade, M. J.; Singh, A. *J. Am. Chem. Soc.* **1983**, *105*, 302.

SCHEME 3. Synthetic Scheme for the Preparation of 11 and 12


Electrochemical Oxidation of the Dianions. The cyclic voltammograms of **11** and **12** in acetonitrile (Figure 1) are nearly identical, suggesting that there is hardly any difference between the abilities of the double and triple bonds to mediate communication between the two anionic centers. The voltammograms show a small prewave at about 1.0 V versus ferrocene (which is at 0.445 V against SCE in acetonitrile) and two anodic peaks. The height and even the presence of the prewave depends on the treatment of the platinum electrode surface, and its occurrence is most probably connected with adsorption phenomena. The height of the first anodic peak slightly exceeds that expected for a one-electron oxidation by comparison with the ferrocene standard, and it is associated with a hint of a reduction peak, especially at higher scan rates, suggesting partial reversibility. Our best estimate of the redox potential for the one-electron couple from a series of repeated measurements is 1.305 V for both **11** and **12**, somewhat higher than the 1.16 V reported^{1,2} for the perfectly reversible oxidation of the dodecamethylated $\text{CB}_{11}\text{Me}_{12}^-$ anion in the same solvent. The second anodic peak is significantly more positive and entirely irreversible. It seems to be a little smaller than the first peak, but a quantitative evaluation is difficult since it appears in the region of supporting electrolyte oxidation, approximately at 1.56 V in **11** and 1.54 V in **12**. Comparison with the cyclic voltammogram of the blank supporting electrolyte strongly suggests that the substrate catalyzes the electrochemical oxidation of acetonitrile or the supporting electrolyte, shifting it to less positive potentials, even though the biradicals appear to be stable in pure acetonitrile. The electrochemical mechanism is undoubtedly more complicated than a simple reversible two-step anodic heterogeneous oxidation dianion \rightleftharpoons anion radical \rightleftharpoons biradical and apparently also involves a comproportionation reaction of the dianion with the biradical. Addition of ferrocene causes an increase of the first peak at the expense of the second peak, which becomes hard to discern. All indications of reversibility disappear, suggesting that oxidized ferrocene acts as a mediator. The complicated behavior calls for an additional future investigation.

Synthesis of the Biradicals. The black biradicals **14** and **15** were obtained as microcrystalline powders by the oxidation of **11** and **12** using $\text{PbO}_2/\text{CF}_3\text{COOH}/\text{CH}_3\text{CN}$ followed by extraction into pentane (Scheme 4). They dissolve to deep blue solutions in CCl_4 , ether, and acetonitrile. They do not yield

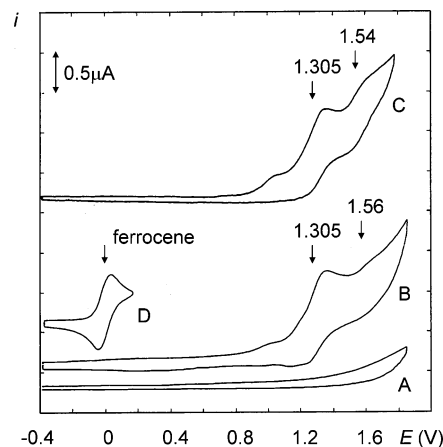
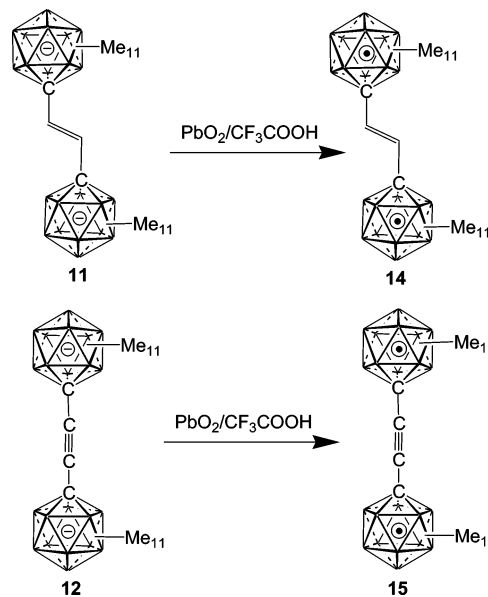


FIGURE 1. Cyclic voltammetry in acetonitrile (0.1 M TBA HFP, $\nu = 100$ mV/s). (A) Blank solution; (B) 5×10^{-4} M **11**; (C) 5×10^{-4} M **12**; (D) 4×10^{-4} M ferrocene.

solution NMR spectra but show broad unresolved EPR signals, similar to that of $\text{CB}_{11}(\text{CH}_3)_{12}^{\bullet}$.² Like this monoradical, the solid biradicals are stable in air at room temperature for a few hours but decay upon prolonged exposure to the atmosphere. They are reduced quantitatively to the starting dianions **11** and **12** upon treatment with lithium amalgam. Along with the mass spectra and the elemental analysis, this leaves no doubt about their structures. We presume that, like **11**, **14** is the trans isomer.

SCHEME 4. Preparation of 14 and 15


We plan to report elsewhere the results of detailed investigations of the physical properties of the new biradicals **14** and **15** and the corresponding radical anions, especially those pertinent to their possible incorporation into magnetic and/or electrically conducting polymers.

Experimental Section

General. All experimental manipulations were carried out using standard vacuum and inert atmosphere techniques. Chemicals were reagent grade; $\text{Me}_3\text{NH}^+\text{HC}(\text{BH})_{11}^-$ was purchased from Katchem, Ltd. (Elišky Krásnohorské 6, 11000 Prague 1, Czech Republic). DME and THF were dried over sodium and distilled before use.

^1H NMR shifts of BH protons were measured with boron decoupling. Chemical shifts are given in parts per million (δ scale). All ^1H chemical shifts were referenced relative to internal residual protons from the lock solvent and ^{11}B shifts to an external reference of $\text{B}(\text{OMe})_3 \cdot \text{Et}_2\text{O}$ (18.1 ppm). The NMR solvent was $(\text{CD}_3)_2\text{CO}$ unless noted otherwise. Electrospray negative and positive ion mass spectra were measured in methanol solution. The matrix for MALDI was 2,5-dihydroxybenzoic acid. The chromatographic purification of compound **8** was performed using silica gel from Aldrich (60–200 mesh, 150 Å), and detection of the target compound was made with a freshly prepared 3% methanolic solution of KMnO_4 . Reverse phase chromatography was performed on C18 columns using buffered (0.7% Et_3N and 1% AcOH) $\text{MeOH}/\text{H}_2\text{O}$ (45:55) as eluent.

Electrochemical Measurements. The electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate (TBAHFP) in nonaqueous acetonitrile (Riedel-deHaen; puriss. p.a., Reag.); the Pt-disk working electrode had a diameter of 1 mm, the auxiliary electrode was a Pt sheet, and the reference electrode was SCE with a nonaqueous bridge or a Pt quasireference electrode. The potentiostat was a PA4 from Laboratorní Přístroje, Praha, Czech Republic. Cyclic voltammetric curves were recorded at a scan rate of $\nu = 100 \text{ mV/s}$ at a concentration of $5 \times 10^{-4} \text{ mol/L}$, prepared by direct dissolution in a solvent deaerated with Ar. Ferrocene was used as the reference.

Preparation of PPh_4^+ Salts. All elemental analyses of anions were performed on PPh_4^+ salts, which have superior combustion properties. An Et_3NH^+ , Me_4N^+ , Me_3NH^+ , or Cs^+ salt (1 equiv, ~0.3 g) was dissolved in MeOH (25 mL) and treated with Ph_4PCl (2 equiv). In the case of **3**, 1.5 equiv of 50% CsOH (aq) was added prior to the addition of Ph_4PCl . Water (5 mL) was added to the clear solution. Upon evaporation of the methanol at ambient temperature, crystals precipitated from the solution. These pure crystals were filtered off and dried under reduced pressure.

1-[2-(Dimethylammonium)ethyl]carba-closo-dodecaborate (–) (3). A 14.9 mL solution of 1.6 M *n*-BuLi in hexane was added dropwise to a stirred solution of $\text{CsCB}_{11}\text{H}_{12}$ (6.00 g, 21.7 mmol) in 150 mL of DME at 0 °C. After complete addition of *n*-BuLi, the resulting mixture was allowed to warm to ambient temperature. Subsequently, a mixture of 2-(dimethylamino)ethyl chloride hydrochloride (4.70 g, 32.6 mmol) and 150 mL of THF was treated with 21.7 mL of 1.6 M *n*-BuLi in hexane at –78 °C and allowed to stand with stirring. After 30 min, the mixture of $\text{CsCB}_{11}\text{H}_{11}^-\text{Li}^+$ and DME was cooled to 0 °C, and the liberated amine in THF was added with a double-ended needle. The resulting mixture was stirred at 0 °C for 4 h and allowed to warm to ambient temperature overnight. The reaction was monitored by ^{11}B NMR. Upon its completion, LiCl was filtered off and the resulting solution was concentrated under reduced pressure. The remaining solid material was dissolved in 50 mL of MeOH, and 15 mL of 4 M HCl was added. The solution was then poured into 300 mL of water at 0 °C. The product precipitated as a white solid and was filtered off. By the subsequent addition of 30% Me_3NHCl (aq) to the filtered solution, the unreacted $\text{CB}_{11}\text{H}_{12}^-$ salt was recovered: Yield 2.60 g, 55% (93% after recovery of starting material); ^1H NMR (δ) 3.09 (m, 2H), 2.95 (s, 6H), 2.34 (m, 2H); ^{13}C NMR (δ) 66.2, 54.7, 29.5; ^{11}B NMR (δ) –9.23 (1B), –13.15 (10B); IR (KBr) 2992, 2900, 2832, 2635, 1472, 1399, 1354, 1277, 918, 845 cm^{-1} ; ESI $m/z = 216$. Anal. Calcd for the Ph_4P^+ salt, $\text{C}_{29}\text{H}_{41}\text{B}_{11}\text{NP}$: C, 62.92; H, 7.47. Found: C, 63.01; H, 7.52.

1-[2-(Trimethylammonium)ethyl]undecamethylcarba-closo-dodecaborate(–) (4). To a vigorously stirred mixture of **3** (2.20 g, 10.2 mmol), sulfolane (80 mL), and CaH_2 (43.0 g, 1.02 mol) was added MeOTf (17.3 mL, 153 mmol) dropwise over a period of 12 h at ambient temperature. Every 7 days, another 5 mL of MeOTf was added until the completion of the reaction (by ^{11}B NMR). After 6 weeks from the initiation of the reaction, the mixture was diluted with 200 mL of EtOAc and filtered. The filtered solid was washed with $3 \times 50 \text{ mL}$ of EtOAc. By careful addition of 50 mL of 28% ammonium hydroxide, excess of MeOTf was quenched.

Upon the addition of water (200 mL), two layers were formed and the aqueous layer was washed with $3 \times 100 \text{ mL}$ of EtOAc. Concentration under reduced pressure gave a thick oil of **4** and sulfolane. The sulfolane was removed at 300 mmHg/150 °C by short-path distillation (Kugelrohr), and the crude **4** recrystallized in 50 mL of water and 100 mL of acetone: Yield 3.20 g, 81%; ^1H NMR (δ) 3.43 (m, 2H), 3.34 (s, 9H), 2.06 (m, 2H), –0.16 (s, 15H), –0.40 (s, 15H), –0.50 (s, 3H); ^{13}C NMR (δ) 65.6, 53.2, 25.6, –2.7 (br m); ^{11}B NMR (δ) 0.59 (1B), –8.43 (5B), –10.96 (5B); IR (KBr) 2930, 2894, 2830, 2625, 1486, 1475, 1437, 1309, 910 cm^{-1} ; ESI $m/z = 533$; mp > 400 °C. Anal. Calcd for $\text{C}_{17}\text{H}_{46}\text{B}_{11}\text{N}$: C, 53.25; H, 12.09. Found: C, 53.30; H, 12.12.

Cs^+ 1-Vinylundecamethylcarba-closo-dodecaborate(–) (5). At 0 °C, 1.6 M *n*-BuLi (23.2 mL, 37.2 mmol) was added dropwise to freshly distilled TMP (6.31 mL, 37.2 mmol) in 20 mL of THF. After 5 min, the resulting LiTMP solution was cannulated to a stirred solution of **4** (2.85 g, 7.43 mmol) in 80 mL of THF at 40 °C. The reaction was quenched after 30 min with 100 mL of 25% CsCl (aq), and THF was evaporated under reduced pressure. From the resulting aqueous mixture, **5** was extracted with $3 \times 100 \text{ mL}$ of EtOEt and concentrated under reduced pressure. The crude product was crystallized from acetone (100 mL) and water (30 mL) to give **5** as white crystals: ESI $m/z = 323$; yield 1.95 g, 57%. Analytical data agreed with those reported.⁶

Cs^+ 1-(trans-2-Bromovinyl)undecamethylcarba-closo-dodecaborate(–) (7). Bromine (0.45 mL, 8.77 mmol) was added dropwise to a solution of **5** (2.00 g, 4.38 mmol) in THF (150 mL) at –78 °C. After 3 h, the reaction was allowed to warm to ambient temperature and 100 mL of CsCl 20% (aq) was added. At 20 °C, the THF and excess bromine were evaporated and the crude **7** was extracted into an ethereal phase ($3 \times 100 \text{ mL}$). After evaporation of the solvent, MeOH (30 mL) and sulfolane (4 mL) were added. Thereafter a $\text{Cs}^+(\text{sulfolane})_2$ complex of **7** was precipitated as a white solid by addition of 150 mL of CsCl 10% (aq) after removal of sulfolane by short-path distillation (Kugelrohr): Yield 2.42 g, 71%; NMR was measured on the PPh_4^+ salt; ^1H NMR (δ) 8.07–7.97 (m, 4H), 7.92–7.81 (m, 16H), 5.82 (d, $J = 14 \text{ Hz}$, 1H), 5.77 (d, $J = 14 \text{ Hz}$, 1H), –0.23 (s, 15H), –0.38 (s, 15H), –0.46 (s, 3H); ^{13}C NMR (δ) 135.7, 135.1, 130.7, 118.3 (d, $J_{\text{p-c}} = 90 \text{ Hz}$), 106.4, 94.6; ^{11}B NMR (δ) 1.80 (1B), –8.37 (5B), –10.48 (5B); IR (KBr) 2928, 2890, 2826, 2650, 1587, 1485, 1435, 1302, 1108, 722, 526 cm^{-1} ; ESI $m/z = 402$; mp 276 °C. Anal. Calcd for the Ph_4P^+ salt, $\text{C}_{38}\text{H}_{55}\text{B}_{11}\text{BrP}$: C, 61.54; H, 7.47. Found: C, 61.52; H, 7.45.

Cs^+ 1-Ethynylundecamethylcarba-closo-dodecaborate(–) (8). A freshly prepared solution of LiTMP (37.4 mmol) in THF (25 mL) was added three times in 12 h intervals to **7** (2.00 g, 3.74 mmol) in THF (100 mL) at ambient temperature. After 36 h, 100 mL of CsCl 20% (aq) was added, and the THF was removed under reduced pressure. The aqueous mixture was washed with diethyl ether ($3 \times 150 \text{ mL}$), the ethereal phase was concentrated, and the resulting crude product was purified by reverse phase chromatography: Yield 1.53 g, 90%; NMR was measured on the PPh_4^+ salt; ^1H NMR (δ) 8.07–7.97 (m, 4H), 7.93–7.82 (m, 16H), 2.26 (s, 1H), –0.20 (s, 15H), –0.36 (s, 15H), –0.46 (s, 3H); ^{13}C NMR (δ) 136.4, 135.8, 131.4, 119.0 (d, $J_{\text{p-c}} = 90 \text{ Hz}$), 70.0; ^{11}B NMR (δ) 1.87 (1B), –8.88 (5B), –9.97 (5B); IR (KBr) 3307, 2888, 2827, 2655, 1587, 1484, 1435, 1301, 1106, 999, 916, 721, 524 cm^{-1} ; ESI $m/z = 321$; mp 328 °C. Anal. Calcd for the Ph_4P^+ salt, $\text{C}_{38}\text{H}_{54}\text{B}_{11}\text{P}$: C, 69.08; H, 8.24. Found: C, 69.14; H, 8.20.

Cs^+ 1-(trans-2-Trimethylsilylvinyl)undecamethylcarba-closo-dodecaborate(–) (9). To a THF solution (25 mL) of **7** (0.150 g, 0.28 mmol) was added *t*-BuLi (0.4 mL of 1.7 M solution) at –78 °C over a period of 30 min. The contents were stirred at that temperature for 20 min and then allowed to come to 0 °C. TMSCl (1.5 equiv, 0.06 mL) was added, and the solution was stirred for 2 h. After 2 h, 20 mL of CsCl 20% (aq) was added and the THF was removed under reduced pressure. The aqueous mixture was washed with diethyl ether ($3 \times 150 \text{ mL}$), the ethereal phase was concen-

trated, and the resulting crude product was purified by reverse phase column chromatography: Yield 0.140 g, 94%; NMR was measured on the PPh_4^+ salt; ^1H NMR (δ) 8.05–7.92 (m, 4H), 7.79–7.88 (m, 16H), 5.85 (d, $J = 12$ Hz, 1H), 5.72 (d, $J = 10$ Hz, 1H), 0.1 (s, 9H), –0.29 (s, 15H), –0.33 (s, 15H), –0.40 (s, 3H); ^{13}C NMR (δ) 136.1, 133.4, 128.3, 115.3; ^{11}B NMR (δ) 1.82 (1B), –8.45 (5B), –10.66 (5B); IR (KBr) 2982, 2875, 2855, 2630, 1560, 1420, 1401, 1310, 1100, 715, 545 cm^{-1} ; ESI $m/z = 395$; mp 296 °C (dec). Anal. Calcd for the Ph_4P^+ salt, $\text{C}_{41}\text{H}_{64}\text{B}_{11}\text{PSi}$: C, 67.01; H, 8.78. Found: C, 66.95; H, 8.80.

Cs⁺ 1-(2-Trimethylsilylethynyl)undecamethylcarba-closo-dodecaborate(–) (10). To a THF solution (25 mL) of **8** (0.150 g, 0.33 mmol) was added *n*-BuLi (0.31 mL of 1.7 M solution, 0.5 mmol) at 0 °C over a period of 30 min. The contents were stirred at that temperature for 20 min and then allowed to come to room temperature. TMSCl (1.5 equiv, 0.06 mL) was added at 0 °C, and the solution was stirred for 2 h. After 2 h, 20 mL of CsCl 20% (aq) was added, and the THF was removed under reduced pressure. The aqueous mixture was washed with diethyl ether (3 × 150 mL), the ethereal phase was concentrated, and the resulting crude product was purified by reverse phase column chromatography: Yield 0.165 g, 89%; NMR was measured on the PPh_4^+ salt; ^1H NMR (δ) 8.05–7.88 (m, 4H), 7.82–7.75 (m, 16H), 0.03 (s, 9H), –0.22 (s, 15H), –0.31 (s, 15H), –0.49 (s, 3H); ^{13}C NMR (δ) 139.0, 130.2, 127.3, 115.0, 75.0; ^{11}B NMR (δ) 1.85 (1B), –8.80 (5B), –9.91 (5B); IR (KBr) 3355, 2875, 2803, 2644, 1520, 1420, 1390, 1305, 1110, 980, 912, 715, 515 cm^{-1} ; ESI $m/z = 393$; mp 370 °C (dec). Anal. Calcd for the Ph_4P^+ salt, $\text{C}_{41}\text{H}_{62}\text{B}_{11}\text{PSi}$: C, 67.19; H, 8.53. Found: C, 67.20; H, 8.50.

Cesium trans-1,2-Ethenebis[1-undecamethylcarba-closo-dodecaborate(–)] (11). To a $(\text{CF}_3)_2\text{CHOH}$ solution (total volume 11 mL) of cesium 1-(2-bromoethyl)undecamethylcarba-closo-dodecaborate(–)⁶ ($\{\text{Cs}^+\}[\text{1-(2-BrC}_2\text{H}_4\text{)-C(BCH}_3\text{)}_{11}\text{]}^-$), 0.100 g, 0.17 mmol) were added **5** (0.078 g, 0.17 mmol) dissolved in $(\text{CF}_3)_2\text{CHOH}$ and 2,6-di-*tert*-butylpyridine (1 mL). The contents were heated to 60 °C, and the reaction course was monitored by NMR. Separation by reverse phase chromatography gave 0.095 g (63%) of **11**, 0.010 g of recovered **5** (13%), and 0.018 g of **13** (17%): ^1H NMR (300 MHz) δ 6.22 (s, 2H, HC=CH, $J_{\text{HH}} = 15.8$ Hz determined from the ^{13}C satellites), –0.62–0.28 (m, 66H, BCH_3); ^{13}C NMR (100 MHz) δ 135.44 (CH=), 128.80 (=CH), 70.53 (C_{cage}), –2.99 (B– CH_3); $^{11}\text{B}\{^1\text{H}\}$ NMR (96 MHz) δ 0.08, –8.2, –10.8; IR (KBr pellet) 2950, 2900, 2830, 2746, 1447, 1232, 1181, 1095, 874, 735 cm^{-1} ; ESI $m/z = 309$. Anal. Calcd for the Ph_4P^+ salt, $\text{C}_{74}\text{H}_{108}\text{B}_{22}\text{P}_2$: C, 68.50; H, 8.39. Found: C, 68.45; H, 8.38.

Cesium 1,2-Ethynabis[1-undecamethylcarba-closo-dodecaborate(–)] (12). To a $(\text{CF}_3)_2\text{CHOH}$ solution (total volume 11 mL) of cesium 1-(2-bromoethyl)undecamethylcarba-closo-dodecaborate(–)⁶ ($\{\text{Cs}^+\}[\text{1-(2-BrC}_2\text{H}_4\text{)-C(BCH}_3\text{)}_{11}\text{]}^-$), 0.100 g, 0.17 mmol) were added **8** (0.077 g, 0.17 mmol) dissolved in $(\text{CF}_3)_2\text{CHOH}$ and 2,6-di-*tert*-butylpyridine (1 mL). The contents were heated to 60 °C, and the reaction course was monitored by NMR. Separation

by reverse phase chromatography gave 0.090 g (60%) of **12**, 0.008 g (11%) of recovered **8**, and 0.015 g (15%) of **13**. NMR was measured on the PPh_4^+ salt: ^1H NMR (δ) 8.02–7.90 (m, 8H), 7.99–7.80 (m, 32H), 0.40 to –0.03 (m, 66H, BCH_3); ^{13}C NMR (δ) 136.4, 135.8, 131.4, 119.0 (d, $J_{\text{p-c}} = 90$ Hz), 68.0; ^{11}B NMR (δ) 1.80 (1B), –8.75 (5B), –9.88 (5B); IR (KBr) 3290, 2770, 2705, 1566, 1466, 1432, 1295, 1111, 907, 753, 520 cm^{-1} ; ESI $m/z = 308$. Anal. Calcd for the Ph_4P^+ salt, $\text{C}_{74}\text{H}_{106}\text{B}_{22}\text{P}_2$: C, 68.61; H, 8.25. Found: C, 68.65; H, 8.22.

trans-1,2-Ethylenebis[1-undecamethylcarba-closo-dodecaboranyl] Biradical (14). PbO_2 (1.50 g) and $\text{Cs}^+\text{11}^-$ (0.050 g, 0.06 mmol) were combined with purified acetonitrile (10 mL) followed by trifluoroacetic acid (5 mL), and the mixture was stirred for 15 min under Ar. The deep blue pentane phase was collected under Ar through a Teflon cannula. Extraction with pentane (15 mL) was repeated until the blue color of **14** was no longer evident. The pentane phase was extracted with acetonitrile (10 mL). Solvent was removed with a stream of Ar giving 28 mg (90%) of pure **14**. No NMR signals: IR (KBr) 3290, 2789, 2712, 1550, 1488, 1414, 1305, 1120, 918, 781, 505 cm^{-1} ; MS (MALDI) $m/z = 310, 620$. Anal. Calcd for $\text{C}_{26}\text{H}_{68}\text{B}_{22}$: C, 50.48; H, 11.08. Found: C, 50.51; H, 11.05.

1,2-Ethynabis[1-undecamethylcarba-closo-dodecaboranyl] Biradical (15). PbO_2 (3.00 g) and $\text{Cs}^+\text{12}^-$ (0.100 g, 0.12 mmol) were combined with purified acetonitrile (15 mL) followed by trifluoroacetic acid (5 mL), and the mixture was stirred for 15 min under Ar. The deep blue pentane phase was collected under Ar through a Teflon cannula. Extraction with pentane (15 mL) was repeated until the blue color of **15** was no longer evident. The pentane phase was extracted with acetonitrile (10 mL). Solvent was removed with a stream of Ar giving 63 mg (85%) of pure **15**. No NMR signals: IR (KBr) 3282, 2779, 2700, 1572, 1458, 1430, 1301, 1104, 913, 761, 525 cm^{-1} ; MS (MALDI) $m/z = 308, 616$. Anal. Calcd for $\text{C}_{26}\text{H}_{66}\text{B}_{22}$: C, 50.64; H, 10.79. Found: C, 50.66; H, 10.81.

Chemical Reduction of 14 and 15. A flask was charged with **14** (20 mg, 0.032 mmol) or **15** (20 mg, 0.033 mmol), and Li (Hg) (85 mg, 0.13 mmol) in THF (15 mL). The progress of the reaction was monitored by NMR spectroscopy. After the reaction was complete, 10 mL of CsCl 20% (aq) was added and the THF was removed under reduced pressure. The aqueous mixture was washed with diethyl ether (3 × 20 mL), the ethereal phase was concentrated, and the resulting crude product was isolated. The products were either **11** (28 mg, 97% based on **14**) or **12** (26 mg, 91% based on **15**).

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