

CB₁₁Me₁₁ Boronium Ylides: Carba-*closo*-dodecaboranes with a Naked Boron Vertex

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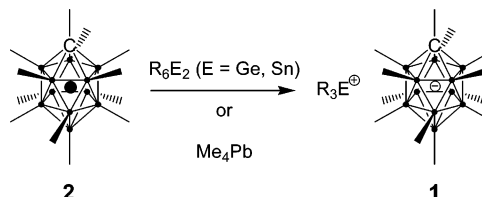
Abstract: In pentane solution, 2 equiv of the icosahedral CB₁₁Me₁₂[•] radical cleaves the Si–Si bond of hexaalkyldisilanes by boron to silicon methyl transfer with formation of 2 equiv of methyltrialkylsilanes. The loss of a methyl radical converts the CB₁₁Me₁₂[•] radical into an internally charge-compensated “boronium ylide” CB₁₁Me₁₁ with a naked vertex, which can be formally viewed as a deprotonated hypercloso carborane. It has been isolated as an air-sensitive solid, stable only below ~ –60 °C. The naked vertex appears to be in position 12 since the material reacts instantaneously with alcohols and ethers to form the 12-alkoxy anions 12-CB₁₁Me₁₁OR. It reacts with many other nucleophiles to yield more complex mixtures containing similar products. DFT calculations for the four CB₁₁Me₁₁ isomers give closed-shell ground-state electronic structures. For the isomer with naked vertex 12, a DFT computational search failed to reveal any skeletal dimers, apparently due to excessive methyl–methyl repulsions, and only a cyclic dimer bound through weak interactions of one of the 7-methyl hydrogen atoms on each cage with the empty exocyclic orbitals on B12 of the other cage was found. Natural hybrid orbital populations suggest that the three possible isomers of monomeric boronium ylides are close to true singlet ylides, with triplet states ~50 kcal/mol higher. The calculated electronic structure of the carbonium ylide is close to a singlet carbene, with a triplet state ~16 kcal/mol higher. An attempted preparation of Me₃C⁺CB₁₁Me₁₂[•] yielded neopentane and products consistent with a sequential loss of methyl groups from the carborane cage with a transient formation of similar boronium ylides. Probable mechanisms of these methyl transfer reactions are considered, and the possibly quite general role of “ylide” structures in Lewis acid induced substitution reactions on the boron vertices of carboranes and boranes is noted.

Introduction

Although polyalkylated CB₁₁ anions have received considerable attention since the preparation of the weakly coordinating permethylated anion CB₁₁Me₁₂[–] (**1**)^{1,2} and its analogues,^{3,4} much of their chemistry remains unknown or poorly understood.

At 1.15 V above the ferrocene/ferrocenium couple in acetonitrile, **1** is reversibly oxidized to the isolable and stable neutral radical CB₁₁Me₁₂[•] (**2**).⁵ This one-electron oxidant is freely soluble in inert nonpolar solvents and is thus suitable for the preparation of salts of highly electrophilic cations with the anion **1** by oxidation of suitable precursors. Oxidation of metal–metal and metal–carbon bonds in germanium, tin, and lead com-

Scheme 1



pounds of the types R₆M₂ and R₃M–R (M = Ge, Sn, Pb, R = alkyl) yielded the salts of the corresponding R₃M⁺ cations with **1** (Scheme 1).^{6,7} The *n*-Bu₃Sn⁺CB₁₁Me₁₂[–] salt has been crystallized from hexane and a disordered single-crystal X-ray diffraction structure obtained,⁶ but the salts of the Me₃M⁺ cations (M = Ge, Sn, and Pb) are insoluble in alkanes and react with other solvents. Structural information for them was obtained only from powder EXAFS measurements.⁷

In the salts of main group^{6–8} and transition metal^{9,10} cations with CB₁₁ anions fully methylated on the boron vertices, the

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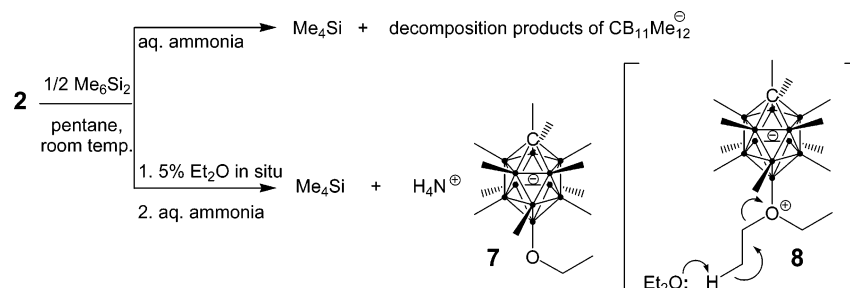
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Scheme 2



cation is coordinated to the carbon of one or more of the methyl groups of the anion, which are calculated⁷ to have considerable methide (methyl anion) character. Under suitable conditions, active metal cations can cause a loss of a methide anion ligand from its boron vertex, and this has led to speculation that the carborane is converted to an internally charge-compensated “boronium ylide” $\text{CB}_{11}\text{Me}_{11}$, an icosahedral cluster with one “naked” vertex that carries neither a substituent nor a lone pair.^{11,12} When one proceeds from $M = \text{Pb}$ to $M = \text{Sn}$ and $M = \text{Ge}$, the observed and calculated structures of $\text{Me}_3\text{M}^+\text{CB}_{11}\text{Me}_{12}^-$ salts provide clear evidence of increasing metal cation–methyl carbon interaction along a reaction path familiar from classical backside $\text{S}_{\text{E}}2$ substitution,⁷ much along the lines of the standard Bürgi–Dunitz analysis.¹³ As we have already indicated,⁷ and now describe in full detail, when $M = \text{Si}$ or $M = \text{C}$, such substitution on the methyl carbon actually takes place and at low temperatures permits a direct observation of the previously only suspected novel structure $\text{CB}_{11}\text{Me}_{11}$, presumably produced by abstraction of a methide anion from the antipodal position 12 (**3**). We have found no unequivocal evidence for the formation of the isomers $\text{CB}_{11}\text{Me}_{11}$ with a naked vertex **7** (**4**), **2** (**5**), or **1** (**6**) in the presently described reactions, but we shall present results of computations for them as well.

The structures **3–5** can be at least formally described as a boronium cation localized on one of the boron vertices, internally charge compensated by the delocalized negative charge on the cage, hence as boronium ylides. The $\text{CB}_{11}\text{Me}_{11}$ isomer with a naked carbon vertex (**6**) has also been postulated as a reaction intermediate;³ its geometry and electronic structure were calculated and described as intermediate between a carbonium ylide and singlet carbene. A more formal description of all four $\text{CB}_{11}\text{Me}_{11}$ isomers is to view them as derivatives of the hypercloso cation $\text{CB}_{11}\text{H}_{12}^+$ deprotonated at one of the vertices.

Results

Oxidation of R_6Si_2 with **2 and In Situ Trapping of **3**.** When 1 equiv of hexamethyldisilane (Me_6Si_2) was added to a solution of 2 equiv of the $\text{CB}_{11}\text{Me}_{12}^\bullet$ radical (**2**) in pentane, no reaction

took place at low temperatures. However, at room temperature, the blue color of the radical disappeared after 30 min, and a precipitate formed. Its analysis revealed the presence of numerous decomposition products of the $\text{CB}_{11}\text{Me}_{12}^-$ anion (**1**). No silicon containing products were found after work up. When the experiment was repeated in an NMR tube and ^{29}Si NMR of the reaction mixture was recorded, only one signal was observed at 0.0 ppm. Its location and splitting pattern due to coupling to ^1H were identical to that of the volatile tetramethylsilane (TMS, Scheme 2). When water, ethanol, or other nucleophiles were added to the room temperature reaction mixture after the blue color disappeared and the precipitate formed, the decomposition products of the carboranyl anion were still observed, and no silicon containing products other than TMS were formed and, in particular, no trapping products expected from the Me_3Si^+ cation.

In an in situ room temperature trapping experiment, with diethyl ether present from the outset, ^{29}Si NMR of the reaction mixture still showed TMS as the only silicon containing product and a new carboranyl anion as another major product. The salt was isolated by HPLC, and the anion was identified as 12-EtO– $\text{CB}_{11}\text{Me}_{11}^-$ (**7**, Scheme 2). Its formation can be explained by a nucleophilic attack by diethyl ether at the naked boron vertex of **3** to produce the zwitterion **8**, which then loses ethylene.

When hexaisopropyldisilane¹⁴ was treated with **2** in pentane, the color of the radical again disappeared only at room temperature in about 1 day. The products were triisopropylmethylsilane,¹⁵ as shown by GC/MS and NMR, and decomposition products of **1**. In contrast, $(i\text{-Pr}_3\text{Si})_2\text{Hg}$ ^{16,17} reacted instantly with **2** in pentane even at -78°C . This reaction also produced only triisopropylmethylsilane (as shown by GC/MS) and decomposition products of the $\text{CB}_{11}\text{Me}_{12}^-$ anion.

Formation of Solid **3 and its Reactions with Alcohols and Ethers.** The reaction of $t\text{-Bu}_6\text{Si}_2$ ¹⁸ with **2** in pentane proceeded rapidly at -78°C and even at -100°C to give a white solid. After warming a mixture of decomposition products of **1** was detected, together with $t\text{-Bu}_3\text{SiMe}$,¹⁹ identified by GC/MS and NMR. Pentane, when carefully removed at temperatures below -60°C , contained only $t\text{-Bu}_3\text{SiMe}$. When the white solid was treated at -78°C with either diethyl ether or ethyl alcohol, the 12-EtO– $\text{CB}_{11}\text{Me}_{11}^-$ anion (**7**) was isolated from the reaction

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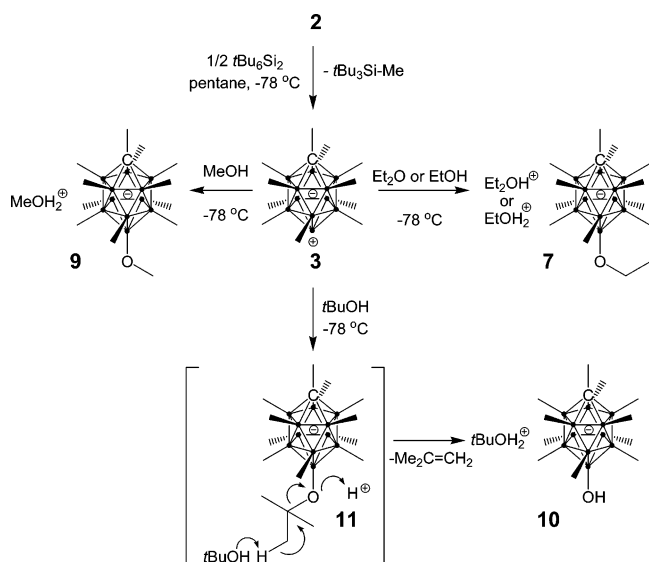
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Scheme 3



mixtures in 93 and 97% yield, respectively. The anion **7** was also formed when the oxidation was conducted in the presence of diethyl ether. These results suggest that the solid is the boronium ylide **3**, stable at this low temperature (Scheme 3).

The reaction of **3** with methanol produced the 12-MeO-CB₁₁Me₁₁⁻ anion (**9**, Scheme 3). The analogous reaction with *tert*-butyl alcohol resulted mostly in the 12-HO-CB₁₁Me₁₁⁻ anion (**10**) and produced only trace amounts of the 12-*t*-BuO-CB₁₁Me₁₁⁻ anion (**11**) as was evident from ES/MS of the reaction mixture, presumably because **11** is unstable in the acidic medium generated and decomposes to **10** with a loss of isobutylene (Scheme 3).

Additional Reactions of Solid 3. Solid **3** was treated with several additional nucleophiles, but in most cases, complicated mixtures of products were formed. In these case, only the structures of the chief products were assigned, based on ES/MS. Thus, diethylzinc produced a mixture containing mainly CB₁₁Me₁₁Et⁻ and some CB₁₁Me₁₁H⁻. Reaction with *tert*-butyllithium produced a mixture containing CB₁₁Me₁₁*t*-Bu⁻ and some CB₁₁Me₁₁H⁻ together with other *t*-Bu-containing products. The reaction with di(*tert*-butyl)mercury²⁰ produced a similar mixture. Neopentyllithium²¹ gave a complicated mixture containing some CB₁₁Me₁₁CH₂-*t*-Bu⁻. Triethylsilyllithium prepared from triethylsilane via bis(triethylsilyl)mercury²² afforded mainly CB₁₁Me₁₁Et⁻. Treatment with carbon monoxide for 3 h followed by the addition of methanol yielded a mixture in which MeOCO-CB₁₁Me₁₁⁻ and MeO-CB₁₁Me₁₁⁻ dominated and some CB₁₁Me₁₁H⁻ was present. Dimethylaminosulfur trifluoride yielded mostly CB₁₁Me₁₁F⁻ and some CB₁₁Me₁₁H⁻. With benzene and pyridine, CB₁₁Me₁₁C₆H₅⁻ and CB₁₁Me₁₁C₅NH₅⁻ were formed, respectively, along with some CB₁₁Me₁₁H⁻.

In most cases where substitution was observed, we expect that it occurred in position 12 of the anion, as in the cleaner trapping reactions described above. However, in some instances, NMR spectra of the mixtures left little doubt that mixtures of two (with benzene and pyridine) or even three (with dimethy-

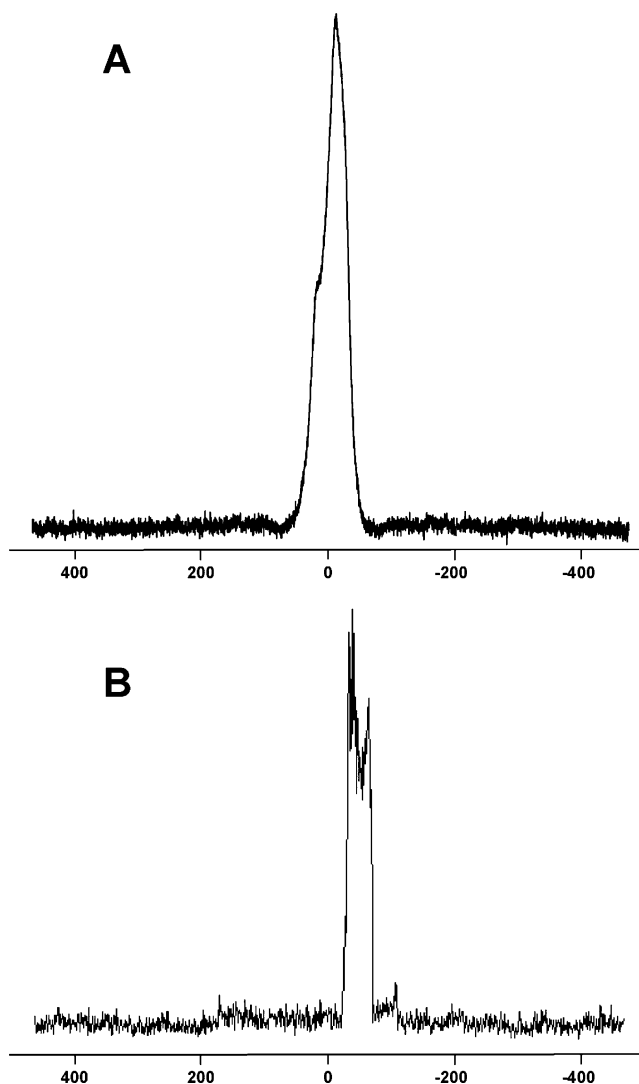


Figure 1. Measured (A) and simulated (B) ¹¹B NMR spectra of **3**. Both spectra have identical spectral width; the measured spectrum was not referenced, while the simulated spectrum was referenced to bare ¹¹B nucleus at 0 ppm.

laminosulfur trifluoride) positional isomers were formed. The exact composition of the reaction mixtures depended on minor changes in the reaction conditions, and we expect that a detailed study of these trapping reactions will be necessary before they are elucidated. Our initial impression is that both **3** and a dimer (**3**)₂ may react with the nucleophile, and that methyl shifts may occur during these trapping reactions.

NMR Spectra of Solid 3. The ¹H, ¹³C, or ¹¹B NMR of pentane or hexane containing the solid **3** below -60 °C did not show any signals attributable to **3**, suggesting that it is insoluble in these solvents at low temperature. Our attempts to grow crystals of **3** by slow diffusion of reagents toward each other through a column filled with Teflon powder at low temperature failed. We were able to characterize the air-sensitive powdery solid **3** by MAS NMR spectroscopy without allowing it to warm above -60 °C (Figure 1), but considerable technical difficulties encountered in the preparation of sealed samples suitable for magic angle spinning forced us to work with only small amounts and caused poor signal-to-noise ratios. We were only able to obtain a qualitative ¹³C NMR spectrum. The results were compared with expectations based on chemical shielding

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Table 1. Calculated^a ¹³C and ¹¹B Isotropic Chemical Shifts and Electric Field Gradient Parameters of the Boronium Ylide **3**

	isotropic shielding ^b	span ^c	C _Q ^d	η _Q ^e
C1	40	43		
CH ₃ at C1	14	24		
CH ₃ at B2 – B12	0 to –2	7–9		
B2–B6	126–127	43–48	1.11	0.69
B7–B11	124	33–34	1.02	0.04
B12	23	130	5.07	0.00

^a GIAO B3LYP/6-31G(d,p). ^b Reported in parts per million from TMS for ¹³C (obtained by taking the calculated value for CH₄ obtained at the same level of theory and adjusting by 7 ppm, the experimental difference between CH₄ and TMS in the gas phase²³), and calculated as shielding value for ¹¹B. ^c Range of diagonal values of the chemical shielding tensor in parts per million. ^d Quadrupole coupling constant in MHz. ^e Asymmetry parameter.

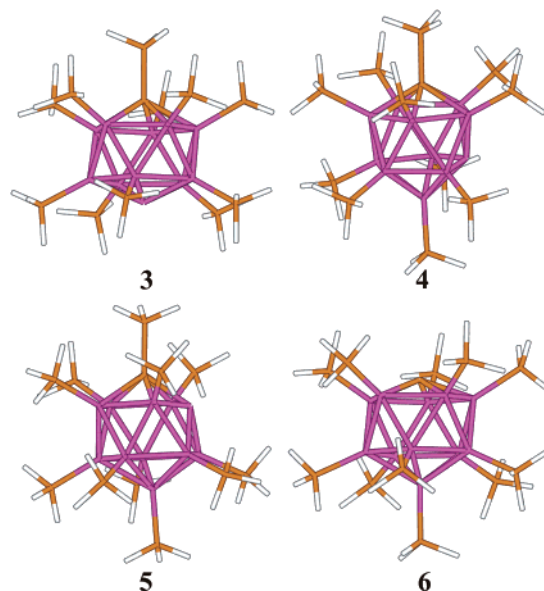
calculations with the GIAO B3LYP/6-31G(d,p) method for monomeric **3**. Since we suspected that **3** may have a tendency to dimerize or form even higher aggregates, we also performed calculations at the same level for the optimized geometry of the weakly bound nearly symmetric dimer (**3**)₂, whose structure will be described below.

In the ¹³C spectrum, three groups of resonances are expected from the calculation for the monomer (Table 1). The results calculated for the dimer are similar except that the cage carbons are shifted to even higher values, about 53 ppm, and the carbons of the two methyl groups that bridge the two cages appear near 35 ppm.

The resonances for the carbon atoms of all methyl groups located at boron vertices are expected to be broadened due to coupling to the boron quadrupole, as is the resonance of the cage carbon, which carries no hydrogens and is expected to have low intensity. Unfortunately, the extremely noisy low-temperature MAS ¹³C NMR spectrum was not very useful. It showed a peak at ~ –2 ppm, along with a weak broader resonance centered at ~40 ppm. The peak anticipated near 14 ppm was not observed and is presumably too weak to be seen above noise. Although the spectrum is compatible with the calculations for the dimer, it cannot be taken for a proof of structure.

The ¹¹B spectrum was of much better quality, but expectations for it are less clear-cut (Table 1). The unsubstituted boron vertex B12 should be strikingly different from the 10 others that carry methyl substituents. The latter should all be very similar to each other and to boron vertices in ordinary methylated carborane anions. The calculated isotropic chemical shift of B12 in monomeric **3** is displaced by 100 ppm toward higher chemical shift (lower shielding) values, has a much larger anisotropy, and has a very different electric field gradient (EFG) tensor. In (**3**)₂, the shielding calculated for B12 is less extreme (about 57 ppm) and less anisotropic (span of about 80 ppm), but this boron atom is still quite distinct from the others. The remaining boron signals calculated for the dimer did not differ much from those calculated for the monomer. The detection of a signal for B12 would thus leave no doubt of the correctness of the structural assignment.

The calculated ¹¹B NMR and EFG parameters of monomeric **3** were used in a series of spectral simulations to determine what should be expected for the observed ¹¹B spectrum, with particular emphasis on the simulation of the peak that would be expected for B12. Unfortunately, they revealed that the

**Figure 2.** Optimized B3LYP/6-31G(d) structures of the isomers of CB₁₁Me₁₁.

resonance of this boron will be exceedingly difficult to observe, due to a combination of factors that include the 10:1 ratio between the methylated borons and B12, the larger span of its very anisotropic chemical shift, its large quadrupolar coupling constant, and its dipolar and quadrupolar coupling to five other borons. In principle, the SIMPSON program that we used has the capability of simulating solid-state NMR spectra for any spin system, but a complete simulation of the 11 boron atoms was too demanding for the computers available to us. Instead, we examined an isolated spin pair, B12 with B7, and found that even in this simple model system the dipolar coupling and the effects of the quadrupolar moment spread the signal of B12 so much that an unrealistically high signal-to-noise ratio would be required to observe it in the presence of the signals from the methylated boron atoms (Figure 1).

As expected from the simulation, the experimental ¹¹B spectrum indeed shows no evidence of B12. Both under slow MAS and static conditions, it contains only one resonance, ~45 ppm at half-height, with a slight shoulder on the higher chemical shift side, and this is attributed to the two groups of similar boron vertices, B2–B6 and B7–B11 (Figure 1).

Attempted Preparation of Me₃C⁺ 1[–]. Treatment of the Ag⁺ salt of **1** with *t*-BuBr in chlorinated solvents (CH₂Cl₂, CHCl₃, CCl₂F–CCl₂F, or CCl₃–CH₃) following a procedure for Ag⁺ CB₁₁H₆X₆[–] salts reported by Reed et al.^{24,25} produced mixtures of carboranyl anions whose ES/MS suggested that they are partially methylated and partially chlorinated. When this reaction was conducted in a sealed NMR tube, no starting *t*-BuBr was found and a new product with ¹H and ¹³C NMR signals similar to those reported for neopentane was observed. On the basis of these observations, we concluded that Me₃C⁺ CB₁₁Me₁₂[–] is unstable and most likely undergoes a series of methide abstraction reactions to give boronium ylides that react with halogenated solvents to abstract chloride anions.

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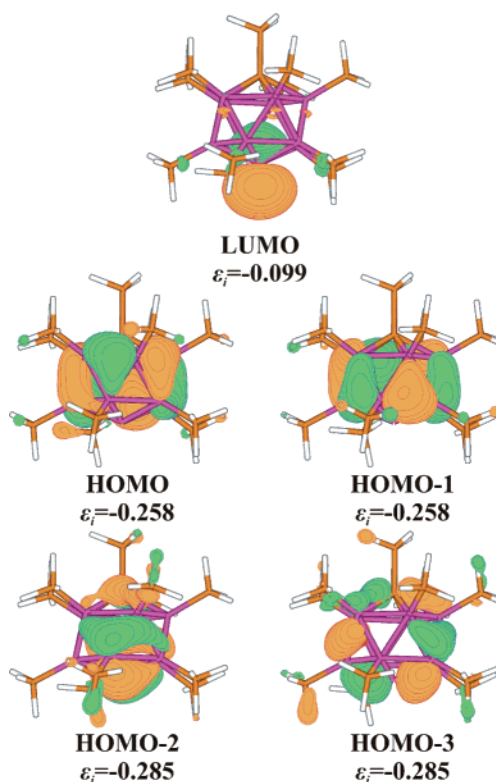
Table 2. B3LYP/6-31G(d) Calculations for the Optimized Lowest Singlet States of **1** and **3–6**

		1	3	4	5	6
E_{rel}^a		-	0	3.2	11.7	36.0
$D_{4,7}$ or $D_{2,10}^b$		3.40	-	3.09	3.07	-
Δ^c		1: 0.82; 12: 0.94	0.64	0.65	0.64	0.53
$D_{1,12}^d$		3.27 ^e	2.94	3.34	3.30	2.95
R^f		1: 1.73; 12: 1.79	1.70	1.70	1.68	1.64
μ^g		-	0.17	2.54	3.90	2.37
n^h	out ⁱ	1: 1.10; 12: 0.77	0.20	0.21	0.25	0.61
	ψ^j	1: 2.32; 12: 1.42	1.54	1.56	1.35	2.51
	in ^k	1: 1.10; 12: 0.68	0.72	0.72	0.76	1.10
$q(\text{B})^l$	12	+0.12	+0.53	+0.11	+0.15	+0.04
	7–11	+0.08	+0.06	+0.49 ^m + 0.05 ⁿ + 0.10	+0.08 ⁿ + 0.10 ^o + 0.05	+0.13
	2–6	+0.26	+0.28	+0.23 ^m + 0.28 ^o + 0.24	+0.62 ^m + 0.24 ⁿ + 0.28	+0.26
$q(\text{C1})^p$	1	-0.52	-0.53	-0.52	-0.56	-0.22
$q(\text{CH}_3)^q$	12	-0.22	-	-0.17	-0.18	-0.13
	7–11	-0.22	-0.17	-0.16 ⁿ - 0.18	-0.17 ⁿ - 0.18 ^o - 0.17	-0.18
	2–6	-0.22	-0.19	-0.17 ⁿ - 0.19 ^o - 0.18	-0.17 ⁿ - 0.19	-0.15
$q(\text{vertex})^r$	1	+0.08	+0.11	+0.11	+0.12	-
	12	-0.10	+0.53	-0.06	-0.03	-0.10
	7–11	-0.13	-0.11	+0.49 ^m - 0.11 ⁿ - 0.08	-0.09 ⁿ - 0.08 ^o - 0.12	-0.04
	2–6	+0.04	+0.09	+0.06 ⁿ + 0.09 ^o + 0.06	+0.62 ^m + 0.07 ⁿ + 0.10	+0.11
	1	-0.45	-0.43	-0.41	-0.44	-0.22

^a Energy in kcal/mol relative to **3** (-750.77248 au). ^b Diameter in Å measured from the naked vertex to its antipode. ^c The distance in Å of the naked vertex to the average plane defined by its five neighboring vertices. ^d Diameter in Å measured from C1 to B12. ^e This also is the value found experimentally (ref 1). ^f Average distance in Å from the naked vertex to its boron neighbors. ^g Dipole moment in Debye. With the negative end located in the center of the icosahedron, a positive entry means that the positive end of the dipole lies in the general direction of the cage carbon atom. ^h Electron populations in the NHOs of the naked vertex atom (three-center bond option used). ⁱ The radial orbital pointing outward. ^j Sum for the two tangential orbitals. ^k The radial orbital pointing inward. ^l Natural atomic charge in units of |e| on vertex boron. Average value where called for by cage symmetry. ^m On the naked vertex. ⁿ On neighbors of the naked vertex. ^o On next nearest neighbors of the naked vertex. ^p Natural atomic charge in units of |e| on the cage carbon. ^q Sum of natural atomic charges on C and H atoms in units of |e|, averaged over vertices related by cage symmetry. ^r Sum of natural atomic charges on B, C, and H atoms on a vertex in units of |e|, averaged over vertices related by cage symmetry.

Density Functional Theory Results for the CB₁₁Me₁₁ Ylides 3–6. The structures of the boronium ylides **3–5** and the carbonium ylide **6** were optimized with the B3LYP/6-31G(d) method (Figure 2) and are compared with that of **1** in Table 2. For each isomer, we performed a few optimizations starting with different methyl orientations, and of the several local minima that differ in methyl group conformation, only the one with the lowest energy was included. Several attempts to find alternative structures for **3** and **6**, in which the empty orbital on the naked vertex would be stabilized by a bridging methyl group, failed. All these structures converged to the global minima shown in Figure 2. The charge distribution was evaluated by NBO analysis with inclusion of three-center bonds. Some of the results for **6** (NBO analysis with three-center bonds) have already been published.³ The LUMO and the two highest-energy pairs of nearly doubly degenerate occupied orbitals, HOMO to HOMO-3, of **3** are depicted in Figure 3.

In an effort to find alternative electronic structures for the reactive intermediates **3–6**, we considered the possibility that they might have a low-energy open-shell state in which the low-lying empty orbital on the naked vertex (the LUMO, Figure 3) has taken an electron from the highest occupied delocalized orbital of the cage (the HOMO, Figure 3) in an intramolecular charge-transfer process (formulas **3R–6R** in Chart 1). After all, the anion **1** can be reversibly oxidized easily, and a HOMO to LUMO excitation might be facile. Since the HOMO of **1** is almost exactly degenerate (except that a methyl substituent has only a 3-fold and not 5-fold axis of symmetry), the radical **2** produced by the removal of one electron is subject to Jahn–Teller distortion, and so will be the open-shell state of **3–6**. A detailed examination that will be described elsewhere²⁶ has shown that there are two inequivalent possible Jahn–Teller distortions of the CB₁₁H₁₂ radical that yield two almost

**Figure 3.** B3LYP/6-31G(d) HOMO to HOMO-3 and LUMO of **3**.

isoenergetic sets of five symmetry-related minima on the ground-state potential energy surface. A similar situation can be anticipated for the HOMO to LUMO excited states of **3**, and related complexity is likely for **4–6**. To develop a feeling for the relative energies of the closed-shell states described in

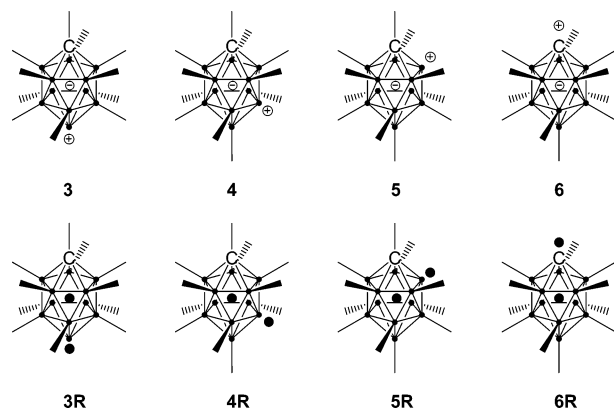
Chart 1. Closed-Shell and Open-Shell (R) Structures of the Ylides 3–6

Table 2 and the biradical “HOMO–LUMO charge transfer” states, we have optimized the structures of the lowest triplets of the boronium ylides **3R–6R**.

Calculations on the parent ylide $\text{CB}_{11}\text{H}_{11}$ suggested the possible existence of A' and A'' states for structures related to **3** and **6** and six (times five, due to the cage symmetry) states for structures related to **4** and **5**. Two of these six states are of A' and A'' symmetry type, with the Jahn–Teller distortion axis passing through the naked vertex. For the four others, the distortion axis is rotated relative to the naked vertex by one or two position, and the A' or A'' electronic state symmetry is approximately kept. The optimizations of ylides **3R–6R** were started from all the structures found for the $\text{CB}_{11}\text{H}_{11}$ system, but with all H atoms replaced with CH_3 groups. They resulted in only one triplet structure for each ylide, with approximately A' electronic structure and C_3 cage symmetry, except that several different conformations of the methyl groups were again possible. As in the case of singlet states, we only present results for the lowest energy conformation of the methyls (Table 3). They show that these states lie well above the closed-shell singlets of Table 2 and will not be easily accessible by thermal excitation at room temperature. Since the two unpaired electrons are well separated in space, the energies of the analogous open-shell singlet states will be similar at approximately vertical geometries, making it unlikely that alternative singlet ground-state structures will result for **3–6**. In their ground state, our intermediates are therefore likely to behave as ylides **3–6** and not as biradicals **3R–6R**.

As mentioned above, we suspect that in solid **3** dimers or even higher aggregates are present, and we have attempted to find the best dimer structure. Since it is likely that dispersion forces play an important role in the stabilization of the dimer, the MP2 method seemed to be the lowest level of calculation that would give reasonable results. Unfortunately, RI-MP2/def-SV(P) geometry optimization was very slow because of the extensive rotational freedom of the methyl groups, and our computer resources did not allow us to reach complete convergence (the optimization was stopped when the rotations of the methyl groups showed only small changes, gradient norm was below the convergence limit, and energy changes, $4 \cdot 10^{-4}$ kcal/mol, were close to the convergence limit). In the end, we used the B3LYP/6-31G(d) method of calculation with the understanding that the dimerization energy will be underestimated. For unmethylated or sparsely methylated boronium

ylides, several types of dimeric cages were found, similar to those known from experimental work on $\text{B}_{10}\text{H}_9^-$.²⁷ However, starting from a geometry in which the two undecamethylated cages were joined by two methyl groups bridging through their carbon atoms, the only bound dimeric structure that was found was held together by two unsymmetrically bridging methyl groups, with a binding energy of only 5.5 kcal/mol. In this cyclic structure, one of the hydrogens of a methyl group in position 7 in each of the two cages is used to form a bridge to the naked B12 atom on the other cage. The MP2 result gave a very similar geometry (Figure 4) with a binding energy of 32 kcal/mol. Because of the known inadequacies of the DFT and MP2 methods in the description of weak complexes, we estimate that the true binding energy is bracketed by the numbers obtained by the two procedures, but we attach only qualitative importance to this result.

Discussion

Boronium Ylides. The mode of formation of the $\text{CB}_{11}\text{Me}_{11}$ product from **2**, its reactions, and its ^{11}B NMR fit the notion that it is the ylide **3**, albeit an ylide of a special kind. Ordinary ylides are species in which two nearby atoms, usually neighbors, carry opposite formal charges. In **3–6**, there are some possibly quite important resonance structures in which the opposite charges are located on the same atom, and it is debatable whether these structures carry enough weight in the ground state to invalidate the description of these molecules as ylides in which one boron or carbon vertex carries a positive charge (a “boronium or carbonium cation”) while the negative charge is delocalized on the cage as in the parent carborane anion **1**. The reactivity of **3** (and **6**)³ toward oxygen-based nucleophiles suggests that at least for some purposes it will be useful to categorize **3–6** as such ylides.

Boron-based ylides are known,^{28–32} but their most common general formula is $^-\text{B}=\text{C}-\text{E}^+$, in which the boron atom carries a negative formal charge. The positive charge resides on a more electronegative atom E (such as phosphorus,²⁸ nitrogen,²⁹ carbon,³⁰ or germanium and tin³¹). Ylides containing a phosphonium³² or ammonium³³ center or the tropylium cation^{34,35} linked to an anionic carborane cage are also known. As discussed earlier,³ the ylides **3–6** are unusual in that some quite reasonable resonance structures carry the positive and the negative charge on the same atom, as in a singlet carbene.

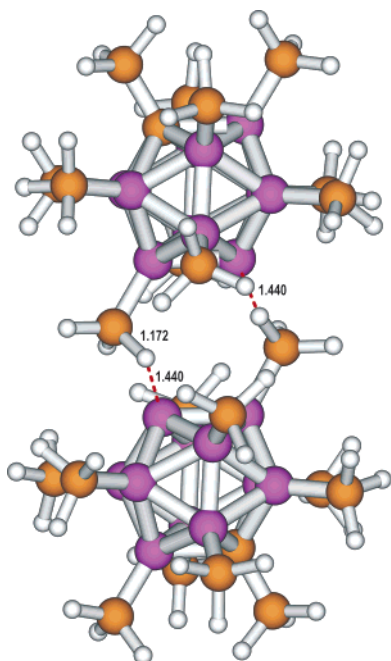
To the best of our knowledge, intermediates with a naked boron vertex carrying a formal positive charge, such as **3**, have never been isolated, but such structures have been postulated as reaction intermediates and suggested computationally. Wierse-

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Table 3. B3LYP/6-31G(d) Calculations for the Optimized Lowest Doublet of **2** and Triplet of **3–6**

	2	3	4	5	6	
E_{ref}^a	-	56.6	56.2	57.2	51.8	
E_{ST}^b	-	56.6	53.1	45.5	15.7	
$D_{4,7}$ or $D_{2,10}^c$	4,7:3.43 2,10:3.46	-	3.38	3.37	-	
Δ^d	1:0.81, 12:0.95	0.86	0.86	0.88	0.68	
$D_{1,12}^e$	3.32	3.24	3.33	3.31	3.17	
R^f	1:1.73, 12:1.81	1.77	1.75	1.75	1.68	
μ^g	2.29	2.84	2.59	2.35	1.15	
n^h	out ⁱ	1:1.12, 12:0.78	0.95	0.94	0.95	
	\uparrow^j	1:2.24, 12:1.14	1.29	1.30	1.15	
	in ^k	1:1.18, 12:0.64	0.62	0.64	0.59	
$q(\text{B})^l$	12	+0.12	+0.12	+0.07	+0.10	
	7–11	+0.16	+0.12	+0.11 ^m + 0.08 ⁿ + 0.25	+0.15 ⁿ + 0.11 ^o + 0.12	+0.12
	2–6	+0.30	+0.31	+0.28 ⁿ + 0.30 ^o + 0.25	+0.29 ^m + 0.24 ⁿ + 0.38	+0.28
$q(\text{C1})^p$	1	-0.55	-0.56	-0.55	-0.59	-0.39
$q(\text{CH}_3)^q$	12	-0.19	-	-0.19	-0.18	-0.18
	7–11	-0.17	-0.29	-0.17 ⁿ - 0.18	-0.17 ⁿ - 0.18 ^o - 0.18	-0.18
	2–6	-0.18	-0.19	-0.18 ⁿ - 0.18 ^o - 0.19	-0.18 ⁿ - 0.19	-0.17
$q(\text{vertex})^r$	1	+0.11	+0.11	+0.11	+0.11	-
	12	-0.07	+0.12	-0.12	-0.09	-0.10
	7–11	-0.01	-0.17	+0.11 ^m - 0.09 ⁿ + 0.07	-0.02 ⁿ - 0.06 ^o - 0.06	-0.01
	2–6	+0.11	0.12	+0.10 ⁿ + 0.11 ^o + 0.06	+0.29 ^m + 0.07 ⁿ + 0.19	+0.11
	1	-0.44	-0.45	-0.44	-0.49	-0.39

^a Energy in kcal/mol relative to the closed-shell singlet state of **3** (Table 2, -750.77248 au). ^b Adiabatic singlet–triplet excitation energy in kcal/mol. ^c Diameter in Å measured from the naked vertex to its antipode. ^d The distance in Å of the naked vertex to the average plane defined by its five neighboring vertices. ^e Diameter in Å measured from C1 to B12. ^f Average distance in Å from the naked vertex to its boron neighbors. ^g Dipole moment in Debye. With the negative end located in the center of the icosahedron, a positive entry means that the positive end of the dipole lies in the general direction of the cage carbon atom. ^h Electron populations in the NHOs of the naked vertex atom (three-center bond option used). ⁱ The radial orbital pointing outward. ^j Sum for the two tangential orbitals. ^k The radial orbital pointing inward. ^l Natural atomic charge in units of |e| on vertex boron. Average value where called for by cage symmetry. ^m On the naked vertex. ⁿ On neighbors of the naked vertex. ^o On next nearest neighbors of the naked vertex. ^p Natural atomic charge in units of |e| on the cage carbon. ^q Sum of natural atomic charges on C and H atoms in units of |e|, averaged over vertices related by cage symmetry. ^r Sum of natural atomic charges on B, C, and H atoms on a vertex in units of |e|, averaged over vertices related by cage symmetry.

**Figure 4.** Optimized RI-MP2/def-SV(P) structure of (**3**)₂, the dimer of **3**.

ma and Middaugh³⁶ oxidized B₁₂H₁₂²⁻ electrochemically and produced the Cs⁺ salt of B₂₄H₂₃³⁻. It is plausible that their initial product was an anion B₁₂H₁₁⁻ missing a hydride ligand on one vertex, and that this then complexed to the B–H bond of another B₁₂H₁₂²⁻, presumably forming a symmetric three-center bond. Hawthorne et al.^{37,38} and Middaugh and Farha³⁹ oxidized B₁₀H₁₀²⁻ and obtained evidence for the intermediacy of B₁₀H₉⁻ in the formation of three distinct dimers B₂₀H₁₈⁻. This chemistry has been thoroughly reviewed.¹⁸ Wiersema and Hawthorne⁴⁰

found a similar behavior in the oxidation of the carborane analogue, 1-CB₉H₁₀⁻. Jelinek et al.⁴¹ proposed the formation of an intermediate with vacant exohedral orbital on a cage boron atom in electrophilically assisted halogenation of 4,5-dicarb-*arachno*-nonaborane(13), 4,5-C₂B₇H₁₃. Hawthorne et al.⁴² found that B₁₀H₁₀²⁻ is phenylated in high yield by reaction with triflic acid and benzene. It has been proposed¹¹ that the Li⁺-catalyzed σ -bond metathesis reaction with arenes that introduces an aryl substituent onto the -CB₁₁Me₁₁⁻ cage proceeds via a boronium ylide. We have already mentioned that evidence for an analogous “carbonium ylide” as a reaction intermediate is quite strong,³ although Tsuji et al.⁴³ were unable to generate a carbocation on a carbon of an analogous but neutral 12-vertex carborane C₂B₁₀H₁₂. More recently, Weller et al.¹⁰ proposed a participation of a boronium ylide when they attempted to combine 1-H-CB₁₁Me₁₁⁻ with certain cationic transition metal species. Also, according to computations by McKee,⁴⁴ protonation of the CB₉H₁₃⁻ anion may lead to the neutral boronium ylide CB₉H₉. Thus, there is considerable indirect evidence for deltahedral boranes and carboranes with a naked vertex, but in the absence of peralkylation, they apparently tend to undergo irreversible dimerization. According to the results of our experiments and calculations, such covalent dimerization is sterically

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prevented by permethylation, and much weaker interactions of the agostic type are likely to be responsible for aggregation in the neat solid.

The Ground State of the Boronium Ylides (Table 2). The computed relative stabilities of **3** and **4** are close, and the involvement of positions 7–11 in reactions of anions of type **1** indeed is close to that of position 12, due to the 5-fold statistical advantage enjoyed by positions 7–11. For example, the reaction of **1** with HF, which we suspect to proceed with intermediate formation of a boronium ylide as discussed further below, is now believed to lead to 30% of substitution in position 7 via **4** and 70% substitution in position 12 via **3**.⁵ The calculated energy of **5** is significantly higher than those of **3** and **4**, and this fits the observation that electrophilically induced nucleophilic substitution in positions 2–6 is rarely if ever observed, although electrophilic substitution in these positions is known (e.g., in the permethylation¹ that leads to **1**). For instance, in the reaction of **1** with HF, substitution in position 2 was not detected. According to the calculations, the carbonium ylide **6** is by far the least stable of the four isomers, and it is puzzling that it should be a viable reaction intermediate³ at all. We are presently examining the properties of this reactive intermediate both experimentally and computationally in an effort to understand this apparent contradiction and to make sure that its structure is indeed **6**.

Presently, we describe primarily the molecular and electronic structure of the boronium ylides **3–5**, as the structure of the carbonium ylide **6** has already been discussed³ and will only be referred to for comparison. Relative to **1**, the main change in the structure brought about by the presence of an empty orbital on one of the boron atoms is a significant compression of the cage along the axis that passes through the naked vertex to the antipodal one, as the naked boron atom moves closer to the center of the cage and shortens the distance to the neighboring vertices significantly, apparently in an effort to increase its interaction with them. At the same time, the icosahedron is expanded in directions perpendicular to this axis. This is very similar to the result³ for the carbonium ylide **6**.

The distribution of atomic charges in the ylides is surprisingly similar to what is calculated for **1** (Table 2; the previously published⁷ results were obtained without the three-center option and are not exactly comparable). In all three boronium ylides **3–5**, the only significant change is the strongly increased positive charge on the naked boron atom. In the carbonium ylide **6**, the naked atom again has much less electron density than in the anion **1**, and in addition, the antipodal position 12 is affected as well: B12 is less positive and its methyl substituent is less negative. The charge distribution in **3** explains why the calculated dipole moment of **3** is so low. While the charge separation between the strongly negatively charged vertex 1 and the strongly positively charged vertex 12 is large, the effect of these charges is almost completely compensated by the effect of charges located on the less strongly positive or negative but more numerous vertices 2–6 and 7–11, respectively.

The population of the individual natural hybrid orbitals on the naked vertex is a more useful indicator of the electronic structure of the ylides. The results for **3** are representative of all three boronium ylides. The outward pointing radial hybrid on the naked atom carries very little electron density, much less than the approximately 3/4 electron in its inward pointing radial

hybrid used for cage bonding, which is similar to what is found in **1**. This corresponds well to expectations for the “empty” orbital of a boronium cation. The tangential hybrids do not carry an especially large compensating electron density, also about 3/4 electron each, and very similar to what is found in **1**. Hence, the overall atomic charge on the naked atom remains quite positive. We propose that the designation of boronium ylide is justified for **3–5**, and that their ground-state structure provides little reason for thinking of them as singlet “borylenoids”. Such structures might possibly become more important along their reaction paths.

This is quite different from the situation in **6**, where the outward pointing radial hybrid still carries fairly low electron density and formally has nearly half an elementary positive charge, while the inward pointing orbital has about one electron, as it did in **1**, and does not contribute significantly to net charge. However, the population of the tangential orbitals is even larger than that in **1**, about 2–1/2 elementary charges, and it is responsible for the overall negative charge on the carbon atom. Both in the limiting “carbenoid”-type structure and in the limiting “ylide”-type structure, one would expect a full positive charge (no electron density) in the outward pointing radial orbital, and formally, one can view the half elementary charge in this orbital as borrowed by polarization from the tangential orbitals, regardless of which description is adopted. One would expect three negative elementary charges in the tangential orbitals (one bond and one lone pair) in the carbenoid structure, and only two (two bonds) in the ylide structure. Thus, from this analysis of natural hybrid orbital populations, which was not available before,³ we now conclude that the best simple description of ground-state **6** is to call it a carbenoid, although it is still true that the structure is intermediate between a carbenoid and an ylide. Of course, unlike a true carbene, in its reactions, **6** generates only one new covalent bond to C1, and the other new bond is ionic, as it would be if an ylide reacted.

Another instructive picture of **3** is provided by Figure 3. As expected, the LUMO is nearly purely the outward facing radial hybrid on the B12 atom, with small contributions from C–C and B–C edges in the rest of the molecule. The degenerate HOMO, HOMO-1 pair is nearly the same as that in **1** and is localized mainly on the B–B bonds of the cage (Figure 2). The degenerate HOMO-2, HOMO-3 pair is responsible for feeding the electron density into the tangential orbitals on vertex 12, whereas the HOMO, HOMO-1 pair has no amplitude there.

Mechanism of Formation of **3 from **2****. Although we established that the oxidation of R₃Si-containing precursors with **2** in alkanes gives the boronium ylide **3**, the mechanism of its formation is presently unclear. For germanium, tin, and lead precursors, this oxidation is believed to proceed in two single electron-transfer steps.⁷ The first one produces a cation radical, whose weak one-electron bond then dissociates to give the cation and the radical. Depending on the nature of the radical, it could be further oxidized to a cation in a second single electron-transfer step, or it could dimerize.

By analogy with R₃E-containing precursors in the case of E = Ge, Sn, and Pb, it is tempting to suggest that, in the case of silicon, R₃Si⁺ cations are formed by a similar sequence of two one-electron oxidations and that this is followed by a fast intramolecular attack by R₃Si⁺ on the anion. Such substitutions by carbenium ions are known,⁴⁵ for example, methide abstrac-

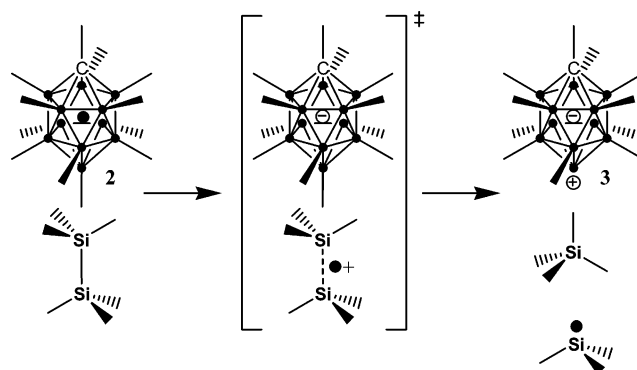
tion by the trityl cation from Cp*WMe₅.⁴⁶ This reaction would also be the reverse of methide anion abstraction by R₃B from Cp₂ZrMe₂,^{47,48} [*t*-BuN-*o*-C₆H₄)₂O]ZrMe₂,⁴⁹ and other^{50,51} transition metal complexes.

Results of calculations suggest that it would be energetically feasible for free R₃Si⁺ to be involved in the formation of **3** in this fashion. The Me₃Si⁺1⁻ ion pair is unstable, and an attempted optimization of its geometry resulted in Me₄Si and **3**. The process in which the 12 methyl group in **1** is abstracted by Me₃Si⁺ to yield **3** and Me₄Si, presumably by a backside S_E2 displacement, is calculated to be exothermic by 20 kcal/mol. The same spontaneous backside S_E2 substitution was found computationally when Me₃Si⁺ was coordinated to the methyl group in position 7 of the anion (exothermic by 17 kcal/mol), but not in positions 2 (exothermic by 8 kcal/mol) or 1 (endothermic by 16 kcal/mol). The leaving power of **3**–**5** as an electrofuge attached to a saturated carbon is thus significantly higher than that of Me₃Si⁺, but of course, the latter can gain much further assistance from an incipient formation of a new bond to silicon on its backside, from the solvent or another suitable nucleophile, whereas steric hindrance prevents **3**–**5** from acquiring much assistance in this fashion. Nevertheless, when **3**–**5**, and apparently even **6**,³ are attached to a saturated hydrocarbon skeleton, they need to be thought of as leaving groups at least as good as a trialkylsilyl substituent. Viewed in this light, the reported failure to isolate the 12-allyl derivative of the parent CB₁₁H₁₂(-) from a Pd-catalyzed Kumada coupling reaction³⁴ may be an expression of an instability of the allylated product to the acidic conditions of the workup procedure rather than a failed coupling reaction, even though in the absence of the methyl substituents the ylide would be harder to form.

However, although the abstraction of a methyl group from **1** with R₃Si⁺ appears perfectly feasible, the fact that the R₃Si⁺ cations could not be trapped in the reactions leading to **3** suggests that free silylium ions are not involved in the reaction of **2** with R₆Si₂. Instead, the reaction apparently leads straight to **3**, R₃SiMe, and R₃Si⁺, which then reacts with a second molecule of **2** to yield **3** and R₃SiMe directly. In Scheme 4, we propose a mechanism in which a methyl radical is transferred from **2** directly to the disilane with a formation of **3**, via a transition state in which electron density has been transferred from the Si–Si bond to the carborane cage. The same would be also true for the transition state of the second step, in which a Me₃Si[•] radical formed in the first step reacts with **2** by a second methyl radical transfer to give Me₄Si and **3**. The action of **2** as a methyl radical transfer agent could be symbolized by use of a resonance structure in which an electron has been transferred from the B12–CH₃ bond to the carborane cage.

There actually is little difference between the two mechanisms considered, the main point being the absence of an intermediate minimum on the potential energy surface of the second mechanism that would correspond to a R₃Si⁺ + **2** + Me₃Si[•]

Scheme 4



combination. This is clear from Figure 5, which shows a schematic view of the reaction potential energy surfaces that we are proposing for the reaction of **2** with M–M bonds, for M = Pb to M = C. The end points of this correlation diagram are anchored by reference to bond strengths. The gradual decrease in the exothermicity of the overall process upon going from Pb to C results in changes in the reaction surface and ion pair structures⁷ that are reminiscent of the changes explored in the classical Bürgi–Dunitz investigations¹³ of reaction paths. The fact that *i*-Pr₃Si₂ reacts with **2** more slowly than Me₆Si₂ is accommodated in our proposal by reference to steric hindrance by *i*-Pr groups in the methyl radical transfer, while faster reaction of *t*-Bu₆Si₂ is ascribed to the ionization potential of the elongated Si–Si bond being much lower⁵² than in other disilanes.

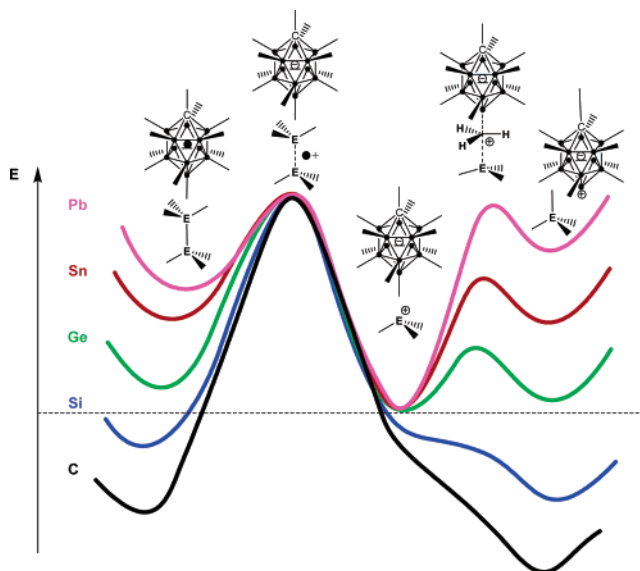


Figure 5. Schematic potential energy surfaces for the reaction of **2** with the dimetallanes R₆M₂.

Potential Role of Boronium Ylides in Substitutions on Carboranes. In addition to recognizing the formation of **3** by methyl radical abstraction, it is tempting to postulate a role for **3** and its analogues as intermediates along the main reaction path or side paths in many Lewis or Brønsted acid promoted substitutions on deltahedral boranes and heteroboranes.⁴¹ These may include the formation of triflylyloxy carrying side products in the substitution of hydrogens by methyls in CB₁₁H₁₂⁻ upon

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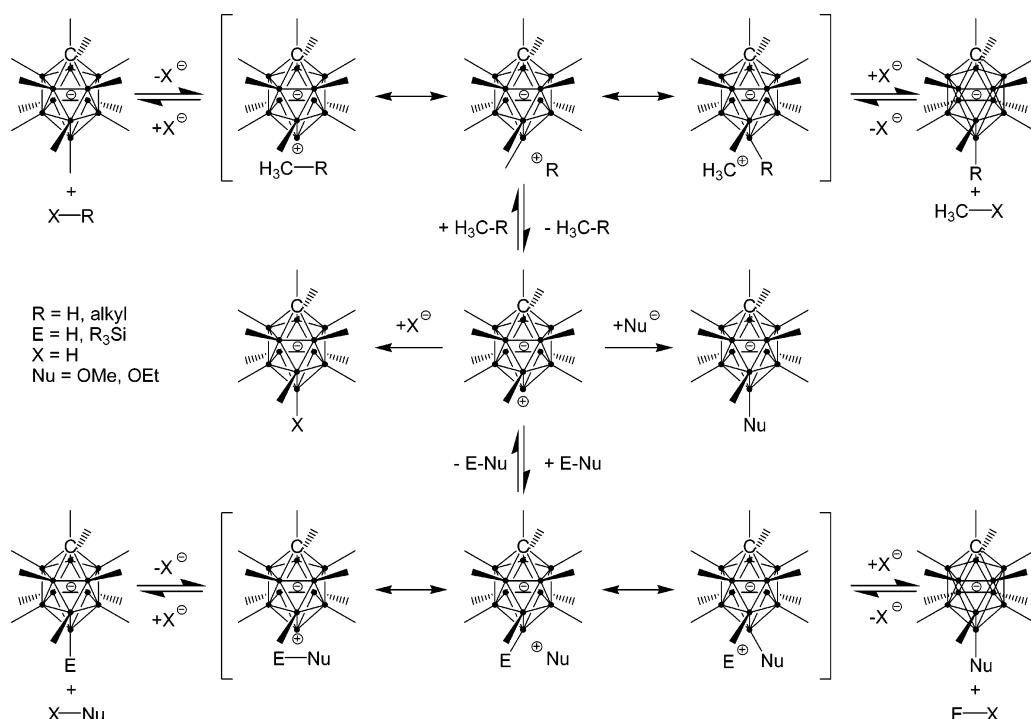
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Scheme 5



treatment with methyl triflate,¹ substitution of methyl groups in $\text{CB}_{11}\text{Me}_{12}^-$ by hydroxide, triflate, fluoride, or trifluoroacetate in its reactions with the corresponding acids,^{5,35} and the formal σ -bond metathesis observed when Li^+ salts of the derivatives of **1** are heated with arenes,¹¹ where the Li^+ cation may play the role of a Lewis acid. A possible general mechanism of such substitution is proposed in Scheme 5. The intermediates in brackets are formulated with three-center two-electron bonds since we concluded above that the boronium ylide formulation is best for **3–5**. However, it is possible that the cage participates by an edge or even a triangular face instead of a vertex as shown. The reactivity of these ylides with other nucleophiles, such as alkenes and aromatics, still remains to be explored.

It is conceivable that in the case of **6** three-center bonded structures similar to those shown in Scheme 5 for **3** also apply, but do not contain pure two-electron three-center bonds. Instead, electrons from the nominally delocalized negative charge on the cage, in reality actually mostly localized on its naked carbon vertex 1, in agreement with the formulation of the electronic structure as carbene-like, could contribute to the formation of a higher bond order between this carbon and its two exocyclic ligands in a way reminiscent of singlet carbene additions to alkenes. However, the ease of formation of the species that reacts as expected for **6**³ makes us wonder whether its true optimal energy and structure or just a local minimum have actually been found despite all the effort expended. Further work will be required to elucidate these issues.

Conclusions

Disilanes react with the $\text{CB}_{11}\text{Me}_{12}^\bullet$ radical (**2**) by methyl transfer from boron to silicon and form a highly reactive intermediate, stable only below -60°C , for which we propose the structure of internally charge-compensated boronium ylide **3**. The structure is compatible with the outcome of trapping experiments with several mostly oxygen-based nucleophiles and

with a solid-state ^{11}B NMR spectrum. Attempted preparation of $\text{Me}_3\text{C}^+\text{CB}_{11}\text{Me}_{12}^-$ by halide metathesis results in products also consistent with the formation of boronium ylides. At the B3LYP/6-31G(d) level of calculation, the isomers **3–5** are far more stable than the carbonium ylide **6**, and their electronic structure corresponds quite closely to that of the label boronium ylide, whereas that of **6** is close to that of a singlet carbene, in which the positive and the negative charges are carried by the same atom.

Experimental Section

General. Standard Schlenk and glovebox techniques were used for handling air-sensitive reagents. Pentane, hexane, cyclohexane, methylcyclohexane, benzene, and Me_6Si_2 were dried over CaH_2 , distilled, and stored under argon, and solvents were stored over a potassium mirror. The following compounds were purchased and used as received: Et_2Zn , $t\text{-BuLi}$, calcium hydride, cesium chloride, $n\text{-BuLi}$ (1.7 M in hexanes), and silver nitrate. $\text{Me}_3\text{NH}^+\text{CB}_{11}\text{Me}_{12}^-$ was purchased from Katchem Ltd., E. Krásnohorské 6, 11000 Prague 1, Czech Republic. Solution ^1H , ^{11}B , ^{13}C , and ^{29}Si spectra were measured with a Varian XRS-300 and a Varian Unity-500 spectrometers. ^1H and ^{13}C chemical shifts were measured relative to the lock solvent. ^{11}B chemical shifts were measured relative to BF_3OEt_2 , with positive chemical shifts downfield. $\text{B}(\text{OCH}_3)_3$ was used as an external standard (18.1 ppm). ^{29}Si chemical shifts were measured relative to Me_4Si . Mass spectra were recorded with a Hewlett-Packard 5989 API/ES/MS. An HPLC system employing a reverse phase C_{18} column (250 \times 4.6 mm, 5 μm) with methanol/water (containing a 1% $\text{AcOH}/0.7\%$ Et_3N buffer) as the mobile phase was used for monitoring reactions, while larger columns of the same phase were used for semipreparative separations. All volatile compounds were analyzed using Varian 3400 analytical GC with 0.2 mm \times 25 m 0.33 μm RSL-150 5% cross-linked silica capillary column. Their separations were performed using Varian 3400 preparative GC with 1/4" \times 21' 5% OV-7 80/100 Chromosorb GHP packed column. Individual compounds were purified to >99.5% purity (by analytical GC).

Solid-State NMR Measurements. Solid-state CP/MAS ^{11}B and ^{13}C NMR spectra were obtained on a Chemagetics CMX-200 spectrometer

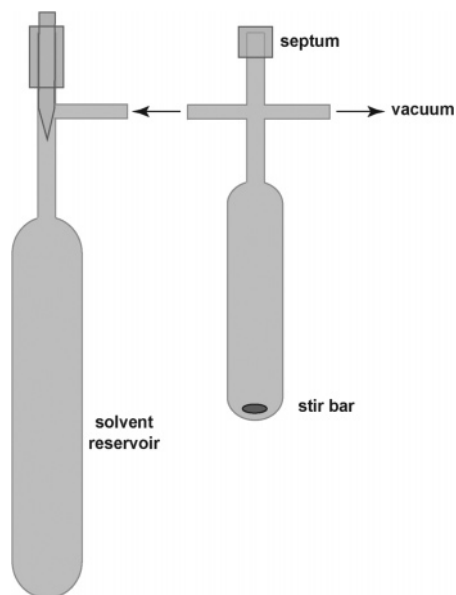


Figure 6. Apparatus for oxidations with **2**.

using a Chemagnetics MAS probe equipped with a 7.5 mm PENCIL rotor at a temperature of $-60\text{ }^{\circ}\text{C}$. The samples were prepared at temperatures below $-60\text{ }^{\circ}\text{C}$ in 5 mm o.d. glass tubes on a vacuum line, followed by solvent removal, and sealing the tubes first off the vacuum line and then to the desired length on a lathe, while maintaining the low temperature. The tubes were packed into the rotor surrounded by KBr (to aid in balancing of the samples for high-speed spinning) below $-60\text{ }^{\circ}\text{C}$. Stable spin rates between 0.5 and 1.0 kHz were attained. The ^{13}C spectrum was externally referenced using HMB, with the methyl resonance of this compound being 17.6 ppm on the TMS scale; the ^{11}B spectra were not referenced.

Calculations. Geometry optimizations (B3LYP/6-31G(d)) were performed using Gaussian98;⁵³ charges were calculated using NBO⁵⁴ using the three-center bond option, and molecular modeling and visualization were performed using Molden 3.6⁵⁵ and Spartan SGI Version 4.1.1, Wavefunction Inc. GIAO calculations of the chemical shift and electric field gradient tensor were completed using revision B.02 of Gaussian03.⁵⁶ These calculations were done on the 6-31G(d) optimized structure and used the B3LYP⁵⁷ hybrid functional and the 6-31G(d,p) basis set. Simulations of the ^{11}B MAS NMR spectrum were completed using the SIMPSON program,⁵⁸ version 1.1.pre28. The geometry of **3** and its dimer (**3**)₂ was optimized with the TURBOMOLE program⁵⁹ using the RI-MP2/def-SV(P) method.

Oxidation with CB₁₁Me₁₂[•]: General Procedures. The CB₁₁Me₁₂[•] radical was placed in a flame-dried ampule (Figure 6) equipped with a stir bar and a septum. The ampule was connected to a dry solvent reservoir and to a vacuum line by thick-walled latex tubing. The system was evacuated (10^{-3} mmHg), the vacuum line disconnected, and the desired amount of solvent was distilled into the ampule cooled in liquid

nitrogen. The system was then filled with argon, and the solution was warmed to the desired temperature with stirring until all radical dissolved. A material to be oxidized was added dropwise with vigorous stirring either neat (dry, degassed) using a syringe or as a dry degassed solution in an alkane solvent via a Teflon cannula. After the blue (pentane, hexane) or green (cyclohexane, methylcyclohexane) color of the radical disappeared, the reaction was complete. Trapping reagents were added to the resulting solution/solids via a syringe or a cannula. For further sample preparations, the solvent can be carefully removed from insoluble products via cannula or evaporated in the case of soluble products, after which the ampule can be sealed.

Cs⁺ 12-EtO-CB₁₁Me₁₁⁻ (7**)** was prepared as a white solid at room temperature in 20 mL of pentane/ether (19:1) solution from 25 mg (0.08 mmol) of the CB₁₁Me₁₂[•] radical and 8.2 μL (5.9 mg, 0.04 mmol) of Me₆Si₂, or at $-78\text{ }^{\circ}\text{C}$ in 20 mL of pentane by reacting 25 mg (0.08 mmol) of the CB₁₁Me₁₂[•] radical with 15.9 mg (0.04 mmol) of *t*-Bu₆Si₂ followed by addition of dry ether or ethanol to the resulting solid. After the reaction was complete, the reaction mixture was quenched with water, and solvents were evaporated. The product was converted into the cesium salt (by shaking its ethereal solution with a 20% aqueous CsCl, followed by removal of ether) and purified by crystallization from water. Yield 35 mg (92%). ^1H NMR (acetone-*d*₆): δ 3.53 (2 H, q, CH₂), 0.926 (3 H, t, CH₃), 0.780 (3 H, s, 1-CH₃), -0.264 (15 H, s, 7-11-CH₃), -0.369 (15 H, s, 2-6-CH₃). ^{11}B { ^1H } NMR (acetone-*d*₆): δ 9.00 (B₁₂), -10.62 (B₇₋₁₁), -12.99 (B₂₋₆). ^{13}C { ^1H , ^{11}B } NMR (acetone-*d*₆): δ 61.60 (H₂C-O), 51.68 (1-C), 23.37 (CH₃), 12.95 (1-CH₃), -3.19 (7-11-CH₃), -3.58 (2-6-CH₃). IR (KBr pellet): 911, 1153, 1252, 1312, 1428, 2827, 2854, 2891, 2928, 2954 cm^{-1} . MS/ES(-) in methanol: base peak at *m/e* 341 with the expected isotopic distribution (M⁻). Anal. Calcd for C₁₄H₃₈B₁₁CsO: C, 35.46; H, 8.08. Found: C, 35.57; H, 8.43.

Cs⁺ 12-MeO-CB₁₁Me₁₁⁻ (9**)** was prepared as a white solid at $-78\text{ }^{\circ}\text{C}$ in 20 mL of pentane by treating 25 mg (0.08 mmol) of the CB₁₁Me₁₂[•] radical with 15.9 mg (0.04 mmol) of *t*-Bu₆Si₂ followed by addition of dry methanol to the resulting solid. After the reaction was complete, the reaction mixture was quenched with water, and solvents were evaporated. The product was converted into the cesium salt (by shaking its ethereal solution with a 20% aqueous CsCl, followed by removal of ether) and purified by crystallization from water. Yield 35 mg (95%). ^1H NMR (acetone-*d*₆): δ 3.25 (3 H, s, H₃C-O), 0.726 (3 H, s, 1-CH₃), -0.260 (15 H, s, 7-11-CH₃), -0.382 (15 H, s, 2-6-CH₃). ^{11}B { ^1H } NMR (acetone-*d*₆): δ 9.07 (B₁₂), -10.47 (B₇₋₁₁), -12.78 (B₂₋₆). ^{13}C { ^1H , ^{11}B } NMR (acetone-*d*₆): δ 54.73 (H₂C-O), 51.68 (1-C), 21.94 (1-CH₃), -3.19 (7-11-CH₃), -3.63 (2-6-CH₃). IR (KBr pellet): 915, 1155, 1252, 1313, 1428, 2827, 2854, 2891, 2928 cm^{-1} . MS/ES(-) in methanol: base peak at *m/e* 327 with the expected isotopic distribution (M⁻). Anal. Calcd for C₁₃H₃₆B₁₁CsO: C, 33.93; H, 7.88. Found: C, 34.17; H, 8.02.

Cs⁺ 12-HO-CB₁₁Me₁₁⁻ (10**)** was prepared as a white solid at $-78\text{ }^{\circ}\text{C}$ in 20 mL of pentane by treating 25 mg (0.08 mmol) of the CB₁₁Me₁₂[•] radical with 15.9 mg (0.04 mmol) of *t*-Bu₆Si₂ followed by addition of dry *tert*-butanol in pentane to the resulting solid. After the reaction was complete, the reaction mixture was quenched with water, and solvents were evaporated. The product was converted into the cesium salt and purified by crystallization from water. Yield 32 mg (89%). ^1H NMR (acetone-*d*₆): δ 0.817 (3 H, s, 1-CH₃), -0.344 (30 H, s, 2-11-CH₃). ^{11}B { ^1H } NMR (acetone-*d*₆): δ 9.32 (B₁₂), -10.15 (B₇₋₁₁), -12.80 (B₂₋₆). ^{13}C { ^1H , ^{11}B } NMR (acetone-*d*₆): δ 49.02 (1-C), 12.92 (1-CH₃), -3.71 (7-11-CH₃), -4.07 (2-6-CH₃). IR (KBr pellet): 909, 1043, 1153, 1312, 1428, 2827, 2854, 2891, 2928, 3245 cm^{-1} . MS/ES(-) in methanol: base peak at *m/e* 313 with the expected isotopic distribution (M⁻). Anal. Calcd for C₁₂H₃₄B₁₁CsO: C, 32.30; H, 7.68. Found: C, 32.16; H, 7.83.

Reactions of **3 with Nucleophiles.** The boronium ylide **3** was prepared as a white solid at $-78\text{ }^{\circ}\text{C}$ in 20 mL of pentane from 25 mg (0.08 mmol) of the CB₁₁Me₁₂[•] radical and 15.9 mg (0.04 mmol) of

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t-Bu₆Si₂. It was treated with pentane solutions of several nucleophiles. After hydrolysis of the reaction mixtures, the following products were observed by ES/MS: with Et₂Zn, *m/e* 325 (CB₁₁Me₁₁Et⁻, major), 297 (CB₁₁Me₁₁H⁻, minor); with *t*-BuLi or *t*-Bu₂Hg, *m/e* 353 (CB₁₁Me₁₁*t*-Bu⁻, major), *m/e* 297 (CB₁₁Me₁₁H⁻, minor); with *t*-BuCH₂Li, a complicated mixture of products with a small amount of an ion with *m/e* 367 (CB₁₁Me₁₁CH₂Bu-*t*⁻); with Et₃SiLi, *m/e* 325 (CB₁₁Me₁₁Et⁻, major); with CO (1 atm, 3 h) followed with MeOH, 355 (CB₁₁Me₁₁COOMe⁻, major) and 327 (CB₁₁Me₁₁OMe⁻, minor); with Et₂NSF₃, 315 (CB₁₁Me₁₁F⁻, major) and 297 (CB₁₁Me₁₁H⁻, minor); with benzene, 373 (CB₁₁Me₁₁C₆H₅⁻, major) and 297 (CB₁₁Me₁₁H⁻, minor); with pyridine, 375 (CB₁₁Me₁₁C₅NH₅⁻, major) and 297 (CB₁₁Me₁₁H⁻, minor). In many cases, singly negatively charged anions with approximately double molecular weight were observed in the mass spectra as well.

Attempted Preparation of Me₃C⁺ CB₁₁Me₁₂⁻. A sample of Ag⁺CB₁₁Me₁₂⁻ was prepared by shaking a solution of 1 g of Cs⁺CB₁₁Me₁₂⁻ in 20 mL of diethyl ether with 20% aqueous AgNO₃ (3 × 20 mL). The organic phase was separated, ether was removed, and the resulting Ag salt dried under vacuum at 80 °C overnight while protected from light. The resulting brownish solid (42 mg, 0.1 mmol) was dissolved in dry dichloromethane (5 mL) under the atmosphere of argon, and 11.5 μL (13.7 mg, 0.1 mmol) of dry *t*-BuBr was added to the solution with a syringe. Negative mode ES/MS (in MeOH) of the reaction mixture showed peaks at *m/e* 331, 351, 371, and 391. Both

m/e and isotopic distribution of these peaks suggested that up to four methyl groups were replaced by chlorine atoms. Similar mixtures of products were found by ES/MS when the above reaction was conducted in CHCl₃, CCl₂F–CCl₂F, and CCl₃–CH₃. When this reaction was conducted in a sealed NMR tube, no starting *t*-BuBr was found and a new product with ¹H NMR signal at 0.91 ppm and ¹³C NMR signals at 31.54 and 27.90 (CD₂Cl₂) was observed. These peaks are similar to those (33.57 and 29.34) reported for neopentane in CCl₄.⁶⁰

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Supporting Information Available: Complete refs 53 and 56, and calculated (DFT) optimized geometries (Cartesian coordinates) and energies (in Hartrees) for structures **1–6**, **3R–6R**, and **(3)₂**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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