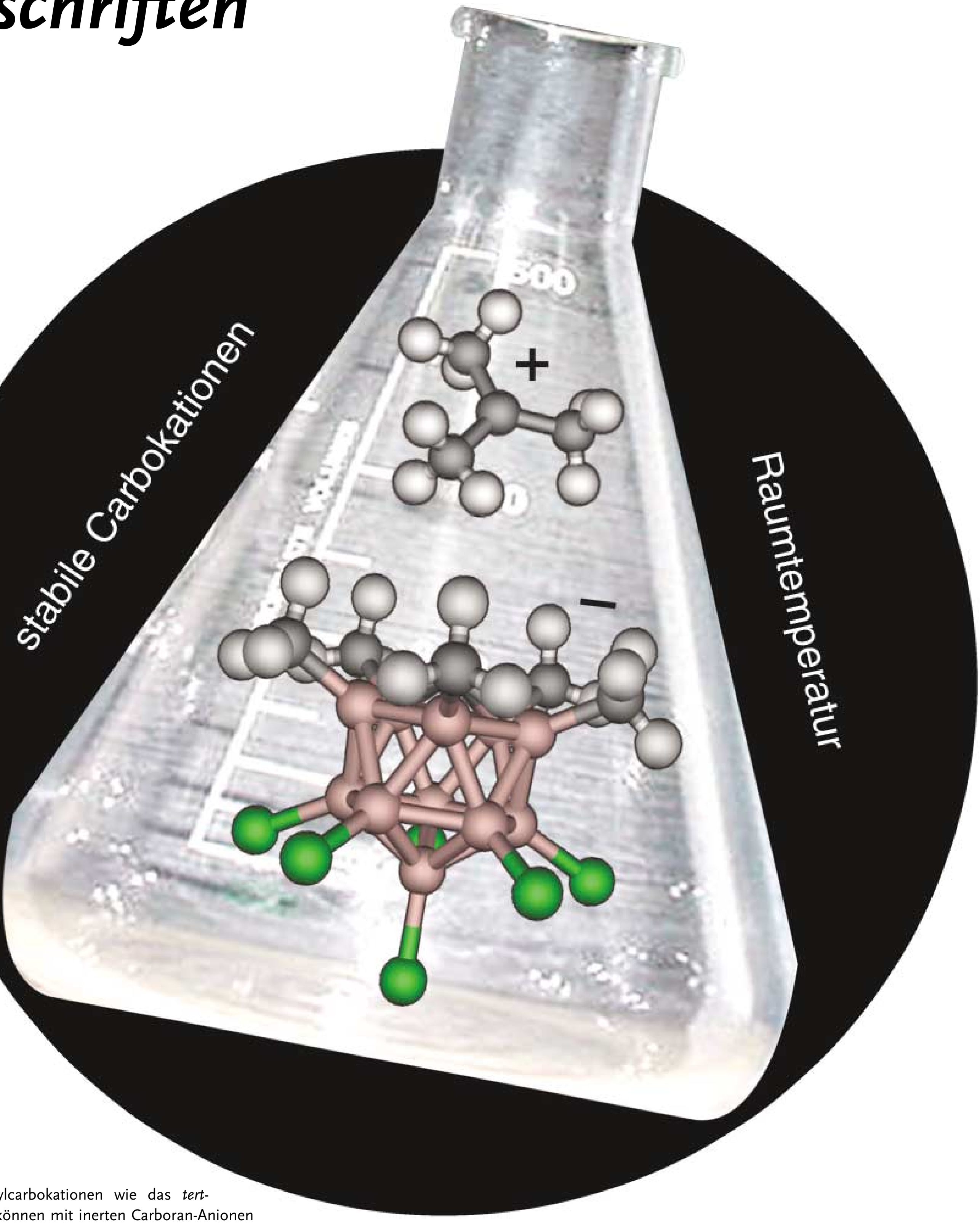
Zuschriften



Einfache Alkylcarbokationen wie das *tert*-Butyl-Kation können mit inerten Carboran-Anionen in Form stabiler Salze bei Raumtemperatur isoliert und “in Flaschen abgefüllt” werden. Die “Me$^+$-Reagentien” $CH_3(CHB_{11}H_5X_6)$ (X = Cl oder Br) sind hinreichend elektrophil, um aus Kohlenwasserstoffen bei Raumtemperatur oder darunter Hydrid-Ionen zu abstrahieren. Näheres hierzu finden Sie in der Zuschrift von C. A. Reed und T. Kato auf den folgenden Seiten.

DOI: 10.1002/ange.200453931

Carbocations

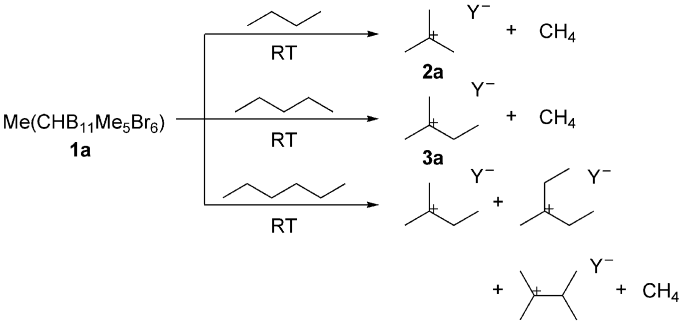
Putting *tert*-Butyl Cation in a Bottle**

*Tsuyoshi Kato and Christopher A. Reed**

The *tert*-butyl cation has a special place in the history of organic chemistry. Tracking its existence from a reactive intermediate postulated on the basis of kinetic measurements to its isolation and characterization at low temperatures in superacidic media is a Nobel Prize winning story.[1] The hexafluoroantimonate salt has been isolated at low temperatures,[2] and solutions containing the *tert*-butyl cation in magic acid ($HFSO_3/SbF_5$) are reportedly stable up to 150 °C.[3] In 1993 a crystal of $[(CH_3)_3C][Sb_2F_{11}]$ suitable for X-ray crystal-structure determination was isolated at $-30\,°C$ from an amyl precursor.[4] A secondary alkyl cation stabilized by Sn hyperconjugation,[5] and a vinyl cation stabilized by Si hyperconjugation,[6] have recently been isolated and structurally characterized. The bridgehead adamantyl cation is stable at room temperature as a fluoroantimonate salt.[2] We now report that *tert*-butyl and other simple tertiary alkyl cations can be isolated at room temperature and their X-ray structures determined.

The external conditions necessary to stabilize alkyl cations are: a) a counterion that is too weakly nucleophilic to form a covalent bond with the cationic carbon atom, and b) high acidity to prevent deprotonation of the carbocation to form an alkene, leading to subsequent oligomerization of the cation. Since icosahedral carborane anions of the type $[CHB_{11}R_5X_6]^-$ (R = H, CH_3; X = halide) have been shown to be the least-coordinating anions towards silylium ions R_3Si^+,[7] they should be excellent candidates for noncoordinating anions with analogous R_3C^+ carbenium ions. The conjugate acids of carborane anions, $H(CHB_{11}H_5X_6)$, are stronger than the strongest oxy superacids (such as $HFSO_3$, CF_3SO_3H),[8,9] which suggests that carborane anions might be sufficiently weak bases not to deprotonate carbocations. The third consideration is a suitable synthetic route.

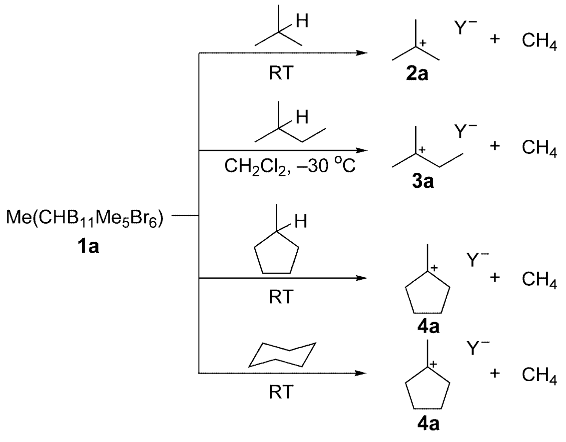
The synthetic route of choice is hydride abstraction from a hydrocarbon since highly electrophilic "Me^+" reagents are known to produce carbocations by methane elimination.[3] In their reactivity towards benzene, methyl carboranes have been shown to be much stronger methylating reagents than methyl triflate.[10] Indeed, they are such strong methyl$^+$ sources that they can abstract a hydride from hydrocarbons at or below room temperature (Scheme 1).



Scheme 1. Reactivity of **1a** with linear alkanes (Y = $CHB_{11}Me_5Br_6$).

The reactions were carried out by stirring solid $CH_3(CHB_{11}H_5Br_6)$, **1a**, in liquefied alkane at room temperature for a few days. As expected, linear hydrocarbons led to branched-chain products reflecting the high thermodynamic stability of tertiary carbocationic centers over primary or secondary, and the facile hydrogen or methyl 1,2 shifts that occur readily in carbenium ions.[11] The colorless microcrystalline $[R_3C]$[carborane] products are stable indefinitely if kept dry and free of nucleophiles. The success of the synthesis probably derives from the very low solubility of the salts in the hydrocarbon solvent. With *n*-heptane as reactant and solvent, a material is obtained that has broad ^1H NMR resonances in the alkane region and no ^{13}C resonances in the carbocationic region. This suggests the formation of an oligomerized product. We surmise that heptyl cations are sufficiently soluble in heptane during the reaction that deprotonation to heptenes can occur, followed by intermolecular reaction of these heptenes with heptyl cations.

Reactions with branched-chain alkanes or cyclic alkanes also give the expected tertiary carbocation products **2a**–**4a** (Scheme 2). When a typical laboratory mixture of hexanes is used, the methylcyclopentyl cation **4a** is exclusively produced, which suggests that the methycyclopentane isomer of hexane undergoes hydride abstraction much faster than the



Scheme 2. Reactivity of **1a** with tertiary and cyclic alkanes.

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[**] We thank Dr. Fook Tham for solution of the X-ray structures and Dr. Evgenii Stoyanov for helpful discussions of the IR spectra. This work was supported by NSF grant CHE-0095206 and NIH grant GM 23851.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

DOI: 10.1002/ange.200453931

other isomers. As indicated in Scheme 2, some reactions were carried out in CH_2Cl_2 at $-30\,°C$ to grow crystals suitable for X-ray crystallography.

Methane was identified as the by-product of these reactions by condensing the head gas from the reaction mixture into an NMR tube and observing in the corresponding spectra the appearance of the ^1H signal at $\delta = 0.158$ ppm due to dissolved methane in C_6D_6.[12] Proof that the methane originated exclusively from the methyl carborane reagent was obtained from a ^{13}C labeling experiment. When 99% enriched $^{13}CH_3(CHB_{11}Me_5Br_6)$ was treated with hexanes, the only ^1H signal showing observable and complete ^{13}C coupling was the methane signal ($J = 125.8$ Hz). Not incidentally, this experiment also shows that the mechanism of hydride abstraction does not involve a five-coordinate carbonium ion since such cation formation would allow scrambling of methyl groups. A μ-hydridobridged cation may be involved.[13]

The carbocations were characterized by ^1H and ^{13}C NMR spectroscopy[14] by dissolution of the crystalline products in liquid SO_2 at $-60\,°C$. The products of Scheme 1 showed clean and quantitative formation of **2a** and **3a**. In the case of hexane, a very similar spectrum to the one previously reported by Olah and Lukas[3] was obtained, indicating formation of an equilibrium mixture of isomers of hexyl cations. The diagnostic downfield carbocation resonances appear in the ^{13}C spectrum at about $\delta = 335$ ppm. Similarly, the cations of Scheme 2 were characterized as single products.

Crystals of the *tert*-butyl- and *tert*-pentyl-cation salts **2a** and **3a** prepared according to Scheme 1 showed unacceptable crystallographic disorder under X-ray examination of their structures. However, single crystals of a *tert*-butyl-cation salt **2b**, without disorder in the cation or anion, could be grown by the reaction of the corresponding hexachloro carborane reagent, $CH_3(CHB_{11}Me_5Cl_6)$ **1b**,[10] with *n*-butane in CH_2Cl_2 at $-30\,°C$. The same conditions gave good single crystals of **3a** and a manageably twinned crystal of **4a**, both with the hexabromo carborane anion.

Figure 1, Figure 2, and Figure 3 show the crystal structures of $[t\mathrm{Bu}][CHB_{11}Me_5Cl_6]\cdot CH_2Cl_2$ (**2b**$\cdot CH_2Cl_2$), $[t\text{-}C_5H_{11}][CHB_{11}Me_5Br_6]\cdot CH_2Cl_2$ (**3a**$\cdot CH_2Cl_2$), and $[c\text{-}MeC_5H_8][CHB_{11}Me_5Br_6]$ (**4a**).[15] As judged by the sum of the C-C$^+$-C angles being $360.0 \pm 0.1°$, the carbocationic centers are planar within experimental error, as expected for sp^2 hybridization. The lattice structures are typical of well-defined salts with separated cations and anions. Halogen atoms from the anions do not approach the carbocationic carbon centers closer than van der Waals separation. Indeed, the closest $C^+\cdots X$ approach is actually shorter for Br than Cl (3.42 vs 3.49 Å) even though Br is the larger atom. This suggests that electrostatic stabilization of the cation through anion approach to the central carbocationic C atom is not as important in carborane salts as in earlier studies with smaller fluoroantimonate anions.[16] On the other hand, there are many close C–H···X interactions. For example, each methyl group of **2b** has one or more H···Cl distances < 2.85 Å, the shortest being 2.71 Å (with a C–H···Cl angle of 161°). Similarly, all methyl or methylene groups adjacent to carbocationic centers in the structures of **3a** and **4a** show one or more close H···Br approaches in the range 2.80–3.08 Å. The shortest Br approach is found to a methyl group in the cation with the fewer C–H bonds adjacent to the carbocationic center, namely the methylcyclopentyl cation, **4a**. These C–H···X interactions are consistent with the survey of C–H hydrogen bonding in the crystallographic database.[17]

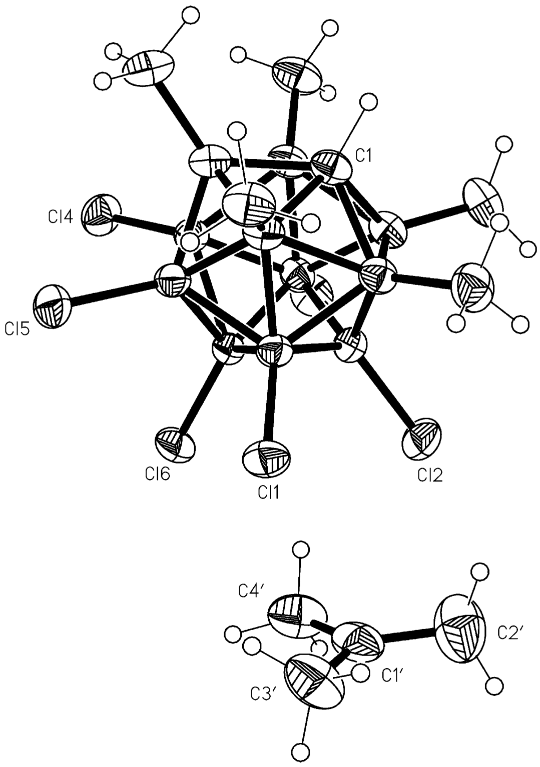

Figure 1. Crystal structure of **2b**$\cdot CH_2Cl_2$. Thermal ellipsoids are shown at the 50% probability level. The disordered solvent molecule CH_2Cl_2 is omitted for clarity. Selected bond lengths [Å] and angles [°]: C1′-C2′ 1.429(4), C1′-C3′ 1.438(4), C1′-C4′ 1.459(4); C2′-C1′-C3′ 120.3(3), C2′-C1′-C4′ 120.0(3), C3′-C1′-C4′ 119.7(3).

These hydrogen-bonding interactions are reflected in the IR spectra of the salts in which νC–H bands from the carbocations are markedly shifted to low frequencies, even lower than those observed in fluoroantimonate salts.[18] The lowest frequency (2695 cm^{-1}) appears in the methylcyclopentyl salt. This may correlate with the shortest C–H···Br distance (2.80 Å), observed for this salt. Together with the X-ray data, these IR indications of significant C–H···X hydrogen bonding to the carborane anions are taken as palpable structural evidence for the very high protic acidity, indeed superacidity, of carbocations.[14,16] Similar IR effects and short C–H···Br distances were observed for the highly acidic protons of the benzenium ion, $C_6H_7^+$, in recently isolated carborane salts.[8]

Perhaps the most interesting new structure is that of **3a**, because the conformation of the C^+-CH_2-CH_3 moiety gives information about the relative importance of C–C versus C–H bond hyperconjugative stabilization of the carbenium-ion center. Theory at the MP4(SDTQ)6-31G**//MP2(FU)/6-31G* + ZPE level finds a negligible energy difference between the conformer having the C–C bond aligned with the

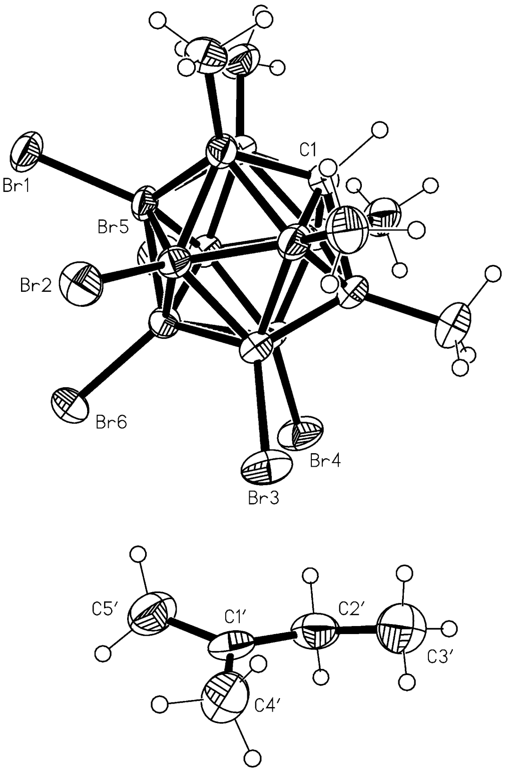

Figure 2. Crystal structure of **3a**·CH_2Cl_2. Thermal ellipsoids are shown at the 50% probability level. The disordered solvent molecule CH_2Cl_2 was omitted for clarity. Selected bond lengths [Å] and angles [°]: C1′-C2′ 1.431(7) C1′-C4′ 1.448(7), C1′-C5′ 1.440(7), C2′-C3′ 1.485(8); C2′-C1′-C4′ 120.4(5), C2′-C1′-C5′ 120.2(5), C4′-C1′-C5′ 119.3(5), C1′-C2′-C3′ 121.3(5).

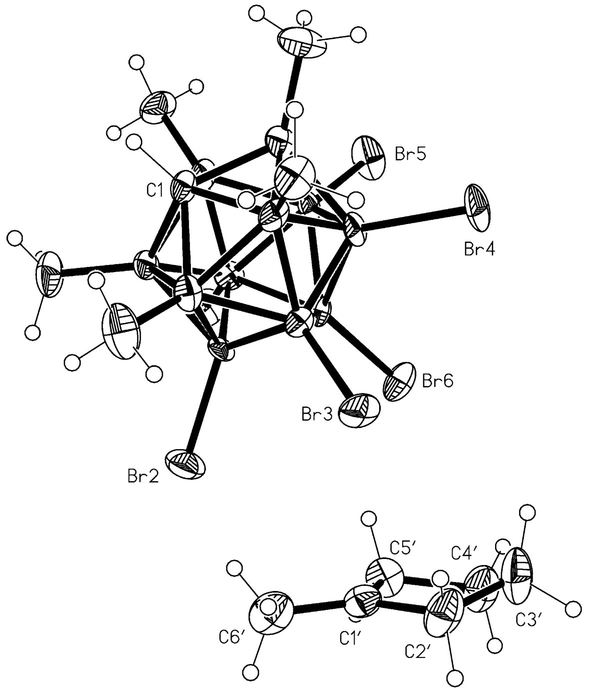

Figure 3. Crystal structure of **4a**. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths [Å] and angles [°]: C1′-C2′ 1.450(11), C1′-C5′ 1.450(10), C1′-C6′ 1.457(11), C2′-C3′ 1.516(12), C3′-C4′ 1.525(12), C4′-C5′ 1.525(11); C2′-C1′-C5′ 109.9(7), C2′-C1′-C6′ 124.9(7), C5′-C1′-C6′ 125.2(7), C1′-C2′-C3′ 106.0(6), C1′-C5′-C4′ 106.8(7), C2′-C3′-C4′ 104.2(7), C3′-C4′-C5′ 102.5(7).

vacant p orbital relative to that having it perpendicular.[19] Preference for the aligned conformation (i.e., having C–C bond hyperconjugation) was made on the basis of better congruence of the computed ^{13}C NMR chemical shifts with those determined experimentally in solution. However, in the X-ray crystal structure (Figure 2), the 25.8° dihedral angle between the carbocationic plane and the C(1)-C(2)-C(3) plane indicates the near absence of C–C bond hyperconjugation. This is consistent with the C(1)-C(2)-C(3) angle of 121.3°, which is close to the value of 119.5° calculated for no C–C bond hyperconjugation (dihedral angle = 0°) and much greater than the 101.7° value calculated for maximum C–C bond hyperconjugation (dihedral angle = 90°). Evidently the torsional potential in the C^+-CH_2-CH_3 moiety is very soft and crystal-packing forces probably dictate the observed orientation, favoring C–H over C–C bond hyperconjugation.

As observed in the X-ray crystal structure of [*t*Bu][Sb_2F_{11}] by Laube and Hollenstein,[4] the C(sp^2)–C(sp^3) distances in the present three tertiary carbocation structures are all short, thus reflecting partial-double-bond character from substantial C–H bond hyperconjugation. The C^+–C bond lengths in the three cations all lie in the narrow range 1.429(4)–1.459(4) Å. The average in **2b** is 1.442(4) Å, identical to that in [*t*Bu][Sb_2F_{11}]. This indicates similar overall influences of the carborane and $[Sb_2F_{11}]^-$ ions on *tert*-butyl cation, even though the carborane favor interactions with C–H bonds rather than the C^+ center. Theory gives a calculated value of 1.458 Å for the C–C bond length in an isolated *tert*-butyl cation.[20] The high level of congruence between calculated and observed bond lengths and angles reflects the intrinsic stability of tertiary carbocations and the relatively insignificant perturbation of their structures by external effects. Their isolation at room temperature simply required shutting down pathways to chemical decomposition.

In summary, we have shown that Me^+ reagents, **1a** and **1b**, based on carborane anions are sufficiently powerful electrophiles that they can abstract hydride from hydrocarbons at or below room temperature. As long as the resulting tertiary carbocation salt is insoluble, it can be synthesized and stored at room temperature. This has allowed the accurate structure determinations of **2b**, **3a**, and **4a** and opens the way for simple tertiary carbocations to be used as reagents, something that has not been practical with carbocations generated in SbF_5-containing superacidic media.

Supporting Information for this article (synthetic procedures, NMR and IR spectra, complete X-ray data) is available for this paper.

Received: February 4, 2004
Revised: March 8, 2004 [Z53931]
Published Online: May 6, 2004

Keywords: carbocations · carboranes · hyperconjugation · structure elucidation

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[15] Crystal data for **2b**·CH_2Cl_2: $C_{11}H_{27}B_{11}Cl_8$, $M = 561.84$, monoclinic $P2(1)/c$, $a = 9.3445(16)$, $b = 9.3140(17)$, $c = 30.929(5)$ Å, $\beta = 94.510(3)°$, $V = 2683.5(8)$ Å^3, $T = 223(2)$ K, $Z = 4$, $\mu(\mathrm{Mo}_{K\alpha}) = 0.841\ \mathrm{mm}^{-1}$, 15280 reflections collected (5475 independent) [$R(\mathrm{int}) = 0.0251$], $R1$ [$I > 2\sigma(I)$] $= 0.0393$, $wR2$ (all data) $= 0.1092$. Crystal data for **3a**·CH_2Cl_2: $C_{12}H_{29}B_{11}Br_6Cl_2$, $M = 842.62$, orthorhombic $Pbca$, $a = 11.9869(17)$, $b = 17.632(2)$, $c = 27.601(3)$ Å, $V = 5833.6(13)$ Å^3, $T = 223(2)$ K, $Z = 8$, $\mu(\mathrm{Mo}_{K\alpha}) = 8.445\ \mathrm{mm}^{-1}$, 29258 reflections collected (5958 independent) [$R(\mathrm{int}) = 0.0713$], $R1$ [$I > 2\sigma(I)$] $= 0.0382$, $wR2$ (all data) $= 0.0980$. Crystal data for **4a**: $C_{12}H_{27}B_{11}Br_6$, $M = 769.71$, monoclinic $P2(1)/c$, $a = 9.183(3)$, $b = 16.157(5)$, $c = 17.810(6)$ Å, $\beta = 98.147(9)°$, $V = 2615.9(15)$ Å^3, $T = 223(2)$ K, $Z = 4$, $\mu(\mathrm{Mo}_{K\alpha}) = 9.209\ \mathrm{mm}^{-1}$, 7787 reflections collected (5158 independent) [$R(\mathrm{int}) = 0.0272$], $R1$ [$I > 2\sigma(I)$] $= 0.0549$, $wR2$ (all data) $= 0.1659$. CCDC-230562 (**2b**) CCDC-230563 (**4a**) and CCDC-230564 (**3a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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