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Isolation of Protonated Arenes (Wheland Intermediates) with BAR^{F} and Carborane Anions. A Novel Crystalline Superacid

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Protonated arenes are widely accepted intermediates in electrophilic aromatic substitution chemistry.¹ Known as Wheland intermediates, but more correctly ascribed to Pfeiffer and Wizinger,^{2,3} they have been characterized by isolation and spectroscopy at low temperatures in superacid media.^{4,5} However, obtaining an X-ray crystal structure of a protonated arene salt is an unrealized experimental challenge,⁵ and thermal instability has prevented their development as useful reagents. In this paper, we show how modern anions lead to readily crystallized salts of remarkable thermal stability. The salt of protonated benzene is a crystalline superacid with distinct advantages over existing superacid media.

The key to the stability of protonated arene salts lies in the choice of counterion. We have had particular success with the carborane $\text{CB}_{11}\text{H}_6\text{Cl}_6^-$ (Figure 1), one of the most useful members of a newly recognized class of large anions with uncommonly low nucleophilicity and exceptional inertness.⁶ Perfluorinated tetraphenylborate ion, $\text{F}_{20}\text{-BPh}_4^-$, is also useful although limited by B–C bond cleavage at higher acidities.

The strong Lewis acidity of the ionlike silylium species, $(\text{Et}_3\text{Si}^{\delta+})(\text{Y}^{\delta-})$ ($\text{Y}^- = \text{CB}_{11}\text{H}_6\text{Cl}_6^-$ or $\text{F}_{20}\text{-BPh}_4^-$),⁷ can be converted to strong Brønsted acidity by treatment with anhydrous HCl. The greater bond strength of Si–Cl (ca. 113 kcal·mol⁻¹) versus H–Cl (103 kcal·mol⁻¹) provides a driving force for this reaction. Added methylated arenes in dry benzene solution are the strongest bases present, and salts of protonated methylated arenes can be isolated upon partial removal of the volatiles, addition of hexanes, and filtration (eq 1).



For hexamethylbenzene, pentamethylbenzene, and mesitylene, respectively, the salts $[\text{C}_6\text{Me}_6\text{H}][\text{CB}_{11}\text{H}_6\text{Cl}_6]$, **1**, $[\text{C}_6\text{Me}_5\text{H}_2][\text{F}_{20}\text{-BPh}_4]$, **2**, $[\text{C}_6\text{Me}_3\text{H}_4][\text{CB}_{11}\text{H}_6\text{Cl}_6]$, **3**, and $[\text{C}_6\text{Me}_3\text{H}_4][\text{F}_{20}\text{-BPh}_4]$, **4** have been isolated.⁸ Yields of the yellow crystalline products are typically ca. 60%. The UV–vis λ_{max} of the $\text{C}_6\text{Me}_6\text{H}^+$ ion in **1** (in dichloromethane) is 398 nm—the same as that of C_6Me_7^+

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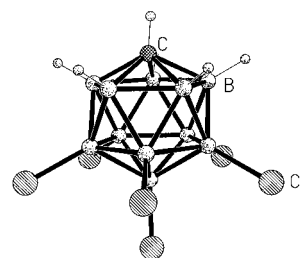


Figure 1. Structure of the hexachlorocarborane anion, $\text{CB}_{11}\text{H}_6\text{Cl}_6^-$.

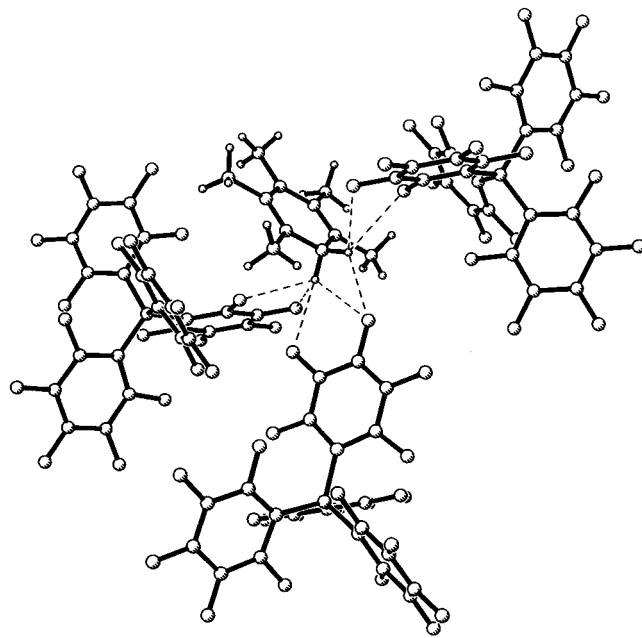


Figure 2. Packing environment of three $[\text{F}_{20}\text{-BPh}_4^-]$ anions around the $[\text{C}_6\text{Me}_5\text{H}_2^+]$ cation in the X-ray structure of **2**. Dashed lines show the $\text{C}\cdots\text{H}\cdots\text{F}\cdots\text{C}$ interactions at $\text{C}\cdots\text{F}$ distances of 2.5–2.8 Å.

and similar to that of $\text{C}_6\text{Me}_6\text{Cl}^+$ (410 nm).⁹ As a solid, **4** has a shelf life of several months but decomposes upon heating above 50 °C to give C_6HF_5 , $\text{B}(\text{C}_6\text{F}_5)_3$, and mesitylene. The structures of **1**, **2**, and **3** have been investigated by X-ray crystallography, but only **2** has an ordered cation.¹⁰ As shown in Figure 2, the order arises from a rare¹¹ example of $\text{C}\cdots\text{H}\cdots\text{F}\cdots\text{C}$ hydrogen bonding between the $\text{H}(\text{pentamethylbenzene})^+$ cation and surrounding anions. The site of protonation is clearly the unmethylated carbon atom, i.e., the structure is a σ complex. The C–C bond lengths (Figure 3) are consistent with predominant cyclohexadienyl character similar to that of the heptamethylbenzenium ion¹² and the very recently reported chlorohexamethylbenzenium ion.⁹ The observed structure is in good agreement with that calculated by a variety of methods,¹³ suggesting that the interaction with the anion is weak. The low temperature ¹H [7.50 (2H), 4.38

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(10) Crystal data for $[\text{C}_6\text{Me}_5\text{H}_2^+][\text{F}_{20}\text{-BPh}_4^-]$, **2**: Orthorhombic, $Fdd2$, $a = 34.1308(10)$, $b = 34.8106(10)$, $c = 10.8128(4)$ Å; $V = 12846.8(7)$ Å³, $Z = 16$, $D_c = 1.713$ g·cm⁻³, $2\theta_{\text{max}} = 52.76^\circ$, 5695 measured unique reflections of which 5319 with $I > 2\sigma(I)$ were used for refinement to give $R = 0.0283$, $R_w = 0.0693$ and $\text{GOF} = 1.07$. The methylene protons were observable in difference-electron density maps; positions were refined in the final model.

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(13) Full geometry optimization of the $[\text{C}_6\text{Me}_5\text{H}_2^+]$ cation used the program Gaussian 94. Calculations at the Hartree–Fock, Møller–Plesset and density functional (B3LYP) levels using a 6-311+G* basis set gave structures of C_s symmetry (neglecting the methyl protons) consistent with the cyclohexadienyl structure: C(1)–C(2) 1.480, 1.473, 1.478 Å, C(2)–C(3) 1.358, 1.386, 1.377 Å, C(3)–C(4) 1.431, 1.428, 1.432 Å, respectively.

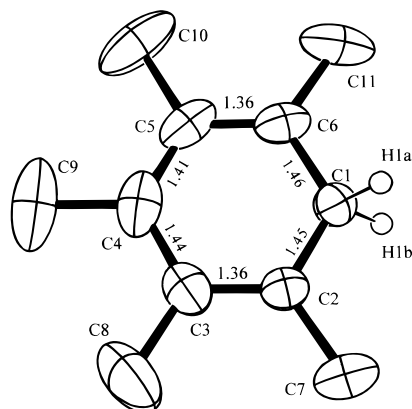


Figure 3. ORTEP plot (50%) and ring C–C bond distances (esd < 0.005 Å) for the $[C_6Me_5H_2^+]$ cation in **2**. C1–H1A = 0.98 (3), C1–H1B = 1.03 (3) Å.

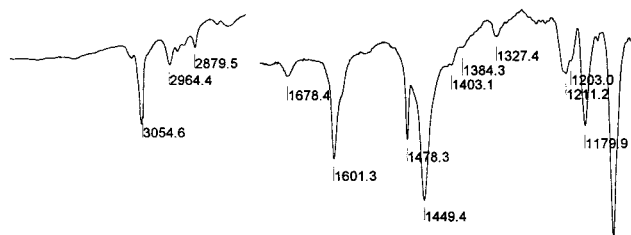


Figure 4. Portions of the IR spectrum (KBr disk) diagnostic of the benzenium cation in $[C_6H_7^+][CB_{11}H_6Cl_6^-]$, **5**.

(2H), 2.83 (3H), 2.66 (6H)] and ^{13}C [193.6, 192.1, 133.8, 51.9, 28.4, 25.8] NMR spectra of **4** in CD_2Cl_2 at -65 °C provide unambiguous identification of the H(mesitylene) $^+$ cation as a σ complex in solution, with protonation at an unmethylated carbon atom.⁵

Remarkably, given that benzene is a weaker base by 10^9 than mesitylene,⁴ eq 1 proceeds in the absence of an added methylated arene. Benzene solvent is a sufficiently good base and $Et_3Si-(CB_{11}H_6Cl_6)$ a sufficiently powerful electrophile⁷ that halide abstraction proceeds. Removal of the volatiles leads to a very pale golden microcrystalline solid, $[C_6H_7][CB_{11}H_6Cl_6]$, **5**, (Anal. Calcd C, 19.63; H, 3.06. Found: C, 19.72; H, 3.98). It is also remarkable that the B–H and B–Cl bonds of the anion are so inert and that neutral benzene is a stronger base than the anionic carborane. The formation of a strong sp^3 C–H bond must compensate for the disruption of aromaticity, allowing benzene to express its basicity. The IR spectrum of **5** in the diagnostic C–C ring vibration region (1601 s, 1478 w, 1449 s, 1327 vw, 1211 & 1203 m, 1180 $s\text{ cm}^{-1}$, see Figure 4) is essentially identical to that obtained at -80 °C in matrix isolation experiments with the $C_6H_6/HCl/GaCl_3$ system: 1595 s, 1475 w, 1445 s, 1328 vw, 1205 m, 1178 s.¹⁴ Several C–H vibrations for **5** are observed: 3065 vw (ν C–H of carborane), 3055 m, 2964 w, 2938 vw, 2916 vw, 2880 w, 2771 vw, 692 vs, and 637 s. Deuteration⁸ gives the expected^{5,14} shifts. The only other IR bands are those of the carborane anion 2613 vs (ν B–H), 1133 vs, 1079 s, 1032 vs, 1019 vs, 992 vs, 941 s, 865 vs, 821 s, 747 s, and 652 s, unperturbed relative to those in $Ag(CB_{11}H_6Cl_6)$, indicating discrete salt character. The 1H NMR spectrum of **5** in CD_2Cl_2 at room temperature shows a single downfield organic resonance—a singlet at 8.17 ppm relative to unprotonated benzene at 7.36 ppm. This corresponds to the weighted average of the shift values reported for the $C_6H_7^+$ cation at -140 °C in a low freezing point solvent/superacid medium.¹⁵ It is consistent with fluxionality of a

σ -complexed static structure, unobservable by NMR in the liquid range of CD_2Cl_2 . A σ -complex is also the lowest energy calculated structure.¹⁶ The CPMAS ^{13}C NMR spectrum of **5** at -120 °C shows peaks centered at 184, 176, 136, and 52 ppm confirming the presence of the σ -complexed benzenium ion.^{8,15,16c} Coalescence of these peaks to 145 ppm at <-60 °C indicates an interesting case of solid-state proton mobility.

It takes several orders of magnitude of acidity above 100% H_2SO_4 to fully protonate benzene, so **5** readily qualifies as a superacid.¹⁷ If kept dry, it is stable for months. This contrasts with all other salts of protonated benzene which are unstable at room temperature.^{15,18} Upon heating slowly in a sealed tube, **5** gradually turns amber (140–250 °C) with loss of benzene and chlorobenzene, becoming a dark brown solid at 350 °C.

The instability of previously isolated arenium ion salts has left the impression that ions such as $C_6H_7^+$ are intrinsically unstable. This is better understood by considering the pathways that particular anions allow for decomposition. Salts formed from nonoxidizing haloacids can simply revert to free arene, hydrogen halide and Lewis acid, e.g., crystalline $[H(\text{toluene})^+][BF_4^-]$ decomposes to toluene, HF, and BF_3 upon warming to -50 °C.¹⁹ Salts formed from oxidizing superacids have anions (e.g., HSO_4^- , SbF_6^- , $Sb_2F_{11}^-$, etc.) capable of irreversible oxidative and nucleophilic destruction. These observations highlight an important property of $[C_6H_7^+][CB_{11}H_6Cl_6^-]$. It is a superacid that is nonoxidizing, not a Brønsted/Lewis acid mixture (compare HF/ SbF_5), and the anion is much less nucleophilic than those previously used. As a stable, weighable reagent, **5** is capable of delivering protons more cleanly and stoichiometrically than previously possible. It represents a new generation of superacids (of which $HN(SO_2CF_3)_2$ may be a member)²⁰ in which oxidation is separated from protonation, Brønsted acidity is separated from Lewis acidity, the anions are as nonnucleophilic as is presently attainable, and protons of superacid strength can be readily delivered to molecules in common organic solvents. This combination of properties gives protonated arene salts potentially wide application in observing the primary protonation of organic and inorganic species that have been heretofore inaccessible in strong and superacid media because of oxidative, nucleophilic, or handling limitations. They also offer considerable opportunity for mechanistic study of H^+ catalyzed reactions (e.g., polymerization) in nearly nucleophile-free environments.

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Supporting Information Available: Details of the synthetic procedures and characterization of products **1–5** and the X-ray crystal structure determination of **2**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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