

The perfluorinated trityl cation accessible as a triflate derivative

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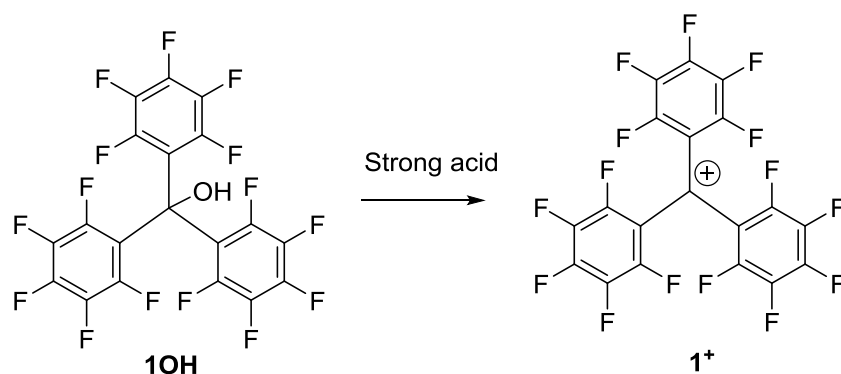
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ABSTRACT

While ultimately not isolable for X-ray structural characterization, the free perfluorinated trityl cation is shown to be observable in neat triflic acid, which represents milder conditions than previous reports of this cation in “magic acid” or oleum. A triflate-bound species can be generated in organic solvents using stoichiometric amounts of triflic acid and is shown to be synthetically viable for hydride abstraction from Et₃SiH. It is demonstrated that the *para* position on the –C₆F₅ rings is the primary point of attack for decomposition of the cation.

INTRODUCTION

The perfluorinated analogue of the trityl cation (1^+) was first observed in superacidic media¹ independently by Filler² and by Olah³ in the 1960s, generated by protonation of an alcohol precursor (1OH , Scheme 1). The stability of 1^+ was limited in oleum, better in “magic acid”, but no salt of the cation could be isolated.



Scheme 1. Generation of trityl cation 1^+ under superacidic conditions.

The electrophilicities of partially fluorinated trityl cations with have been studied recently by Mayr and co-workers,^{4,5} but the fully fluorinated analogue was not included. Given the explosion in utility observed for the boron counterpart, trispentafluorophenyl borane,^{6,7} and the availability of new counterions for reactive cations^{8,9} we proposed in a theoretical paper in 2014 that it was time to revisit the fully fluorinated analogue of the trityl cation.¹⁰ We predicted that its fluoride and hydride affinities would be very high, much higher than those of trityl cation and trispentafluorophenyl borane. Stephan and co-workers studied the perfluorinated trityl cation as an extreme Lewis acid showing good correlation between predicted Global Electrophilicity Indexes and Lewis acidity.¹¹

Herein we report on our efforts to observe and isolate cation 1^+ as a triflate or carborane salt in non-superacidic media along with an exploration of its chemistry.

RESULTS AND DISCUSSION

Our initial goal was to prepare a halo derivative of **1OH** for use in halide abstraction routes to form **1⁺**. The starting alcohol **1OH** was initially synthesized by Filler *et al.* by reacting LiC_6F_5 with decafluorobenzophenone.² They reported being unable to synthesize a halogenated derivative. We repeated their synthesis of **1OH** and further verified its structure by X-ray (Figure 1). *Caution: in the course of a routine 2 g synthesis, we experienced an explosion from LiC_6F_5 despite the mixture being held in a dry-ice/ EtOH bath.* We subsequently found that replacing the lithium reagent with the Grignard reagent $\text{BrMg-C}_6\text{F}_5$, generated from Mg metal and $\text{Br-C}_6\text{F}_5$, provides a suitable alternative route to **1OH**, albeit with a somewhat lower yield.

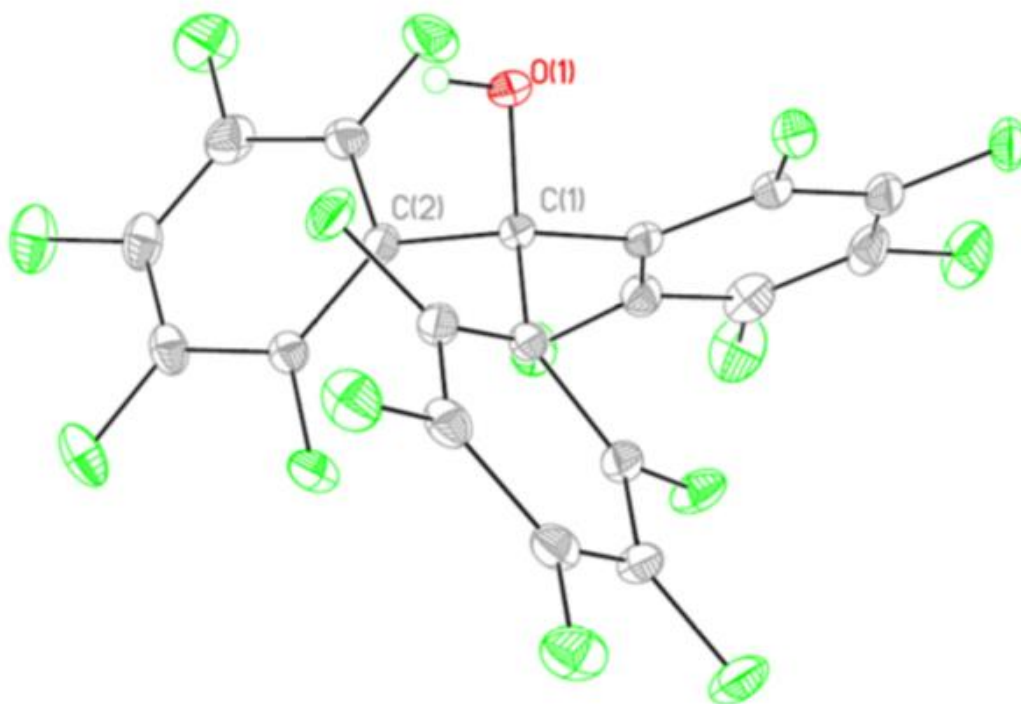


Figure 1. Solid-state structure of **1OH**. Thermal ellipsoids are depicted at the 50% probability level.

In an attempt to form the bromo derivative, **1OH** was reacted with neat acetyl bromide, following the reported procedure for the formation of trityl bromide from trityl alcohol.¹² Fluorine-19 NMR of the reaction mixture and isolated material gave the expected three resonances, shifted from those from **1OH**. However, X-ray studies revealed the presence of the acetate derivative, **1OAc**, rather than the targeted bromide (Figure 2). The ¹H NMR spectrum of the isolated powder contained a singlet, confirming identity of the bulk material with the single crystal.

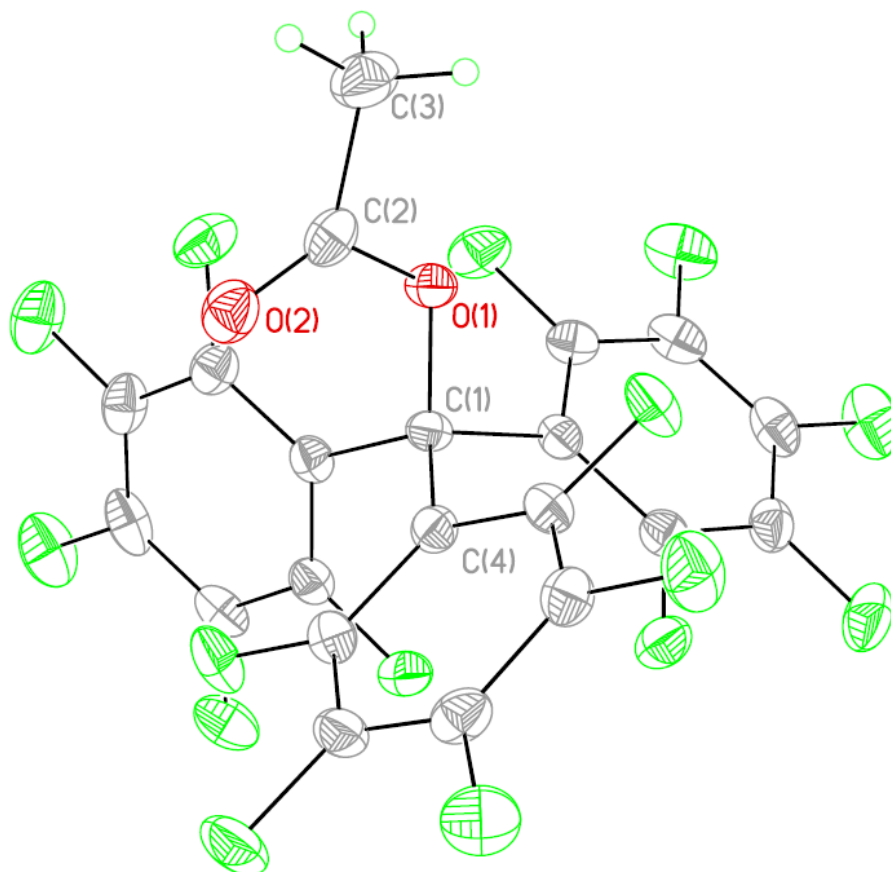
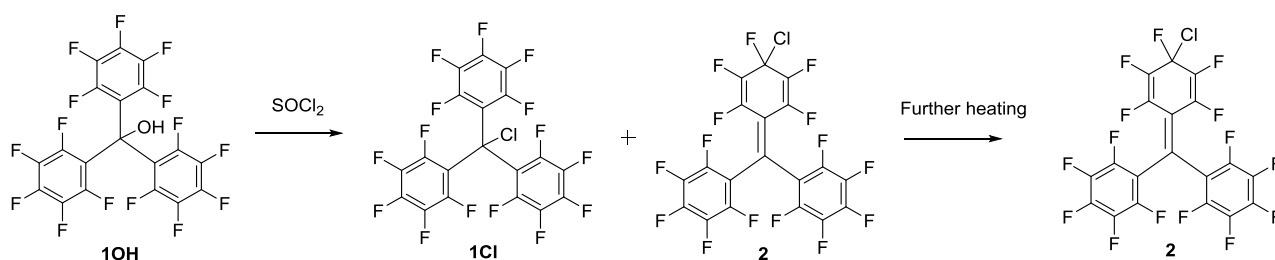


Figure 2. Solid-state structure of **1OAc**. Thermal ellipsoids are depicted at the 50% probability level.

We next used SOCl_2 to form the chloro derivative (Scheme 2). Reaction in *p*-xylene at 142 °C consistently resulted in a crude product showing nine ^{19}F NMR signals. The mixture could be chromatographically separated into two compounds, one showing six signals, the other showing the expected three signals from symmetric $-\text{C}_6\text{F}_5$ groups. X-ray diffraction revealed the latter structure to be the targeted chloroalkane **1Cl** (Figure 3). The former compound, with six ^{19}F signals, was revealed to be chlorinated at the *para*-position with sp^3 hybridized carbon, **2** (Figure 4). Heating **1Cl** to high temperatures results in transformation to **2**, presumably by attack from chlorine onto the *para* position, which is known to be a reactive site on $-\text{C}_6\text{F}_5$ rings with respect to nucleophilic attack.¹³ Efforts to minimize formation of this *para*-substituted isomer through various synthetic modifications (lower reaction temperatures, Vilsmeier-Haack chemistry or alternative chlorinating agents) failed to give better yields of the desired **1Cl**. Indeed, **2** often became the sole product. This suggests product formation is under kinetic control, favoring less sterically hindered attack of the chloride ion at the *para* position. Nevertheless, under milder reaction temperatures (≤ 80 °C approx.) **2** shows significantly reduced solubility relative to the desired chloroalkane, allowing isolation of **1Cl** in reasonable purity.



Scheme 2. Generation of chloro-derivatives **1Cl** and **2**.

Examination of the solid-state contacts in **1Cl** shows that the intermolecular contact for the chloride atom and the *para* carbon position is 3.35 Å, less than the sum of their Van der Waals radii of ~3.5

Å. These are the closest contacts for these atoms, indicative of the Lewis basic nature of the terminal chloride and more importantly, the Lewis acidic nature of the para carbon atom.

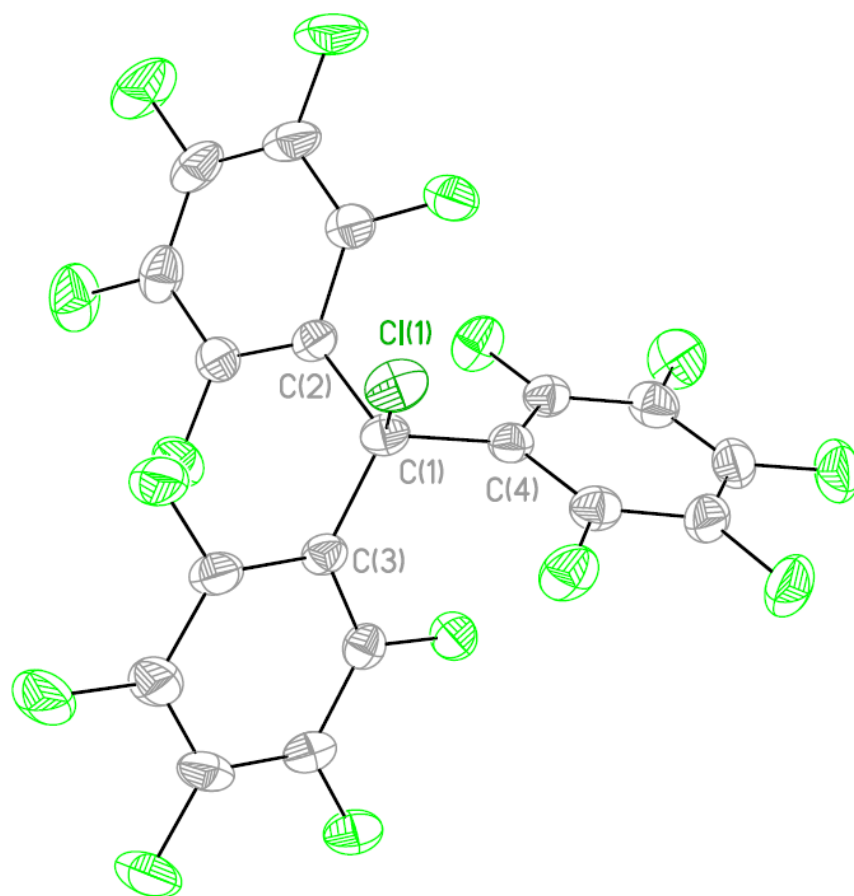


Figure 3. Solid-state structure of **1Cl**. Thermal ellipsoids are depicted at the 50% probability level.

Selected bond distances (Å): C(1)-Cl(1) 1.845(2), C(1)-C(4) 1.538(3).

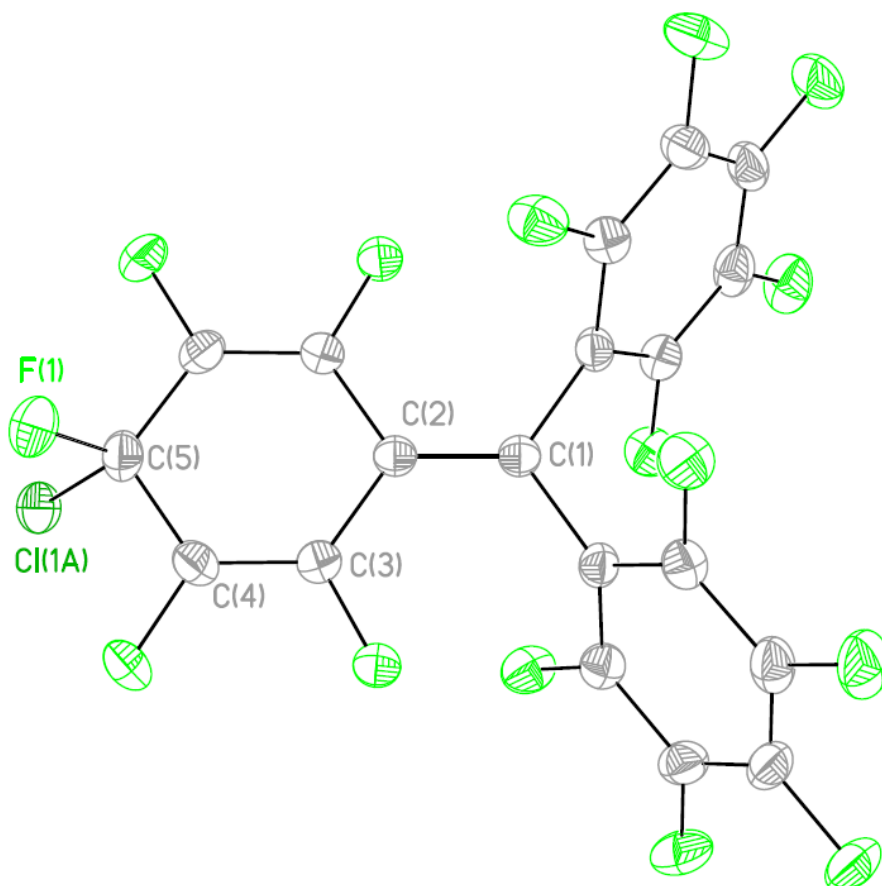
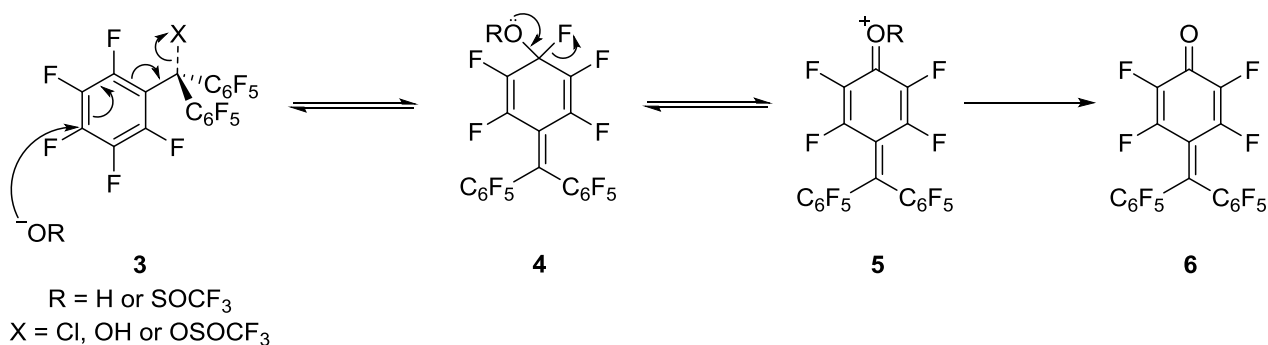


Figure 4. Solid-state structure of **2**. Thermal ellipsoids are depicted at the 50% probability level. Selected bond distances (Å): C(5)-Cl(1A) 1.727(3), C(5)-F(1) 1.415(5), C(4)-C(5) 1.484(2), C(3)-C(4) 1.327(2), C(2)-C(3) 1.466(2), C(1)-C(2) 1.355(3).

With the requisite chloroalkane in hand, we set about investigating its reaction with various halide abstraction agents. ^{19}F NMR analysis of a 1:1 mixture of **1Cl** and silver triflate (AgOTf) after stirring at ambient temperature for 20 hours in acetonitrile indicated formation of a new species having similar characteristics to the starting material. However, concentration of the colourless reaction mixture resulted in isolation of a new red solid whose ^{19}F NMR showed five new resonances. X-ray analysis revealed this compound to be the dienone **6** (Scheme 3, Figure 5), previously reported from quenching reactions between **1OH** and H_2SO_4 with water.¹⁴ Although

employing stringent anhydrous conditions, we surmised that trace amounts of water lead to its formation. Thus, despite all reasonable efforts to exclude water from the system, we continued to isolate **6** as the sole reaction product. The same outcome was observed when employing a stoichiometric amount of trimethylsilyl triflate (TMSOTf) instead of AgOTf. Attempts at using $\text{Ag}_2[\text{B}_{12}\text{Cl}_{12}]$ as a halide abstraction agent introducing the weakly coordinating $[\text{B}_{12}\text{Cl}_{12}]^{2-}$ anion¹⁵ resulted in no reaction.

A plausible reaction pathway to rationalize this reproducible formation of **6** is proposed in Scheme 3. In solution, chloroalkane **1Cl** undergoes gradual conversion to its *para*-chloro isomer **2** (*vide supra*). Similarly, the kinetically-controlled attack of a nucleophile (in this case, water or triflate anion) at the *para* position of one perfluorinated aryl ring results in formation of alkene **4** through loss of leaving group X. In this case, the leaving group may be a chloride ion or hydroxyl/triflate group (given the appearance of resonances correlating well to the perfluorinated alcohol in crude ¹⁹F NMR spectra). Subsequent elimination of F^- yields the more stable conjugated dienone **6** *via* **5**.



Scheme 3. Proposed mechanism for the generation of ketone **6**.

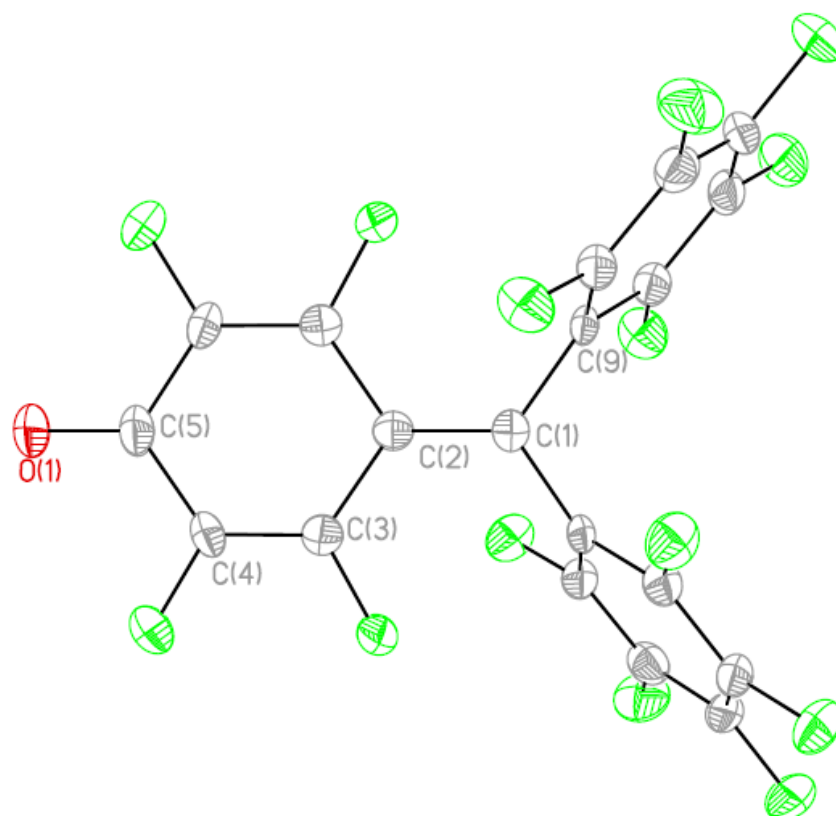
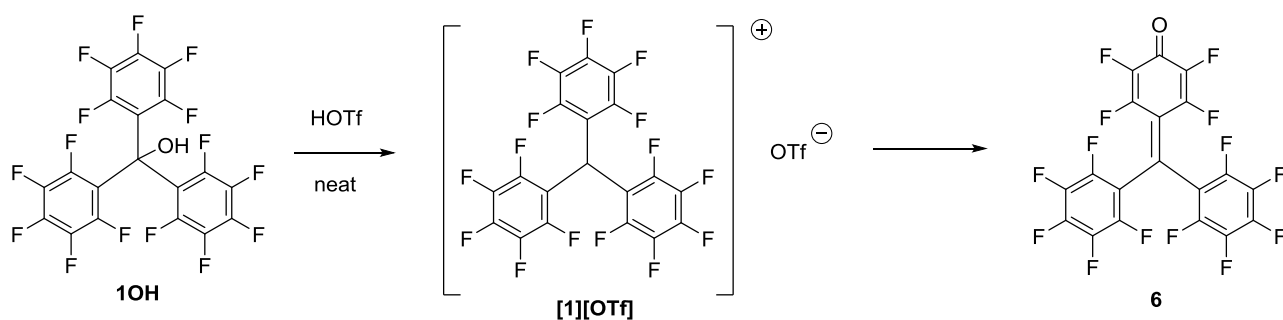


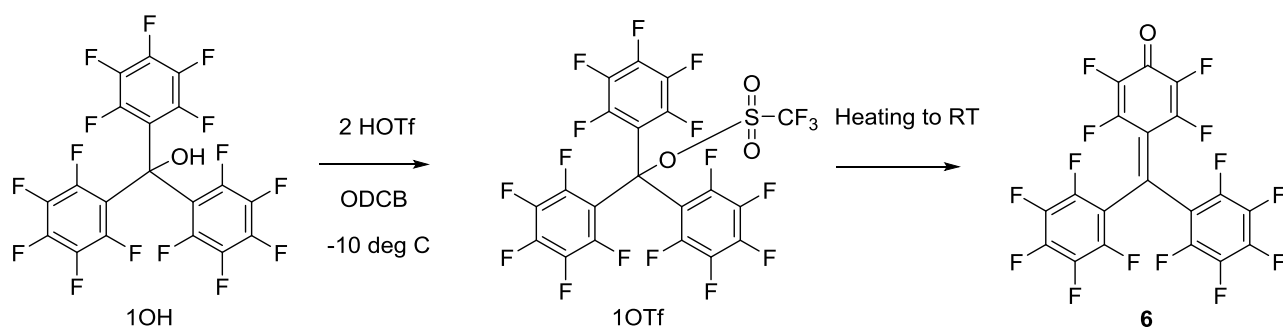
Figure 5. Solid-state structure of **6**. Thermal ellipsoids are depicted at the 50% probability level. Selected bond distances (Å): C(5)-O(1) 1.214(3), C(4)-C(5) 1.460(2), C(3)-C(4) 1.329(2), C(2)-C(3) 1.462(2), C(1)-C(2) 1.357(3), C(1)-C(9) 1.494(2).

The addition of neat triflic acid to solid **1OH** at $-30\text{ }^{\circ}\text{C}$ resulted in immediate generation of a deep maroon solution (Scheme 4). ^{19}F NMR spectroscopy of the solution with the NMR probe set at $-30\text{ }^{\circ}\text{C}$ revealed three signals at -115 , -128 , and -157 ppm. The strongly downfield shift of the *para* and *ortho* fluorine atoms is consistent with the observations of Olah and co-workers for ionized **1⁺** in strongly acidic media.³ While this cation is stable for at least two hours at $-30\text{ }^{\circ}\text{C}$, warming to room temperature results in decomposition, with ketone **6** being the main product after a sample was held overnight.



Scheme 4. Generation of **1⁺** as a triflate salt in neat HOTf and decomposition to **6** upon warming.

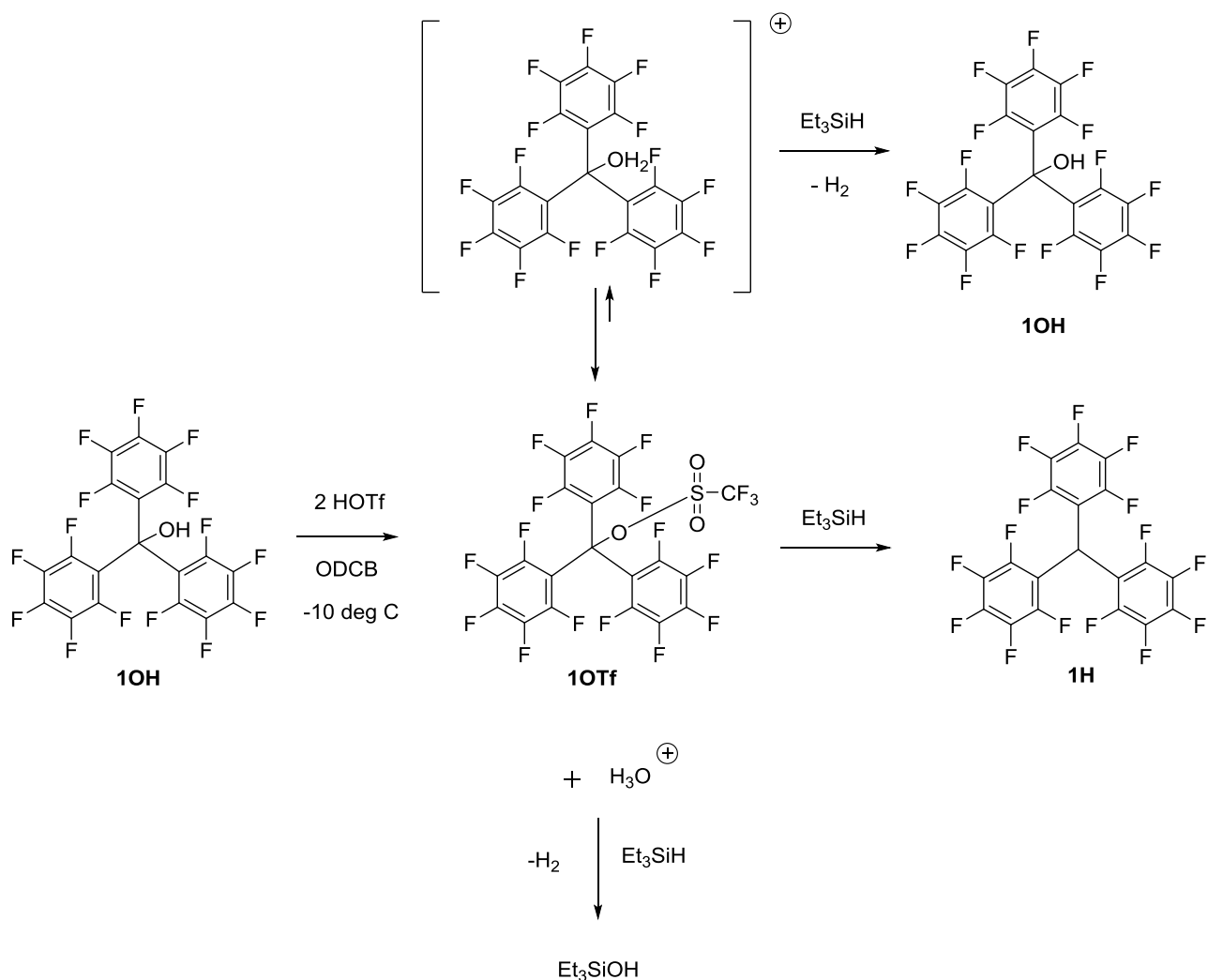
Neat triflic acid is a harsh medium and likely precludes the synthetic use of **1⁺**. We therefore explored its formation in organic solvents. Reacting two equivalents of TfOH (one to protonate the alcohol, and the second to sequester the resulting equivalent of H₂O) with **1OH** in *ortho*-dichlorobenzene (ODCB) resulted in the immediate formation of a dark red colored solution (Scheme 5). The ¹⁹F NMR spectrum of the reaction mixture at -10 °C was relatively clean, with three ¹⁹F signals at -142.5, -153.6, and -162.8 ppm. These signals are distinctly different from those of **1OH** in the same solvent and far upfield to what is consistent with a free cation, as observed with neat triflic acid. Warming to room temperature resulted in decomposition of the mixture to signals consistent with **6** as the main product after 48 hours. The data is consistent with the formation of **1OTf**, with the triflate fragment remaining bound to the carbon centre.



Scheme 5. Generation of **1OTf** and decomposition to **6** upon warming.

To lend support to the proposed formation of **1OTf** and explore its synthetic utility, we explored its ability to act as a hydride acceptor. This is expected behavior, as triflate is an excellent leaving group bound to electron-deficient carbon.

Addition of Et₃SiH as a hydride donor to a solution of **1OTf** prepared from **1OH** and two equivalents of HOTf at -10 °C in *ortho*-dichlorobenzene (Scheme 6), resulted in an NMR spectrum consistent with the presence of two species, one the regenerated alcohol **1OH**, and the other as tris(pentafluorophenyl)methane **1H**.¹⁶ Performing the reaction in toluene at low temperature allowed for simpler isolation of **1H** in a pure form, because toluene is more easily removed under vacuum. We hypothesize that the competing reactions shown in Scheme 6 account for this distribution of products. Nevertheless, the generation of **1H** is supportive of the generation of **1OTf**. The anion is too strongly coordinating to allow ionization to **1**⁺ in low dielectric media.



Scheme 6. Reaction pathways of **1OTf** with hydride donor Et₃SiH.

Carborane anions are much less coordinating than triflate and often allow isolation of extremely reactive cations.⁸ To determine if the *closo*-carborane anion [HCB₁₁Cl₁₁]⁻ might allow isolation of “free” **1**⁺ in non-super acidic media, solid alcohol **1OH** was mixed with two equivalents of solid [C₆H₇][HCB₁₁Cl₁₁], the protonated benzene salt of the carborane. IR spectroscopy indicated that mixing the two solids did not result in any reaction but the addition of a drop of benzene resulted in the immediate generation of a maroon slurry, followed by immediate evaporation. IR spectroscopy of the resulting solid indicated loss of **1OH**. The vibrations associated with stretching of C_{central}-C_{ipso} bonds are shifted to lower frequencies (1604-1611 cm⁻¹) compared to **1OH** (1653 cm⁻¹). For comparison, calculated vibration frequencies using B3LYP-D3(BJ)/def2-TZVPP give 1671-1678

cm⁻¹ for **1OH** and 1667 cm⁻¹ for **1**⁺. For comparison, the IR spectrum for the trityl salt of the same carborane anion shows stretches associated with the central-*ipso* C-C bonds at 1577 cm⁻¹ while the computationally predicted vibration for the trityl cation is found at 1630 cm⁻¹. The blue shift for the perfluorinated compound is likely a result of a stronger C-C bond induced by the π donor ability of the fluorine atoms.

Despite this evidence for the existence of **1**⁺ in the solid state, it does not appear that the cation is stable in low polarity solvents. Although addition of 2 equivalents of [C₆H₇][CHB₁₁Cl₁₁] to a solution of **1OH** in a variety of arene solvents (toluene, benzene, *ortho*-dichlorobenzene) did result in the immediate formation of red solutions, they underwent decolorization within minutes and we were unable to identify any ¹⁹F NMR signals consistent with formation of **1**.

CONCLUSIONS

We have demonstrated that the perfluorinated trityl cation exists in neat triflic acid. In less polar organic solvents it exists with bound triflate but nevertheless shows reactivity as a hydride acceptor with silanes. The free cation appears to exist in the solid state when the counterion is switched to an ultra-inert carborane but intrinsic decomposition prevents its full characterization. It is apparent that the para-carbon position of the -C₆F₅ ring is the Achilles heel of this reactive species.

ASSOCIATED CONTENT

Supporting Information. Experimental details with associated ^1H , ^{19}F , IR spectra of synthesized compounds and reaction mixtures. Computational details and Cartesian coordinates for calculated species. X-ray crystallographic details in .cif format.

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