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View Article Online
View Journal | View IssueCite this: *Chem. Sci.*, 2022, 13, 4972

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Isolable fluorinated triphenylmethyl cation salts of $[\text{HCB}_{11}\text{Cl}_{11}]^-$: demonstration of remarkable hydride affinity†

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Significantly fluorinated triarylmethyl cations have long attracted attention as potentially accessible highly reactive carbocations, but their isolation in a convenient form has proved elusive. We show that abstraction of chloride with a cationic silylium reagent leads to the facile formation of di-, tetra-, and hexafluorinated trityl cations, which could be isolated as analytically pure salts with the $[\text{HCB}_{11}\text{Cl}_{11}]^-$ counterion and are compatible with (halo)arene solvents. The F_6Tr^+ cation carrying six *meta*-F substituents was computationally predicted to possess up to 20% higher hydride affinity than the parent triphenylmethyl cation Tr^+ . We report that indeed F_6Tr^+ displays reactivity unmatched by Tr^+ . F_6Tr^+ at ambient temperature abstracts hydrides from the C–H bonds in tetraethylsilane, mesitylene, methylcyclohexane, and catalyzes Friedel–Crafts alkylation of arenes with ethylene, while Tr^+ does none of these.

Received 27th October 2021

Accepted 2nd April 2022

DOI: 10.1039/d1sc05936j

rsc.li/chemical-science

Introduction

The triphenylmethyl or trityl cation (Ph_3C^+ or Tr^+) is a textbook example of a carbocation that is isolable owing to the high degree of benzylic conjugation and the steric protection afforded to the central carbon by the three phenyl substituents.¹ In organometallic chemistry and catalysis, salts of Tr^+ are frequently used to study the thermodynamics and kinetics of hydride transfer,^{2,3,4} or to generate reactive main-group and transition-metal cations through hydride or alkyl anion abstraction.^{5,6,7} Tr^+ can also serve as a convenient one-electron oxidant.⁸ Trityl cation derivatives bearing stabilizing electron-donating groups can even exist in aqueous solutions, with a rich history of use as indicators and dyes.⁹ The trityl cation versions bearing electron-withdrawing substituents have proven more challenging to obtain. Fluorinated trityl cations, up to $(\text{C}_6\text{F}_5)_3\text{C}^+$ (**A**, Fig. 1), have been of particular fundamental interest,^{10–12} including as isoelectronic analogs of the widely used borane $(\text{C}_6\text{F}_5)_3\text{B}$,^{13,14} and more recently have been studied by Horn and Mayr¹⁵ and Dutton *et al.*¹⁶ The more reactive **A** or other *ortho*- and/or *meta*-fluorinated trityl cations were not isolated in those studies, but were generated *in situ*, or their intermediacy was indicated by kinetic studies. While generation

of fluorinated trityl cations in oleum and other superacidic media,^{10–12,16} or by *in situ* abstraction of halides with element halide Lewis acids¹⁵ is possible, these media and counteranions are not fully compatible with either the more electron-deficient trityl cations themselves or with their potential use in the synthesis of other reactive main-group or transition metal cations. Thus, the full extent of the reactivity of the fluorinated trityl cations can only be accessed when paired with more robust weakly coordinating anions in weakly coordinating solvents.¹⁷ The only example of an isolated trityl-type cation

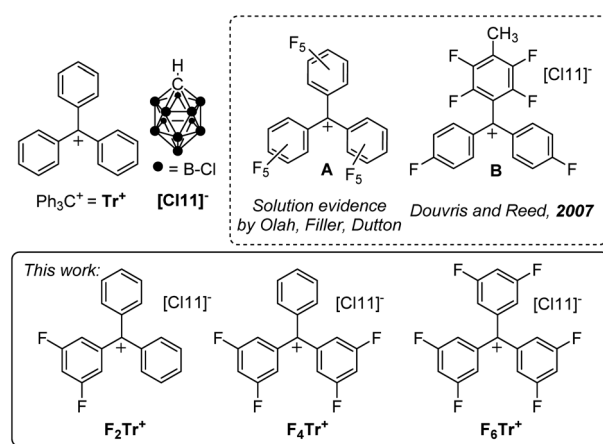


Fig. 1 The parent trityl cation Tr^+ , selected literature examples of fluorinated trityls, and the fluorinated trityl salts prepared and studied in this work.

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† Electronic supplementary information (ESI) available: Experimental details and pictorial NMR spectra, details of the computational studies and the coordinate files. CCDC 2079761 and 2079762. For ESI and crystallographic data in CIF or other electronic format see <https://doi.org/10.1039/d1sc05936j>

fluorinated in the *ortho*-/*meta*-positions is **B** (Fig. 1), obtained by Douvris and Reed in an undefined yield, and not studied further.¹⁸ The perchlorotriptyl cation has also been isolated.¹⁹

Our group has been attracted to the highly reactive carbo- and main-group cations in the context of our work on silylium and alumenium cation-catalyzed activation of aliphatic C–F bonds,^{20–23} which permitted exhaustive defluorination of perfluoroalkyl groups under mild conditions. The chemistry of abstraction of fluoride from certain fluoroarenes with silylium cations has led to innovative reactivity, as well.^{24,25} Trialkylsilylium cations are typically generated by hydride abstraction from trialkylsilanes (R_3SiH) using Tr^+ ,²⁶ but our theoretical analysis suggested that the parent Tr^+ only barely has the thermodynamic hydride affinity (HA) to abstract hydrides from even the relatively electron-rich SiH bonds in trialkylsilanes. Given the perceived challenge^{10,16} in the isolation of the fully fluorinated $(C_6F_5)_3C^+$, we decided to first explore the partially fluorinated derivatives. Here, we report the isolation of analytically pure di-, tetra-, and hexafluorosubstituted triptyl cation salts, and the remarkable contrast in the hydride abstraction reactivity with the parent Tr^+ .

Results and discussion

Theoretical HA analysis

Wilson and Dutton calculated gas-phase and CH_2Cl_2 solvent continuum HA values for a series of symmetric polychloro- and polyfluorosubstituted triptyl cations.²⁷ They discussed the fit to the known experimental values provided by the various computational methods and settled on the use of B3LYP/aug-cc-pVTZ//B3LYP/def2-TZVPP.^{28,29}

The Wilson–Dutton calculations showed that replacement of H with F in the *para*-position has an essentially zero effect on HA, whereas introduction of each *ortho*- or a *meta*-fluorine increases HA by *ca.* 2.4–2.7 kcal mol^{−1} (CH_2Cl_2 continuum) or *ca.* 3.5 kcal mol^{−1} (gas phase). This is in line with the more negative pK_{R^+} values for the various *ortho*- and *meta*-fluorinated triptyls compared to Tr^+ or the *para*-F substituted triptyls, determined by Filler *et al.*¹⁰ The *ortho*- and *para*-CF positions are conjugated to the central carbon by resonance and the *para*-CF has been identified as a site of alternative nucleophilic attack on $(C_6F_5)_3C^+$ related to its decomposition pathways.^{10,16} We decided to avoid fluorination in the *ortho*- or *para*-positions and focus on *meta*-fluorination. The Wilson–Dutton HA values for F_6Tr^+ (213.0 and 108.3 kcal mol^{−1}) were 11% and 17% higher than for Tr^+ (191.4 and 92.5 kcal mol^{−1}) in the gas phase and CH_2Cl_2 continuum, respectively.

In 2011,³⁰ we analyzed the HA and FA values for a series of cations relevant to the silylium-catalyzed HDF using the M05-2X functional with the basis sets 6-311+G(d) for F, and 6-31++G(d,p) for C and H.³¹ Utilizing the DFT approach from our 2011 paper, we calculated the gas-phase and the chlorobenzene solvent continuum HA values for F_6Tr^+ to be 229.4 and 135.0 kcal mol^{−1}, representing a 13% and a 20% increase *vs.* Tr^+ . These relative increases are similar to those in the Wilson–Dutton work.²⁷ The substantial increase suggests that the HA of F_6Tr^+ is thermodynamically sufficient to abstract a hydride from

a range of Si–H containing molecules, and rivals the HA values calculated (also in PhCl) for Me_3C^+ (126.6 kcal mol^{−1}), $PhCH_2^+$ (137.8 kcal mol^{−1}), and Me_2CH^+ (138.9 kcal mol^{−1}).³⁰ Without assessing quantitative accuracy, we nonetheless surmised that F_6Tr^+ might be able to abstract hydrides from tertiary and possibly secondary and benzylic C(sp³)–H bonds.

Synthesis and characterization of F_xTr^+ salts

We envisioned the synthesis of fluorinated triptyl cations partnered with the exceptionally robust and weakly coordinating $[HCB_{11}Cl_{11}]^-$ anion ($[Cl11]$, Fig. 1)^{18,32–35} *via* abstraction of a chloride anion from the corresponding F_2TrCl , F_4TrCl , and F_6TrCl .^{36,37} $Na[Cl11]$ can abstract a chloride from $TrCl$ ³⁸ and from F_2TrCl in *o*- $C_6H_4Cl_2$ at ambient temperature, giving a 97% isolated yield of $F_2Tr[Cl11]$ after workup. Attempts to use $Na[Cl11]$ to generate $F_4Tr[Cl11]$ and $F_6Tr[Cl11]$ were unsuccessful and we moved to a more powerful^{39–41} chloride abstractor $[(Me_3Si)_2OTf][Cl11]$ ($Si[Cl11]$).^{38,42}

Indeed, treatment of F_2TrCl with $Si[Cl11]$ in a 2 : 1 C_6D_6/o - $C_6H_4Cl_2$ solvent mixture at ambient temperature (Fig. 2) resulted in rapid color change. Analysis of the resultant solution by NMR spectroscopy after 10 min revealed the expected formation of equimolar amounts of Me_3SiCl and Me_3SiOTf and 96% yield of F_2Tr^+ (¹⁹F NMR evidence, δ −104.6 ppm). The analogous reactions with F_4TrCl and F_6TrCl also proceeded smoothly. The resultant $F_4Tr[Cl11]$ and especially $F_6Tr[Cl11]$ are less soluble than $F_2Tr[Cl11]$ or $Tr[Cl11]$, and precipitate readily out of fluoro-*benzene*, allowing isolation of analytically pure solids in 96% and 70% yields.

The ¹³C NMR chemical shifts of the central carbons of $F_2Tr[Cl11]$, $F_4Tr[Cl11]$, and $F_6Tr[Cl11]$ in the 208–210 ppm range,⁴³ as well as the ¹H and ¹⁹F NMR spectral data did not suggest any significant interaction of the cations with the $[Cl11]^-$ anion, the

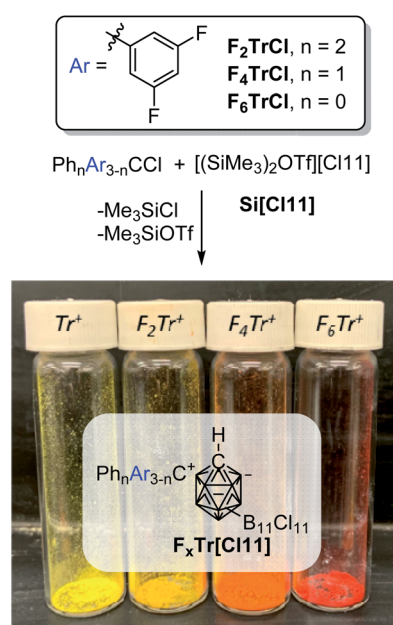


Fig. 2 Synthesis of fluorinated triptyl cation salts and their appearance.



arene or CD_2Cl_2 solvents, or the $\text{Me}_3\text{SiCl}/\text{Me}_3\text{SiOTf}$ by-products. Single-crystal X-ray diffractometry (Fig. 3) revealed that the central carbons in $\text{F}_2\text{Tr}[\text{Cl11}]$ and $\text{F}_6\text{Tr}[\text{Cl11}]$ possessed a planar environment in all the crystallographically independent cations (the sums of C–C–C angles are *ca.* 360°), and the aryl groups splay out in a pinwheel pattern about the central carbon. The closest approach of any chlorine to the central carbon in $\text{F}_2\text{Tr}[\text{Cl11}]$ is at least 3.7 Å, and 3.25 Å in $\text{F}_6\text{Tr}[\text{Cl11}]$, consistent with the well-separated, ionic nature of the $\text{F}_x\text{Tr}[\text{Cl11}]$ salts.

Reactivity of F_6Tr^+ vs. Tr^+ with Et_3SiH

It was previously shown that Tr^+ is not capable of abstracting the full hydride equivalent from Et_3SiH in non-coordinating solvents and that two equivalents of R_3SiH are needed for complete formation of TrH .⁴⁴ Our observations are similar: treatment of either $\text{F}_6\text{Tr}[\text{Cl11}]$ or $\text{Tr}[\text{Cl11}]$ with two equivalents of Et_3SiH in a $\text{C}_6\text{D}_6/o\text{-C}_6\text{H}_4\text{Cl}_2$ solvent mixture led to the quantitative formation of F_6TrH or TrH , respectively. The fate of the “ Et_3Si^+ ” species in arene solvents is not straightforward, as has been studied in detail⁴⁵ by Heinekey and coworkers: the presence of varying amounts of Et_4Si betrays complexity arising from the H/Et redistribution in the Si species and/or reactions with the arenes.

The reaction of $\text{Tr}[\text{Cl11}]$ with a substoichiometric (0.9 equiv.) amount of Et_3SiH did not lead to the complete disappearance of the Si–H moiety (16% of the original Si–H intensity remained) and only 82% of the possible TrH was observed (Fig. 4). In contrast, the reaction of $\text{F}_6\text{Tr}[\text{Cl11}]$ with substoichiometric (0.75

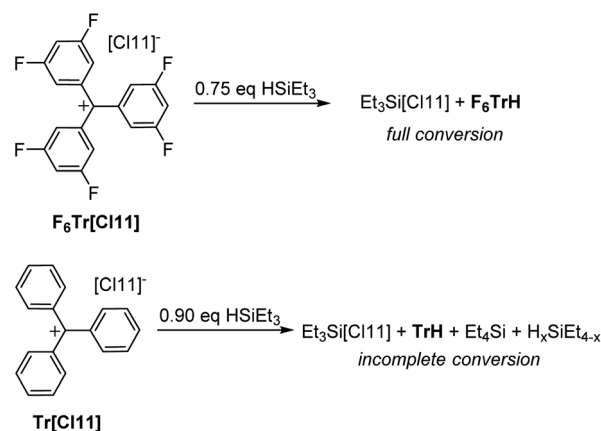


Fig. 4 Reactions of Tr^+ and F_6Tr^+ with a substoichiometric amount of HSiEt_3 .

equiv.) amount of Et_3SiH led to the production of the expected quantity of F_6TrH , the complete disappearance of the Si–H signals, and without the concomitant observation of Et_4Si .

H–D exchange

In the reactions of $\text{F}_6\text{Tr}[\text{Cl11}]$ with Et_3SiH , significant H/D scrambling was observed among the neutral aromatic compounds present in solution: C_6D_6 , $o\text{-C}_6\text{H}_4\text{Cl}_2$, and F_6TrH (but the $\text{C}(\text{sp}^3)\text{--H}$ bond in F_6TrH was never deuterated). The extent of H–D exchange was analyzed *via* ^1H , ^{13}C , or ^{19}F NMR spectroscopy (see ESI† for details). The mechanism of the H/D exchange likely involves the generation of superacidic protonated arenes *in situ*,⁴⁷ which should enable rapid H/D exchange *via* H^+/D^+ shuttling (Fig. S4†).^{47,48} The product of addition of either Et_3Si^+ or F_6Tr^+ to a neutral arene can be alternatively viewed as a protonated arene.⁴⁷ It is also possible that analogous cations are accessed *via* reactions involving the minor components of the mixture. The Oestreich group recently examined this type of H/D exchange catalysis in greater detail.⁴⁹

Abstraction of hydride from C–H bonds

Given the computational prediction of the enhanced hydride affinity of F_6Tr^+ vs. Tr^+ , we wished to examine their reactivity towards benzylic and aliphatic C–H bonds. As expected, no reaction was observed between $\text{Tr}[\text{Cl11}]$ and (1) 1 equiv. of mesitylene or (2) 1 equiv. of methylcyclohexane in $o\text{-C}_6\text{H}_4\text{Cl}_2$ after 1 week at ambient temperature. In contrast, the reaction of $\text{F}_6\text{Tr}[\text{Cl11}]$ with mesitylene (as solvent) resulted in 66% yield (NMR evidence) or F_6TrH after 48 h. We propose that hydride abstraction from mesitylene by $\text{F}_6\text{Tr}[\text{Cl11}]$ generates a 3,5-dimethylbenzyl cation, which rapidly undergoes Friedel–Crafts^{20,21} addition to mesitylene. GC–MS analysis of the mixture after quenching with water showed the presence of a m/z signal at 238, consistent with compound 4 (Fig. 5). Treatment of $\text{F}_6\text{Tr}[\text{Cl11}]$ in $o\text{-C}_6\text{H}_4\text{Cl}_2$ with 1 equiv. of methylcyclohexane resulted in the >95% yield (NMR evidence) of F_6TrH after 96 h. The aliphatic region of the ^1H NMR spectrum presented a large

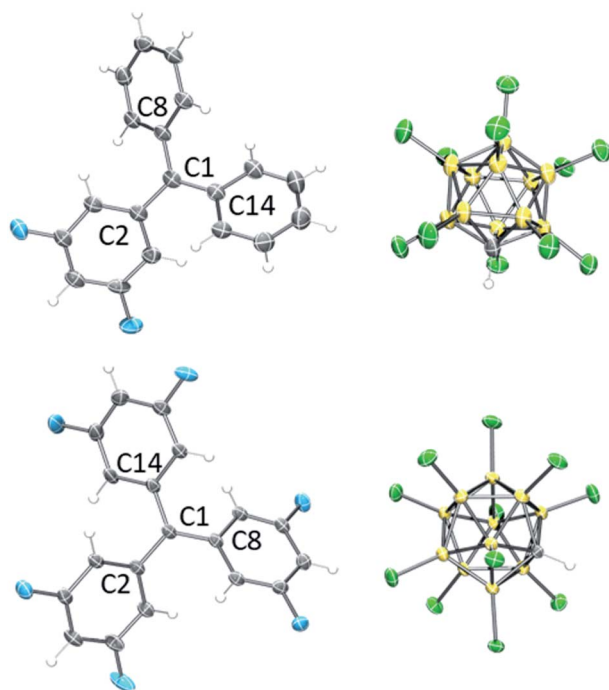


Fig. 3 POV-Ray rendition of the ORTEP (50% probability ellipsoids) drawing of $\text{F}_2\text{Tr}[\text{Cl11}]$ (top) and $\text{F}_6\text{Tr}[\text{Cl11}]$ (bottom). Only one cation and one anion from each asymmetric unit is shown. Solvent and disorder are omitted for clarity.



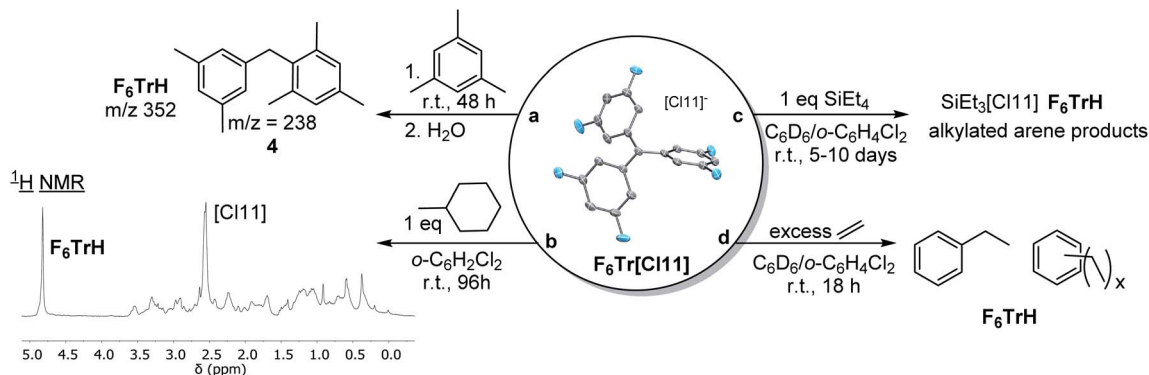


Fig. 5 Reactions of $F_6Tr[Cl11]$ resulting in the abstraction of a hydride from $C(sp^3)-H$ bonds.

number of overlapping aliphatic signals, indicating a complex mixture (Fig. 5b).

The methylcyclohexyl cation presumed to be formed initially may undergo isomerization⁵⁰ and Friedel–Crafts addition to $o-C_6H_4Cl_2$, with many potential products. Abstraction of a hydride from alkanes, with generation of rearranged tertiary carbocations, was previously reported by the Reed group using $Me[HCB_{11}Me_5Br_6]$.^{51,52} The key difference between Reed's “ Me^+ ” reagents and the F_6Tr^+ reported here is that the latter can be prepared in bulk analytical purity and is stable in haloarene solutions.

Abstraction of a hydride from the β -position in tri-alkylaluminums with Tr^+ has been used to generate reactive alumenium (R_2Al^+) cations.^{6,22,53} The analogous abstraction of β -hydride from alkylsilanes by Tr^+ is not known, and we have confirmed that no reaction takes place between $Tr[Cl11]$ and Et_4Si in $C_6D_6/o-C_6H_4Cl_2$. However, an analogous reaction of Et_4Si with $F_6Tr[Cl11]$ resulted in the formation of 82% F_6TrH after 96 h (and complete disappearance of Et_4Si after 10 d). The major Si product appeared to be “ Et_3Si ”, but instead of the stoichiometric complement of free ethylene, we observed ethane and other aliphatic resonances. Ethane may result from the protonolysis of Et_4Si by the highly Brønsted acidic cations generated in the reaction (extensive H/D exchange was concomitantly observed), a process reported on by Oestrich and co-workers.⁵⁴ As a control experiment, we examined the reaction of $F_6Tr[Cl11]$ with 6.3 equiv. of ethylene in $C_6D_6/o-C_6H_4Cl_2$. Within 18 h at ambient temperature, all ethylene had been consumed, with the concomitant generation of ethylbenzene (1.8 equiv.) and other alkylarenes, and quantitative production of F_6TrH . It is reasonable to propose that $F_6Tr[Cl11]$ abstracts a hydride from the benzylic positions of ethylbenzene or other alkylarenes generated through Friedel–Crafts alkylation. In complete contrast, no reaction occurred between $Tr[Cl11]$ and ethylene under analogous conditions.

Conclusion

Introduction of six *meta*-F substituents in F_6Tr^+ brought about remarkable contrast with the reactivity of the parent triphenylmethyl (Tr^+) cation, understood primarily through the

greatly enhanced hydride affinity of especially the hexafluorinated F_6Tr^+ . Interestingly, while F_6Tr^+ catalyzes the Friedel–Crafts alkylation of arenes with ethylene, and generates alkyl cations *via* hydride abstraction which then readily engage in Friedel–Crafts addition, F_6Tr^+ itself is stable in combination with (halo)arene solvents and dichloromethane. This shows that fluorinated trityl cations represent a promising class of reagents for achieving the extremes of hydride affinity while minimizing reactivity with other potential substrates.

Data availability

Data for this manuscript are available in the ESI.†

Author contributions

S. O. G. and C. I. L. performed the syntheses and obtained the characterization data. E. S. performed the DFT calculations. N. B. carried out the X-ray diffraction studies on the crystals grown by S. O. G. S. O. G. and O. V. O. wrote the manuscript with assistance of the other co-authors. O. V. O. directed the overall effort.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This research was supported by the Naval Research Laboratory (grant N00173-20-1-G010 to O. V. O.). We thank Dr Manoj Kolevteel for insightful discussions. The authors acknowledge the High-Performance Research Computing Center at Texas A&M University for providing access to supercomputing clusters, software, and computing time. We thank R. A. Gholson for assistance with manuscript formatting.

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