


Cite 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  $\text{F}_6\text{Tr}^+$  cation carrying six *meta*-F substituents was computationally predicted to possess up to 20% higher hydride affinity than the parent triphenylmethyl cation  $\text{Tr}^+$ . We report that indeed  $\text{F}_6\text{Tr}^+$  displays reactivity unmatched by  $\text{Tr}^+$ .  $\text{F}_6\text{Tr}^+$  at ambient temperature abstracts hydrides from the C–H bonds in tetraethylsilane, mesitylene, methylcyclohexane, and catalyzes Friedel–Crafts alkylation of arenes with ethylene, while  $\text{Tr}^+$  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 ( $\text{Ph}_3\text{C}^+$  or  $\text{Tr}^+$ ) 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.<sup>1</sup> In organometallic chemistry and catalysis, salts of  $\text{Tr}^+$  are frequently used to study the thermodynamics and kinetics of hydride transfer,<sup>2,3,4</sup> or to generate reactive main-group and transition-metal cations through hydride or alkyl anion abstraction.<sup>5,6,7</sup>  $\text{Tr}^+$  can also serve as a convenient one-electron oxidant.<sup>8</sup> Trityl cation derivatives bearing stabilizing electron-donating groups can even exist in aqueous solutions, with a rich history of use as indicators and dyes.<sup>9</sup> 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,<sup>10–12</sup> including as isoelectronic analogs of the widely used borane  $(\text{C}_6\text{F}_5)_3\text{B}$ ,<sup>13,14</sup> and more recently have been studied by Horn and Mayr<sup>15</sup> and Dutton *et al.*<sup>16</sup> 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,<sup>10–12,16</sup> or by *in situ* abstraction of halides with element halide Lewis acids<sup>15</sup> 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.<sup>17</sup> The only example of an isolated trityl-type cation

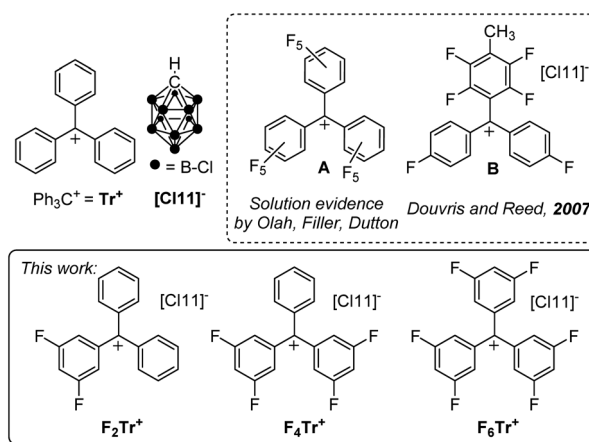


Fig. 1 The parent trityl cation  $\text{Tr}^+$ , selected literature examples of fluorinated trityls, and the fluorinated trityl salts prepared and studied in this work.

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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.<sup>18</sup> The perchlorotryl cation has also been isolated.<sup>19</sup>

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,<sup>20–23</sup> 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.<sup>24,25</sup> Trialkylsilylium cations are typically generated by hydride abstraction from trialkylsilanes ( $R_3SiH$ ) using  $Tr^+$ ,<sup>26</sup> 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<sup>10,16</sup> 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 trityl 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 trityl cations.<sup>27</sup> 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.<sup>28,29</sup>

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<sup>−1</sup> ( $CH_2Cl_2$  continuum) or *ca.* 3.5 kcal mol<sup>−1</sup> (gas phase). This is in line with the more negative  $pK_{R^+}$  values for the various *ortho*- and *meta*-fluorinated trityls compared to  $Tr^+$  or the *para*-F substituted trityls, determined by Filler *et al.*<sup>10</sup> 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.<sup>10,16</sup> 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<sup>−1</sup>) were 11% and 17% higher than for  $Tr^+$  (191.4 and 92.5 kcal mol<sup>−1</sup>) in the gas phase and  $CH_2Cl_2$  continuum, respectively.

In 2011,<sup>30</sup> 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.<sup>31</sup> 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<sup>−1</sup>, representing a 13% and a 20% increase *vs.*  $Tr^+$ . These relative increases are similar to those in the Wilson–Dutton work.<sup>27</sup> 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<sup>−1</sup>),  $PhCH_2^+$  (137.8 kcal mol<sup>−1</sup>), and  $Me_2CH^+$  (138.9 kcal mol<sup>−1</sup>).<sup>30</sup> Without assessing quantitative accuracy, we nonetheless surmised that  $F_6Tr^+$  might be able to abstract hydrides from tertiary and possibly secondary and benzylic  $C(sp^3)$ –H bonds.

### Synthesis and characterization of $F_xTr^+$ salts

We envisioned the synthesis of fluorinated trityl cations partnered with the exceptionally robust and weakly coordinating  $[HCB_{11}Cl_{11}]^-$  anion ( $[Cl11]$ , Fig. 1)<sup>18,32–35</sup> *via* abstraction of a chloride anion from the corresponding  $F_2TrCl$ ,  $F_4TrCl$ , and  $F_6TrCl$ .<sup>36,37</sup>  $Na[Cl11]$  can abstract a chloride from  $TrCl$ <sup>38</sup> 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<sup>39–41</sup> chloride abstractor  $[(Me_3Si)_2OTf][Cl11]$  ( $Si[Cl11]$ ).<sup>38,42</sup>

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

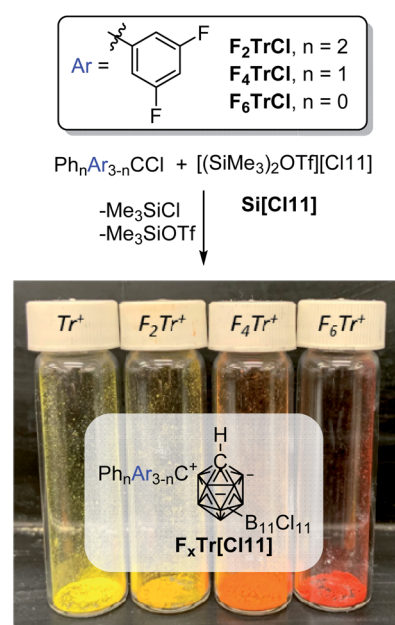


Fig. 2 Synthesis of fluorinated trityl cation salts and their appearance.



arene or  $\text{CD}_2\text{Cl}_2$  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.*  $360^\circ$ ), 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 $\text{F}_6\text{Tr}^+$ vs. $\text{Tr}^+$ with $\text{Et}_3\text{Si-H}$

It was previously shown that  $\text{Tr}^+$  is not capable of abstracting the full hydride equivalent from  $\text{Et}_3\text{SiH}$  in non-coordinating solvents and that two equivalents of  $\text{R}_3\text{SiH}$  are needed for complete formation of  $\text{TrH}$ .<sup>44</sup> Our observations are similar: treatment of either  $\text{F}_6\text{Tr}[\text{Cl11}]$  or  $\text{Tr}[\text{Cl11}]$  with two equivalents of  $\text{Et}_3\text{SiH}$  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  $\text{F}_6\text{TrH}$  or  $\text{TrH}$ , respectively. The fate of the “ $\text{Et}_3\text{Si}^+$ ” species in arene solvents is not straightforward, as has been studied in detail<sup>45</sup> by Heinekey and coworkers: the presence of varying amounts of  $\text{Et}_4\text{Si}$  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  $\text{Et}_3\text{SiH}$  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  $\text{TrH}$  was observed (Fig. 4). In contrast, the reaction of  $\text{F}_6\text{Tr}[\text{Cl11}]$  with substoichiometric (0.75

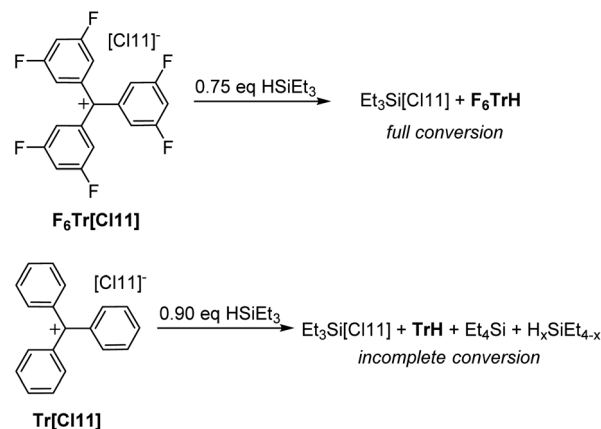


Fig. 4 Reactions of  $\text{Tr}^+$  and  $\text{F}_6\text{Tr}^+$  with a substoichiometric amount of  $\text{HSiEt}_3$ .

equiv.) amount of  $\text{Et}_3\text{SiH}$  led to the production of the expected quantity of  $\text{F}_6\text{TrH}$ , the complete disappearance of the Si–H signals, and without the concomitant observation of  $\text{Et}_4\text{Si}$ .

### H–D exchange

In the reactions of  $\text{F}_6\text{Tr}[\text{Cl11}]$  with  $\text{Et}_3\text{SiH}$ , significant H/D scrambling was observed among the neutral aromatic compounds present in solution:  $\text{C}_6\text{D}_6$ ,  $o\text{-C}_6\text{H}_4\text{Cl}_2$ , and  $\text{F}_6\text{TrH}$  (but the  $\text{C}(\text{sp}^3)\text{-H}$  bond in  $\text{F}_6\text{TrH}$  was never deuterated). The extent of H–D exchange was analyzed *via*  $^1\text{H}$ ,  $^{13}\text{C}$ , or  $^{19}\text{F}$  NMR spectroscopy (see ESI† for details). The mechanism of the H/D exchange likely involves the generation of superacidic protonated arenes *in situ*,<sup>47</sup> which should enable rapid H/D exchange *via*  $\text{H}^+/\text{D}^+$  shuttling (Fig. S4†).<sup>47,48</sup> The product of addition of either  $\text{Et}_3\text{Si}^+$  or  $\text{F}_6\text{Tr}^+$  to a neutral arene can be alternatively viewed as a protonated arene.<sup>47</sup> 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.<sup>49</sup>

### Abstraction of hydride from C–H bonds

Given the computational prediction of the enhanced hydride affinity of  $\text{F}_6\text{Tr}^+$  vs.  $\text{Tr}^+$ , 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  $\text{F}_6\text{TrH}$  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<sup>20,21</sup> 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  $\text{F}_6\text{TrH}$  after 96 h. The aliphatic region of the  $^1\text{H}$  NMR spectrum presented a large

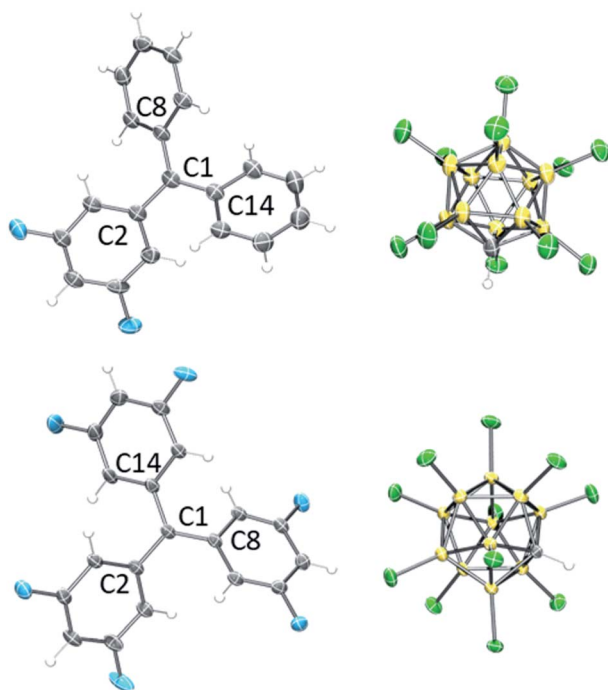


Fig. 3 POV-Ray rendition of the ORTEP (50% probability ellipsoids) drawing of  $\text{F}_2\text{Tr}[\text{Cl11}]$  (top) and  $\text{F}_6\text{Tr}[\text{Cl11}]$  (bottom). Only one cation and one anion from each asymmetric unit is shown. Solvent and disorder are omitted for clarity.



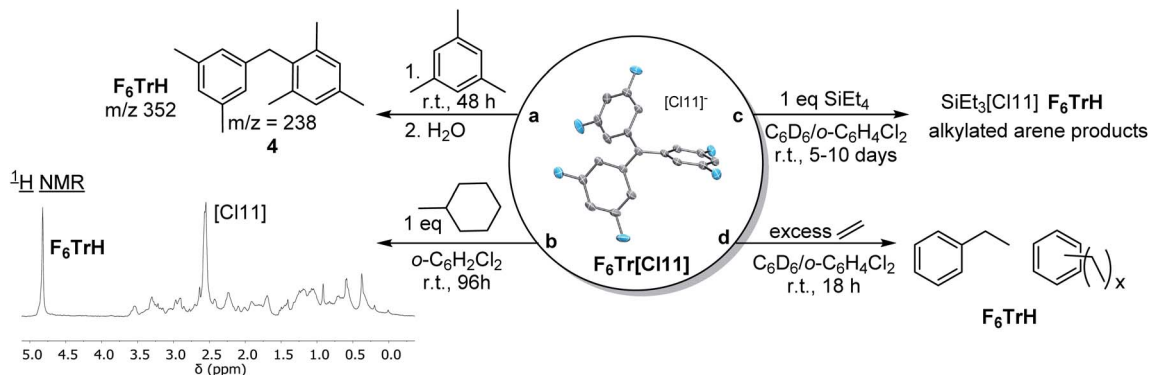


Fig. 5 Reactions of  $F_6Tr[Cl11]$  resulting in the abstraction of a hydride from  $C(sp^3)-H$  bonds.

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

The methylcyclohexyl cation presumed to be formed initially may undergo isomerization<sup>50</sup> 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  $Me[HCB_{11}Me_5Br_6]^+$ .<sup>51,52</sup> 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  $\beta$ -position in trialkylaluminums with  $Tr^+$  has been used to generate reactive alumenium ( $R_2Al^+$ ) cations.<sup>6,22,53</sup> The analogous abstraction of  $\beta$ -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<sub>3</sub>Si", 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.<sup>54</sup> 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 Kolevtevil 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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