Synthetic Methods

Deutsche Ausgabe: DOI: 10.1002/ange.201510494
Internationale Ausgabe: DOI: 10.1002/anie.201510494

Use of Trifluoromethyl Groups for Catalytic Benzylation and Alkylation with Subsequent Hydrodefluorination

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Abstract: *The electrophilic organofluorophosphonium catalyst $[(C_6F_5)_3PF][B(C_6F_5)_4]$ is shown to effect benzylation or alkylation by aryl and alkyl CF_3 groups with subsequent hydrodefluorination, thus resulting in a net transformation of CF_3 into CH_2–aryl fragments. In the case of alkyl CF_3 groups, Friedel–Crafts alkylation by the difluorocarbocation proceeded without cation rearrangement, in contrast to the corresponding reactions of alkyl monofluorides.*

C–F bonds are thermodynamically strong and generally kinetically inert. These attributes together with increased hydrophobicity and metabolic stability are important features that have led to the incorporation of fluorine into over 200 pharmaceuticals currently in use.[1] This resistance to reactivity has also been exploited for materials development. Perhaps the best known example is the perfluorinated polymer Teflon,[2] which is used as a chemically resistant coating or as a container for corrosive materials. On the other hand, the lack of reactivity means that organofluorocarbons are environmentally persistent and pervasive.[3] For example, the highly toxic perfluorooctanoic acid derivatives used in surfactants and the production of fluorinated polymers have been found even in arctic snow.[4] Furthermore, the adverse effects of chlorofluorocarbons (CFCs) and other low-molecular-weight fluorinated alkanes, which act as potent greenhouse gases, are well-established.[5]

Strategies for the installation of C–F bonds or fluorinated organic fragments have drawn considerable attention in recent years, largely because of the potential for pharmaceutical applications.[6] On the other hand, strategies designed to cleave C–F bonds for the degradation of environmental toxins have seen more limited development.[7] The research groups of Jones,[8] Grushin,[9] Oestreich,[10] and others[1,11] have developed transition-metal species that activate aryl or monofluoroalkyl C–F bonds stoichiometrically, whereas a recent report described the abstraction of fluoride by $B(C_6F_5)_3$ from a hexafluoropropylene–palladium species to give a cationic perfluoroallylpalladium complex.[12]

An alternative strategy for C–F bond activation involves the use of main-group reagents or catalysts. To this end, Ozerov and co-workers described the hydrodefluorination of C–F bonds in the presence of silanes and silylium cations.[13] The following year, Müller and co-workers reported the use of disilyl cations in related dehydrofluorination reactions of C–F bonds.[14] In 2007, Terao and co-workers described the alkylation of a CF_3 species in a stoichiometric reaction with an aluminum alkyl species.[15] In 2008, Douvris and Ozerov reported the use of a trialkylsilylium cation in the hydrodefluorination of trifluoromethyl and nonafluorobutyl groups by silanes under mild conditions.[16] The Ozerov group subsequently described the use of $AlMe_3$ and an alumenium cation to alkylate C–F bonds.[17] In 2012 and 2013, our research group reported the use of the electrophilic Lewis acid catalysts $B(C_6F_5)_3$ and $[(C_6F_5)_3PF][B(C_6F_5)_4]$ in hydrodefluorination reactions of fluoroalkanes.[18] Whereas the former is a classic Lewis acid based on the vacant p orbital on B, the latter exploits the σ* orbital oriented opposite to the P–F bond. A recent review by Oestreich et al. provides an excellent overview of main-group Lewis acids for C–F bond activation.[19]

Friedel–Crafts products were identified in several of the above studies,[13,16,17,20] although it was Olah and Kuhn in 1964 who first reported the Friedel–Crafts alkylation of alkyl fluorides by the use of BF_3.[21] In 2011, Siegel and co-workers exploited Friedel–Crafts reactions of polyaromatic monofluoroarenes initiated by protons or silylium cations to effect intramolecular cyclization reactions affording polyaromatic species.[22] Kemnitz and co-workers reported C–C bond formation through reactions of fluoromethanes and benzene in the presence of the heterogeneous catalyst aluminum chlorofluoride.[20b] Recently, Paquin and co-workers developed an acid-mediated Friedel–Crafts arylation of benzyl fluorides that was enabled by hydrogen bonding.[23] We previously observed that whereas $[(C_6F_5)_3PF][B(C_6F_5)_4]$ mediated hydrodefluorination in CD_2Cl_2, the use of arene solvents afforded Friedel–Crafts by-products. In this study, we optimized the use of $[(C_6F_5)_3PF][B(C_6F_5)_4]$ as a catalyst for Friedel–Crafts benzylation or alkylation with aryl or alkyl trifluoromethyl derivatives and subsequent hydrodefluorination. In this fashion, CF_3 groups were converted catalytically into a variety of CH_2–aryl fragments.

We explored the notion of the Lewis acid activation of CF_3 fragments by treating p-$BrC_6H_4CF_3$ in C_6D_6 in the presence of Et_3SiH (3.6 equiv) with 10 mol % of the Lewis acids $B(C_6F_5)_3$, $FeCl_3$, $InCl_3$, and $ZnCl_2$. In these cases, no reaction was observed over the course of 16 h at 80 °C. In contrast, the use of $AlCl_3$ (1.5 mol %) as the catalyst under the same conditions afforded the product p-$BrC_6H_4CH_2C_6D_5$ (**1**) in 15 % yield after 16 h at 25 °C. Furthermore, the use of the Lewis acid $[(C_6F_5)_3PF][B(C_6F_5)_4]$ (1.5 mol %) gave the product

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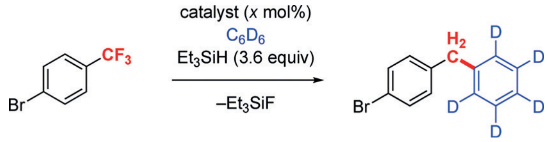
Supporting information and ORCID(s) from the author(s) for this article are available on the WWW under http://dx.doi.org/10.1002/anie.201510494.

Table 1: Benzylation/hydrodefluorination of $BrC_6H_4CF_3$: Catalysis by Lewis acids.

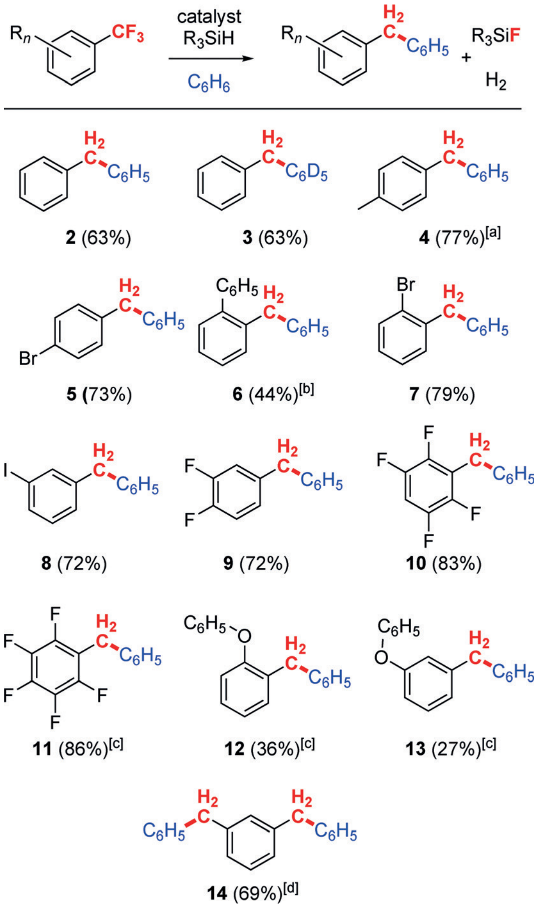


Catalyst	Loading [mol %]	*t* [h]	*T* [°C]	Conversion [%]
$AlCl_3$	10	16	80	60
$[(C_6F_5)_3PF][B(C_6F_5)_4]$	1.5	4	60	99
$AlCl_3$	1.5	16	25	15
$[(C_6F_5)_3PF][B(C_6F_5)_4]$	1.5	16	25	99

p-$BrC_6H_4CH_2C_6D_5$ in quantitative yield in 16 h at 25 °C or in just 4 h at 60 °C (Table 1).

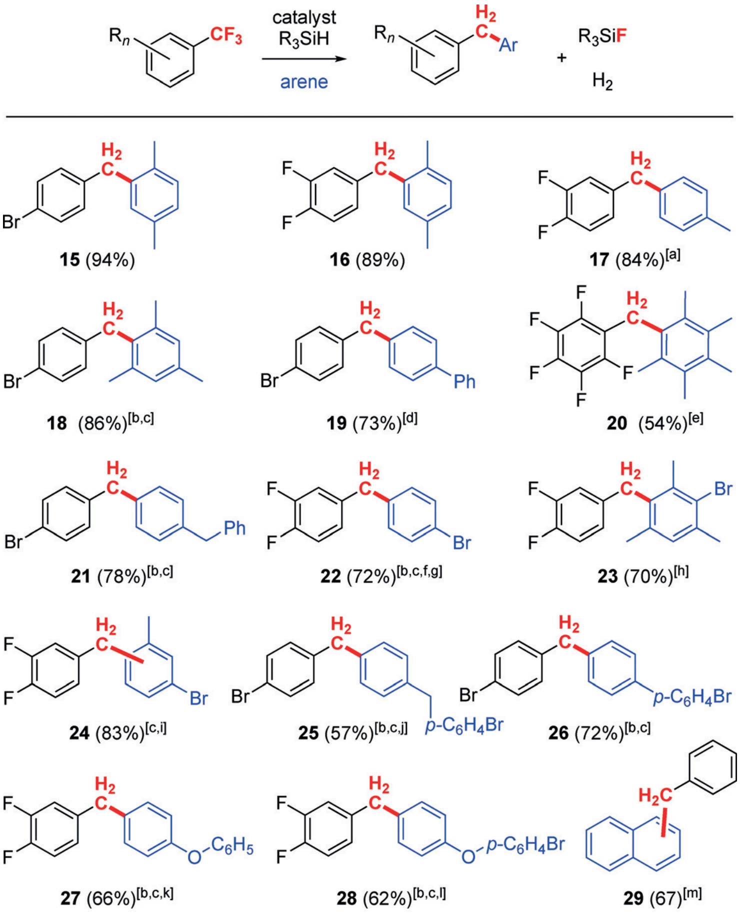
The formation of 4-$BrC_6H_4CH_2C_6D_5$ (**1**) reveals the ability of Lewis acids to mediate the arylation of the CF_3 group with concurrent hydrodefluorination. To probe the generality of this reactivity, we treated a series of substituted trifluorotoluene derivatives in C_6H_6 with Et_3SiH (3.6 equiv) in the presence of $[(C_6F_5)_3PF][B(C_6F_5)_4]$ (1.5 mol %) at temperatures ranging from 25 to 80 °C (Scheme 1). In this fashion, $C_6H_5CF_3$ was converted into Ph_2CH_2 (**2**) or $PhCH_2C_6D_5$ (**3**; when the reaction was carried out in C_6D_6) in 63 % yield in 4 h at 60 °C. This functionalization of the CF_3 fragment tolerated a variety of alkyl and halogen substituents, thus enabling the conversion of the CF_3 groups in 4-$MeC_6H_4CF_3$, 2-$PhC_6H_4CF_3$, 4-$BrC_6H_4CF_3$, 2-$BrC_6H_4CF_3$, 3-$IC_6H_4CF_3$, 3,4-$F_2C_6H_3CF_3$, 2,3,4,5-$F_4C_6HCF_3$, and $C_6F_5CF_3$ into substituted benzyl groups; the products **4**–**11** were isolated in 44–86 % yield. The aryl ether derivatives 2-$(PhO)C_6H_4CF_3$ and 3-$(PhO)C_6H_4CF_3$ reacted similarly, although the products 2-$(PhO)C_6H_4CH_2Ph$ (**12**) and 3-$(PhO)C_6H_4CH_2Ph$ (**13**) were isolated in pure form in modest yields of 36 and 27 %, respectively. Interestingly, the reaction of 1,3-$(CF_3)_2C_6H_4$ with 7.2 equivalents of Et_3SiH in the presence of the phosphonium catalyst at 60 °C for 16 h afforded the doubly functionalized species 1,3-$(PhCH_2)_2C_6H_4$ **14** in 69 % yield.

The above reactions of CF_3 derivatives are not limited to benzene. A variety of arenes, including *p*-xylene, toluene, mesitylene, 1,1′-biphenyl, diphenylmethane, bromobenzene, bromomesitylene, 3-methylbromobenzene, (4-bromophenyl)-phenylmethane, 4-bromophenylbenzene, phenoxybenzene, 4-bromophenoxybenzene, and naphthalene, reacted with trifluoromethyl aryl species to give diarenes linked by a common benzylic methylene group in moderate to high yields (products **15**–**29**; Scheme 2). These reactions could also be performed in CH_2Cl_2 or C_6H_5Br with 5.0 equivalents of the arene. The reaction of perfluorotoluene with 1,2,3,4,5-pentamethylbenzene is an remarkable example, as it provided a diphenylmethane derivative **20** that incorporates both electron-rich and electron-poor phenyl rings. In general, these reactions were selective and tended to give the product of *para* substitution with monosubstituted arenes. In the reactions to form **17**, **22**, **25**, **27**, and **28**, a varying but smaller amount of the *ortho* isomer was also observed. Products **24** and **29** were formed as a 1:1 mixture of the *ortho* and *para* and 1- and 2-substituted isomers, respectively. Although in some cases the arene was used as the solvent, it is also possible to use C_6H_5Br as the solvent, as the reaction proceeds more quickly with a stoichiometric excess of a more electron rich arene than with C_6H_5Br. Nonetheless, the benzylation of C_6H_5Br is possible, although an increased catalyst loading (5 mol %) is required (product **22**). Such reactions can also proceed well on a preparative scale: 0.5 mol % of the catalyst was used to prepare 0.952 g of **18** (97 % yield) in 4 h at 25 °C.



Scheme 1. Benzylation/hydrodefluorination with trifluorotoluene derivatives and benzene. Reported yields are for the isolated product. Reaction conditions, unless otherwise stated: $[(C_6F_5)_3PF][B(C_6F_5)_4]$ (1.5 mol %), Et_3SiH (3.6 equiv), 60 °C, 4 h. [a] The reaction was carried out at 25 °C. [b] with iPr_3SiH (3.6 equiv) at 80 °C for 16 h. [c] 25 °C for 16 h. [d] The reaction was carried out with 7.2 equivalents of Et_3SiH for 16 h.

Despite the well-established stability of aliphatic CF_3 groups, the discovery of the above reactions of aryl CF_3 species suggested the possibility of analogous reactivity of alkyl CF_3 substrates. Indeed, when 1,1,1-trifluorohexane, (2,2,2-trifluoroethyl)benzene, and (trifluoromethyl)cyclohexane were treated with benzene and Et_3SiH in the presence of the catalyst under conditions similar to those employed for the corresponding reactions of trifluoromethyl aryl substrates, the alkyl–aryl coupling products **30**–**32** were obtained in high yields (Scheme 3). It is most notable that this protocol gave exclusively linear alkyl substituents. Moreover, these reactions were tolerant of both iodide and bromide substituents



Scheme 2. Benzylation/hydrodefluorination with trifluoroaryl species. Reported yields are for the isolated product. Reaction conditions, unless otherwise stated: $[(C_6F_5)_3PF][B(C_6F_5)_4]$ (1.5 mol%), Et_3SiH (3.6 equiv), 60 °C, 4 h. [a] Reaction time: 6 h; product ratio (*p*/*o*): 2:1. [b] Reaction time: 2 h. [c] The reaction was carried out at 80 °C. [d] The reaction was carried out at 25 °C for 16 h. [e] Reaction time: 10 h [f] Product ratio (*p*/*o*): 3:1. [g] The reaction was carried out with 5 mol% of the catalyst. [h] The reaction was carried out at 25 °C for 60 h. [i] Product ratio (*p*/*o*): 1:1. [j] Product ratio (*p*/*o*): 7.2:1. [k] Product ratio (*p*/*o*): 8:1. [l] Product ratio (*p*/*o*): 5:1. [m] Product ratio (1-/2-naphthyl): 1:1.

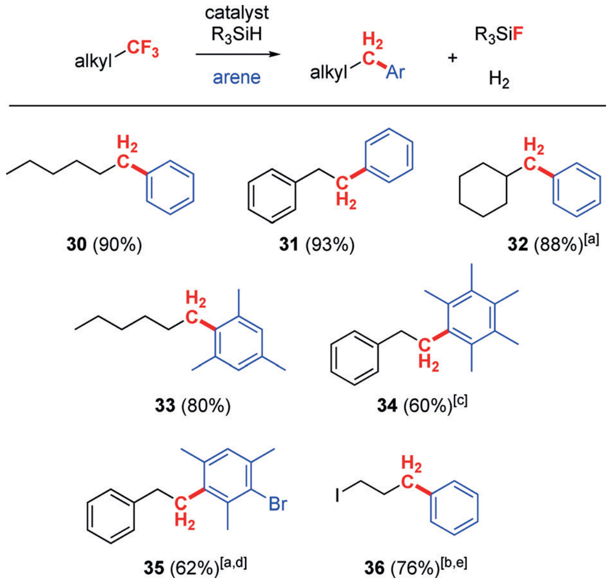
on the trifluoromethyl-substituted alkane. Conventional methods based on intermolecular alkylation for the synthesis of such aryl derivatives are palladium-catalyzed Suzuki coupling reactions of alkyl or aryl bromides or chlorides and borates; however, these reactions are inoperative for fluorides. Thus, the present protocol provides an unprecedented avenue for the conversion of a CF_3 fragment into a functional group suitable for further derivatization by cross-coupling methods.

An interesting alternative for the formation of **31** involves the use of a readily available aryl ketone, 2,2,2-trifluoro-1-phenylethan-1-one. We have previously established the ability of the catalyst $[(C_6F_5)_3PF][B(C_6F_5)_4]$ to effect the deoxygenation of alkyl aryl ketones in the presence of a silane. Thus, the treatment of 2,2,2-trifluoro-1-phenylethan-1-one under catalytic conditions with an excess of triethylsilane effected concurrent deoxygenation/benzylation/hydrodefluorination to afford compound **31**, which was isolated in 74% yield (Scheme 4).

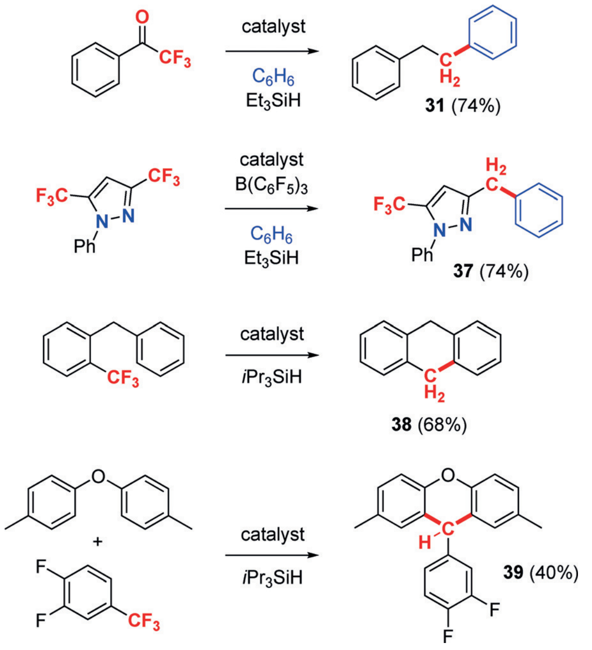
Attempts to employ the above protocol for the derivatization of 2-(trifluoromethyl)quinoline or 2-bromo-5-(trifluoromethyl)pyridine were unsuccessful. Similar treatment of 1-*N*-phenyl-3,5-bis(trifluoromethyl)-1*H*-pyrazole, an analogue of the commercial drug celecoxib, led to no reaction. This result was attributed to coordination of the pyrazole derivative to the phosphonium Lewis acid catalyst. However, the addition of 1 equivalent of $B(C_6F_5)_3$ to the reaction mixture of the pyrazole, the silane, and the phosphonium catalyst and heating at 80 °C for 48 h resulted in the clean formation of the benzylated product **37**, which was obtained in 74% yield after purification by chromatography. This result suggests that coordination of the pyrazole to the more accessible borane allows C–F activation and electrophilic substitution to take place.

These C–F activation reactions can also be applied to effect ring closure. For example, the treatment of 2-benzyl-1-(trifluoromethyl)benzene with iPr_3SiH and the catalyst for 48 h at 60 °C resulted in the formation of 9,10-dihydroanthracene (**38**). Notably, for a related intramolecular benzylation reported by Fuchibe and Akiyama, stoichiometric $NbCl_5$ and excess $LiAlH_4$ were used to produce fluorenes.[24] In a similar fashion, and perhaps more interestingly, 1,2-difluoro-4-(trifluoromethyl)benzene reacted with di-*p*-tolyl ether to give the intermolecular tricyclic ring-closure product **39** in 40% yield after 2 h at 80 °C.

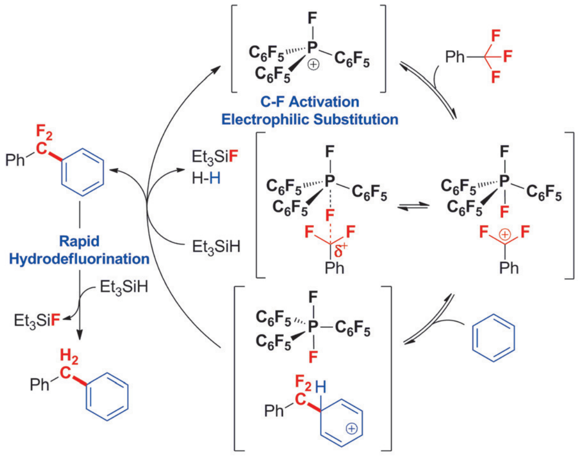
The mechanism of these reactions begins with the activation of the trifluoromethyl group by the fluorophosphonium cation. We have previously described an independent reaction of fluoroalkanes with fluorophosphonium cations that yielded the corresponding difluorophosphorane.[20a] Thus, in the present case, we propose that a difluorocarbocation is generated and then undergoes electrophilic aromatic substitution (Scheme 5). Although the degree to which the free carbocation is generated is unknown, this mechanism is closely related to that proposed by Kemnitz and co-workers for the heterogeneous catalyst aluminum chlorofluoride.[20b] Analogous fluorocarbocations are well-established,[25] and Reutrakul and co-workers proposed the intermediacy of related cations in recent studies of the reaction of $RSCF_2Br$ with silver salts.[26] The liberated proton reacts with the silane to generate H_2, and the resulting silylium cation abstracts fluoride from the difluorophosphorane to regenerate the fluorophosphonium cation catalyst. Hydrodefluorination (HDF) at the secondary carbon center of the transient difluorobenzyl product to afford the observed benzylic products is thought to be rapid. Indeed, the independent reaction of difluorodiphenylmethane with triethylsilane in the presence of a catalytic amount of the fluorophosphonium cation resulted in rapid HDF and the generation of diphenylmethane in just 20 min at 25 °C (Scheme 6). These observations indicate that the difluorocation reacts more rapidly with



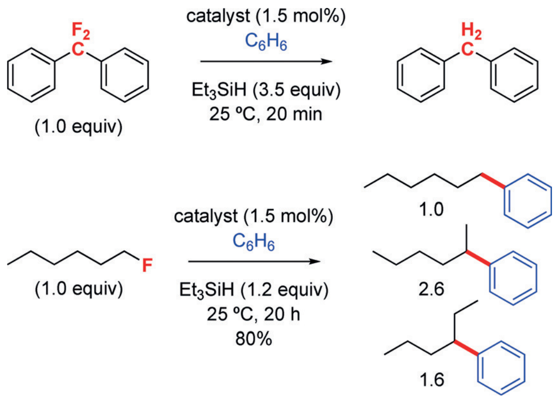
Scheme 3. Alkylation/hydrodefluorination with trifluoroalkyl derivatives. Reaction conditions, unless otherwise stated: $[(C_6F_5)_3PF][B(C_6F_5)_4]$ (1.5 mol%), Et_3SiH (3.6 equiv), 80 °C, 4 h. [a] The reaction was carried out at 25 °C. [b] The reaction was carried out at 60 °C. [c] Reaction time: 10 h. [d] The reaction was carried out in CH_2Cl_2. [e] The reaction was carried out in benzene for 2 h.



Scheme 4. More examples of benzylation/hydrodefluorination catalysis.



Scheme 5. Reactions steps in benzylation/hydrodefluorination catalysis.



Scheme 6. Reactions in support of the proposed mechanism.

the arene, whereas the subsequently produced monofluorocation and carbocation react more rapidly with the silane. The differing reactivities of these cations reflect both their differing steric environment and their differing electrophilicity.

Further support for the proposed mechanism was provided by experiments comparing the reactivity of 1,1,1-trifluorohexane and 1-fluorohexane. As described above, the reaction of 1,1,1-trifluorohexane with triethylsilane in the presence of a catalytic amount of the fluorophosphonium cation afforded exclusively *n*-hexylbenzene. In contrast, the corresponding reaction of 1-fluorohexane afforded a mixture of *n*-hexylbenzene, 2-phenylhexane, and 3-phenylhexane in a 1:2.6:1.6 ratio (Scheme 3). These observations are consistent with the generation of carbocations that effect electrophilic aromatic substitution and indicate that the difluorohexyl cation is conformationally more robust, whereas the transient hexyl carbocation undergoes rearrangements, thus accounting for the mixture of products. This finding further illustrates the important advantage of this protocol, which provides exclusively linear products of arene alkylation.

In summary, we have described a Lewis acid catalyzed derivatization of aryl and alkyl CF_3 groups with a range of arenes to give CH_2–aryl fragments. This metal-free procedure involves sequential benzylation or alkylation and hydrodefluorination reactions. It is based on that previously used for hydrodefluorination,[20a] with the simple inclusion of an arene nucleophile in the reaction medium. In the case of alkyl CF_3 derivatives, only linear products of arene alkylation were observed. The further application of this methodology in the derivatization of CF_3 groups in organic and inorganic systems is the subject of ongoing studies.

Acknowledgements

D.W.S. gratefully acknowledges the financial support of the NSERC of Canada through the award of a Canada Research Chair. C.B.C. is grateful for the support of an NSERC-CGS-D Scholarship.

Keywords: alkylation · benzylation · electrophilic phosphonium cations · hydrodefluorination · trifluoromethyl groups

How to cite: *Angew. Chem. Int. Ed.* **2016**, *55*, 1417–1421
Angew. Chem. **2016**, *128*, 1439–1443

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Received: November 11, 2015