CHEMISTRY
A European Journal

A Journal of
ChemPubSoc Europe

Accepted Article

Title: C-F Bond Activation by Silylium Cation/Phosphine Frustrated Lewis Pairs: Mono-Hydrodefluorination of PhCF3, PhCF2H and Ph2CF2

Authors: Ian Mallov, Adam Ruddy, Hui Zhu, Stefan Grimme, and Douglas Wade Stephan

To be cited as: *Chem. Eur. J.* 10.1002/chem.201705276

Link to VoR: http://dx.doi.org/10.1002/chem.201705276

Supported by
ACES

WILEY-VCH

10.1002/chem.201705276

WILEY-VCH

COMMUNICATION

C-F Bond Activation by Silylium Cation/Phosphine Frustrated Lewis Pairs: Mono-Hydrodefluorination of $PhCF_3$, $PhCF_2H$ and Ph_2CF_2

Ian Mallov, Adam J. Ruddy, Hui Zhu, Stefan Grimme* and Douglas W. Stephan*

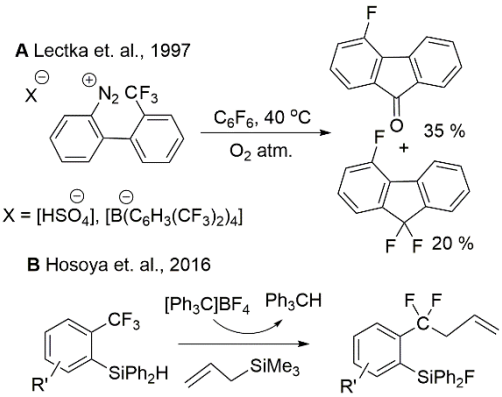
Dedicated to the memory of Professor Samuel Mallov, State University of New York

Abstract: *Single defluorination of aryl trifluoromethyl functionalities is achieved by both intra- and intermolecular silylium cation/phosphine Lewis pairs. Phosphine-captured aryl fluoromethyl cations are then treated with Brønsted base to complete mono-hydrodefluorinations of $PhCF_3$, Ph_2CF_2, and $PhCF_2$.*

The electronegative element fluorine is currently included in over 200 commercial pharmaceuticals including such block-buster drugs as Crestor, Prozac and Celebrex. Fluorinated fragments are bioisosteric units that are chemically resistant to metabolic oxidation. While a growing range of protocols for fluorination or trifluoromethylation have been established, the inclusion of CF_2 units is much less common.[1] Nonetheless, CF_2H units have recently been shown to be unique, biologically-relevant hydrogen bond donors.[2]

One conceivable strategy to CF_2H fragments is the derivatization of CF_3 units. However, the relatively strong nature of C-F bonds (ca. D_e = 120-130 kcal/mol),[3] makes this approach challenging and accounts for the long environmental lifetimes of molecules containing CF_3 fragments.[4] In 1964 Olah *et al*. reported the first Friedel−Crafts alkylation of alkyl monofluorides using BF_3.[5] Subsequently, C-F bond activations using transition metal species have been studied by the groups of Jones,[6] Grushin,[7] Oestreich[8] and others;[9] these systems effect stoichiometric activations of aryl or monofluoroalkyl C–F bonds.

Avenues to chemistry of CF_3 units have also utilized strong main group Lewis acids.[4a] The alkylation of CF_3 species has also been carried out via stoichiometric reactions of aluminum alkyl species.[10] Kemnitz and coworkers described alkylation of benzene with fluoromethanes using the heterogeneous catalyst, aluminum-chlorofluoride.[11] While Ozerov described the hydrodefluorination of C-F bonds catalyzed by silylium cations in the presence of silane,[12] Reed and coworkers used silylium cations with a carborane-based anion to isolate fluorinated carbon-cations.[13] Müller and coworkers subsequently described the use of disilyl-cations in hydrodefluorination reactions,[14] while we described hydrodefluorinations of fluoroalkanes catalyzed by $B(C_6F_5)_3$[15] or electrophilic phosphonium cation salts such as $[(C_6F_5)_3PF][B(C_6F_5)_4]$.[15-16] These latter catalysts have also been used in Friedel-Crafts couplings, of alkyl or aryl-CF_3 species or benzyl fluorides.[17] In a related vein, Paquin *et. al.* have described acid mediated Friedel-Crafts arylation of benzyl fluorides.[18]



Scheme 1: Previous aryl-CF_3 to aryl-CF_2 conversions reported by Lectka (A) and Hosoya (B).

Reactions achieving mono-defluorinations of CF_3 fragments are rare. Electrochemical methods,[19] or use of excess Mg[20] or SmI,[21] have been used to form CF_2-C derivatives. In 1997, Lectka described a cyclic CF_2 linked diarene via the intramolecular reaction of aryl-CF_3 and diazonium fragments.(Scheme 1A).[22] In 2016, Hosoya and co-workers described reactions in which silylium cations *ortho* to CF_3 groups effected single fluoride abstraction permitting reaction with vinyl silanes to generate new CF_2-vinyl moieties with adjacent SiF units (Scheme 1B).[23] Most recently, Ishikawa used CF_3-derived alkenes to effect difluoroallylation of arenes.[24] In this communication, we describe our efforts to develop an FLP strategy to effect selective stoichiometric mono-hydrodefluorination of di- and trifluoromethyl functionalities without the requirement of C-F activation by an *ortho*-silylium cation. Wedemonstrate the first conversions of CF_3 to CF_2H and CF_2H to CH_2F.

[*] I. Mallov, Dr. A. J. Ruddy Prof. Dr. D. W. Stephan
Department of Chemistry, University of Toronto
80 St. George St, Toronto Ontario M5S 3H6 (Canada)
E-mail: dstephan@chem.utoronto.ca

Dr. Hui Zhu, Prof. Dr. S. Grimme, Mulliken Center for Theoretical Chemistry, Institut für Physikalische und Theoretische Chemie
Universität Bonn, Beringstr. 4, 53115 Bonn (Germany).
Email: grimme@thch.uni-bonn.de

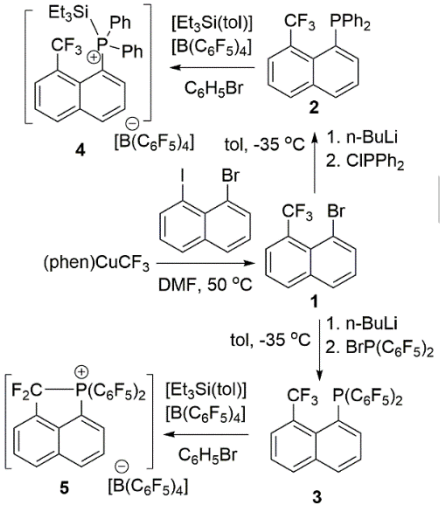
[**] The authors gratefully acknowledge the financial support of the NSERC of Canada and the Deutsche Forschungsgemeinschaft in the framework of the Leibniz prize. DWS is also grateful for the award of a Canada Research Chair and an Einstein Fellowship at TU Berlin. Dr. Timothy Johnstone is thanked for helpful discussion.

Supporting information for this article is given via a link at the end of the document.

10.1002/chem.201705276

In an initial effort, we targeted the activation of a CF_3 fragment adjacent a phosphine donor. Using our previously-reported synthesis of 1-(bispentafluorophenylphosphino)-8-trifluoromethylnaphthalene, $C_{10}H_6(1\text{-}P(C_6F_5)_2)(8\text{-}CF_3)$ **3** [25] based on protocols developed by Hartwig,[26] we also prepared 1-(diphenylphosphino)-8-trifluoromethylnaphthalene, $C_{10}H_6(1\text{-}PPh_2)(8\text{-}CF_3)$ **2** in 60% yield. Treatment of **2** with $[Et_3Si(tol)][B(C_6F_5)_4]$ did not lead to C-F activation. Rather than the combined action of the Lewis acid and Lewis base on the CF_3 fragment, a classical Lewis acid-base adduct was derived via coordination of the phosphine to the $[Et_3Si]$ cation affording $[C_{10}H_6(1\text{-}PPh_2SiEt_3)(8\text{-}CF_3)]$ $[B(C_6F_5)_4]$ **4** in 88% yield. This was evidenced by a shift in the ^{31}P NMR resonance from –2.5 ppm to 5.0 ppm.[27] Diminished through-space coupling between the ^{19}F nuclei of the CF_3 group and the ^{31}P nucleus from 110 Hz in the free phosphine to 29 Hz is consistent with formation of the adduct **4**.[28] P-Si satellites were not observed for **4**. A previous report reveals P-Si couplings in phosphine-silylium adduct to be of similar magnitude to the observed P-F coupling.[29] Indeed, this P-Si bond remained intact even upon heating to 100 °C and no evidence of C-F bond activation was observed (Scheme 2).

In a subsequent effort, the corresponding reaction of **3,** which incorporates a phosphine donor of reduced basicity, was undertaken, anticipating that this would deter classical adduct formation. Treatment of **3** with 0.9 equivalents of $[Et_3Si(tol)][B(C_6F_5)_4]$ gave rise to a new species **5** in 91 % yield. This species exhibits a triplet in the $^{31}P\{^1H\}$ NMR spectrum at 11.5 ppm with a typical $^2J_{P\text{-}F}$ coupling constant of 108 Hz. The corresponding ^{19}F resonance was the expected doublet of quintets at -84.7 ppm, with $^5J_{F\text{-}F}$ coupling to the four *ortho*-fluorine atoms of 7 Hz. These data support the formulation of **5** as $[C_{10}H_6(1\text{-}P(C_6F_5)_2)(8\text{-}CF_2)][B(C_6F_5)_4]$ (Scheme 2) in which the phosphorus atom is bonded to a CF_2 fragment generated by fluoride ion abstraction by silylium cation. Monitoring the reaction mixture by ^{19}F NMR spectroscopy confirmed the formation of the corresponding triethylsilylfluoride. This formulation of **5** was further confirmed crystallographically (Figure 1).



Scheme 2: Synthesis of **2**-**5**.

The solid-state structure of **5** shows an unusually long P-C_{CF2} bond of 1.915(2) Å to the difluoro-substituted carbon atom, which is significantly longer than the P-C bonds to the fluoroarene rings (1.788(2) and 1.797(2) Å). The corresponding C-F bonds are on the short end of the spectrum for aliphatic C-F bonds (av. 1.358 (3) Å). These parameters are consistent with the poor donor ability of the phosphorus centre, and reflect the considerably electrophilic nature of the carbon centre The formation of **5** arises by trapping of the difluoro-carbocation generated by fluoride abstraction from CF_3. This can be viewed as the action of the Si^+/P FLP on the CF_3 fragment. A critical feature in this reactivity is the electron-poor nature of the phosphine which affords the FLP in the presence of the highly electrophilic and fluorophilic silylium cation. As such **5** is, to the best of our knowledge, the first case in which a phosphine donor intercepts a difluoro-carbocation affording a CF_2-P linkage.

Figure 1: POV-ray depiction of the cation of **5**. C: black, P: orange, F: pink. H-atoms have been omitted for clarity.

Extensive DFT calculations at the PW6B95-D3/def2-QZVP + COSMO-RS(C_6H_5Br) // TPSS-D3/def2-TZVP + DCOSMO-RS($CHCl_3$) level were performed to probe the mechanism of this C-F activation of **3** by cation $[Et_3Si(tol)]^+$.[30] Geometry optimization calculations were carried out at the TPSS-D3/def2-TZVP + DCOSMO-RS($CHCl_3$) level of theory, which included the solvation effects using $CHCl_3$ (ε = 4.81) whose dielectric constant is similar to the experimental solvent C_6H_5Br (ε = 5.17). Frequency analysis was used to confirm the nature of stationary points and to calculate thermal free energy corrections G_c at 298 K and 1 atm. Single-point energies were computed at the PW6B95-D3/def2-QZVP level of theory and using better solvation free energies (G_{sol}) based on the COSMO-RS (C_6H_5Br) calculations The final free energies at the highest PW6B95-D3 level including both thermal and solvation free energy corrections are used in our discussion. Two energetically similar free energy pathways for the formation of **5** were computed, with the $[Et_3Si(tol)]^+$ cation complexes interacting with either the *ortho*- or *para*-carbon atom (see SI). Interactions of the silylium ion Et_3Si^+ with the *ortho*- *or para*-fluorine atoms of the borate anion were also considered but shown to be less stable than the silylium-toluene adducts, consistent with the reported solid-state structure showing Et_3Si^+ as the toluene adduct.[31] In all cases, Si-F bond formations followed by ring-closure via P-C bond formation afforded the products in overall exergonic reactions. The reaction between $[Et_3Si(tol)]^+$ and **3** is 46.2 kcal/mol exergonic with a free energy barrier of 19.7 kcal/mol to form product **5** together with Et_3SiF.(See SI).

In furthering this FLP approach to C-F activation, the conversion of $C_6H_5CF_3$ to $C_6H_5CF_2H$ was targeted. To this end, the intramolecular FLP containing a phosphorus donor and a silylium cation was prepared from the known species $C_6H_4(1\text{-}PPh_2)(2\text{-}SiHPh_2)$[32] via reaction with $[Ph_3C][B(C_6F_5)_4]$. The salt $[C_6H_4(1\text{-}PPh_2)(2\text{-}SiPh_2)][B(C_6F_5)_4]$ **6** was isolated in 77% yield. This species gave a resonance in the ^{31}P NMR spectrum at +11.6 ppm, consistent with an intramolecular interaction between P and

10.1002/chem.201705276

COMMUNICATION

Si. Although minor impurities were persistent in syntheses of **6**, a ^{29}Si-^{1}H HMBC spectrum revealed a ^{29}Si NMR chemical shift at +12.8 ppm. Despite an apparent dative interaction between P and Si, ring strain of the four-membered ring is thought to provide access to the open form of the FLP for reactivity. This situation is directly analogous to the now classic Erker FLP system, $Mes_2PCH_2CH_2B(C_6F_5)_2$ where the open-FLP is accessed as a result of similar ring strain. Probing this aspect via reaction, freshly prepared and isolated **6** was combined with a solution of $C_6H_5CF_3$ in fluorobenzene. Stirring for 24 h at room temperature, followed by NMR analysis of the reaction mixture indicated the formation of a new product **7** in 52% yield. This species exhibited the diagnostic triplet in the ^{31}P{^{1}H} NMR spectrum at 23.8 ppm with a $^{2}J_{P\text{-}F}$ coupling constant of 104 Hz. The corresponding doublet was seen at –94.7 ppm in the ^{19}F NMR spectrum. This species was isolated by column chromatography. These data indicate the FLP activation of the CF_3 fragment affording difluoro-benzyl substituted phosphonium salt $[C_6H_4(1\text{-}P(CF_2Ph)Ph_2)(2\text{-}SiFPh_2)][B(C_6F_5)_4]$ **7**. It is thought that the proximity of the Lewis acid and base centre in **6** is key to trapping the CF_2Ph fragment as efforts to effect analogous chemistry with intermolecular FLPs were unsuccessful (eg $[Et_3Si(tol)]^+$ and $P(C_6F_5)_2Ph$). It is also noteworthy that this reaction was most favourable in fluorobenzene as the generation of difluorocarbocations in more electron-rich aromatic solvents has been shown to afford Friedel-Crafts chemistry.

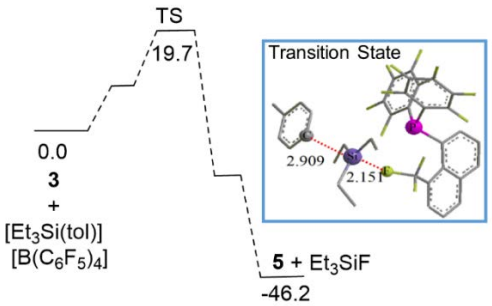


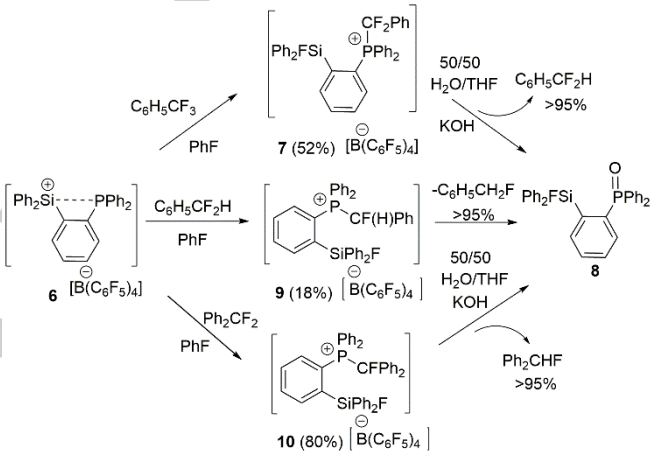
Figure 2: The computed reaction free energy profile (in kcal/mol) for the formation of **5**. (see SI for more details).

Similar DFT calculations reveal the Lewis acidic Si-centre of cation **6**$^{+}$ abstracts fluoride from $C_6H_5CF_3$ directly affording the Si-P bond of **6**$^{+}$ opposite to the breaking C-F bond of $C_6H_5CF_3$. This step is 7.1 kcal/mol endergonic over a moderate barrier of 21.7 kcal/mol. In the computations, the transient solvated $C_6H_5CF_2^+$ cation combines rapidly with the neutral acyclic $C_6H_4(1\text{-}PPh_2)(2\text{-}SiFPh_2)$ to form the product cation $[C_6H_4(1\text{-}P(CF_2Ph)Ph_2)(2\text{-}SiFPh_2)]^+$ of **7** giving an overall reaction that is exergonic by –17.2 kcal/mol.

Treatment of phosphonium cations with Brønsted bases is a well-established route[33] to effect P-C bond cleavage, with liberation of the most apicophilic substituent.[34] Treatment of **7** with a 0.40 M solution of KOH in 50:50 water:THF affords the liberation of $C_6H_5CF_2H$ (Scheme 3) in >95% yield, demonstrating selective cleavage of the difluorinated substituent, with concurrent formation of the phosphine oxide **8** while $C_6H_5CF_2H$ could be separated by column chromatography for spectral confirmation.

The analogous reaction of $PhCF_2H$ with **6** was performed in in fluorobenzene and allowed to react for 24 h. While the reaction was far from complete, a doublet at +21.1 ppm in the ^{31}P NMR spectrum with a coupling constant of 81 Hz and a doublet of doublets was observed at -184.9 ppm in the ^{19}F NMR spectrum with a $^{2}J_{PF}$ and $^{2}J_{FH}$ coupling of 81 Hz and 57 Hz, respectively were consistent with the formation of $[C_6H_4(1\text{-}P(CFHPh)Ph_2)(2\text{-}SiFPh_2)]^+[B(C_6F_5)_4]^-$ **9** (Scheme 3). This was generated in only 18% yield; nonetheless, subsequent treatment of **9** with a 0.40 M solution of KOH in 50:50 H_2O/THF mixture gave **8** in >95% conversion from **9** and permitted the isolation of $PhCH_2F$ by column chromatography.

Similarly, ^{31}P and ^{19}F NMR spectroscopy confirmed that treatment of Ph_2CF_2 with one equivalent of **6** led to the formation of the product $[C_6H_4(1\text{-}P(CFPh_2)Ph_2)(2\text{-}SiFPh_2)][B(C_6F_5)_4]$ **10** in 80% yield (Scheme 3). In this case, the additional phenyl substituent is postulated to lower the energy of the transition state as well as stabilize the transient carbenium cation. Again, treatment under the conditions described above resulted in the isolation of mono-hydrodefluorinated product Ph_2CHF in >95% yield.



Scheme 3: Reactions of **6** with $C_6H_5CF_3$, $C_6H_5CF_2H$ and Ph_2CF_2, conversions as determined by NMR are provided.

It is important to note that previous reports using Lewis acids to mediate hydrodefluorination converted CF_3 to CH_3 fragments regardless of the stoichiometry. In the present report, the use of an Si+/P FLP reagent is shown to facilitate a two-step process involving initial activation of a C-F bond and subsequent hydrolysis of the generated P-C bond to give the conversion of $PhCF_3$ to $PhCF_2H$, $PhCF_2H$ to $PhCFH_2$ and Ph_2CF_2 to Ph_2CHF. The yields of the initial C-F activations are not optimal, and particularly the poorer yield of **9** relative to those of **7** and **10** suggests the FLP is more effective when capturing more stable carbocations. Nonetheless, these findings demonstrate the viability of this strategy CF_3 derivatization.

In summary, the chemistry described herein exploits a FLP derived from silylium cations and phosphine donors to activate C-F bonds and capture the resulting carbocations. Subsequent hydrolysis of the P-C bonds affording the first stoichiometric protocol for mono-hydrodefluorinations. While this work demonstrates that a FLP strategy is conceptually viable, we are continuing to explore applications of other FLPs in CF_3 chemistry, specifically targeting more controlled stoichiometric and selective reagents for derivatization or functionalization of CF_3 moieties.

Keywords: silylium cations • FLP • CF bond activation • hydrodefluorination •

References

[1] L. Xu, D. A. Vicic, *J. Am. Chem. Soc.* **2016**, *138*, 2536-2539.
[2] C. D. Sessler, M. Rahm, S. Becker, J. M. Goldberg, F. Wang, S. J. Lippard, *J. Am. Chem. Soc.* **2017**, *139*, 9325-9332.
[3] A. Karton, S. Daon, J. M. L. Martin, B. Ruscic, *Chem. Phys. Lett.* **2011**, *510*, 165-178.
[4] (a) T. Stahl, H. F. T. Klare, M. Oestreich, *ACS Catal.* **2013**, 1578–1587; (b) Q. Shen, Y.-G. Huang, C. Liu, J.-C. Xiao, Q.-Y. Chen, Y. Guo, *J. Fluorine Chem.* **2015**, *179*, 14-22.
[5] (a) G. A. Olah, S. Kuhn, *J. Org. Chem.* **1964**, *29*, 2317-2320; (b) G. A. Olah, T. Yamato, T. Hashimoto, J. G. Shih, N. Trivedi, B. P. Singh, M. Piteau, J. A. Olah, *J. Am. Chem. Soc.* **1987**, *109*, 3708-3713.
[6] B. M. Kraft, R. J. Lachicotte, W. D. Jones, *J. Am. Chem. Soc.* **2001**, *123*, 10973-10979.
[7] V. V. Grushin, *Acc. Chem. Res.* **2010**, *43*, 160-171.
[8] T. Stahl, H. F. T. Klare, M. Oestreich, *J. Am. Chem. Soc.* **2013**, *135*, 1248-1251.
[9] (a) U. Rosenthal, V. V. Burlakov, P. Arndt, A. Spannenberg, U. Jaeger-Fiedler, M. Klahn, M. Hapke, in *Act. Unreact. Substrates*, **2009**, pp. 165-182; (b) Z. Jin, G. B. Hammond, B. Xu, *Aldrichimica Acta* **2012**, *45*, 67-83; (c) J. Wang, M. Sanchez-Rosello, J. L. Acena, C. del Pozo, A. E. Sorochinsky, S. Fustero, V. A. Soloshonok, H. Liu, *Chem. Rev.* **2014**, *114*, 2432-2506; (d) X. Lin, Z. Weng, *Dalton Trans.* **2015**, *44*, 2021-2037; (e) A. M. Traff, M. Janjetovic, G. Hilmersson, *Chem. Commun.* **2015**, *51*, 13260-13263; (f) A. Kethe, A. F. Tracy, D. A. Klumpp, *Org. Biomol. Chem.* **2011**, *9*, 4545-4549; (g) F. Wang, J. Hu, *Chin. J. Chem.* **2009**, *27*, 93-98; (h) M. F. Kuehnel, D. Lentz, T. Braun, *Angew. Chem. Int . Ed.* **2013**, *52*, 3328-3348; (i) S. Sabater, J. A. Mata, E. Peris, *Nature Comm.* **2013**, *4*, 2553-2560.
[10] (a) J. Terao, M. Nakamura, N. Kambe, *Chem. Commun.* **2009**, 6011-6013; (b) J. Terao, S. A. Begum, Y. Shinohara, M. Tomita, Y. Naitoh, N. Kambe, *Chem. Commun.* **2007**, 855-857; (c) W. Gu, M. R. Haneline, C. Douvris, O. V. Ozerov, *J. Am. Chem. Soc.* **2009**, *131*, 11203-11212.
[11] M. Ahrens, G. Scholz, T. Braun, E. Kemnitz, *Angew. Chem. Int . Ed.* **2013**, *52*, 5328-5332.
[12] (a) V. J. Scott, R. Celenligil-Cetin, O. V. Ozerov, *J. Am. Chem. Soc.* **2005**, *127*, 2852-2853; (b) C. Douvris, O. V. Ozerov, *Science* **2008**, *321*, 1188-1190; (c) C. Douvris, C. M. Nagaraja, C.-H. Chen, B. M. Foxman, O. V. Ozerov, *J. Am. Chem. Soc.* **2010**, *132*, 4946-4953.
[13] C. Douvris, E. S. Stoyanov, F. S. Tham, C. A. Reed, *Chem. Commun.* **2007**, 1145-1147.
[14] R. Panisch, M. Bolte, T. Müller, *J. Am. Chem. Soc.* **2006**, *128*, 9676-9682.
[15] C. B. Caputo, D. W. Stephan, *Organometallics* **2012**, *31*, 27-30.
[16] (a) L. J. Hounjet, C. B. Caputo, D. W. Stephan, *Dalton Trans.* **2013**, *42*, 2629-2635; (b) C. B. Caputo, L. J. Hounjet, R. Dobrovetsky, D. W. Stephan, *Science* **2013**, *341*, 1374-1377.
[17] (a) J. T. Zhu, M. Pérez, D. W. Stephan, *Angew. Chem. Int . Ed.* **2016**, *55*, 8448-8451; (b) J. Zhu, M. Pérez, C. B. Caputo, D. W. Stephan, *Angew. Chem. Int . Ed.* **2016**, *55*, 1417-1421.
[18] P. A. Champagne, Y. Benhassine, J. Desroches, J. F. Paquin, *Angew. Chem. Int. Ed.* **2014**, *53*, 13835-13839.
[19] C. Saboureau, M. Troupel, S. Sibille, J. Perichon, *Chem. Commun.* **1989**, 1138-1139.
[20] (a) Y. Nakamura, Y. Ozeki, K. Uneyama, *J. Fluorine Chem.* **2008**, *129*, 274-279; (b) H. Amii, T. Kobayashi, Y. Hatamoto, K. Uneyama, *Chem. Commun.* **1999**, 1323-1324; (c) N. V. Moskalev, S. P. Zhuravkov, V. D. Ogorodnikov, *Russ. Chem. Bull.* **1996**, *45*, 2461-2461.
[21] J. Wettergren, T. Ankner, G. Hilmersson, *Chem. Commun.* **2010**, *46*, 7596-7598.
[22] D. Ferraris, C. Cox, R. Anand, T. Lectka, *J. Am. Chem. Soc.* **1997**, *119*, 4319-4320.
[23] S. Yoshida, K. Shimomori, Y. Kim, T. Hosoya, *Angew. Chem. Int . Ed.* **2016**, *55*, 10406-10409.
[24] K. Fuchibe, H. Hatta, K. Oh, R. Oki, J. Ichikawa, *Angew. Chem. Int. Ed.* **2017**, *56*, 5890-5893.
[25] I. Mallov, T. C. Johnstone, D. C. Burns, D. W. Stephan, *Chem. Commun.* **2017**, *53*, 7529-7532.
[26] (a) H. Morimoto, T. Tsubogo, N. D. Litvinas, J. F. Hartwig, *Angew. Chem. Int . Ed.* **2011**, *50*, 3793-3798; (b) F. Cottet, E. Castagnetti, M. Schlosser, *Synthesis* **2005**, 798-803.
[27] M. H. Holthausen, J. M. Bayne, I. Mallov, R. Dobrovetsky, D. W. Stephan, *J. Am. Chem. Soc.* **2015**, *137*, 7298-7301.
[28] T. Tuttle, J. Grafenstein, D. Cremer, *Phys. Chem. Lett.* **2004**, *394*, 5-13.
[29] T. J. Herrington, B. J. Ward, L. R. Doyle, J. McDermott, A. J. P. White, P. A. Hunt, A. E. Ashley, *Chem. Commun.* **2014**, *50*, 12753-12756.
[30] (a) TURBOMOLE 2015, TURBOMOLE GmbH, ; (b) J. Tao, J. P. Perdew, V. N. Staroverov, G. E. Scuseria, *Phys. Rev. Lett.* **2003**, *91*, 146401; (c) S. Grimme, S. Ehrlich, H. Krieg, *J. Chem. Phys.* **2010**, *132*, 154104-; (d) S. Grimme, S. Ehrlich, L. Goerigk, *J. Comput. Chem.* **2011**, *32*, 1456-1465; (e) F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297-3305; (f) F. Weigend, M. Häser, H. Patzelt, R. Ahlrichs, *Chem. Phys. Lett.* **1998**, *143*, 294; (g) A. Schaefer, C. Huber, R. Ahlrichs, *J. Chem. Phys.* **1994**, *100*, 5829-5835; (h) P. Deglmann, K. May, F. Furche, R. Ahlrichs, *Chem. Phys. Lett.* **2004**, *384*, 103; (i) K. Eichkorn, F. Weigend, O. Treutler, R. Ahlrichs, *Theor. Chem. Acc.* **1997**, *97*, 119; (j) COSMOtherm, Version C3.0, Release 14.01, 2013, COSMOlogic GmbH & Co., Leverkusen, Germany, ; (k) F. Eckert, A. Klamt, *AIChE J.* **2002**, *48*, 369-385; (l) A. J. Klamt, *Phys. Chem.* **1995**, *99*, 2224-2235; (m) Y. Zhao, D. G. Truhlar, *J. Phys. Chem. A* **2005**, *109*, 5656-5667; (n) S. Grimme, *Chem. Eur. J.* **2012**, *18*, 9955; (o) S. Sinnecker, A. Rajendran, A. Klamt, M. Diedenhofen, F. Neese, *J. Phys. Chem. A* **2006**, *110*, 2235-2245.
[31] J. B. Lambert, S. Zhang, C. L. Stern, J. C. Huffman, *Science* **1993**, *260*, 1917-1918.
[32] F. Zhang, L. Wang, S.-H. Chang, K.-L. Huang, Y. Chi, W.-Y. Hung, C.-M. Chen, G.-H. Lee, P.-T. Chou, *Dalton Trans.* **2013**, *42*, 7111-7119.
[33] (a) S. A. Bone, S. Trippett, P. J. Whittle, *J. Chem. Soc. Perkin Trans.1* **1977**, 437-438; (b) M. Zanger, C. A. Vander-Werf, W. E. McEwen, *J. Am. Chem. Soc.* **1959**, *81*, 3806-3807; (c) S. M. Cairns, W. E. McEwen, *J. Org. Chem.* **1987**, *52*, 4829-4831.
[34] (a) Z. Deng, J.-H. Lin, J.-C. Xiao, *Nat. Commun.* **2016**, *7*, 10337-10344; (b) Z. Deng, C. Liu, X. L. Zeng, J. H. Lin, J. C. Xiao, *J Org Chem* **2016**, *81*, 12084-12090.

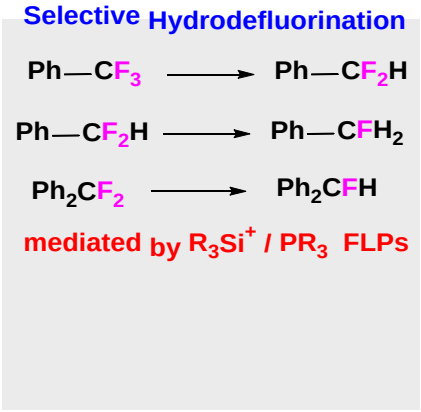
10.1002/chem.201705276

WILEY-VCH

Layout 1:

COMMUNICATION

Reactions of CF_3: Silylium / phosphine- based FLPs are shown to effect the selective abstraction of fluoride ion from aryl-CF_3 and CF_2 groups, ultimate converting CF_3 to CF_2H to CFH_2 fragments.



Ian Mallov, Adam J. Ruddy, Hui Zhu, Stefan Grimme and Douglas W. Stephan**

Page No. – Page No.
C-F Bond Activation by Silylium/Phosphine Frustrated Lewis Pairs: Mono-Hydrodefluorination of $PhCF_3$, $PhCF_2H$ and Ph_2CF_2