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Perfluoroalkylation of Alkenes by Frustrated Lewis Pairs

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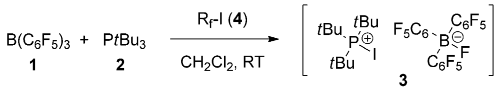
Abstract: The activation of perfluoroalkyl iodides by the frustrated Lewis pair tris(pentafluorophenyl)borane and tri-*tert*-butylphosphine is described. By abstraction of both a fluorine and an iodine atom, an iodophosphonium fluoroborate salt is formed. In the presence of alkenes the corresponding iodoperfluoroalkylation products are generated regioselectively. First mechanistic investigations support a radical mechanism.

Pairs of a Lewis acid and a Lewis base which are sterically too demanding to form adducts are known as frustrated Lewis pairs (FLPs).[1] Their chemistry has evolved dramatically from curiosities to a vivid research area since the first reports that small molecules such as dihydrogen can be activated.[2] Since then, hydrogenation protocols for unsaturated hydrocarbons and reductions of C=N bonds have been well-documented.[3] Apart from dihydrogen also other small molecules, such as silanes,[4] carbon monoxide,[5] carbon dioxide,[6] sulfur dioxide,[7] nitrogen oxides[8] as well as alkyl fluorides and bromides,[9] were successfully activated. It was also shown that the element–halogen bond (E–X) in X_2, HX, BX_3, $SOCl_2$, and CX_4 can be broken by Lewis pairs.[9e,10] The first FLPs were based on an electron-deficient borane and an electron-rich phosphine either as separate molecules or sharing a bridging scaffold. Today, this concept has been extended also to transition-metal complexes and chiral catalysts.[1,11]

Recently, we have developed a stereoselective hydroperfluoro-alkylation protocol of electron-deficient C=C bonds for the synthesis of amino acids and butanolides.[12] Due to the great importance of fluorinated compounds in pharmacy, agrochemistry, and materials science, past years have witnessed a substantial expansion of available synthetic tools for their efficient preparation.[13] Fluorine and organofluorine compounds have a number of unique properties, such as high (group) electronegativity, low polarizability, and bond dissociation energies. They differ significantly from the heavier halogens and require special functionalization protocols.[14] Based on the reported activation of the non-polarized H–H bond by FLPs we became interested in a potential related activation of perfluoroiodoalkanes R_f–I and subsequent functionalization of unsaturated hydrocarbons such as alkenes or alkynes.[15]

We started our investigation with the well-established FLP system $B(C_6F_5)_3$/P*t*Bu_3 (**1**/**2**).[2b] Upon addition of different perfluoroalkyl iodides to a solution of the FLP in dichloromethane the salt [*t*Bu_3PI][$(C_6F_5)_3$BF] (**3**) was generated and isolated in 54–85 % yield (Table 1). This result raised the question for the process leading to this fluoroborate salt.[10c] In the case of perfluorocyclohexyl iodide (**4e**) the formation of perfluorocyclohexene (**5**)[16] was evident by ^{19}F NMR spectroscopy indicating a β-fluoride elimination process (Scheme 1). Such a mechanism is not possible for perfluoroiodoalkanes such as CF_3I (**4a**) or perfluorobenzyl iodide (**4f**). For these substrates an α-fluoride elimination with concomitant perfluorocarbene formation needs to be considered.

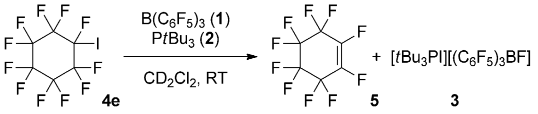
Table 1. Formation of [*t*Bu_3PI][$(C_6F_5)_3$BF] (**3**) from perfluoroiodoalkanes.[a]



Entry	Perfluoroiodoalkane (R_f–I)	Time	Yield (**3**) [%]
1	F_3C-I (**4a**)	20 min	65
2	F_3C-CF_2-CF_2-CF_2-I (**4b**)	24 h	62
3	F_3C-$(CF_2)_6$-CF_2-I (**4c**)	24 h	54
4	F_3C-CFI-CF_3 (**4d**)	20 min	85
5	C_6F_{11}-I (**4e**)	60 min	75
6	$C_6F_5CF_2$-I (**4f**)	30 min	70

[a] Reactions were performed in CH_2Cl_2 at RT for the time indicated.

We became interested whether such a carbene intermediate may be trapped in the presence of an alkene. Surprisingly,



Scheme 1. FLP-mediated dehalogenation of perfluorocyclohexyl iodide.

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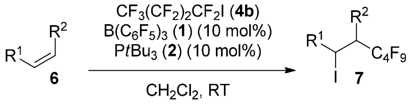
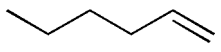
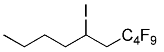
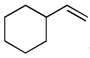
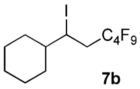
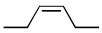
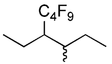
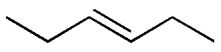
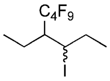
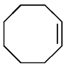
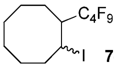
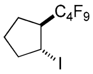
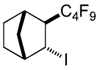
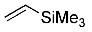
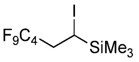
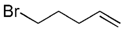
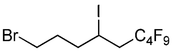
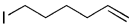
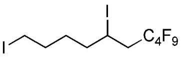
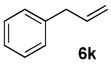
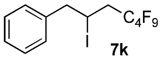
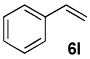
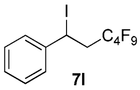
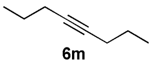
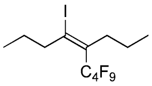
Table 2. Iodoperfluoroalkylation of unsaturated hydrocarbons by FLPs.[a]



Entry	Alkene	Product	Time [h]	Yield [%]
1	 **6a**	 **7a**	12	73
2	 **6b**	 **7b**	12	95
3	 **6c**	 **7c** 62:38 d.r.	22	33
4[b]	 **6d**	 **7c**	24	–
5	 **6e**	 **7e** 53:47 d.r.	12	55
6	 **6f**	 **7f**	20	54
7	 **6g**	 **7g**	12	37
8	 **6h**	 **7h**	12	81
9	 **6i**	 **7i**	17	56
10	 **6j**	 **7j**	24	84
11	 **6k**	 **7k**	40	56
12[b]	 **6l**	 **7l**	12	–
13	 **6m**	 **7m**	24	18

[a] Reactions were performed in CH_2Cl_2 at RT for the time indicated. [b] No reaction was observed.

when perfluorobutyl iodide (**4b**) was added in excess to $B(C_6F_5)_3/PtBu_3$ (**1**/**2**) in the presence of 1-hexene (**6a**) the corresponding iodoperfluoroalkylation product **7a** was formed and isolated in 73% yield (Table 2, entry 1). The reaction proceeded completely regioselective with the iodo substituent located in the former 2-position.

Control experiments revealed that both borane **1** and phosphine **2** need to be present for this transformation; no product was obtained in the absence of any of them. In addition, no reaction was observed when 2,2,2-trifluoro-1-iodoethane was submitted to the reaction conditions indicating that sufficient polarization of the C–I bond is essential.

The perfluoroalkylation reaction requires only substoichiometric amounts of the FLP. In fact, in the presence of 10 mol% of both borane **1** and phosphine **2** terminal as well as internal *cis*-alkenes **6** react with perfluorobutyl iodide (**4b**) to the corresponding addition products **7** (Table 2). In the case of *trans*-olefins as well as styrenes no apparent reaction was observed and the starting material was reisolated (Table 2, entries 4 and 12). In polar solvents, such as THF, the reaction proceeds very slowly. This may be explained by an unfavorable Lewis adduct formation with the highly electron-deficient borane. For a similar reason, substrates incorporating polar heteroatoms are not transformed efficiently. When 4-octyne was submitted to the Lewis pair mediated perfluoroalkylation reaction the corresponding tetrasubstituted alkene was obtained (Table 2, entry 13).

In order to get insight into the mechanism of the observed iodoperfluoroalkylation reaction we first investigated potential interactions between perfluoroalkyl iodide and the individual members of the Lewis pair. Mixtures of the electron-deficient borane $B(C_6F_5)_3$ (**1**) and either perfluorobutyl iodide (**4b**) or 1-hexene (**6a**) showed no significant shift in the ^1H and ^{19}F NMR spectra compared to the starting material. In contrast, when equal amounts of the perfluoroalkyl iodide **4b** and the electron-rich phosphine **2** were dissolved in CD_2Cl_2 the ^{31}P NMR spectrum showed a significant upfield shift by 6 ppm.[17] Likewise, in the ^{19}F NMR spectrum a upfield shift of the RCF_2I signal by 12 ppm was observed (Figure 1). This result is in agreement with the assumption of an iodine-phosphorous interaction.

A mechanistic rationale for the observed activation of perfluoroalkyl iodides and subsequent addition to alkenes may follow an ionic pathway (**a**) via intermediate **I** or radical pathways (**b**, **c**, and **d**) via intermediate **II** (Figure 2). The electron-rich phosphine **2** forms a halogen bond to the perfluoroalkyl iodide **4**. Potentially supported by a coordination of the borane to a fluorine substituent either heterolytic (upper path) or homolytic (lower path) R_f–I bond cleavage occurs. Following the upper pathway an iodophosphonium species is formed. The cyclic iodonium intermediate **I** obtained upon halogen transfer to the alkene (pathway **a**) is then opened on the sterically more accessible site by the perfluoroalkyl anion. Alternatively, the interaction of $B(C_6F_5)_3$ with the alkene **6** may result in the attack of the perfluoroalkyl anion (pathway **b**). It is known that electron-deficient boranes can activate alkenes, as it has been shown specifically for the addition of FLP **1**/**2** to different alkenes such as 1-hexene forming a betaine product.[18] However, such alkyltris(pentafluorophenyl)borates are known to be stable and are therefore not likely to form radical intermediate **II**.[19] Through pathway **c** the electron-rich phosphine **2** may reductively form a perfluoroalkyl radical, which adds to the alkene followed by radical chain iodine transfer from R_f–I to intermediate **II**.[20] Furthermore, a perfluoroalkyl borate could be formed by means of pathway **d**. Homolytic bond cleavage and formation of a radical pair may then be the initiation step of a radical iodoperfluoroalkylation from **II**.

In a test reaction 1,6-heptadiene (**6n**) was added to perfluorobutyl iodide (**4b**) in the presence of 10 mol% of the FLP **1**/**2**. A product mixture of the double-addition product **7n** and the corresponding cyclopentane derivative **8** (as mixture of *cis*/

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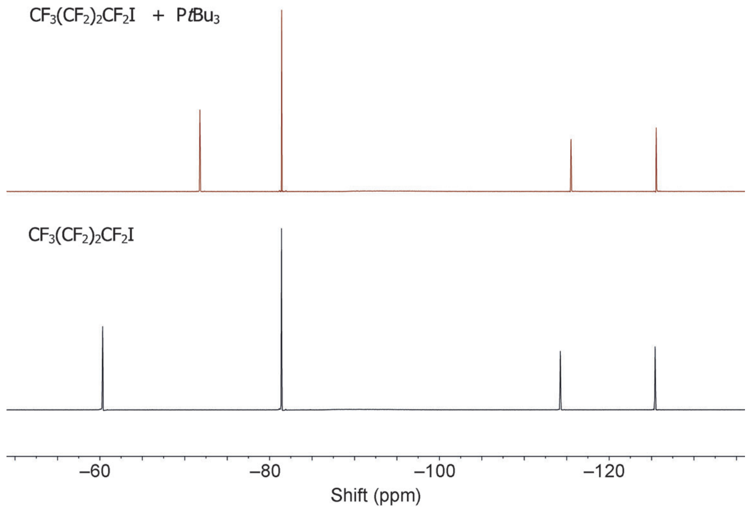


Figure 1. ^{19}F NMR spectrum (376 MHz, 298 K, CD_2Cl_2) of a mixture of P*t*Bu$_3$ and perfluorobutyl iodide compared to free perfluorobutyl iodide.

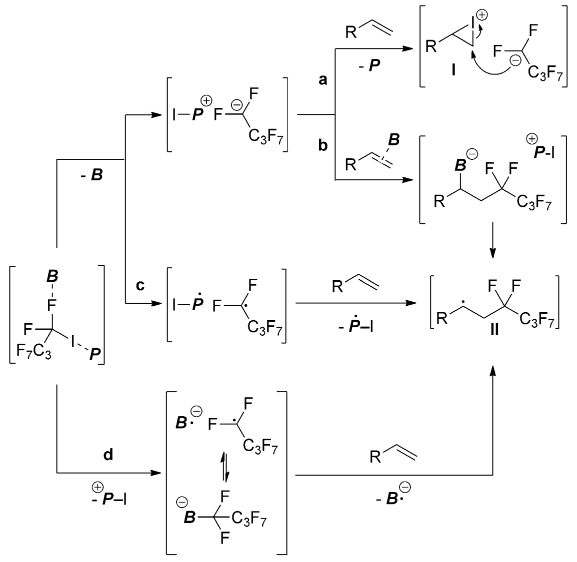
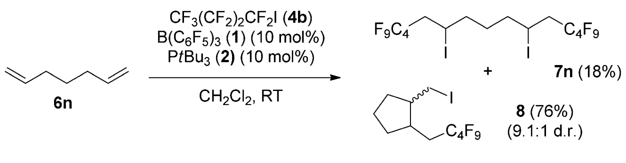


Figure 2. Mechanistic rationale for the activation of perfluoroiodoalkanes. ***B***$=B(C_6F_5)_3$ (**1**); ***P***$=$P*t*Bu$_3$ (**2**).



Scheme 2. Iodoperfluoroalkylation of 1,6-heptadiene (**6n**).

trans isomers) was formed (Scheme 2).[21] This regioselective ring closure of the diene is more consistent with the assumption of a step-wise perfluoroalkyl and halogen atom transfer via a radical rather than by a cationic intermediate.[22] In addition, the iodoperfluoroalkylation of substrate **6c** gave the product as a mixture of *syn*/*anti*-diastereomers, which would not be expected for the nucleophilic ring opening of a putative iodonium intermediate or a potential synchronous process. These results suggest paths **c** or **d** as potential mechanistic routes. However, as no radical intermediates could be detected by EPR so far, no reaction or polymerization was found with styrene as substrate,[23] and addition of stoichiometric amounts of the radical scavenger BHT[24] had no impact on the conversion rate, other mechanisms should not be excluded at this point and will be in the focus of future investigations.

In summary, we have shown that frustrated Lewis pairs can activate perfluoroalkyl iodides. In the presence of alkenes a regioselective iodoperfluoroalkylation reaction occurs while in their absence an iodophosphonium fluoroborate salt is formed. Studies aiming at a better understanding of the mechanism as well as a potential development of a stereoselective process are under way and will be reported in due course.

Experimental Section

Representative procedure for the iodoperfluoroalkylation of alkenes: Tris(pentafluorophenyl)borane (**1**) (46.4 mg, 90.6 μmol, 10 mol %) and tri-*tert*-butylphosphine (**2**) (18.4 mg, 90.9 μmol, 10 mol %) were dissolved in dichloromethane (2.0 mL). Afterwards, vinylcyclohexene (**6b**, 120 μL, 0.877 mmol) and perfluorobutyl iodide (**4b**, 150 μL, 0.877 mmol) were added by syringe. The reaction mixture was stirred overnight at room temperature. After removal of the solvent the crude product was purified by column chromatography (silica gel, eluent: cyclohexane) to give the desired product **7b** (380 mg, 95 %) as a colorless viscous liquid. ^{1}H NMR (500 MHz, 298 K, $CDCl_3$): $\delta=4.35$ (td, $J=6.7$ Hz, $J=3.0$ Hz, 1 H; CHI), 2.84 (m$_c$, 2 H; CH_2CF_2), 1.82–1.78 (m, 2 H; CH_2^{Cy}), 1.73–1.65 (m, 3 H; CH_2^{Cy}), 1.43–1.29 (m, 2 H; CH_2^{Cy}), 1.26–1.08 (m, 3 H; CH_2^{Cy}), 0.82 ppm (tq, $J=11.1$ Hz, $J=3.1$ Hz, 1 H; CH^{Cy}); $^{13}C\{^1H\}$ NMR (126 MHz, 298 K, $CDCl_3$): $\delta=120.9$–108.0 (m, CF_3, CF_2), 44.3 (s$_{br}$, CH^{Cy}), 39.1 (t, $J=20.8$ Hz, CH_2CF_2), 33.9 (CH_2Cy), 30.5 (s$_{br}$, CHI) 29.9, 26.2, 25.9, 25.7 ppm (CH_2^{Cy}); ^{19}F NMR (376 MHz, 298 K, $CDCl_3$): $\delta=-80.9$ (t, $J=10.0$ Hz, 3F, CF_3), -113.8 (m$_c$, 2F, CF_2), -124.4 (m$_c$, 2F, CF_2), -125.8 ppm (m$_c$, 2F, CF_2). IR (film): $\tilde{\nu}=2930$ (s), 2857 (s), 1451 (m), 1433 (w), 1349 (s), 1134 (s), 1051 (w), 903 (w), 880 (m), 768 (m), 650 (w), 521 cm^{-1} (w); MS (EI) calcd (*m/z*) for $[M-I]^+$: 329.0952, found: 329.0941; elemental analysis calcd (%) for $C_{12}H_{14}F_9I$: C 31.60, H 3.09; found: C 31.60, H 3.09.

Acknowledgements

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Keywords: alkenes · boranes · fluoroalkylation · frustrated Lewis pairs · halogenation

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[24] BHT = 2,6-bis(*tert*-butyl)-4-methylphenol.

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COMMUNICATION

Fluorine Chemistry

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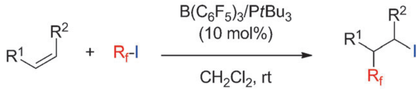
Perfluoroalkylation of Alkenes by Frustrated Lewis Pairs



Frustrated Lewis pairs mediate the regioselective addition of perfluoroalkyl iodides to non-activated olefins. In the absence of an alkene, an iodophosphonium fluoroborate salt is formed by a fluoride elimination process. For the activation of the C–I bond, dual action of both the phosphine and the borane is required (see scheme).

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