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# Straightforward synthesis of bench-stable heteroatom-centered difluoromethylated entities *via* controlled nucleophilic transfer from activated TMSCHF<sub>2</sub><sup>†</sup>

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The commercially available and experimentally convenient (bp 65 °C) difluoromethyltrimethylsilane (TMSCHF<sub>2</sub>) is proposed as a valuable difluoromethylating transfer reagent for delivering the CHF<sub>2</sub> moiety to various heteroatom-based electrophiles. Upon activation with an alkoxide, a conceptually intuitive nucleophilic displacement directly furnishes in high yields the bench-stable analogues.

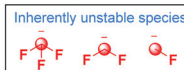
Among the techniques enabling the modulation of pivotal physical-chemical properties of organic arrays, the introduction of fluorine atoms has become a powerful tool, nowadays thoroughly applied in chemistry.<sup>1</sup> Synthetic chemists tackling the challenge of embodying fluorine into molecules quickly recognized that well-established methodologies in classical halogen chemistry could not be validated for this member of the series.<sup>2</sup> Ideally, the use of fluorinated carbanion-like entities would enable – upon a conceptually intuitive nucleophile-electrophile logic – the forging of a new carbon–carbon bond presenting the exact and desired fluorination degree of the targeted compound (Scheme 1).<sup>3</sup> However, F-containing nucleophiles are notoriously reluctant species mainly due to their inherent limited chemical integrity, which for a long time eclipsed their employment in synthesis.<sup>2a,4</sup> In this sense, the introduction of trifluoromethyltrimethylsilane (TMSCF<sub>3</sub>, Ruppert–Prakash reagent)<sup>5</sup> allowed productive trifluoromethylations under nucleophilic regimes by exploiting the stabilizing effect imparted by the silicon atom. Analogous nucleophilic difluoromethylations<sup>6</sup> and monofluoromethylations<sup>7</sup> remained

somehow obscured and thus, underdeveloped until recently because of the high tendency of MCHF<sub>2</sub> and MCH<sub>2</sub>F carbanions to undergo α-elimination. On the other hand, the introduction of difluoromethyltrimethylsilane (TMSCHF<sub>2</sub>), a commercially available and experimentally convenient CHF<sub>2</sub>-donor source (bp 65 °C)<sup>8</sup> boosted the flourishing of synthetic protocols for the introduction of this group<sup>9</sup> featuring some unique properties – H-bond donor, weakly acidic, lipophilic isostere of OH and SH motifs – which make it highly valuable *inter alia* in drug design.<sup>10</sup> Compared to the Ruppert–Prakash reagent, the reactivity of TMSCHF<sub>2</sub> is tamed<sup>11</sup> and its proper activation under Lewis basic conditions is essential, as demonstrated by Hu in 2011 in the course of difluoromethylations of ketones and imines,<sup>12</sup> and later extended also to other sp<sup>2</sup>-hybridized carbon electrophiles by our group.<sup>13</sup> Collectively, these precedents showcase that replacing a putative ionic (*e.g.* Li) M–CHF<sub>2</sub> bond with a covalent one (*e.g.* Si) represents the *conditio sine qua non* for accessing bench stable difluoromethylating agents. With this rationale in mind, we wondered if a unified strategy enabling the release of the nucleophilic CHF<sub>2</sub> moiety from a competent donor to a recipient heteroatom-centered

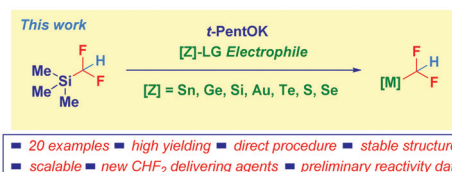
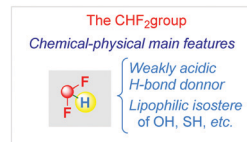
## Forming C–C bond with fluorinated nucleophiles



## Use of Fluoro-containing carbanions



Requirement for stabilizing elements (*e.g.* Si as in TMSCF<sub>3</sub>)



Scheme 1 General context of the presented work.

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electrophile – [Z]-LG, Z = heteroatom, LG = leaving group – could be designed. Should this concept be experimentally validated, we would establish a smooth access to versatile Z-CHF<sub>2</sub> agents not relying on more complex routes such as the Prakash-Olah modification<sup>14</sup> of the Cullen CF<sub>2</sub> carbene insertion into the Sn-H bond of a trialkyltin hydride.<sup>15</sup> Herein, we present the feasibility of this rationale through an alkoxide mediated activation of TMSCHF<sub>2</sub>: we anticipate that the protocol – working like a CHF<sub>2</sub> shuttle – enables the preparation in high chemical yields of  $\alpha,\alpha$ -difluoromethyl-derivatives of diverse heteroatoms.

We selected the commercially available chloro-stannatrane **1** as the model substrate for evaluating the strategy proposed (Table 1). This choice was motivated by the following reasons: (a) the stannatrane backbone – introduced in synthesis by Vedejs<sup>16</sup> – due to the constitutive apical nitrogen atom which enlarges the Sn–C bond, manifests a higher tendency to transmetallate and thus, to be engaged in nucleophilic transfer operations;<sup>17</sup> (b) as showcased in illuminating works by Biscoe,<sup>18</sup> stannatranes are particularly suited for coupling (enantioenriched) secondary systems; (c) the expected difluoromethyl analogue **2** is, to the best of our knowledge, an unknown reagent, potentially useful in fluorination chemistry, thus substituting inherently less reactive “dummy”-based species (e.g. R<sub>3</sub>SnCHF<sub>2</sub>).<sup>19</sup>

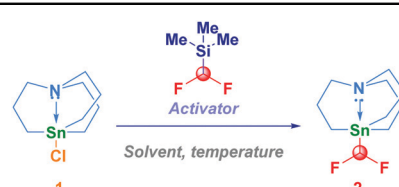
Activating the pronucleophile with CsF (in toluene or DMF) or with TBAT (tetrabutylammonium difluorodiphenylsilicate) was not effective and, the starting chloro-stannatrane **1** was fully recovered (entries 1–3). The adoption of a Lewis base activation protocol with a commercially available solution of potassium *tert*-pentoxide (amylate) in toluene enabled a clean

transformation in THF at –50 °C, thus giving **2** in 79% isolated yield (entry 4). Increasing the temperature – *coeteris paribus* – to –20 °C and 0 °C, respectively, was beneficial (entries 5–6). The stoichiometric ratio between TMSCHF<sub>2</sub> and *t*-PentOK could be dwindled to 1.5:1.4 without significantly affecting the transformation efficiency (entry 7), whereas a further decrease was detrimental (entry 8). Some additional aspects merit mention: (a) a slight excess (0.1 equiv.) of the pronucleophile compared to the alkoxide was essential for the complete genesis of the difluoromethyl carbanion-like species and thus, for suppressing the (non isolable) stannatrane nucleophilic substitution adduct [Sn–O(*t*-Pent), entry 9]; (b) using Barbier-type conditions was crucial for observing reactivity, thus remarking the limited chemical integrity of this carbanion (entry 10).

With the optimal conditions for the direct homologative transfer of the CHF<sub>2</sub> unit to a halostannane-type derivative,<sup>20</sup> we then investigated the scope of the reaction (Scheme 2). Pleasingly, tricyclohexyl- and tri(*n*-butyl)-stannanes smoothly underwent the transformation, furnishing analogues **3** and **4** in comparable high yield. Switching to aromatic substituents (**5**) on tin did not affect the effectiveness. Previously undisclosed difluoromethyl derivatives of organogermanium compounds could also be prepared under our conditions in the case of both trialkyl-(**6**) and triphenyl-(**7**) systems. This is particularly intriguing since organogermaniums recently emerged as more sustainable and attractive alternatives to the more common organotin compounds.<sup>21</sup> Notably, dichlorodiphenylgermanium was a competent electrophile for the double functionalization, conducting to the bis-(difluoromethyl) derivative **8** in a very good 83% isolated yield. The difluoromethyl fragment released by the silicon atom of TMSCHF<sub>2</sub> could be efficiently transferred to a different silicon center by reacting with a halo-silane, thus conducting to the unprecedented difluoromethylsilanes **9** (*t*-butyldiphenyl, 78%) and **10** (triphenyl, 81%). The combined electronic and steric factors imparted by these substituents may be advantageously employed for modulating the reactivity of difluoromethylsilane (*vide infra*). Furthermore, the NHC–Au(I)–Cl complex could be engaged in the transformation, giving the corresponding –CHF<sub>2</sub> adduct **11** in high yield. The scalability of the transformation (15 mmol) was deduced by high-yielding processes for compounds **2** (90%) and **10** (85%).

The formal nucleophilic substitution process was not only achieved on heteroatom-halide functionalities but, was also effective in the case of symmetrical RZ-ZR moieties acting as convenient starting materials. An organotellurium analogue smoothly underwent the reaction, giving (**12**) in a very good 90% isolated yield. Organosulfur compounds acted as competent substrates for the transformation regardless of the different electronic behaviour displayed by the substituent on the aromatic ring, as evidenced by reactions involving the *p*-methoxy-(**13**) and the 2,4,5-trichloro-(**14**) systems. Notably, engaging a highly sterically hindered material (2,4,6-tri-*i*-propyl, **15**) aromatic disulfide further validated the protocol. Moreover, an excellent chemoselective profile was deduced in the presence of a nitro moiety which remained unaffected, thus

Table 1 Reaction optimization

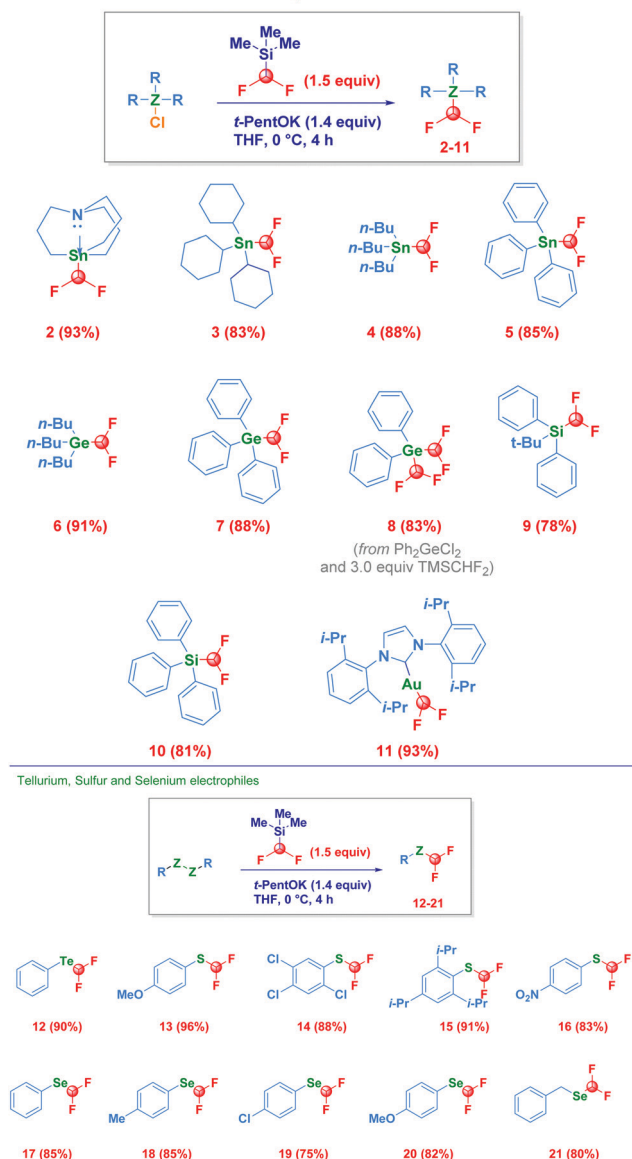


Entry	Activator (equiv.)	TMSCHF <sub>2</sub> (equiv.)	Solvent/Temp. (°C)	Yield of <b>2</b> (%) <sup>a</sup>
1	CsF (1.8)	2.0	Toluene/90	—
2	CsF (1.8)	2.0	DMF/90	—
3	TBAT (1.8)	2.0	DMF/90	—
4	<i>t</i> -PentOK (1.8)	2.0	THF/–50	79
5	<i>t</i> -PentOK (1.8)	2.0	THF/–20	87
6	<i>t</i> -PentOK (1.8)	2.0	THF/0	94
7	<i>t</i> -PentOK (1.4)	1.5	THF/0	91
8	<i>t</i> -PentOK (1.2)	1.1	THF/0	83
9 <sup>b</sup>	<i>t</i> -PentOK (1.5)	1.5	THF/0	85
10 <sup>c</sup>	<i>t</i> -PentOK (1.4)	1.5	THF/0	—

<sup>a</sup> Yields refer to isolated and purified compound on a model reaction run at 0.68 mmol scale. <sup>b</sup> <sup>1</sup>H-NMR and GCMS analyses of the reaction crude indicate the presence of a stannatrane-O-*t*-Pent adduct whose purification was unfortunately not effective. <sup>c</sup> Reaction carried out under *non* Barbier-type conditions. Entries 1–3 run for 6 h. Entries 4–10 run for 1 h.



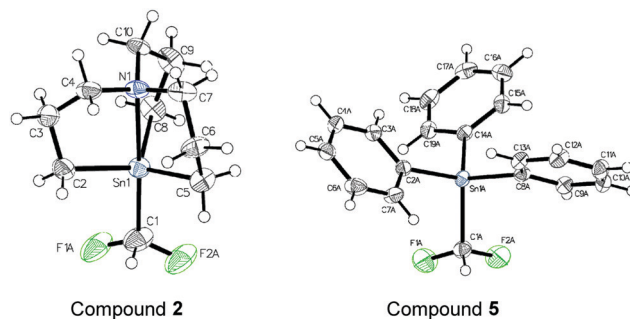
Tin, Germanium, Silicon and Gold electrophiles



**Scheme 2** Difluoromethyl-group transfer under the nucleophilic regime from TMSCH<sub>2</sub> to different heteroatom-based electrophiles.

furnishing exclusively the difluoromethyl sulfide (**16**). We further extended the technique to diselenides, it being applicable to both aromatic (**17–20**) and alkyl analogues (**21**). The proposed strategy favourably compares with reported protocols, as for example the use of the non-commercially available PhSeCN with the same TMSCH<sub>2</sub>F<sub>2</sub><sup>22</sup> or, the use of the gaseous species chlorodifluoromethane.<sup>23</sup>

With the aim to gain insights into structural features of difluoromethyl-tin analogues **2** and **5**, their crystallographic X-ray analysis revealed some important aspects (Fig. 1). In the case of stannatrane, the Sn1–C1 bond has a length of 2.233 Å, significantly longer compared to classical organotin (R<sub>3</sub>SnR<sup>1</sup>).<sup>24</sup> This element is in agreement with the reasons accounting for the chemical profile of the stannatrane



**Fig. 1** X-ray structures of selected difluoromethyltin derivatives (**2** CCDC 2150362 and **5** CCDC 2150363).

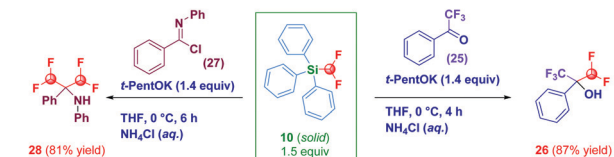
backbone: the enlarged Sn–C bond makes it more labile and thus, confers a high reactivity. In fact, the analogous bond Sn1–C1 in the triphenyltin analogue **5** is 2.197 Å. Moreover, the Sn1–N1 distance in the stannatrane is 2.478 Å, whereas the two carbon-fluorine bonds in both structures are comparable (1.313 Å and 1.317 Å in stannatrane **2** and, 1.225 Å and 1.338 Å in triphenyltin- **5**). The angle C1–Sn1–C2 (102.66°) matches with the analogous C1–Sn1–C5 (103.77°) and C1–Sn1–C8 (102.27°) in the stannatrane, which also shows a characteristic planar orientation N1–Sn1–C6 (178.61°). The absence of the rigidifying backbone in **5** is evident from the values of the angles C1–Sn1–C8 (107.36°), C1–Sn1–C14 (110.30°) and C1–Sn1–C2 (103.13°).

The synthetic potential of selected prepared compounds was then evaluated (Scheme 3). Difluoromethyl stannatrane **2** acted as a versatile coupling agent in two recently developed protocols by Biscoe,<sup>18a,d</sup> namely: (a) the Pd-catalyzed cross-coupling with bromobenzene furnishing **22** in 76% yield and, (b) the Pd-catalyzed acylation with an acyl chloride **23** which resulted in the clean formation of difluoromethylketone **24** in 83% yield (path a). As an additional proof of the enhanced reactivity conferred by the stannatrane backbone, it is worth noting that Sn-CHF<sub>2</sub> analogues **3**, **4** and **5** did not promote at any extent both transformations. Intrigued by the solid physical state of the triphenylsilane derivative **10**, upon the usual activation with potassium *tert*-pentoxide and reaction with

a) Use of CHF<sub>2</sub>-stannatrane in Pd-catalyzed cross-coupling and acylation



b) Use of CHF<sub>2</sub>-triphenylsilane in nucleophilic additions



**Scheme 3** Synthetic uses of CHF<sub>2</sub>-stannatrane and CHF<sub>2</sub>-triphenylsilane.



$\alpha,\alpha,\alpha$ -trifluoroacetophenone **25**, we were delighted to observe the preparation of the *gem*-difluoromethyl-trifluoromethyl carbinol **26** in 87% yield (path b).<sup>25</sup> Although reactive, the process carried out with the *tert*-butyldiphenyl analogue **9**, gave **26** in 54% yield, probably as a consequence of the increased steric hindrance on the Si-atom. The same activated form of the triphenylsilane derivative **10** accomplished also a double nucleophilic attack on the azomethinic carbon of *N*-phenylbenzimidoyl chloride **27 en route** to bis(difluoromethyl) amine **28** (81% yield). Collectively, these experiments indicate derivative **10** as a valuable difluoromethylating agent form whose solid state – although not suitable for X-ray analysis – may have advantages on the liquid TMSCHF<sub>2</sub>.

In summary, we reported the direct nucleophilic transfer of a difluoromethyl unit to a series of heteroatom-centered electrophiles (Sn, Ge, Si, Au, Se, S, Te) for forging bench stable analogues. The procedure is levered on the Lewis base mediated activation (potassium *tert*-pentoxide) of the commercially available and experimentally convenient TMSCHF<sub>2</sub>. Not only chlorinated starting materials could be employed, but also chalcogenides of general structure RZ-ZR, thus giving straightforward access to the title compounds through a flexible and intuitive logic. Among the prepared motifs, the following deserve a particular mention: (i) the stannatrane analogue for which structural aspects deduced by the X-ray crystallographic analysis support a unique reactivity in Pd-catalyzed cross-coupling or acylation processes and, (ii) the triphenylsilyl-derivative, which can be regarded as a valuable alternative to the starting TMSCHF<sub>2</sub> for the delivery of the CHF<sub>2</sub> unit to electrophilic linchpins (ketone and imidoyl chloride).

Dedicated to Professor Helmut Spreitzer in on the occasion of his retirement.

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## Conflicts of interest

There are no conflicts to declare.

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