

VIP Very Important Paper

# Structural Characterization of Hydro-, Chloro- and Fluoroorganylsilanes with Substituents of Varying Electron Withdrawing Character

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We report on the molecular structure of trimethylsilanes Si(CH<sub>3</sub>)<sub>3</sub>X in which the substituents X, namely (Z)-pentafluoropropen-1-yl, trifluoropropyn-1-yl, pentafluoroethyl, trifluorovinyl, vinyl, propyn-1-yl, di- and trichloromethyl, display electron withdrawing effects of varying strength. The lengths of the bonds between the silicon and the carbon atoms of X correlate with the hybridization of the respective orbitals and the steric demand of X rather than with the electron withdrawing capability. In case of chlorinated substituents dispersion effects

seem to shorten the Si–C bond. Furthermore, a route for generating trifluoropropyn-1-yllithium from the cryogen 2,3,3,3-tetrafluoropropene (HFO-1234yf) and *n*-butyllithium is described. Tetrafluoropropen-1-yllithium is slowly formed at –80 °C but even at this temperature spontaneous elimination of LiF occurs. Deprotonation of the formed 3,3,3-trifluoropropene requires temperatures of above –60 °C leading to trifluoropropyn-1-yllithium which appears as relatively stable at room temperature.

## Introduction

Electron withdrawing substituents are imperative in all fields of chemistry. The strength of electron withdrawing effects of the substituents significantly influences the Lewis acidity of molecules. Such substituents are of interest to finetune the Lewis acidic character of catalysts employed in organic<sup>[1]</sup> and polymer chemistry<sup>[2]</sup> as well as for the design of frustrated Lewis pairs.<sup>[3]</sup>

The calculation of the C–O bond length of a *para* or *meta* substituted phenolate ion provides a convenient way to classify the strength of this effect. A shortened C–O bond corresponds with an increased electron withdrawing activity of a substituent X. The difference  $\Delta(O^-)_{m,p}$  between this bond length  $d(XC_6H_4-O^-)$  and the C–O bond length of the non-substituted phenolate  $d(C_6H_5-O^-)$  provides parameters in good agreement with the well-established Hammett constants.<sup>[4]</sup>

Due to the high electronegativity of fluorine perfluoroorganyl groups are powerful electron withdrawing substituents. Their transfer is not trivial but over the years efficient methods have been established, for example nucleophilic perfluoroalkylation with various types of organometallic reagents, electrophilic perfluoroalkylation with reagents such as iodonium salts, and radical perfluoroalkylation with iodides.<sup>[5]</sup>

One convenient approach is based upon usage of trimethylperfluoroorganylsilanes, which as mostly stable liquids are easy to handle and often commercially available. They are

activated by catalytic amounts of nucleophiles, typically fluoride ions. After activation the perfluoroorganyl groups exhibit nucleophilic character and are smoothly transferred upon electrophilic compounds (Scheme 1).<sup>[6]</sup>

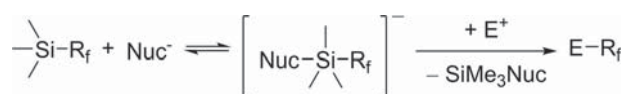
One of the preparatively most relevant silanes of this kind is the Ruppert-Prakash reagent, trimethyl(trifluoromethyl)silane. For its preparation tris(diethylamino)phosphane, bromotrifluoromethane and chlorotrimethylsilane are employed. Supposedly the phosphane activates bromotrifluoromethane leading to a trifluoromethanide synthon which reacts with chlorotrimethylsilane under formation of a phosphonium chloride and trimethyl(trifluoromethyl)silane.<sup>[7]</sup> However, most perfluoroorganylsilanes are nowadays prepared from the respective lithium reagent, provided that it is sufficiently stable, with bromo- or chlorotrimethylsilane under liberation of lithium bromide or chloride as byproduct.

Those lithium reagents have been synthesized by transmetalation and deprotonation processes. Unsaturated perfluoroorganyllithium reagents are available either by deprotonation of the corresponding perfluoroalkene or perfluoroalkyne or else by treatment of di- and trihydrofluoroalkanes with appropriate lithium bases. In the latter reactions several deprotonation steps are followed by elimination of lithium fluoride yielding targeted species.

The preparation of trifluorovinyl lithium via transmetalation from trifluorovinyltin compounds and phenyllithium was first published 1960.<sup>[8]</sup> However, it is more conveniently accessible by treatment of 1,1,1,2-tetrafluoroethane with two equivalents

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**Scheme 1.** Transfer of perfluoroorganyl groups R<sub>f</sub> upon electrophilic reagents E<sup>+</sup> using nucleophiles Nuc<sup>−</sup> for activation of the respective perfluoroorganylsilane.