(9*H*-FLUOREN-9-YLIDENE)FLUOROMETHYLLITHIUM, A STABILIZED FLUOROALKENYL CARBANION. PREPARATION, REACTIONS, ^{13}C AND ^{19}F NMR SPECTRA+

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(9*H*-Fluoren-9-ylidene)fluoromethyllithium (**1**) was prepared by a low-temperature transmetallation of bromo(9*H*-fluoren-9-ylidene)fluoromethane (**2**). Whereas the synthesis of unlabeled bromofluoroalkene **2a** was based on Wittig–Horner reaction of fluorenone (**3**) with ethyl (diethoxyphosphoryl)fluoroacetate (**4**), (1-^{13}C)-labeled compound **2b** was obtained *via* an addition of labeled lithium 1-ethoxy-2-fluoro(2-^{13}C)ethen-1-olate (**5**) to ketone **3**. Fluoroethenyllithium **1** was found by a low-temperature ^{19}F NMR spectroscopy to be stable up to –40 °C; it was reacted with the series of electrophiles, *e.g.* benzaldehyde (**6**), methyl iodide (**7**) or chloro(trimethyl)silane (**8**). ^{13}C NMR experiments with (1-^{13}C)-labeled **1a** proved that fluorocarbenoid **1** is probably monomeric in THF solution in analogy to other halocarbenoids.

Keywords: 1-Fluoro-1-lithioalkene; Carbenoids; Carbanions; Fluorocarbenoids; Fluorocarbanions; Fluoroalkenes; Fluoroorganometallics; NMR spectroscopy.

Carbanions which contain both electropositive metal and electronegative halogen atoms at the central atom are called carbenoids as they often behave similarly to carbenes. Chemistry of carbenoids is governed by a strong interaction between the metal and halogen atoms. This interaction lowers characteristically the carbenoid stability[1] and hence limits their synthetic use. Although bromo- and chlorocarbenoids have been intensively studied[1], little attention have been paid to fluorocarbenoids[2]. Organolithium compounds are widely used in synthetic organic chemistry[3]. However, in con-

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trast to other metals such as zinc or cadmium, highly electropositive lithium brings additional instability to the fluorocarbenoid molecule and the ways of decomposition of both alkane-[4] and alkene-based[5] fluorocarbenoids have been studied. Until now, only one example of the synthetic use of the non-stabilized alkane-based fluorocarbenoid, dibromofluoromethyllithium, at low temperature is known[6], and few others rely on adjacent heteroatom, like sulfur[7], phosphorus[8] or silicon[9], stabilization. Due to these limitations, much more attention has been paid to more stable alkenyl fluorocarbenoids.

Although 1-fluoroethenyllithium was proved to be unstable[10,11], stabilizing β-substituents such as fluorine, phenyl or trifluoromethyl groups enhanced the stability of corresponding 1-fluoro-1-lithioethenes, which have been employed in organic syntheses[12]. Their stability could be estimated by a low-temperature ^{19}F NMR spectroscopy[11] and in most cases significant differences in stabilities of both geometric isomers have been observed[11,12]. Recently, surprisingly stabilizing role of oxygen substituent in a greater distance from the carbenoid centre has been reported[13].

Most organolithium compounds form oligomers in solution. Thus, with the aid of a low-temperature ^{13}C NMR spectroscopy, ethenyllithium proved to form tetramers in THF (ref.[14]). On the other hand, bromo- and chlorocarbenoids are only monomeric in solution[15] and this has been confirmed by X-ray spectroscopy of the 2,2-diaryl-1-chloroethenyllithium–THF–TMEDA complex[16]. In contrast to this experimental observation, calculations of fluoromethyllithium in simulated solvent suggested that dimers containing two C–F–Li–C linkages could also be formed[17].

Aryl substituents in the β-position stabilize halocarbenoids, but are prone to the Fritsch–Buttenberg–Wiechell rearrangement[1]. This can be efficiently suppressed by connecting aromatic rings[1]. We published preliminary notes about synthesis and low-temperature NMR spectra of (9*H*-fluoren-9-ylidene)fluoromethyllithium[18,19] (**1**). Here we wish to report full experimental details of this work, as well as some reactions of carbenoid **1** which show the scope and limitations of its use.

EXPERIMENTAL

General Comments

Temperature data are uncorrected. Low-temperature NMR experiments have been performed in a Wilmad narrow mouth NMR tubes equipped with a Wilmad Omnivalve adapter. ^{1}H NMR 1D and 2D spectra were recorded with a Varian Gemini 300 HC spectrometer at 400.1 MHz using TMS as internal standard, other NMR spectra were recorded with a Bruker AM 400

spectrometer, *viz*. ^{1}H NMR spectra at 400.1 MHz in $CDCl_3$ and ^{13}C NMR spectra at 100.6 MHz in $CDCl_3$ using TMS as internal standard, ^{19}F NMR at 376.5 MHz using $CFCl_3$ as internal standard with upfield values designed negative. In NMR spectra, chemical shifts are given in ppm (δ-scale), coupling constants (*J*) in Hz. FTIR spectra were recorded with a Nicolet 740 instrument in $CHCl_3$.

All manipulations and reactions including organometallic reagents were performed with an exclusion of moisture and atmospheric oxygen in oven-dried apparatuses. Ethyl bromo(2-^{13}C)acetate (**12**) was purchased from Aldrich. KF (Aldrich) was dried by heating to 150 °C/100 Pa prior to use. THF was dried over sodium benzophenone ketyl and distilled prior to use. Ethyl (diethoxyphosphoryl)fluoroacetate (**4**) was prepared according to ref.[20]. Concentrations of BuLi and MeLi solutions were estimated by titration prior to use according to ref.[21].

Fluoro(9*H*-fluoren-9-ylidene)acetic Acid (**9a**)

A flask was charged with ethyl (diethoxyphosphoryl)fluoroacetate (**4**; 12.11 g, 49.9 mmol) and dry THF (100 ml). The mixture was cooled to –80 °C and BuLi (23.3 ml, 2.15 M solution in hexanes, 50.1 mmol) was added. The mixture was allowed to warm to –30 °C and a solution of fluoren-9-one (**3**; 8.55 g, 47.5 mmol) in THF (20 ml) was dropwise added to it. The mixture was stirred at –30 °C for 30 min and at 0 °C for 2 h. Solvents were removed on a vacuum rotary evaporator and the residue was partitioned between CH_2Cl_2 (100 ml) and water (100 ml). The water layer was extracted twice with CH_2Cl_2 (50 ml), organic layers were combined, washed with water (50 ml) and dried with anhydrous $MgSO_4$. Evaporation of solvent afforded crude ethyl fluoro(9*H*-fluoren-9-ylidene)acetate (**10a**; 13.26 g), which was added to a mixture of dioxane (90 ml) and aqueous (90 ml) NaOH (7.60 g, 190 mmol) solution. This mixture was stirred at room temperature for 24 h, acidified by 5% HCl (150 ml) and extracted with CH_2Cl_2 (70 + 3 × 40 ml). Combined organic layers were dried with anhydrous $MgSO_4$ and solvent removed on a vacuum rotary evaporator to afford crude acid **9a** (11.52 g), which was washed four times with hot petroleum ether and recrystallized from MeCN to afford pure fluoro acid **9a** (8.61 g, 75.5%, m.p. 228–230 °C). ^{1}H NMR: 7.34 dt, 1 H, $^3J_{HH}$ = 7.9, $^4J_{HH}$ = 1.2; 7.37 t, 1 H, $^3J_{HH}$ = 7.7; 7.44 t, 1 H, $^3J_{HH}$ = 7.5; 7.47 dt, 1 H, $^3J_{HH}$ = 7.6, $^4J_{HH}$ = 0.8; 7.84 d, 1 H, $^3J_{HH}$ = 6.1; 7.85 d, 1 H, $^3J_{HH}$ = 6.9; 7.98 d, 1 H, $^3J_{HH}$ = 7.7; 8.64 d, 1 H, $^3J_{HH}$ = 7.9; 14.3 bs, 1 H. ^{13}C NMR: 120.1 s; 126.3 d, $^2J_{CF}$ = 15; 127.3 s; 127.4 s; 127.5 s; 127.7 s; 128.2 s; 130.0 s; 130.2 s, 7 C; 133.0 d, $^3J_{CF}$ = 8; 135.6 s; 139.5 s; 140.9 d, J_{CF} = 3; 147.5 d, $^1J_{CF}$ = 276; 162.2 d, $^2J_{CF}$ = 35. ^{19}F NMR: –105.4 s. IR: 923 s, 946 s, 1 146 s, 1 203 s, 1 285 s, 1 304 s, 1 423 s, 1 438 s, 1 496 s, 1 623 s, 1 685 s, 1 708 s, 2 520 m, 2 970 m, 3 000 m. For $C_{15}H_9FO_2$ (240.2) calculated: 75.0% C, 3.8% H; found: 75.1% C, 3.7% H.

Bromo(9*H*-fluoren-9-ylidene)fluoromethane (**2a**)

A flask was charged with fluoro acid **9a** (3.60 g, 15.0 mmol) and $CHCl_3$ (50 ml). Bromine (2.52 g, 15.8 mmol) was dropwise added to the stirred dispersion formed, the flask was stoppered and the reaction mixture was stirred at room temperature while irradiated by an infrared lamp for 6 h. Evaporation of solvent on a vacuum rotary evaporator afforded crude bromo(9-bromo-9*H*-fluoren-9-yl)fluoroacetic acid (**11a**; 6.55 g), which was added to the suspension of $NaHCO_3$ (2.52 g, 30.0 mmol) in acetone (50 ml). The mixture was refluxed for 16 h. Solvent was then removed on a vacuum rotary evaporator to afford crude product (4.04 g),

which was purified by short column chromatography (SiO_2; column length 4 cm, eluent petroleum ether) to afford fluoroethene **2a** (3.94 g, 95.6%, m.p. 80–84 °C; ref.[22] 87–88 °C). ^{1}H NMR: 7.29 dt, 1 H, $^3J_{HH}$ = 7.5, $^4J_{HH}$ = 1.2; 7.30 dt, 1 H, $^3J_{HH}$ = 7.6, $^4J_{HH}$ = 1.3; 7.35 dt, 1 H, $^3J_{HH}$ = 7.5, $^4J_{HH}$ = 1.2; 7.37 dt, 1 H, $^3J_{HH}$ = 7.5, $^4J_{HH}$ = 1.1; 7.66 dt, 1 H, $^3J_{HH}$ = 7.5, $^4J_{HH}$ = 1.1; 7.68 dd, 1 H, $^3J_{HH}$ = 7.0, $^4J_{HH}$ = 0.7; 7.85 dd, 1 H, $^3J_{HH}$ = 7.5, $^4J_{HH}$ = 0.8; 8.15 dd, 1 H, $^3J_{HH}$ = 7.7, $^4J_{HH}$ = 0.8. ^{13}C NMR: 119.6 s; 120.0 s; 121.3 d, $^2J_{CF}$ = 14; 123.4 s; 125.3 d, $^4J_{CF}$ = 15; 127.0 s; 127.8 s; 128.6 s; 128.7 s; 134.4 d, $^1J_{CF}$ = 288; 134.2 s; 136.2 s; 138.3 s; 140.5 s. ^{19}F NMR: –54.6 s. IR: 938 s, 1 200 s, 1 212 s, 1 442 s, 1 665 s, 3 080 m. For $C_{14}H_8BrF$ (275.1) calculated: 61.1% C, 2.9% H; found: 61.0% C, 2.7% H.

Ethyl Fluoro(2-^{13}C)acetate (**13**)

A flask topped by a Hickmann still was charged with ethyl bromo(2-^{13}C)acetate (**12**; 1.00 g, 5.95 mmol), anhydrous KF (689 mg, 11.9 mmol) and 18-crown-6 ether (162 mg, 0.61 mmol). The mixture was heated to 140 °C for 2 h, during which fluoro ester **13** (610 mg, 95.7%) was collected in the adapter.

Ethyl Fluoro(9-hydroxy-9*H*-fluoren-9-yl)(2-^{13}C)acetate (**14**)

A flask was charged with hexamethyldisilazane (0.33 g, 2.4 mmol) and THF (15 ml), and MeLi (1.45 ml, 1.5 mol l^{-1}, 2.18 mmol, mixture with LiBr) was added. After the gas evolution ceased (15 min), the mixture was cooled to –110 °C and HMPA (0.91 g, 5.0 mmol) was added followed by labeled fluoro ester **13** (180 mg, 1.68 mmol). The mixture was kept at –110 °C while stirred for 30 min and fluoren-9-one (**3**; 357 mg, 1.98 mmol) was added. The mixture was then stirred at –110 °C for 2 h, at –90 °C for 15 min and quenched at –90 °C with saturated aqueous NH_4Cl solution (1 ml). The mixture was then allowed to heat to room temperature and 30 ml of petroleum ether was added. This solution was extracted with water (5 × 25 ml) and dried with anhydrous $MgSO_4$. Solvents were removed on a vacuum rotary evaporator and pure fluoro ester **14** (225 mg, 46.6%) was obtained by column chromatography (SiO_2, column length 8 cm, diameter 1 cm, eluent CH_2Cl_2). ^{1}H NMR: 0.90 t, 3 H, $^3J_{HH}$ = 7.1; 3.34 dd, 1 H, *J* = 3.5, *J* = 1.1; 3.94 q, 2 H, $^3J_{HH}$ = 7.1; 5.29 dd, 1 H, $^1J_{HC}$ = 159.6, $^2J_{HF}$ = 48.4; 7.32 dt, 1 H, $^3J_{HH}$ = 7.5, $^4J_{HH}$ = 1.1; 7.33 dt, 1 H, $^3J_{HH}$ = 7.5, $^4J_{HH}$ = 1.1; 7.41 dt, 1 H, $^3J_{HH}$ = 7.5, $^4J_{HH}$ = 1.1; 7.57 d, 1 H, $^3J_{HH}$ = 7.5; 7.62 m, 3 H. ^{13}C NMR: 13.5 s; 61.5 s; 81.9 dd, $^1J_{CC}$ = 45, $^2J_{CF}$ = 20; 92.0 d (strong signal due to labeling), $^1J_{CF}$ = 195; 120.1 s; 120.1 s; 124.8 s; 125.1 s; 140.1 s; 140.3 s; 143.4 s; 143.6 s; 167.0 dd, $^1J_{CC}$ = 60, $^2J_{CF}$ = 20. ^{19}F NMR: –195.6 dd, $^1J_{CF}$ = 195, $^2J_{HF}$ = 48.

(9*H*-Fluoren-9-ylidene)fluoro(2-^{13}C)acetic Acid (**9b**)

A flask was charged with toluene (25 ml), 4-methylbenzene-1-sulfonic acid (14 mg, 74 μmol) and labeled fluoro ester **14** (215 mg, 0.75 mmol). The mixture was heated to reflux for 48 h and toluene was removed on a vacuum rotary evaporator. Ethyl (9*H*-fluoren-9-ylidene)-fluoro(2-^{13}C)acetate (**10b**; 164 mg) was obtained by column chromatography (SiO_2, column length 8 cm, diameter 1 cm, eluent petroleum ether–CH_2Cl_2 5 : 1) of the residue. Ester **10b** (164 mg, 0.61 mmol) was added to the mixture of THF (8 ml) and aqueous solution (8 ml) of NaOH (114 mg, 2.85 mmol), followed by stirring at room temperature for 12 h. THF was removed on a vacuum rotary evaporator. The obtained aqueous suspension of crude acid **9b** was extracted with Et_2O (4 × 20 ml), organic layers were combined and dried with anhy-

drous $MgSO_4$. Solvent was removed on a vacuum rotary evaporator to afford labeled fluoro acid **9b** (145 mg, 80.3%), which had identical properties and NMR spectra as unlabeled fluoro acid **9a** with the exception of two signals in ^{13}C NMR spectra: 147.9 d (strong signal due to labeling), $^1J_{CF}$ = 276; 162.4 dd, $^1J_{CC}$ = 85, $^2J_{CF}$ = 45, and the ^{19}F NMR signal: 107.4 d, $^1J_{CF}$ = 276.

Bromo(9*H*-fluoren-9-ylidene)fluoro(1-^{13}C)methane (**2b**)

A flask was charged with labeled fluoro acid **9b** (135 mg, 0.52 mmol), $CHCl_3$ (50 ml) and bromine (100 mg, 0.63 mmol), stoppered and the reaction mixture was stirred at room temperature for 8 h while irradiated with a infrared lamp. Evaporation of solvents by vacuum rotary evaporator afforded crude bromo(9-bromo-9*H*-fluoren-9-yl)fluoro(2-^{13}C)acetic acid (**11b**; 247 mg), which was added to the suspension of $NaHCO_3$ (82 mg, 0.98 mmol) in acetone (15 ml). The mixture was refluxed for 12 h, cooled to room temperature and solvent was removed on a vacuum rotary evaporator. Pure labeled bromofluoroethene (**2b**; 92 mg, 59.5%) was obtained by column chromatography (SiO_2, column length 8 cm, diameter 1 cm, eluent petroleum ether) of the residue. The product had identical physical properties and NMR spectra with the exception of one signal in the ^{13}C NMR spectra: 134.6 d (strong signal due to labeling), $^1J_{CF}$ = 331, and the ^{19}F NMR signal: –53.2 d, $^1J_{CF}$ = 332.

Formation of (9*H*-Fluoren-9-ylidene)fluoromethyllithium (**1a**) and Its Reaction with Electrophiles. General Procedure

A flask was charged with bromofluoroalkene **2a** (275 mg, 1.00 mmol) and THF (10 ml), cooled to –110 °C and BuLi solution in hexanes (1.10 mmol) was slowly (15 min) dropwise added. The mixture was stirred at –110 °C for 15 min forming (9*H*-fluoren-9-ylidene)-fluoromethyllithium (**1a**), followed by addition of an electrophile. The mixture was then stirred at –110 °C for 10 min, at 90 °C for 30 min and allowed slowly (2 h) to warm to room temperature The product was obtained after removal of a solvent on a vacuum rotary evaporator by column chromatography.

Reaction of Fluoroethenyllithium **1a** with Trifluoroacetic Acid

(9*H*-Fluoren-9-ylidene)fluoromethyllithium (**1a**), formed by reaction of **2a** with 2.28 M BuLi solution (0.44 ml), was quenched with a solution of trifluoroacetic acid (228 mg, 2.00 mmol) in THF (1 ml) affording after column chromatography (SiO_2, column length 8 cm, diameter 1.5 cm, eluent petroleum ether) *9-(fluoromethylidene)-9H-fluorene* (**15**; 148 mg, 75.5%, m.p. 58–62 °C; in ref.[24] not given).

Reaction of Fluoroethenyllithium **1a** with Deuteriotrifluoroacetic Acid

(9*H*-Fluoren-9-ylidene)fluoromethyllithium (**1a**), formed by reaction of **2a** with 2.28 M BuLi solution (0.44 ml), was quenched with a solution of deuteriotrifluoroacetic acid (230 mg, 2.00 mmol) in THF (1 ml) affording after column chromatography (SiO_2, column length 8 cm, diameter 1.5 cm, eluent petroleum ether) *9-[fluoro(²H-methylidene)]-9H-fluorene* (**16**; 167 mg, 84.7%, m.p. 63–65 °C). ^1H NMR: 7.23 dt, 1 H, $^3J_{HH}$ = 7.5, $^4J_{HH}$ = 1.2; 7.32 dt, 1 H, $^3J_{HH}$ = 7.4, $^4J_{HH}$ = 1.8; 7.32 tm, 1 H, $^3J_{HH}$ = 6.8; 7.36 dt, 1 H, $^3J_{HH}$ = 7.4, $^4J_{HH}$ = 1.3; 7.49 dd, 1 H, $^3J_{HH}$ = 7.6, $^4J_{HH}$ = 1.6; 7.68 dd, 1 H, $^3J_{HH}$ = 7.6, $^4J_{HH}$ = 1.8; 7.69 dd, 1 H, $^3J_{HH}$ = 7.2, $^4J_{HH}$ = 1.3;

7.96 dm, 1 H, $^3J_{HH}$ = 6.3. ^{13}C NMR: 119.8 s; 119.8 s; 120.2 s; 121.6 d, $^2J_{CF}$ = 8; 125.9 d, J_{CF} = 11; 127.0 s; 128.0 s; 128.5 s; 134.7 s; 136.0 d, $^3J_{CF}$ = 12; 139.4 s; 139.5 d, J_{CF} = 5; 147.6 dt, $^1J_{CF}$ = 277, $^1J_{CD}$ = 26. ^{19}F NMR: –126.3 t, $^2J_{DF}$ = 12. IR: 977 s, 1 065 s, 1 119 s, 1 177 s, 1 196 s, 1 231 s, 1 442 s, 1 473 s, 1 642 s, 1 662 s, 3 030 m, 3 080 s. For $C_{14}H_8DF$ (197.2) calculated: 85.3% C, 5.1% H + D; found: 85.0% C, 4.8% H + D.

Reaction of Fluoroethenyllithium **1a** with Methyl Iodide (**7**)

A flask was charged with bromofluoroethene **2a** (275 mg, 1.00 mmol), THF (10 ml), cooled to –110 °C while stirred and 2.28 M BuLi solution (0.48 ml) was dropwise added. After stirring at –110 °C for 45 min, methyl iodide (**7**; 284 mg, 2.00 mmol) dissolved in THF (1 ml) was dropwise added. The mixture was then stirred at –90 °C for 2 h and more methyl iodide (**7**; 150 mg, 1.06 mmol) was added, followed by 1 h stirring. More methyl iodide (**7**; 142 mg, 1.00 mmol) was added and the mixture stirred at –90 °C for 30 min, at –70 °C for 30 min and at –40 °C for 30 min. Then it was cooled to –90 °C and quenched by a solution of trifluoroacetic acid (250 mg, 2.17 mmol). After allowing the mixture to warm to room temperature, solvents were removed on a vacuum rotary evaporator and *9-(1-fluoroethylidene)-9H-fluorene* (**17**; 100 mg, 47.6%, m.p. 89–91 °C) was obtained by repeated column chromatography (SiO_2, first column length 6 cm, diameter 1.5 cm; second column length 25 cm, diameter 2.5 cm, eluent petroleum ether). ^{1}H NMR: 2.63 d, 3 H, $^3J_{HF}$ = 18.5; 7.33 m, 4 H; 7.60 d, 1 H, $^3J_{HH}$ = 8.0; 7.76 m, 2 H; 8.00 dd, 1 H, $^3J_{HH}$ = 5.6, $^4J_{HH}$ = 2.6. ^{13}C NMR: 18.4 d, $^2J_{CF}$ = 29; 117.9 d, $^2J_{CF}$ = 12; 119.4 s; 120.0 s; 122.7 s; 125.6 d, J_{CF} = 15; 126.8 s; 127.0 s; 127.3 s; 127.4 s; 136.1 d, J_{CF} = 12; 136.4 s; 138.1 s; 140.0 s; 159.7 d, $^1J_{CF}$ = 265. ^{19}F NMR: –74.4 q, $^3J_{HF}$ = 19. IR: 938 s, 1 200 s, 1 212 s, 1 442 s, 1 665 s, 3 080 m. For $C_{15}H_{11}F$ (210.3) calculated: 85.7% C, 5.3% H; found: 85.6% C, 5.1% H.

Reaction of Fluoroethenyllithium **1a** with Chloro(trimethyl)silane (**8**)

To the solution of (9*H*-fluoren-9-ylidene)fluoromethyllithium (**1a**), formed by reaction of **2a** with 2.28 M BuLi solution (0.48 ml) at –110 °C, chloro(trimethyl)silane (**8**; 130 mg, 1.20 mmol) in THF (1 ml) was dropwise added. The mixture was then stirred at –90 °C for 30 min and allowed to warm slowly to room temperature (2 h). Evaporation of solvents followed by repeated column chromatography (SiO_2, first column length 6 cm, diameter 1.5 cm; second column length 25 cm, diameter 2.5 cm, eluent petroleum ether) afforded *[(9H-fluoren-9-ylidene)fluoromethyl]trimethylsilane* (**18**; 107 mg, 39.9%, m.p. 60–64 °C). ^{1}H NMR: 0.49 s, 9 H; 7.16 t, 1 H, $^3J_{HH}$ = 7.6; 7.33 m, 3 H; 7.63 d, 1 H, $^3J_{HH}$ = 7.7; 7.71 m, 2 H; 8.13 d, 1 H, $^3J_{HH}$ = 7.5. ^{13}C NMR: –1.6 d, $^3J_{CF}$ = 4; 119.3 s; 120.0 s; 123.3 s; 126.4 s; 127.3 d, J_{CF} = 18; 127.6 s; 127.7 s; 128.2 s; 132.6 d, $^2J_{CF}$ = 7; 136.0 d, J_{CF} = 15; 136.5 s; 138.7 s; 140.3 s; 173.2 d, $^1J_{CF}$ = 297. ^{19}F NMR: –94.0 bs. IR: 865 s, 931 s, 1 077 s, 1 254 s, 1 442 s, 1 473 m, 1 592 m, 1 612 m, 1 712 m, 2 910 m, 2 970 m, 3 060 m. For $C_{17}H_{17}FSi$ (268.4) calculated: 76.1% C, 6.4% H; found: 76.3% C, 6.3% H.

Reaction of Fluoroethenyllithium **1a** with Benzaldehyde (**6**)

To the solution of (9*H*-fluoren-9-ylidene)fluoromethyllithium (**1a**), formed by reaction of **2a** with 1.98 M BuLi solution (0.51 ml) at –110 °C, benzaldehyde (**6**; 106 mg, 1.00 mmol) in THF (1 ml) was dropwise added. The mixture was then stirred at –90 °C for 30 min and allowed to warm slowly to room temperature (2 h). Evaporation of solvents followed by col-

umn chromatography (SiO_2, column length 6 cm, diameter 1.5 cm, eluent petroleum ether–dichloromethane 4 : 1) afforded *2-(9H-fluoren-9-ylidene)-2-fluoro-1-phenylethanol* (**19**; 178 mg, 58.9%, m.p. 98–104 °C). ^{1}H NMR: 2.76 d, 1 H, $^3J_{HH}$ = 6.8; 6.40 dd, 1 H, $^3J_{HH}$ = 6.4, $^3J_{HF}$ = 25.3; 7.26 dt, 1 H, $^3J_{HH}$ = 7.7, $^4J_{HH}$ = 1.2; 7.30 dt, $^3J_{HH}$ = 7.5, $^4J_{HH}$ = 1.3; 7.32 dt, 1 H, $^3J_{HH}$ = 7.7, $^4J_{HH}$ = 1.2; 7.32 dt, 1 H, $^3J_{HH}$ = 7.4, $^4J_{HH}$ = 1.4; 7.36 m, 4 H; 7.56 d, 2 H, $^3J_{HH}$ = 7.3; 7.66 d, 1 H, $^3J_{HH}$ = 7.8; 7.72 d, 1 H, $^3J_{HH}$ = 7.5; 7.76 d, 1 H, $^3J_{HH}$ = 7.6; 8.01 d, 1 H, $^3J_{HH}$ = 7.7. ^{13}C NMR: 70.6 d, $^2J_{CF}$ = 26; 119.5 d, $^3J_{CF}$ = 15; 119.5 s; 120.3 s; 126.3 d, $^4J_{CF}$ = 17; 126.3 s; 127.3 s; 127.8 s; 128.2 s; 128.4 d, J_{CF} = 2; 128.6 s; 128.8 s; 134.7 d, $^2J_{CF}$ = 11; 136.2 s; 138.4 s; 139.0 s; 140.7 ; 159.1 d, $^1J_{CF}$ = 275. ^{19}F NMR: –108.0 d, $^3J_{HF}$ = 26. IR: 942 s, 1027 s, 1 173 s, 1 219 s, 1 442 s, 1 473 m, 1 488 m, 1 542 s, 1 658 s, 2 940 m, 3 050 m, 3 070 m, 3 450 m, 3 610 m. For $C_{21}H_{15}FO$ (302.4) calculated: 83.4% C, 5.0% H; found: 83.2% C, 5.0% H.

Reaction of Fluoroethenyllithium **1a** with Tributyl(chloro)stannane (**20**)

To the solution of (9*H*-fluoren-9-ylidene)fluoromethyllithium (**1a**), formed by reaction of **2a** with 1.85 M BuLi solution (0.57 ml) at –110 °C, tributyl(chloro)stannane (**20**; 395 mg, 1.21 mmol) in THF (1 ml) was dropwise added. The mixture was stirred at –90 °C for 1 h and at –70 °C for 1 h and then allowed to warm slowly to room temperature (2 h). Evaporation of solvents followed by repeated column chromatography (SiO_2, first column length 6 cm, diameter 1.5 cm; second column length 25 cm, diameter 2.5 cm, eluent petroleum ether) afforded *tributyl[(9H-fluoren-9-ylidene)fluoromethyl]stannane* (**21**; 231 mg, 47.6%). ^{1}H NMR: 0.89 t, 9 H, $^3J_{HH}$ = 7.3; 1.29 m, 6 H; 1.36 sextet, 6 H, $^3J_{HH}$ = 7.4; 1.62 m, 6 H; 7.24 dt, 1 H, $^3J_{HH}$ = 7.4, $^4J_{HH}$ = 1.6; 7.33 t, 1 H, $^3J_{HH}$ = 6.9; 7.34 t, 1 H, $^3J_{HH}$ = 7.3; 7.49 d, 1 H, $^3J_{HH}$ = 7.7; 7.73 dd, $^3J_{HH}$ = 7.5, $^4J_{HH}$ = 0.9; 7.74 dd, 1 H, $^3J_{HH}$ = 7.5, $^4J_{HH}$ = 0.9; 8.14 d, 1 H, $^3J_{HH}$ = 7.1. ^{13}C NMR: 10.9 s; 13.6 s; 27.2 s; 28.9 s; 119.3 s; 120.0 s; 120.5 s; 126.2 s; 126.7 d, J_{CF} = 16; 127.2 s; 127.5 s; 127.7 s; 133.5 d, J_{CF} = 3; 135.8 d, J_{CF} = 6; 137.3 d, $^2J_{CF}$ = 17; 138.1 s; 139.8 d, J_{CF} = 4; 181.0 d, $^1J_{CF}$ = 334. ^{19}F NMR: –82.0 s. IR: 931 s, 1 035 s, 1 046 s, 1 442 s, 1 461 s, 1 592 s, 1 608 s, 2 860 s, 2 920 s, 2 970 s, 3 060 m. For $C_{26}H_{35}FSn$ (485.3) calculated: 64.4% C, 7.3% H; found: 64.6% C, 7.5% H.

Reaction of Fluoroethenyllithium **1a** with Trifluoroacetic Anhydride (**22**)

To the solution of (9*H*-fluoren-9-ylidene)fluoromethyllithium (**1a**), formed by reaction of **2a** with 1.85 M BuLi solution (0.57 ml) at –110 °C, trifluoroacetic anhydride (**22**; 252 mg, 1.20 mmol) in THF (1 ml) was dropwise added. The mixture was stirred at –90 °C for 1 h and then allowed to warm slowly to room temperature (2 h). Evaporation of solvents followed by column chromatography (SiO_2, column length 6 cm, diameter 1.5 cm, eluent petroleum ether, then petroleum ether–CH_2Cl_2, finally CH_2Cl_2) afforded *1,3-di(9H-fluoren-9-ylidene)-1,3-difluoro-2-(trifluoromethyl)propan-2-ol* (**23**; 130 mg, 53.3%, m.p. 190–194 °C). ^{1}H NMR: 4.60 s, 1 H; 7.06 dt, 2 H, $^3J_{HH}$ = 7.7, $^4J_{HH}$ = 1.2; 7.25 t, 2 H, $^3J_{HH}$ = 7.5; 7.28 dt, 2 H, $^3J_{HH}$ = 7.7, $^4J_{HH}$ = 1.1; 7.35 dt, 2 H, $^3J_{HH}$ = 7.5, $^4J_{HH}$ = 1.0; 7.61 d, 2 H, $^3J_{HH}$ = 7.5; 7.63 d, 2 H, $^3J_{HH}$ = 7.0; 8.01 d, 2 H, $^3J_{HH}$ = 7.7; 8.16 d, 2 H, $^3J_{HH}$ = 8.0. ^{13}C NMR: 79.0 sextet, $^2J_{CF}$ = 28; 119.4 s; 119.6 s; 124.1 q, $^1J_{CF}$ = 285; 125.1 d, J_{CF} = 16; 127.0 s; 127.3 s; 127.6 s; 128.0 s; 129.0 d, J_{CF} = 2; 129.3 s; 132.9 d, J_{CF} = 9; 136.2 s; 139.5 s; 141.2 d, J_{CF} = 4; 152.3 d, $^1J_{CF}$ = 273. ^{19}F NMR: –76.1 t, 3 F, $^4J_{FF}$ = 14; –97.8 q, 2 F, $^4J_{FF}$ = 14. IR: 1 104 s, 1 119 s, 1 150 s, 1 208 s, 1 258 s, 1 450 s, 1 473 m, 1 596 m, 1 642 m, 3 470 m. For $C_{30}H_{17}F_5O$ (488.5) calculated: 73.8% C, 3.5% H; found: 72.6% C, 3.4% H.

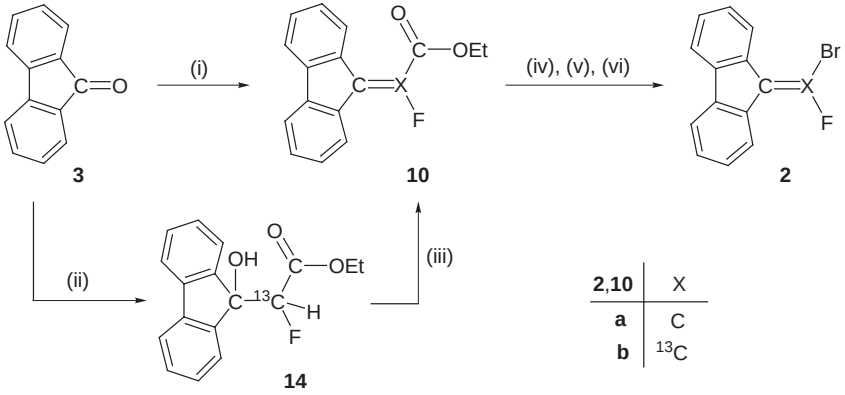
NMR Observations of Fluoroethenyllithium **1**

A Wilmad narrow-mouth NMR tube was charged with bromofluoroalkene **2** (13.8 mg, 50 μmol) and closed with a Wilmad Omnivalve adapter. THF (0.5 ml) and THF-d_8 (dried, 150 μl) were syringed to the tube, the tube was shaken and cooled to –110 °C. BuLi (65 μl) was carefully syringed to the tube and the tube was alternatively cooled and quickly several times reverted to mix the components while preventing overheating of the reaction mixture. When homogenization was achieved, the NMR observations were started.

RESULTS AND DISCUSSION

*Preparation of Bromo(9H-fluoren-9-ylidene)fluoromethane (**2a**)*

Bromo(9*H*-fluoren-9-ylidene)fluoromethane (**2a**) was originally prepared by reaction of 9-diazo-9*H*-fluorene with bromofluorocarbene[22]. We preferred a methodology developed by Eddarir and coworkers[23], which employed the Wittig–Horner reaction of lithium salt of ethyl (diethoxyphosphoryl)fluoroacetate (**4**) with fluoren-9-one (**3**) to form substituted fluoropropenoate **10a**, which on bromination followed by debromodecarboxylation afforded the target bromofluoroalkene **2a** (Scheme 1). What makes the procedure used attractive is that only the final product has to be purified and all previous steps can be performed with crude reaction products.



(i) $(EtO)_2POCHFCO_2Et$ (**4**), BuLi, THF, -30 °C, 30 min; (ii) $^{13}CH_2FCO_2Et$ (**13**), HMDS, MeLi, LiBr,THF, HMPA, -110 °C, 2 h; (iii) TsOH, toluene, reflux, 48 h; (iv) NaOH, dioxane or THF, r.t., 24 h, then HCl; (v) Br_2, $CHCl_3$, irradiation, r.t., 6 h; (vi) $NaHCO_3$, acetone, reflux, 16 h

SCHEME 1

*Preparation of Bromo(9H-fluoren-9-ylidene)fluoro(^{13}C)methane (**2**)*

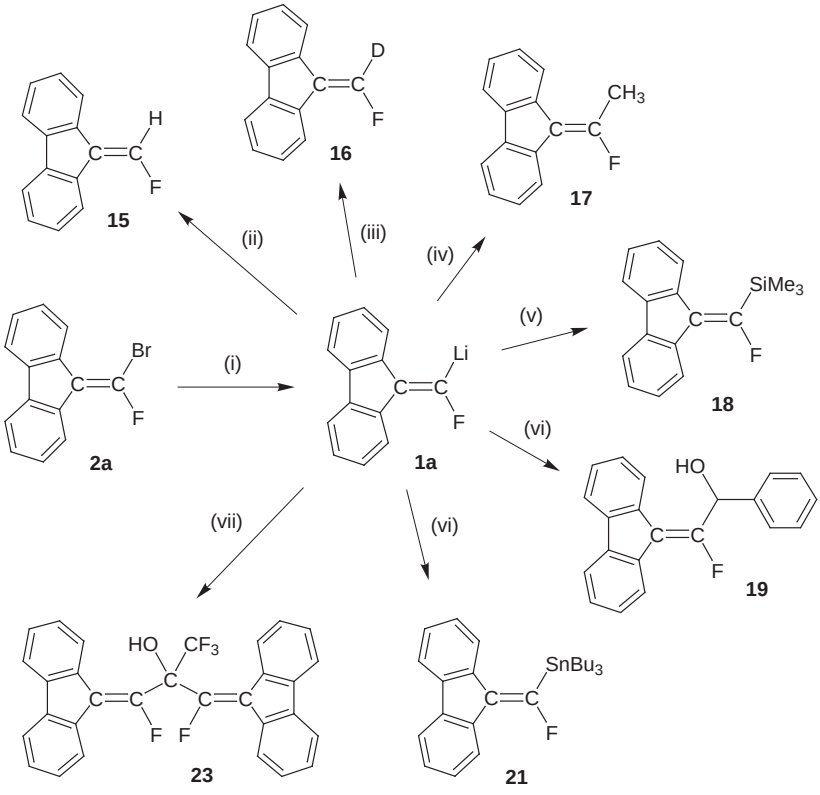
Due to low intensity of signals, large half-line width and splitting of carbon atom by fluorine and lithium atoms, low-temperature ^{13}C NMR spectra of fluorocarbenoids has to be taken with ^{13}C labeled compounds. Neither labeled dibromofluoromethane, nor labeled ethyl (diethoxyphosphoryl)-fluoroacetate (**4**) are easily accessible compounds and we hence had to found another reaction pathway. Fortunately, labeled ethyl bromo-(2-^{13}C)acetate (**12**) is commercially available and can be easily converted to the corresponding labeled fluoro ester **13** (ref.[24]). Directed aldol condensation of lithium 1-ethoxy-2-fluoro(2-^{13}C)ethen-1-olate (**5**) with various ketones has been published[25]. We obtained excellent yield of labeled fluoroacetate **13** by fluorination with anhydrous potassium fluoride under PTC conditions (18-crown-6 ether) without any solvent. Directed aldol condensation of the fluoroenolate **5** with fluoren-9-one (**3**) under sligthly modified conditions afforded labeled fluoro(hydroxy)propanoate **14**, which was dehydrated under mild conditions to labeled fluoropropenoate **10b** and, in analogy to unlabeled ester **10a**, further transformed to labeled bromofluoroethene **2b**.

*Formation of (9H-Fluoren-9-ylidene)fluoromethyllithium (**1a**) and Its Reaction with Electrophiles*

We prepared fluorocarbenoid **1a** by lithium–halogen exchange with BuLi in THF at –110 °C. We decided for this way for two reasons. First, lithium–halogen exchange is more rapid and selective than lithiation of a carbon–hydrogen bond[1], second, nonbrominated analog **15** of bromofluoroethene **2a** is not long stable and tends to polymerize spontaneously. The formation of fluorocarbenoid **1a** has to be performed slowly, as the mixture is highly sensitive to overheating followed by decomposition of flluorocarbenoid **1a**.

The *in situ* preformed fluorocarbenoid was reacted with a series of electrophiles to find scope and limitations of its use (Scheme 2). In most cases, the reactions with electrophiles were performed at –90 °C. Tributyl(chloro)stannane (**20**) had to be reacted at slightly higher temperature, –70 °C, to complete the conversion. The less reactive electrophile successfully used was methyl iodide (**7**). To obtain acceptable yields, still higher temperature (–40 °C) and a large excess of electrophile **7** had to be employed. Moreover, the reaction mixture had to be acidified with trifluoroacetic acid before work-up. The reaction with trifluoroacetic anhydride (**22**) afforded mostly the 2 : 1 product, fluorinated diol **23**, and only traces of trifluoromethyl

ketone were identified in the crude reaction mixture even if large excess of fluoro anhydride **23** was applied. Attempts to react fluorocarbenoid **1a** with benzyl bromide or benzyl iodide failed completely.



(i) BuLi, THF, -110 °C, 30 min; (ii) CF_3COOH, THF, -110 °C, 5 min; (iii) CF_3COOD, THF, -110 °C, 5 min; (iv) CH_3I (**7**), THF, -70 to -40 °C, 1 h, then CF_3COOH; (v) Me_3SiCl (**8**), THF, -90 °C, 30 min; (vi) PhCHO (**6**), THF, -90 °C, 30 min; Bu_3SnCl (**20**), THF, -70 °C, 30 min; (vii) $(CF_3CO)_2O$ (**22**), THF, -90 °C, 30 min.

SCHEME 2

*NMR Observations of Fluoroethenyllithium **1***

After preparing fluorocarbenoid **1a** in the NMR tube at –110 °C, we gradually rose the ^{19}F NMR observation temperature to find the limits of the temperature stability of fluorocarbenoid **1a**. Whereas no change was observed at –40 °C, at –30 °C fluorocarbenoid **1a** slowly started to decompose with a

half-life of 12 h. The decomposition was reasonably faster at –20 °C (half-life 0.8 h). When two-fold molar excess of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) was added to the reaction mixture, two signals could be observed at –110 °C (Fig. 1). The first one, at –40.6 ppm, corresponds to the signal of fluorocarbenoid **1a** from experiment without TMEDA addition which is coordinated according to calculations[26] to three molecules of THF. The second one, at –38.9 ppm, arises probably from coordination to one molecule of TMEDA and one of THF in agreement with published[16] X-ray of substituted chloroethenyllithium. Both signals coalesce at –70 °C.

In ^{13}C NMR spectra of labeled fluorocarbenoid **1b**, broad doublet (188.8 ppm) of the ^{13}C-1 carbon arising from the carbon-fluorine coupling could be observed at –70 °C. Its half-line width grew as the temperature was lowered to –90 °C and finally the signal was splitted to a doublet of quartet at –110 °C as a result of carbon–lithium coupling (Fig. 1). This is in agreement with ^{13}C NMR spectra of other halocarbenoids observed by Seebach and coworkers[15] and shows that fluorocarbenoid **1b** forms either solvated monomer in solution as is supported by the X-ray of analogous chlorocarbenoid[16], or a dimer with a C–F–Li–C linkage, which was computed[17] to be the preferred structure for fluoromethyllithium.

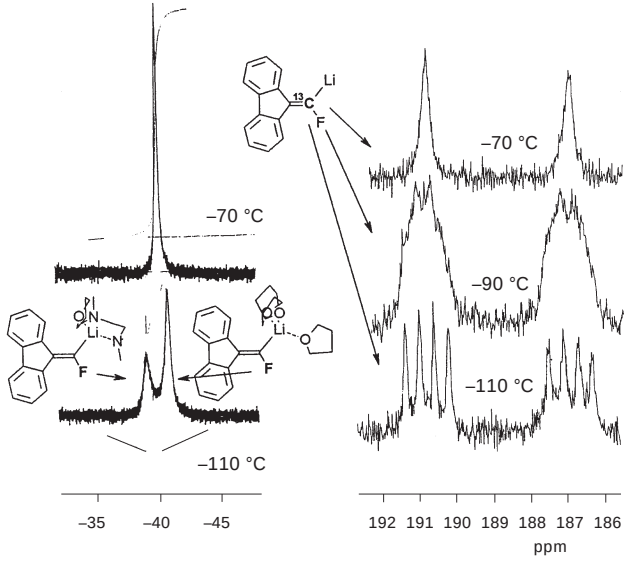


FIG. 1
^{19}F and ^{13}C NMR spectra of (9*H*-fluoren-9-ylidene)fluoromethyllithium (**1a**)

We thus synthesized the first fluorocarbenoid which is not stabilized by heteroatom. We for the first time observed low-temperature ^{13}C and ^{19}F NMR spectra of fluorocarbenoid with the aim to find limits of its stability and the level of aggregation in solution. We also studied its reactivity with the aim to find scope and limitations of its use.

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