Electronic Supplementary Material (ESI) for Chemical Communications

Supplementary Information

Metal Free and Selective Activation of one C–F Bond in a Bound CF_3 Group

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EXPERIMENTAL SECTION

Syntheses were carried out under an inert gas atmosphere of dinitrogen in oven dried glassware using standard Schlenk techniques and other manipulations were accomplished in a dinitrogen filled glove box. Solvents were purified by MBRAUN solvent purification system MB SPS-800. All chemicals were purchased from Aldrich and used without further purification. Compounds **1** and **2** were prepared as reported in the literature.[S1,S2] ^{1}H, ^{19}F, and ^{29}Si NMR spectra were recorded with a Bruker Avance DPX 300, or a Bruker Avance DRX 500 spectrometer, using C_6D_6 as solvent. Chemical shifts δ are given relative to $SiMe_4$. EI-MS spectra were obtained using a Finnigan MAT 8230 instrument. Elemental analyses were performed by the Institut für Anorganische Chemie, Universität Göttingen.

Synthesis of 3. Toluene (30 mL) was added to a 100 mL Schlenk flask containing **1** (0.35 g, 1.19 mmol) and to this was added PhN=C(CF$_3$)$_2$ (0.29 g, 1.20 mmol) in toluene (30 mL) at room temperature. The reaction mixture was stirred for 6 h. Then it was filtered and the solvent was removed *in vacuo* to 10 mL and stored at –26 ºC in a freezer to obtain colorless crystals of **3** (0.51 g, 80%). Elemental analysis (%) calcd for $C_{24}H_{28}ClF_6N_3Si$ (536.03): C, 53.78; H, 5.27; N, 7.84. Found: C, 53.72; H, 5.21; N, 7.78. ^{1}H NMR (500 MHz, C_6D_6, 25 °C): δ 0.79 (s, 9H, C(C*H*$_3$)$_3$), 1.15 (s, 9H, C(C*H*$_3$)$_3$), 6.83–7.31 (m, Ar) ppm; ^{19}F{^{1}H} NMR (282.40 MHz, C_6D_6, 25 °C): δ –60.81 to –60.95 (m, 3F, C*F*$_3$), –72.89 (b, 1F, Si*F*), –83.60 to –83.78 (m, 1F, C*F*$_2$),–84.52 to –84.73 (m, 1F, C*F*$_2$) ppm; ^{29}Si{^{1}H} NMR (59.63 MHz, C_6D_6, 25 °C): δ –106.9 ppm (J_{SiF} = 251 Hz). EI-MS: *m/z*: 516 [M$^+$–F].

Synthesis of 4. Hexane (30 mL) was added to a 100 mL Schlenk flask containing **2** (0.26 g, 0.58 mmol) and to this was added PhN=C(CF$_3$)$_2$ (0.14 g, 0.58 mmol) in hexane (30 mL) at room temperature. The reaction mixture was stirred for 6 h. Then it was filtered and the solvent was reduced *in vacuo* to 20 mL and stored at –26 ºC in a freezer to obtain colorless crystals of **4** (0.33 g, 83%). Elemental analysis (%) calcd for $C_{38}H_{45}F_6N_3Si$ (685.86): C,

66.55; H, 6.61; N, 6.13. Found: C, 66.52; H, 6.53; N, 6.97. ^{1}H NMR (500 MHz, C_6D_6, 25 °C): δ 1.08–1.12 (m, 9H, CH(CH_3)$_2$), 1.15 (d, 6H, J = 7 Hz, CH(CH_3)$_2$), 1.19 (d, 3H, J = 7 Hz, CH(CH_3)$_2$),1.27 (d, 3H, J = 7 Hz, CH(CH_3)$_2$), 1.40 (b, 3H, CH(CH_3)$_2$), 1.49 (s, 3H, NCCH_3), 3.25 (m, 2H, CH(CH$_3$)$_2$), 3.37 (s, 1H, NCCH_2), 3.59 (m, 2H, CH(CH$_3$)$_2$), 4.01 (s, 1H, NCCH_2), 5.40 (s, 1H, γ – CH), 6.72–7.13 (m, 11 H, C_6H_5, 2 x *i*Pr$_2$C$_6H_3$) ppm.^{19}F{^{1}H} NMR (282.40 MHz, C_6D_6, 25 °C): δ –62.08 to –62.51 (m, 3F, CF_3), –77.19 to –77.34 (m, 1F, CF_2), –80.51 to –80.93 (m, 1F, CF_2), –137.35 (s, 1F, SiF) ppm; ^{29}Si{^{1}H} NMR (99.36 MHz, C_6D_6, 25 °C): δ –65.1 ppm (J_{SiF} = 286 Hz). EI-MS: *m/z*: 685 [M$^+$].

Crystal Structure Determination. Suitable single crystals for X-ray structural analysis of **3** and **4** were mounted at low temperature in an inert oil under argon atmosphere by applying the X-Temp2 device.[S3] The diffraction data for **3** was collected at 100 K on a Bruker D8 three circle diffractometer equipped with a SMART APEX II CCD detector and a rotating anode with INCOATEC Quazar mirror optics (λ = 0.71073 Å). The diffraction data for **4** was collected at 100 K on a Bruker D8 three circle diffractometer equipped with a SMART APEX II CCD detector and an INCOATEC Mo microsource with INCOATEC Quazar mirror optics (λ = 0.71073 Å). The data were integrated with SAINT[S4] and an empirical absorption correction with SADABS[S5] was applied. The structures were solved by direct methods (SHELXS-97) and refined against all data by full-matrix least-squares methods on F^2 (SHELXL-97).[S6] All non-hydrogen-atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined isotropically on calculated positions using a riding model with their U_{iso} values constrained to 1.5 U_{eq} of their pivot atoms for terminal sp^3 carbon atoms and 1.2 times for all other carbon atoms. The disordered groups in **4** are refined with distance restraints and restraints for the anisotropic displacement parameters.

Table 1. Crystal and Structure Refinement parameters for compounds **3** and **4**.

Parameters	**3**	**4**
Empirical formula	$C_{24}H_{28}ClF_6N_3Si$	$C_{38}H_{45}F_6N_3Si$
Formula Weight	536.03	685.86
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/n$	*Pnma*
Unit cell dimensions	a = 10.617 (2) Å	a = 16.937 (6) Å
	b = 16.479 (3) Å	b = 20.574 (6) Å
	c = 14.578 (2) Å	c = 10.082 (4) Å
	β = 93.59 (2)°	
Volume, Z	2545.5 (8) $Å^3$, 4	3513 (2) $Å^3$, 4
Density (Calculated)	1.399 g/cm^3	1.297g/cm^3
Absorption coefficient	0.259 mm^{-1}	0.130 mm^{-1}
F (000)	1112	1448
Crystal size [mm^3]	0.10 x 0.10 x 0.05	0.02 x 0.02 x 0.01
θ range for data collection	1.87 to 25.36°	1.98 to 21.27°
Limiting indices	$-12\le h\le 12$,	$-17\le h\le 17$,
	$-19\le k\le 19$,	$-20\le k\le 20$,
	$-17\le l\le 17$	$-10\le l\le 10$
Reflections collected	18144	15989
Independent reflections	4661 (R_{int} = 0.0441)	2024 (R_{int} = 0.0505)
Completeness to θ	100% (θ = 25.36)	99.9% (θ = 21.27)
Refinement method	Full - matrix least - squares on F^2	Full - matrix least - squares on F^2
Data/ restraints/ parameters	4661 / 0 / 322	2024 / 176 / 288
Goodness - of - fit on F^2	1.042	1.055
Final R indices [$I>2\sigma(I)$]	$R1$ = 0.0399, $wR2$ = 0.0839	$R1$ = 0.0388, w$R2$ = 0.0902
R indices (all data)	$R1$ = 0.0652, $wR2$ = 0.0904	$R1$ = 0.0548, $wR2$ = 0.0971
g_1, g_2	0.0413, 0.4441	0.0447, 2.8243
Largest diff. peak and hole	0.251 and –0.311 $eÅ^{-3}$	0.204 and –0.229 $eÅ^{-3}$

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