Supporting Information
© Wiley-VCH 2007
69451 Weinheim, Germany
Supporting Information

for

Catalytic C–F Activation of Hexafluoropropene at Rhodium:

Formation of (3,3,3-Trifluoropropyl)silanes.**

Thomas Braun*, Falk Wehmeier and Kai Altenhöner
Experimental Section

All solvents were purified and dried by conventional methods and distilled under argon before use. Benzene-$d_6$ was dried by stirring over potassium and then distilled under vacuum. The silanes were obtained from Aldrich and ABCR and have been crystallized or distilled before use. Hexafluoropropene was obtained from Lancaster. [RhH(PEt$_3$)$_3$] (1a), [RhH(PEt$_3$)$_4$] (1b) and [Rh{(Z)-CF=CF(CF$_3$)}(PEt$_3$)$_3$] (2) were prepared according to the literature.$^{[1,2]}$

The NMR spectra were recorded with a Bruker DRX 500 spectrometer. The $^1$H NMR chemical shifts were referenced to residual C$_6$D$_5$H at $\delta$ 7.15. The $^{19}$F NMR spectra were referenced to external C$_6$F$_6$ at $\delta$ –162.9 ppm. The $^{31}$P{$^1$H} NMR spectra were referenced externally to H$_3$PO$_4$ at $\delta$ 0 ppm; the $^{29}$Si{$^1$H} NMR spectrum to TMS.

Formation of 4a: A solution of [Rh{(Z)-CF=CF(CF$_3$)}(PEt$_3$)$_3$] (2) (50 mg, 0.26 mmol) in benzene (10 mL) was treated with Ph$_3$SiH (90 mg, 0.35 mmol). The solution was stirred for 20 h at room temperature and the volatiles were then removed under vacuum. NMR spectroscopic data of the residue reveal the presence of triphenylfluorosilane as well as of 2 and Ph$_3$SiCH$_2$CH$_2$CF$_3$ (4a) (ratio: 2:1). Addition of an excess Ph$_3$SiH leads to a full consumption of 2 and gives additionally rise to the formation of complex cis-fac-[Rh(H)$_2$(SiPh$_3$)(PEt$_3$)$_3$] (5)$^{[3]}$.

Catalytic experiments for the formation of 4a – 4e from hexafluoropropene. In a typical catalytic experiment, a solution of 2 (20 mg, 34 µmol) in benzene (10 mL) was analyzed by $^{19}$F NMR spectroscopy using 4-fluorotoluene as external standard to determine the exact concentration of 2 in situ. Hexafluoropropene was bubbled carefully though the solution for 3 min. Then the tertiary silane (5.1 mmol) was added. In one case additional amounts of Et$_3$N (0.2 g, 1.98 mmol) and Cs$_2$CO$_3$ (0.6 g 1.84 mmol) were also added (see Table 1, entry 7). The mixture was stirred for 20 h at room temperature and again analyzed by NMR spectroscopy using the same external standard to
determine the turnover number for the formation of the (3,3,3-trifluoropropyl)silane. The solution was then filtered over silica and the silica gel was washed with hexane. The filtrate was analyzed by GC/MS. Each filtrate contained R₃SiCH₂CH₂CF₃ (4a: R₃ = Ph₃, 4b: R₃ = Ph₂Me, 4c: R₃ = PhMe₂, 4d: R₃ = Et₃, 4e: R₃ = (OMe)₃) and the corresponding fluorosilane R₃SiF, only. The solvent was then removed from the filtrate in vacuo. Pure samples can be obtained by washing the residue with hexane (5 mL) to give a colorless solid (4a, 4b). 4c - 4e have been obtained as colorless oils, which can purified by distillation. Analytical data: 4a: ¹H NMR (C₆D₆, 500 MHz): δ = 1.57 (m, 2 H, SiCH₂), 2.13 (m, 2 H, CH₂CF₃), 7.11-7.69 (m, 15 H, Ph) ppm; ¹⁹F NMR (C₆D₆, 470 MHz): δ = −67.3 (t, CF₃, 3 J(HF) = 11 Hz) ppm; ²⁹Si NMR (C₆D₆, 99 MHz) δ = −10.8 ppm. MS (EI, m/z): 356 (M⁺), 279 (Ph₃SiHF⁺), 259 (Ph₂Si⁺). Elemental analysis calcd. (%) for C₂₁H₁₉F₃Si: C 70.76, H 5.37; Found: C 71.32, H 5.87. 4b: ¹H NMR (C₆D₆, 500 MHz): δ = 0.46 (s, 3 H, CH₃), 1.03 (m, 2 H, SiCH₂), 1.74 (m, 2 H, CH₂CF₃), 7.02-7.52 (m, 10 H, Ph) ppm; ¹⁹F NMR (C₆D₆, 470 MHz): δ = −67.4 (t, CF₃, 3 J(HF) = 10 Hz) ppm; MS (EI, m/z): 217 (Ph₂MeSiHF⁺), 197 (Ph₂MeSi⁺). Elemental analysis calcd. (%) for C₁₆H₁₇F₃Si: C 65.28, H 5.82; Found: C 65.88, H 5.87. Compound 4e has been identified by comparison of NMR and MS data with these of an authentic sample; 4c and 4d have been described before and have also been identified by their NMR and MS data.³

Parts of the simulated ¹H NMR (δ in ppm) spectra of 4a:
**Figure S1:** part of the $^1$H NMR spectrum of complex 4a; simulated (below) and observed (above) using the following coupling constants: $J(H^aH^a') = J(H^bH^b') = -13.9$, $J(H^aH^b) = J(H^aH^b') = 13.8$, $J(H^a'H^b) = J(H^a'H^b') = 3.9$, $(H^bX) = J(H^bX) = 10.7$ Hz

**Catalytic formation of 4a hexafluoropropene in the presence of hydrogen.** Dihydrogen was bubbled into a suspension of Ph$_3$SiH (0.95 g, 3.65 mmol), Et$_3$N (0.5 g, 4.94 mmol) and Cs$_2$CO$_3$ (1.5 g, 4.60 mmol) in benzene (3 mL) for 3 minutes. A solution of 2 (20 mg, 34 µmol) in benzene (3 mL) was analyzed by $^{19}$F NMR spectroscopy using 4-fluorotoluene as external standard to determine the exact concentration of 2 *in situ*. Hexafluoropropene was then bubbled carefully through this solution for 3 min. The solution of 2 and hexafluoropropene was then added to the mixture of Ph$_3$SiH, Et$_3$N and Cs$_2$CO$_3$ and the reaction vessel was purged with hydrogen (1 atm). The mixture was stirred for 20 h at room temperature and again analyzed by NMR spectroscopy using the same external standard to determine the turn over number for the formation of the 4a. The solution was then filtered over silica and the silica gel was washed with hexane. The filtrate was analyzed by GC/MS.

**Synthesis of cis-fac-[Rh(H)$_2$(Si(OMe)$_3$)(PEt$_3$)$_3$] (6).** (a) A solution of [Rh{(Z)-CF=CFCF$_3$}(PEt$_3$)$_3$] (2) (180 mg, 0.31 mmol) in benzene (5 mL) was treated with HSi(OMe)$_3$ (180 µl, 1.50 mmol). The NMR spectroscopic data of the reaction mixture reveal the formation of 4e and 6. (b) [RhH(PEt$_3$)$_3$] (1a) (140 mg, 0.24 mmol) was dissolved in benzene (5 mL), and HSi(OMe)$_3$ (30 µl, 0.25 mmol) was added. The red solution went immediately colorless. The reaction mixture was then stirred for 30 min at room temperature and the volatiles were removed under vacuum. The remaining pink solid was suspended in hexane (10 mL) and the suspension was filtered through a cannula. The filtrate was brought to dryness to give a light yellow powder, which loses HSi(OMe)$_3$ *in vacuo*. Yield 100 mg (72%). Analytical data for 6: IR (n-hexane): $\tilde{\nu} = 2063, 1955$ cm$^{-1}$ (Rh-H). $^1$H NMR (C$_6$D$_6$, 500 MHz): $\delta = -11.34$ (m, see Figure S2), 0.98 (m, 9 H, P$^b$CH$_2$CH$_3$), 1.05 (m, 18
H, P(CH₂CH₃), 1.20 (m, 6 H, P(CH₂CH₃)), 1.44 (m, 12 H, P(CH₂CH₃)), 3.80 (s, 9 H, Si(OMe)₃) ppm.

³¹P NMR (202 MHz): δ = 5.9 (dt, ¹J(RhP) = 85.1, ²J(PbP) = 23.8 Hz, Pb), 15.1 (dd, ¹J(RhP) = 101.6, ²J(PbP) = 23.8 Hz, Pb) ppm.

**Figure S2:** ¹H NMR spectrum (hydride region) of complex 6; computed (below) and observed (above) using the following coupling constants: ¹J(RhH) = ¹J(RhH') = 18.1, ²J(PaH) = ²J(Pa'H') = −130.5, ²J(PaH) = ²J(Pa'H) = 22.5, ²J(PbH) = ²J(Pb'H) = 18.2, ²J(HH') = 32.4 Hz.

**Catalytic hydrosilylation of 3,3,3-trifluoropropene with Ph₃SiH.**

A solution of [RhH(PEt₃)₄] (1b) (40 mg, 0.07 mmol) in C₆D₆ (6 mL) was analyzed by ¹H NMR spectroscopy using 4-fluorotoluene as external standard to determine the exact concentration of 1b in situ. After adding Ph₃SiH (2.7 g, 10.7 mmol), 3,3,3-trifluoropropene was bubbled carefully though the solution for 5 min. The mixture was stirred for 6 h at room temperature and again analyzed by ¹⁹F NMR spectroscopy using the same external standard to determine a turn over number for the formation of the (3,3,3-trifluoropropyl)triphenylsilane. The data reveal that the reaction was quantitative with a TON = 138. The solution was then filtered over silica and the filtrate was brought to dryness. The residue was washed with hexane (3 mL) to give a colorless solid. Yield 967 mg (30%, not optimized).
