Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

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 $[Rh\{(Z)\text{-}CF{=}CF(CF_3)\}(PEt_3)_3]$ (**2**) were prepared according to the literature.[1,2]

The NMR spectra were recorded with a Bruker DRX 500 spectrometer. The ^1H NMR chemical shifts were referenced to residual C_6D_5H at δ 7.15. The ^{19}F NMR spectra were referenced to external C_6F_6 at δ –162.9 ppm. The $^{31}P\{^1H\}$ NMR spectra were referenced externally to H_3PO_4 at δ 0 ppm; the $^{29}Si\{^1H\}$ NMR spectrum to TMS.

Formation of 4a: A solution of $[Rh\{(Z)\text{-}CF{=}CFCF_3\}(PEt_3)_3]$ (**2**) (50 mg, 0.26 mmol) in benzene (10 mL) was treated with Ph_3SiH (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 $Ph_3SiCH_2CH_2CF_3$ (**4a**) (ratio: 2:1). Addition of an excess Ph_3SiH 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_3N (0.2 g,1.98 mmol) and Cs_2CO_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 turn over 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 $R_3SiCH_2CH_2CF_3$ (**4a**: R_3 = Ph_3, **4b**: R_3 = Ph_2Me, **4c**: R_3 = $PhMe_2$, **4d**: R_3 = Et_3, **4e**: R_3 = $(OMe)_3$) and the corresponding fluorosilane R_3SiF, 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 (C_6D_6, 500 MHz): $\delta = 1.57$ (m, 2 H, $SiCH_2$), 2.13 (m, 2 H, CH_2CF_3), 7.11-7.69 (m, 15 H, Ph) ppm; ^{19}F NMR (C_6D_6, 470 MHz): $\delta = -67.3$ (t, CF_3, $^3J(HF) = 11$ Hz) ppm; ^{29}Si NMR (C_6D_6, 99 MHz) $\delta = -10.8$ ppm. MS (EI, m/z): 356 (M^+), 279 (Ph_3SiHF^+), 259 (Ph_3Si^+). Elemental analysis calcd. (%) for $C_{21}H_{19}F_3Si$: C 70.76, H 5.37; Found: C 71.32, H 5.87. **4b**: ^1H NMR (C_6D_6, 500 MHz): $\delta = 0.46$ (s, 3 H, CH_3), 1.03 (m, 2 H, $SiCH_2$), 1.74 (m, 2 H, CH_2CF_3), 7.02-7.52 (m, 10 H, Ph) ppm; ^{19}F NMR (C_6D_6, 470 MHz): $\delta = -67.4$ (t, CF_3, $^3J(HF) = 10$ Hz) ppm; MS (EI, m/z): 217 ($Ph_2MeSiHF^+$), 197 (Ph_2MeSi^+). Elemental analysis calcd. (%) for $C_{16}H_{17}F_3Si$: 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**:

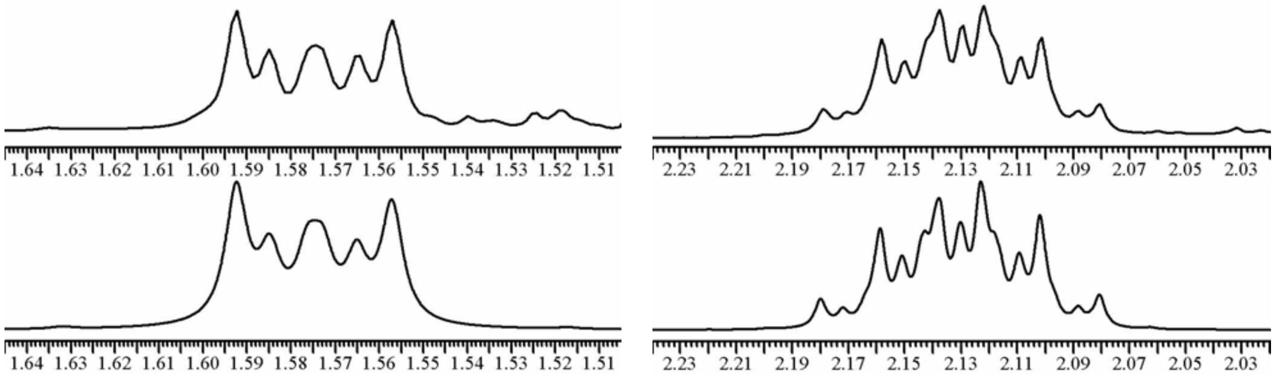

Figure S1: part of the ^{1}H NMR spectrum of complex **4a**; simulated (below) and observed (above) using the following coupling constants: $J(H^aH^{a'})$ = $J(H^bH^{b'})$ = -13.9, $J(H^aH^b)$ = $J(H^{a'}H^{b'})$ = 13.8, $J(H^{a'}H^b)$ = $J(H^aH^{b'})$ = 3.9, (H^bX) = $J(H^{b'}X)$ = 10.7 Hz

Catalytic formation of 4a hexafluoropropene in the presence o f hydrogen. Dihydrogen was bubbled into a suspension of Ph_3SiH (0.95 g, 3.65 mmol), Et_3N (0.5 g, 4.94 mmol) and Cs_2CO_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_3SiH, Et_3N and Cs_2CO_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_6D_6, 500 MHz): δ = −11.34 (m, see Figure S2), 0.98 (m, 9 H, $P^bCH_2CH_3$), 1.05 (m, 18

H, $\mathrm{P^aCH_2}\mathit{CH_3}$), 1.20 (m, 6 H, $\mathrm{P^b}\mathit{CH_2}\mathrm{CH_3}$), 1.44 (m, 12 H, $\mathrm{P^a}\mathit{CH_2}\mathrm{CH_3}$), 3.80 (s, 9 H, $\mathrm{Si(OMe)_3}$) ppm. ^{31}P NMR (202 MHz): $\delta = 5.9$ (dt, $^1J(\mathrm{RhP}) = 85.1$, $^2J(\mathrm{P^bP^a}) = 23.8$ Hz, $\mathrm{P^b}$), 15.1 (dd, $^1J(\mathrm{RhP}) = 101.6$, $^2J(\mathrm{P^bP^a}) = 23.8$ Hz, $\mathrm{P^a}$) ppm.

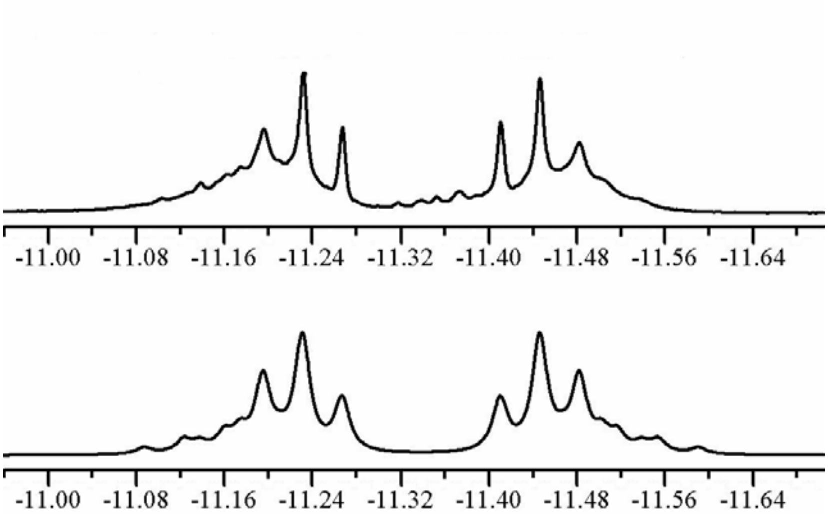

Figure S2: ^{1}H NMR spectrum (hydride region) of complex **6**; computed (below) and observed (above) using the following coupling constants: $^1J(\mathrm{RhH}) = {}^1J(\mathrm{RhH'}) = 18.1$, $^2J(\mathrm{P^aH}) = {}^2J(\mathrm{P^{a'}H'}) = -130.5$, $^2J(\mathrm{P^aH'}) = {}^2J(\mathrm{P^{a'}H}) = 22.5$, $^2J(\mathrm{P^bH}) = {}^2J(\mathrm{P^bH'}) = 18.2$, $^2J(\mathrm{HH'}) = 32.4$ Hz.

Catalytic hydrosilylation of 3,3,3-trifluoropropene with $\mathrm{Ph_3SiH}$.

A solution of $[\mathrm{RhH(PEt_3)_4}]$ (**1b**) (40 mg, 0.07 mmol) in $\mathrm{C_6D_6}$ (6 mL) was analyzed by ^{1}H NMR spectroscopy using 4-fluorotoluene as external standard to determine the exact concentration of **1b** *in situ*. After adding $\mathrm{Ph_3SiH}$ (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 ^{19}F 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).

[1] T. Yoshida, D. L. Thorn, T. Okano, S. Otsuka, J. A. Ibers, *J. Am. Chem. Soc.* **1980**, *102*, 6451-6457.

[2] a) T. Braun, D. Noveski, B. Neumann, H.-G. Stammler, *Angew. Chem. Int. Ed.* **2002**, *41*, 2745-2748; b) T. Braun, D. Noveski, B. Neumann, H.-G. Stammler, *Angew. Chem.* **2002**, *114*, 2870-2873.

[3] I. Ojima, T. Fuchikami, M. Yatabe, *J. Organomet. Chem.* **1984**, *260*, 335-346.