Supplementary Material

Consecutive C–F Bond Activation and C–F Bond Formation at Heteroaromatics at Rhodium: The Peculiar Role of $FSi(OEt)_3$

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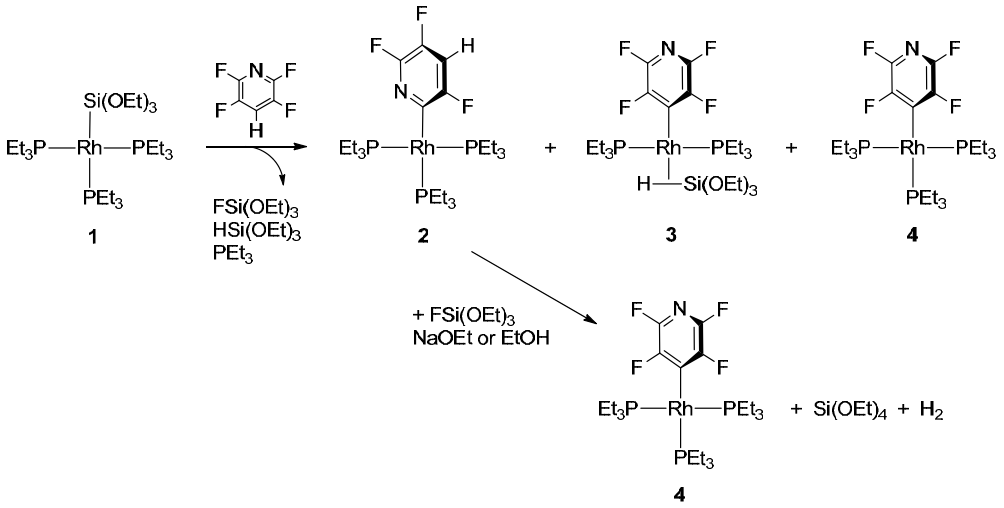
Experimental section

The synthetic work was carried out with a Schlenk line under an atmosphere of argon or in an argon-filled glove-box with oxygen levels below 10 ppm. All solvents were dried and purified by conventional methods and distilled under argon before use. [D_6]benzene, [D_8]toluene and [D_8]THF were purified by distillation from Na/K under argon. [Rh{$Si(OEt)_3$}(PEt_3)$_3$] (**1**), [Rh(H)(PEt_3)$_3$] (**6**), [Rh(CH_3)(PEt_3)$_3$] (**9**), $FSiEt_3$ and $FSi(OEt)_3$ were prepared according to the literature.[1] Alternatively, the latter was formed *in situ*. Compound **1** was freshly prepared before usage. In all experiments with **9** as starting compound, **9** was employed as a solution with a concentration of 0.106 mmol·mL^{-1}. 2,3,5,6-Tetrafluoropyridine, 2,3,4,6-tetrafluorobenzene, 2,3,5,6-tetrafluorobenzene, 2,3,5-trifluoropyridine and 2,3,6-trifluoropyridine were supplied from ABCR. TASF was obtained from Sigma-Aldrich.

The NMR spectra were acquired on a Bruker DPX 300, Bruker Avance 300 or a Bruker AV 400 NMR spectrometer. The ^{1}H chemical shifts were referenced to the residual signal of non-deuterated solvents at δ = 7.16 ppm for benzene, δ = 2.08 ppm for toluene and δ = 3.58 ppm for THF. ^{29}Si NMR spectra were referenced to external TMS at δ = 0 ppm. ^{19}F NMR spectra were referenced externally to $CFCl_3$ at δ = 0 ppm and ^{31}P NMR spectra were referenced externally to H_3PO_4 at δ = 0 ppm. As internal standards, capillaries with C_6F_6/C_6D_6 or H_3PO_4/D_2O were used. Liquid injection field desorption ionization (LIFDI) mass spectra were measured at a Micromass Q-TOF 2 mass spectrometer equipped with a LIFDI 700 (Linden CMS) ion source.

General procedure for the activation of 2,3,5,6-tetrafluoropyridine at [Rh{Si(OEt)$_3$}(PEt$_3$)$_3$] (1) and the subsequent generation of [Rh{2-(3,5,6-C$_5$F$_3$HN)}(PEt$_3$)$_3$] (2) in the presence of triethoxyfluorosilane



2,3,5,6-Tetrafluoropyridine (5.5 µL, 0.054 mmol) was added to a freshly prepared solution of [Rh{Si(OEt)$_3$}(PEt$_3$)$_3$] (**1**) (0.053 mmol) in [D$_8$]-toluene (0.4 mL) or as an alternative in [D$_8$]-THF (0.4 mL) in a glass NMR tube. The C–F activation reaction was monitored by ^{31}P{^{1}H} NMR spectroscopy until the silyl complex **1** was quantitatively converted into [Rh{2-(3,5,6-C$_5$F$_3$HN)}(PEt$_3$)$_3$] (**2**), [Rh(4-C$_5$F$_4$N){η^2-HSi(OEt)$_3$}(PEt$_3$)$_2$] (**3**) and [Rh(4-C$_5$F$_4$N)(PEt$_3$)$_3$] (**4**) (ratios between 74:14:12 and 80:8:12). Then NaOEt or EtOH was added (Table 1). The formation of [Rh(4-C$_5$F$_4$N)(PEt$_3$)$_3$] (**4**) from [Rh{2-(3,5,6-C$_5$F$_3$HN)}(PEt$_3$)$_3$] (**2**) and [Rh(4-C$_5$F$_4$N){η^2-HSi(OEt)$_3$}PEt$_3$)$_2$] (**3**) was monitored by ^{31}P{^{1}H} and ^{19}F{^{1}H} NMR spectroscopy. Internal standards revealed a full conversion of **2** (between 4.5 and 18.5 h). The ^{1}H,^{29}Si HMBC NMR spectrum showed the formation of tetraethoxysilane, which was identified by comparison of its NMR spectroscopic data with the literature.[2] The formation of pyridyl complexes (**4**, **5**, **7**) and of dihydrido silyl complex [Rh(H)$_2${Si(OEt)$_3$}(PEt$_3$)$_3$] (Table 1) was observed in a ratio of 94:6 . In subsequent reactions with intermediary H$_2$ the hydrodefluorination product [Rh{4-(2,3,5-C$_5$F$_3$HN)}(PEt$_3$)$_3$] (**7**) was formed from [Rh{2-(3,5,6-C$_5$F$_3$HN)}(PEt$_3$)$_3$] (**2**) and the product of the oxidative addition [Rh(H)$_2$(4-C$_5$F$_4$N)(PEt$_3$)$_3$] (**5**) was generated from [Rh(4-C$_5$F$_4$N)(PEt$_3$)$_3$] (**4**). Competing reactions are shown in the Scheme below. The stoichiometry of the reactions, the reaction times and product ratios are listed in Table 1.

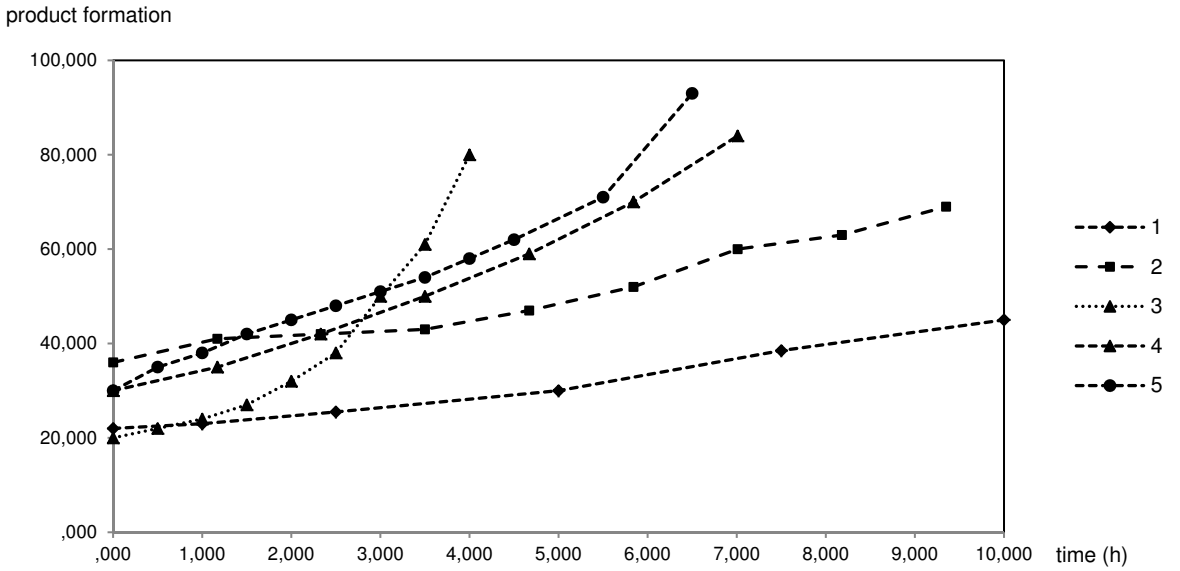
MS (LIFDI, [D$_8$]toluene): m/z = 620 [M]$^+$ (**1**), 589 [M]$^+$ (**2**), 607 [M]$^+$ (**4**).

Tabel S1: Additives, reaction times and observed ratios of the rhodium pyridyl complexes [Rh(4-C_5F_4N)(PEt_3)$_3$] (**4**), [Rh(H)$_2$(4-C_5F_4N)(PEt_3)$_3$] (**5**) and [Rh{4-(2,3,5-C_5F_3HN)}(PEt_3)$_3$] (**7**) that were obtained after the conversion of [Rh{2-(3,5,6-C_5F_3HN)}(PEt_3)$_3$] (**2**) was completed. Ratios were determined by integration of $^{31}P\{^1H\}$ NMR spectra.

entry	additive	mmol	time (h)	**3**	**4**	**5**	**7**
1	none		18.5	2	89		
2	EtOH	0.04 (2.5 µL)	6,5		58	11	31
3	NaOEt	0.06 (4 mg)	9	2	82	traces	16
4	NaOEt	0.03 (2 mg)	7	4	70	7	19
5	NaOEt, [D_8]THF	0.03 (2 mg)	4,5	2	80	11	7
6[a]	CsF	0.01 (2 mg)	–				
7[a]	LiF	0.06 (1.5 mg)	–				
8[a,b]	$FSiEt_3$	0.06 (10 µL)	–				

[a] No conversion of [Rh{2-(3,5,6-C_5F_3HN)}(PEt_3)$_3$] (**2**) was observed. [b] $FSiEt_3$ and small amounts of PEt_3 were added after removing $FSi(OEt)_3$ in vacuum and dissolving the residue in [D_8]toluene.

Figure S1: Plot of the ratio of the fluorination products (sum of the integrals of the signals for the complexes **3**, **4** and **5**) as a function of the reaction time (h). Plots 1-5 correspond to the entries in Table S1. Reaction conditions are listed in Table S1.



Competing reaction routes of [Rh{2-(3,5,6-C_5F_3HN)}(PEt_3)$_3$] (**2**) after treatment with triethoxyfluorosilane to yield **4** by fluorination. The reactions are induced by the intermediate generation of dihydrogen and $HSiOEt_3$ from **3**.

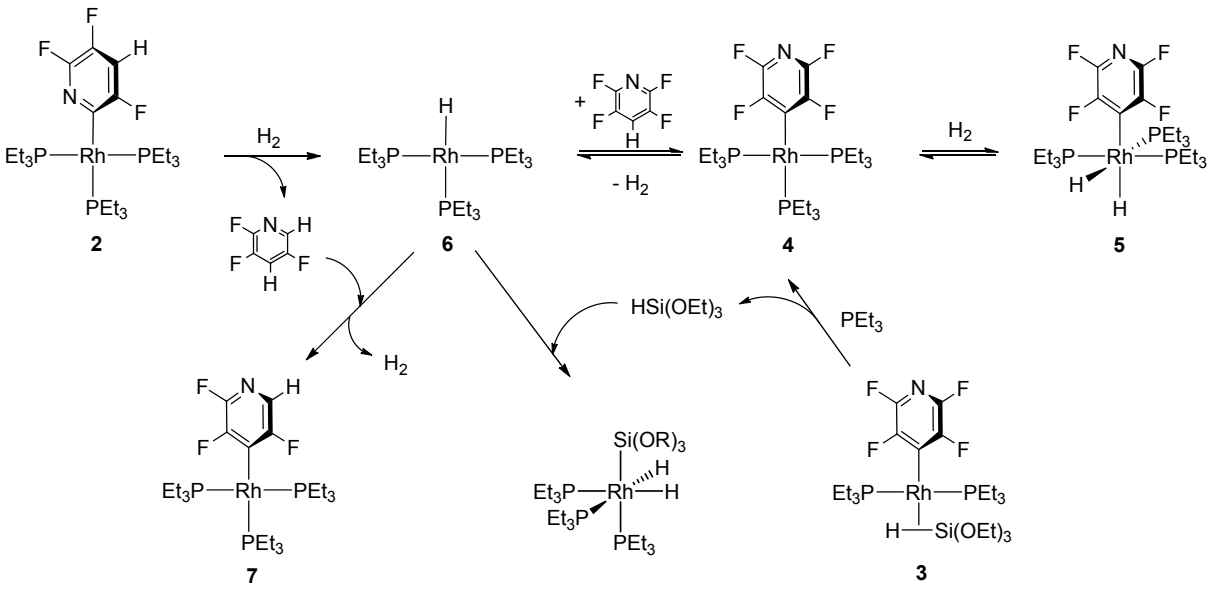
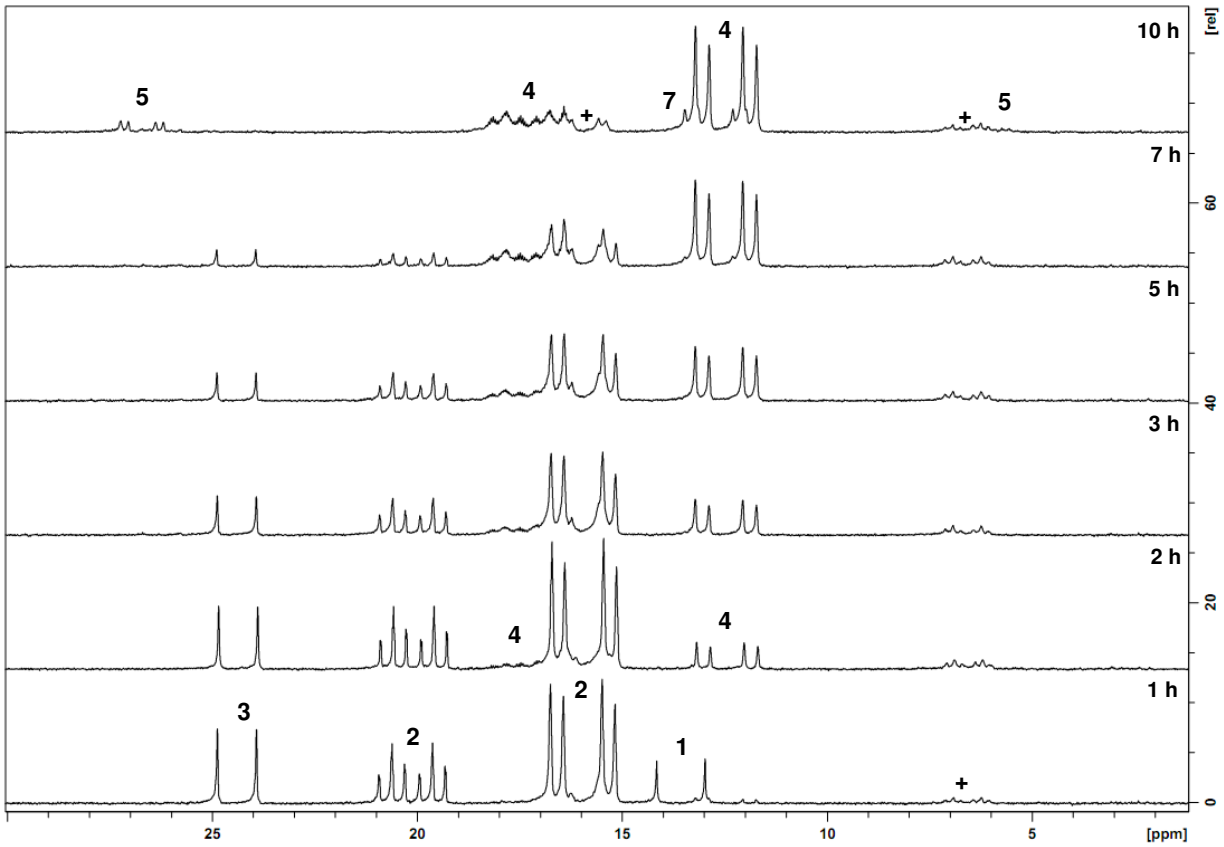
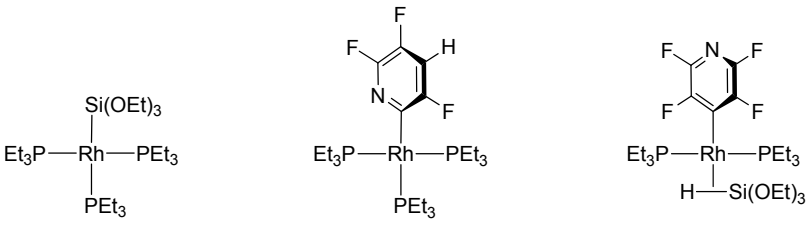


Figure S2: Part of the $^{31}P\{^{1}H\}$ NMR spectra of the fluorination of [Rh{2-(3,5,6-C_5F_3HN)}(PEt_3)$_3$] (**2**) in presence of $FSi(OEt)_3$ and NaOEt (entry 3, Table S1; recorded on a Bruker Avance 300 spectrometer at 282.4 MHz in [D_8]toluene).





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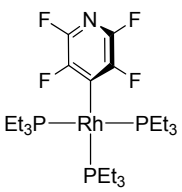

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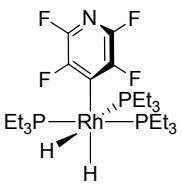

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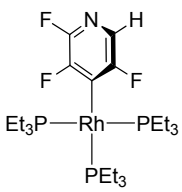

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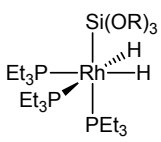

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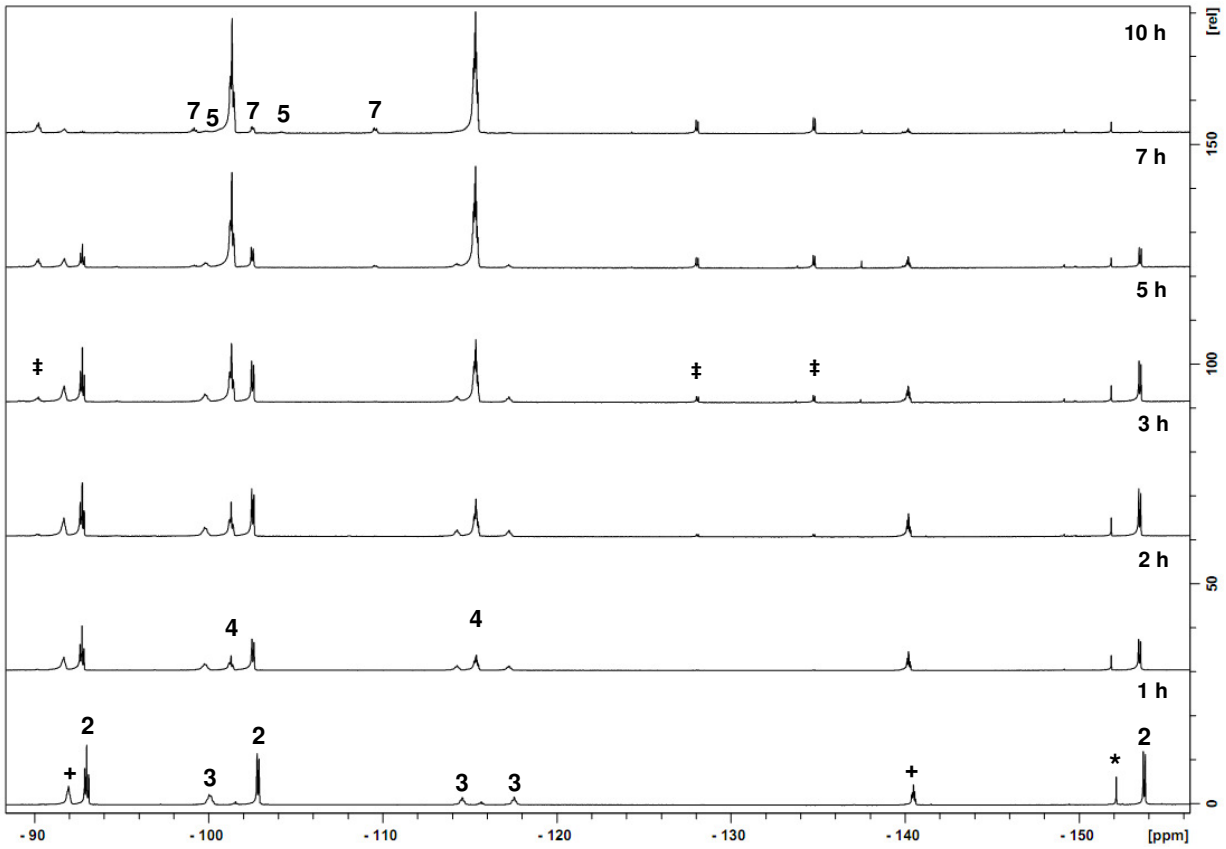
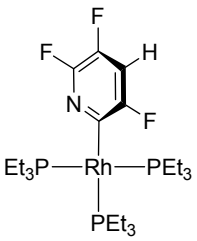
Figure S3: Part of the $^{19}F\{^{1}H\}$ NMR spectra of the fluorination of [Rh{2-(3,5,6-C_5F_3HN)}(PEt_3)$_3$] (**2**) in presence of $FSi(OEt)_3$ and NaOEt (entry 3, Table S1; recorded on a Bruker Avance 300 spectrometer at 282.4 MHz in [D_8]toluene).





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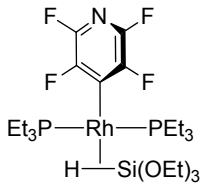

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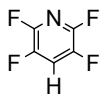

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$FSi(OEt)_3$

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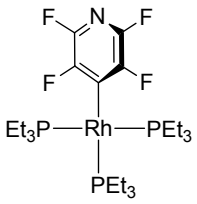

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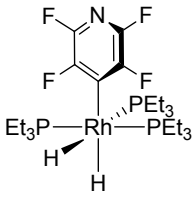

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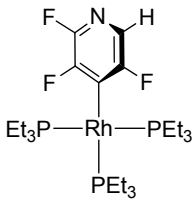

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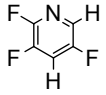

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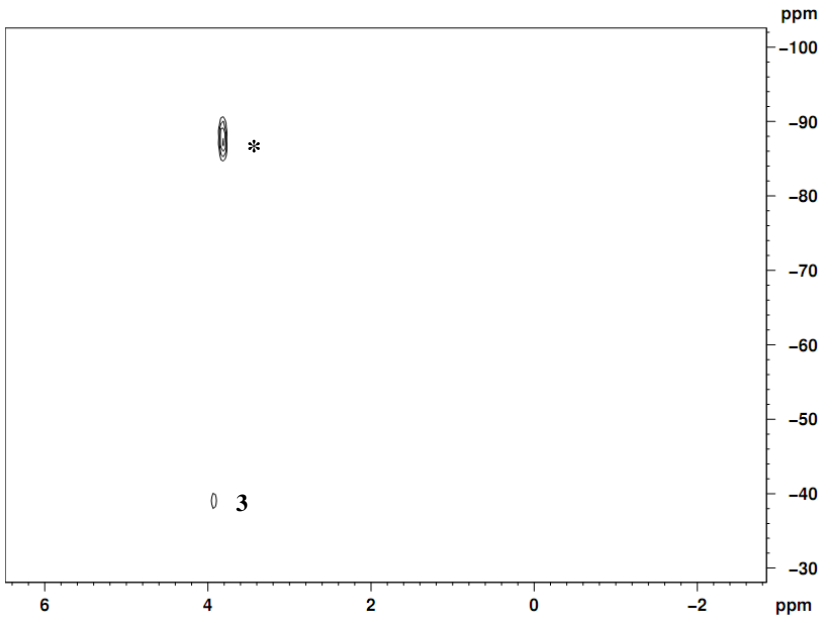
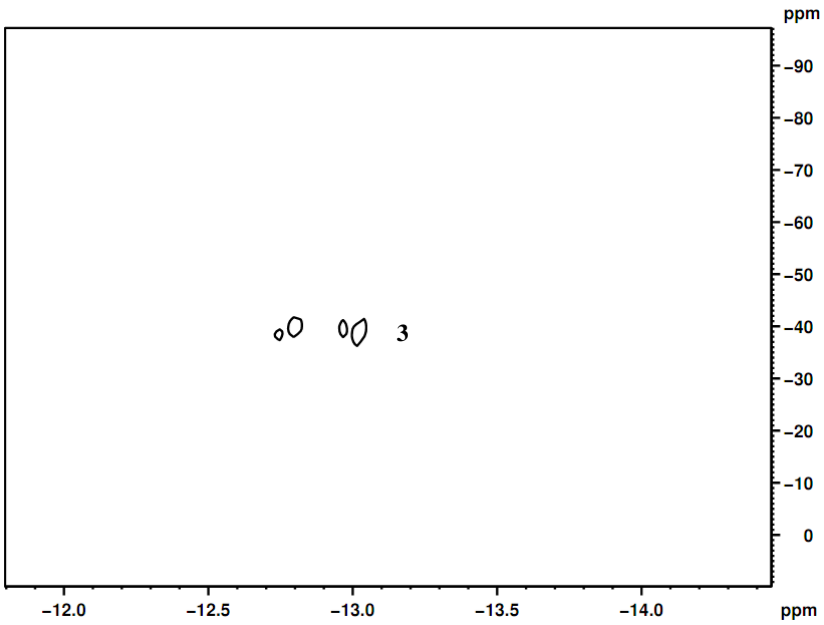
Figure S4: Part of the $^{1}H,^{29}Si$ HMBC NMR spectrum of the formation of [Rh{2-(3,5,6-C_5F_3HN)}$(PEt_3)_3$] (**2**) and subsequent fluorination in presence of $FSi(OEt)_3$ and NaOEt (entry 3, Table S1; recorded on a Bruker Avance 300 spectrometer at 59.6 MHz in [D_8]toluene); a) during C-F activation phase; b) after fluorination.

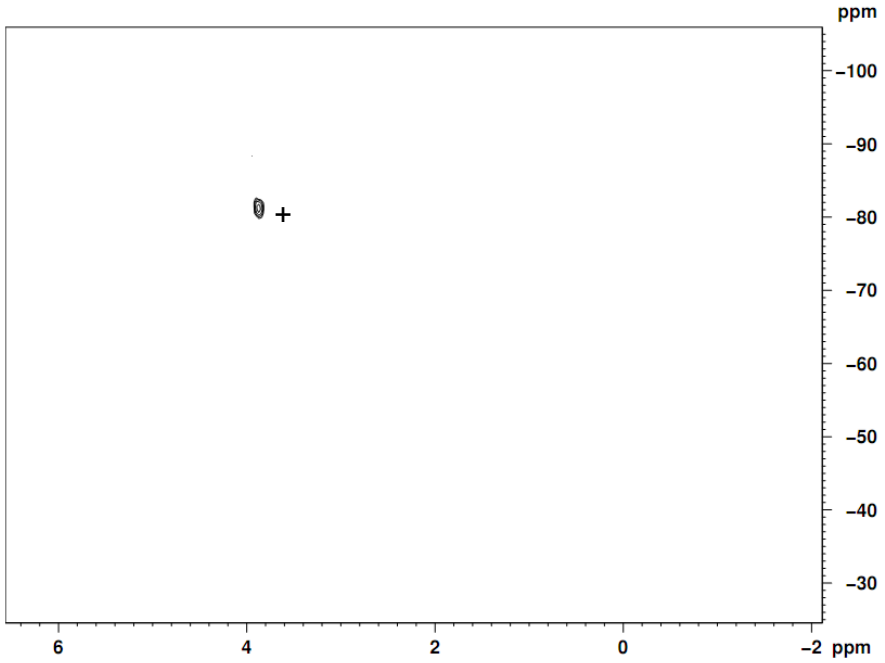
a) [Rh(4-C_5F_4N){η^2-$HSi(OEt)_3(PEt_3)_3$] (**3**) (above: correlation to CH_2 hydrogens of the Si bound Et groups; below: cross peak to the hydrogen atom of the silane ligand)

* fluorotriethoxysilane

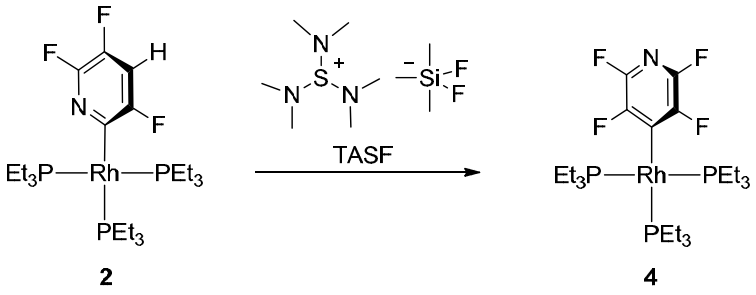




b) + tetraethoxysilane



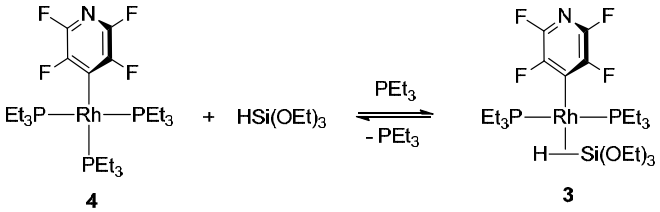
Fluorination of [Rh{2-(3,5,6-C_5F_3HN)}(PEt_3)$_3$] (2) by reaction of 2 with TASF



2 **4**

2,3,5,6-Tetrafluoropyridine (5.3 µL, 0.053 mmol) was added to a solution of [Rh{Si(OEt)$_3$}(PEt_3)$_3$] (**1**) (33 mg, 0.053 mmol) in [D_8]-toluene (0.3 mL). The reaction progress was monitored by NMR spectroscopy until the silyl complex **1** was fully consumed to give [Rh{2-(3,5,6-C_5F_3HN)}(PEt_3)$_3$] (**2**), [Rh(4-C_5F_4N){η^2-HSi(OEt)$_3$}(PEt_3)$_2$] (**3**) and [Rh(4-C_5F_4N)(PEt_3)$_3$] (**4**) (ratio: 68:17:15 after 1.5 h). All volatile compounds were removed in vacuum and the residue was dissolved in [D_8]-THF (0.35 mL) and triethyphoshine (1 µL, 0,007 mmol) was added. The solution was added to TASF (15 mg, 0.054 mmol) in an NMR tube. The formation of [Rh(4-C_5F_4N)(PEt_3)$_3$] (**4**) was monitored by $^{31}P\{^1H\}$ and $^{19}F\{^1H\}$ NMR spectroscopy. After 0.7 h the $^{31}P\{^1H\}$ NMR spectrum reveals the presence of [Rh{2-(3,5,6-C_5F_3HN)}(PEt_3)$_3$] (**2**), [Rh(4-C_5F_4N)(PEt_3)$_3$] (**4**), [Rh{4-(2,3,5-C_5F_3HN)}(PEt_3)$_3$] (**7**), [RhF(PEt_3)$_3$] (**8**) and additional rhodium complexes, that could not be characterized further, in a ratio of 3:35:13:10:39.[3]

Synthesis of [Rh(4-C_5F_4N){η^2-HSi(OEt)$_3$}(PEt_3)$_2$] (3)



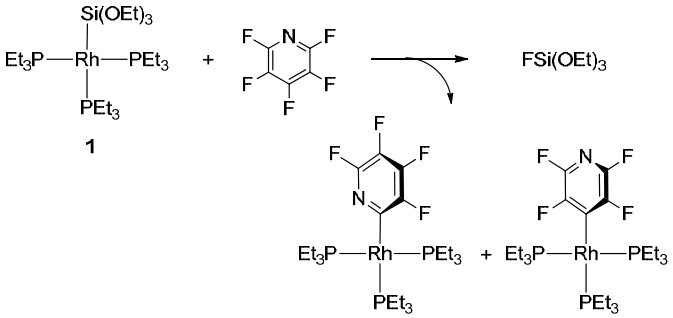
4 **3**

To a solution of Rh(4-C_5F_4N)(PEt_3)$_3$] (**4**) (32 mg, 0.053 mmol) triethoxysilane was added (10 µL, 0.054 mmol). After 20 min the formation of [Rh(4-C_5F_4N){η^2-HSi(OEt)$_3$}(PEt_3)$_2$] (**3**) and triethylphosphine was observed. Compounds **3** and **4** are present in a 1:3 ratio according the $^{31}P\{^1H\}$ NMR spectra.

NMR data of **3**: ^1H NMR (300.1 MHz, [D_8]toluene, 300 K): δ = 3.9 (q, ^3J(H,H) = 6.8 Hz, 6H, HSiOCH_2CH$_3$), −12.9 ppm (m, dt in the $^1H\{^{19}F\}$ NMR spectrum, ^1J(H,Rh) = 20 Hz, ^2J(H,P) = 14 Hz, 1H, *H*SiOCH$_2$CH$_3$). The resonances for the ethyl groups of the phosphine ligands and the methyl

group of the ethoxy substituents in **3** are covered by signals of **4**, triethoxysilane and triethylphosphine; ^{19}F NMR (282.4 MHz, [D$_8$]toluene, 300 K): δ = −99.8 (m, 2F), −114.3 (m, 1F), −117.2 ppm (m, 1F); ^{31}P{^{1}H} NMR (121.5 MHz, [D$_8$]toluene, 300 K): δ(ppm) = 24.4 (d, ^1J(Rh,P) = 117 Hz); ^{1}H,^{29}Si HMBC NMR (300.1/59.6 MHz, [D$_8$]toluene, 300 K): δ {^{1}H/^{29}Si} = 4/−39 (HSiOC*H*$_2$CH$_3$), −13/−39 ppm (*H*SiOCH$_2$CH$_3$, dd in the ^{1}H domain ^1J(H,Si) = 65 Hz, ^1J(H,Rh) = 20 Hz).

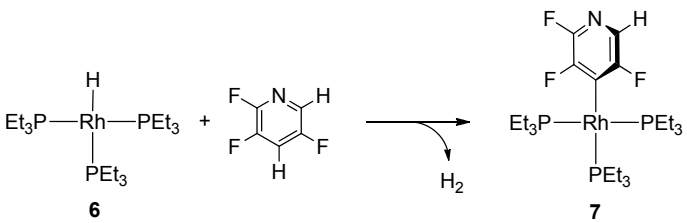
Formation of FSi(OEt)$_3$



Pentafluoropyridine (4.5 µL, 0.04 mmol) was added to a solution of [Rh{Si(OEt)$_3$}(PEt$_3$)$_3$] (**1**) (0.053 mmol) in [D$_8$]-toluene (0.4 mL). After 15 min all volatile compounds were removed in vacuum and collected in a cold trap. NMR spectra of the solution show the presence of solely FSi(OEt)$_3$. The latter was used in the reaction with the complexes **7** and **10**-**12** (see page 15).

NMR data of FSi(OEt)$_3$: ^{1}H NMR (300.1 MHz, [D$_8$]toluene, 300 K): δ = 3.8 (q, ^3J(H,H) = 7.0 Hz, 6H, SiOC*H*$_2$CH$_3$), 1.1 ppm (t, ^3J(H,H) = 7.0 Hz, 9H, SiOCH$_2$C*H*$_3$); ^{19}F NMR (282.4 MHz, [D$_8$]toluene, 300 K): δ = −152.2 ppm (s, ^{29}Si satellites, J(Si,F) = 204 Hz, 1F); ^{1}H,^{29}Si HMBC NMR (300.1/59.6 MHz, [D$_8$]toluene, 300 K): δ {^{1}H/^{29}Si} = 4/−89 ppm (SiOC*H*$_2$CH$_3$).

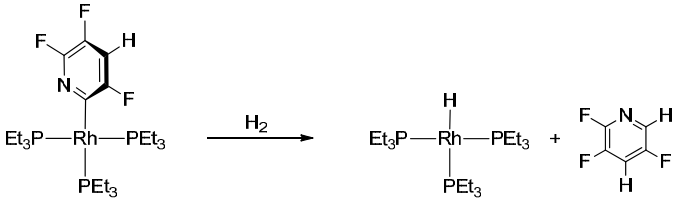
Formation of [Rh{4-(2,3,5-C$_5$F$_3$HN)}(PEt$_3$)$_3$] (7) via C-H Activation at [RhH(PEt$_3$)$_3$] (6)



2,3,5-Trifluoropyridine (2.8 µL, 0.032 mmol) was added to a solution of [RhH(PEt_3)$_3$] (**6**) (0.032 mmol) in [D_6]-benzene (0.4 mL). After 1 h the $^{19}F\{^1H\}$ NMR spectrum reveals the formation of [Rh{4-(2,3,5-C_5F_3HN)}(PEt_3)$_3$] (**7**) and the presence of residual 2,3,5-trifluoropyridine in a 1:1 ratio.

NMR data for **7**: ^1H NMR (300.1 MHz, [D_8]toluene, 300 K): δ = 7.6 (m, 1H, C_5F_3HN), 1.5 (m, q in the $^1H\{^{31}P\}$ NMR spectrum, ^3J(H,H) = 7.6 Hz, 6H, PC***H***$_2$CH$_3$), 1.4 (m, q in the $^1H\{^{31}P\}$ NMR spectrum, ^3J(H,H) = 7.4 Hz, 12H, PC***H***$_2$CH$_3$), 1.1 (m, t in the $^1H\{^{31}P\}$ NMR spectrum , ^3J(H,H) = 7.6 Hz, 9H, PCH$_2$C***H***$_3$), 1.0 ppm (m, t in the $^1H\{^{31}P\}$ NMR spectrum, ^3J(H,H) = 7.4 Hz, 18 H, PCH$_2$C***H***$_3$). ^{19}F NMR (282.4 MHz, [D_8]toluene, 300 K): δ = −103.8 (m, 1F), −107.5 (m, 1F), −114.5 ppm (m, 1F). $^{31}P\{^1H\}$ NMR (121.5 MHz, [D_8]toluene, 300 K): δ = 17.5 (dtm, ^1J(Rh,P) = 128 Hz, ^2J(P,P) = 40 Hz, 1P), 13.3 ppm (dd, ^1J(Rh,P) = 144 Hz, ^2J(P,P) = 40 Hz, 2P).

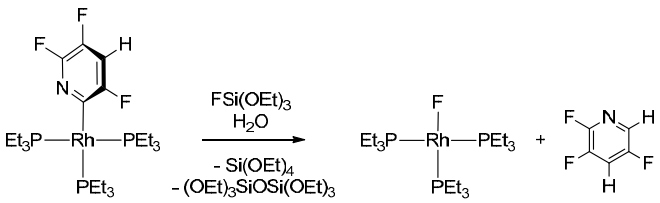
Formation of 2,3,5-trifluoropyridine from [Rh{2-(3,5,6-C_5F_3HN)}(PEt_3)$_3$] (2)



2 **7**

A reaction mixture of [Rh{2-(3,5,6-C_5F_3HN)}(PEt_3)$_3$] (**2**), [Rh(4-C_5F_4N){η^2-HSi(OEt)$_3$}(PEt_3)$_2$] (**3**) and [Rh(4-C_5F_4N)(PEt_3)$_3$] (**4**) (ratio: 81:16:3) was prepared via the described procedure (see page 2). All volatile compounds were removed in vacuum and a solution of PEt_3 (2 µL, 0.014 mmol) in [D_8]toluene (0.4 mL) was added. Hydrogen was bubbled for 20 sec into the solution. After 30 min the $^{31}P\{^1H\}$ NMR spectrum revealed the formation of [RhH(PEt_3)$_3$] (**7**), [Rh(H)$_2${Si(OEt)$_3$}(PEt_3)$_3$], [Rh(4-C_5F_4N)(PEt_3)$_3$] (**4**) and [Rh(H)$_2$(4-C_5F_4N)(PEt_3)$_3$] (**5**) in a ratio of 53:21:4:10. In the ^{19}F NMR spectrum 2,3,5-trifluoropyridine and 2,3,5,6-tetrafluoropyridine were detected additionally.

Formation of [RhF(PEt_3)$_3$] (8) by reaction of of 2 with water and FSi(OEt)$_3$

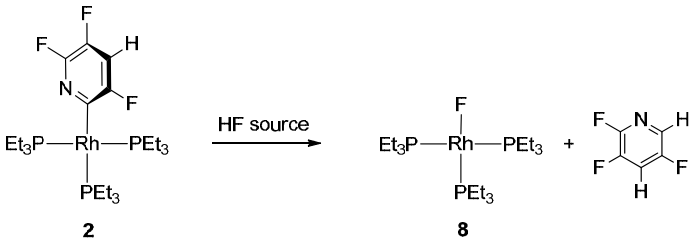


2 **8**

A reaction mixture of [Rh{2-(3,5,6-C_5F_3HN)}(PEt_3)$_3$] (**2**), [Rh(4-C_5F_4N){η^2-HSi(OEt)$_3$}(PEt_3)$_2$] (**3**), [Rh(4-C_5F_4N)(PEt_3)$_3$] (**4**), PEt_3 and FSi(OEt)$_3$ was prepared via the described procedure (76:16:8; see

page 2). Water (0.5 µL, 0.28 mmol) was added. Monitoring the reaction by $^{31}P\{^{1}H\}$ NMR spectroscopy revealed after 4.5 h the formation of $[RhF(PEt_3)_3]$ (**8**) from $[Rh\{2\text{-}(3,5,6\text{-}C_5F_3HN)\}(PEt_3)_3]$ (**2**). Complex **8** was identified by its NMR spectroscopic data.[3]

Formation of $[RhF(PEt_3)_3]$ (8) from $[Rh\{2\text{-}(3,5,6\text{-}C_5F_3HN)\}(PEt_3)_3]$ (2) and an HF source

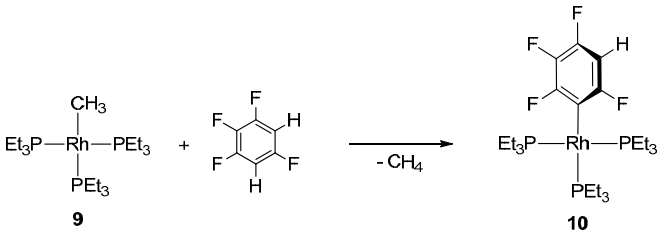


2 **8**

HF source: $Et_3N{\cdot}3HF$, HF (aq), HF (EtOH)

A reaction mixture of $[Rh\{2\text{-}(3,5,6\text{-}C_5F_3HN)\}(PEt_3)_3]$ (**2**), $[Rh(4\text{-}C_5F_4N)\{\eta^2\text{-}HSi(OEt)_3\}(PEt_3)_2]$ (**3**), $[Rh(4\text{-}C_5F_4N)(PEt_3)_3]$ (**4**), PEt_3 and $FSi(OEt)_3$ was prepared via the described procedure (see page 2). All volatile compounds were removed in vacuum and the residue was disolved in $[D_8]$-toluene (0.4 mL) and triethyphoshine (1 µL, 0.007 mmol). In a PFA NMR tube a HF source was added. This was either $3HF{\cdot}NEt_3$ (2 µL) or a solution in water (2.5 µL of a 40 % solution) or ethanol (4 µL of a 18 M solution). Monitoring the reaction by $^{31}P\{^{1}H\}$ NMR spectroscopy revealed after 1.5 h in each case the formation of $[RhF(PEt_3)_3]$ (**8**) from $[Rh\{2\text{-}(3,5,6\text{-}C_5F_3HN)\}(PEt_3)_3]$ (**2**), whereas **3** and **4** did not react. Complex **8** was identified by its NMR spectroscopic data.[3]

Formation of $[Rh(2,3,4,6\text{-}C_6F_4H)(PEt_3)_3]$ (10)



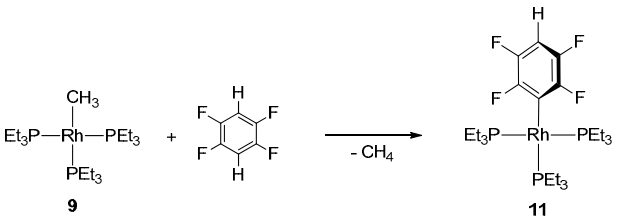
9 **10**

2,4,5,6-Tetrafluorobenzene (10 µL, 0.089 mmol) was added to a solution of $[Rh(CH_3)(PEt_3)_3]$ (**9**) (0.053 mmol) in $[D_8]$-toluene (0.5 mL) and the reaction mixture was stirred for 30 min at 70 °C. The $^{31}P^{1}\{H\}$ spectrum reveals the conversion of the methyl complex **9** into **10** and $[Rh(p\text{-}tol)(PEt_3)_3]$.[1b] The ^{1}H NMR spectrum reveals a ratio of **10** and $[Rh(p\text{-}C_6D_4CD_3)(PEt_3)_3]$ of 97:3. The formation of the latter results from a C–H activation reaction of toluene at **9**.[4] Evaporation of the solvent and residual 2,4,5,6-tetrafluorobenzene yielded a yellow solid.

NMR data for **10**: ^{1}H NMR (300.1 MHz, [D$_8$]toluene, 300 K): δ = 6.4 (m, s, br in the ^{1}H{^{19}F} NMR spectrum, 1H, C_6F_4H), 1.4 (m, q in the ^{1}H{^{31}P} NMR spectrum,^{3}J(H,H) = 7.4 Hz, 6H, PC***H***$_2$CH$_3$), 1.3 (m, q in the ^{1}H{^{31}P} NMR spectrum,^{3}J(H,H) = 7.6 Hz, 12H, PC***H***$_2$CH$_3$), 1.0 (m, t in the ^{1}H{^{31}P} NMR spectrum , ^{3}J(H,H) = 7.4 Hz, 9H, PCH$_2$C***H***$_3$), 0.9 ppm (m, t in the ^{1}H{^{31}P} NMR spectrum, ^{3}J(H,H) = 7.6 Hz, 18 H, PCH$_2$C***H***$_3$). ^{19}F NMR (282.4 MHz, [D$_8$]toluene, 300 K): δ = −88.5 (m, 1F), −107.6 (m, 1F), −149.4 (m, 1F), −174.1 ppm (m, 1F). ^{31}P{^{1}H} NMR (121.5 MHz, [D$_8$]toluene, 300 K): δ = 13.9 (dtm, ^{1}J(Rh,P) = 132 Hz, ^{2}J(P,P) = 39 Hz, 1P), 9.6 ppm (dd, ^{1}J(Rh,P) = 144 Hz, ^{2}J(P,P) = 39 Hz, 2P).

MS (LIFDI, [D$_8$]toluene): m/z = 606 [M]$^{+}$.

Formation of [Rh(2,3,5,6-C$_6$F$_4$H)(PEt$_3$)$_3$] (11)

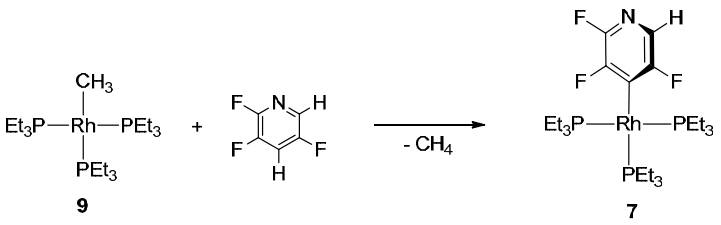


1,2,4,5-Tetrafluorobenzene (10 µL, 0.089 mmol) was added to a solution of [Rh(CH$_3$)(PEt$_3$)$_3$] (**9**) (0.053 mmol) in [D$_8$]-toluene (0.5 mL) and the reaction mixture was stirred for 30 min at 70 °C. The ^{31}P^{1}{H} spectrum reveals the conversion of the methyl complex **9** into **11**. As additional product [Rh(*p*-C$_6$D$_4$CD$_3$)(PEt$_3$)$_3$], resulting from C–H activation of toluene with **9**, was observed.[1b,4] **11** and [Rh(*p*-C$_6$D$_4$CD$_3$)(PEt$_3$)$_3$] were obtained in a ratio of 98:2 (determined via integration in the ^{1}H NMR spectrum). Evaporation of the solvent and residual 1,2,4,5-tetrafluorobenzene yielded a yellow solid.

NMR data for **11**: ^{1}H NMR (300.1 MHz, [D$_8$]toluene, 300 K): δ = 6.5 (m, s in the ^{1}H{^{19}F} NMR spectrum, 1H, C_6F_4H), 1.4 (m, q in the ^{1}H{^{31}P} NMR spectrum,^{3}J(H,H) = 7.6 Hz, 6H, PC***H***$_2$CH$_3$), 1.3 (m, q in the ^{1}H{^{31}P} NMR spectrum,^{3}J(H,H) = 7.7 Hz, 12H, PC***H***$_2$CH$_3$), 1.0 (m, t in the ^{1}H{^{31}P} NMR spectrum , ^{3}J(H,H) = 7.6 Hz, 9H, PCH$_2$C***H***$_3$), 0.9 ppm (m, t in the ^{1}H{^{31}P} NMR spectrum, ^{3}J(H,H) = 7.7 Hz, 18 H, PCH$_2$C***H***$_3$). ^{19}F NMR (282.4 MHz, [D$_8$]toluene, 300 K): δ = −110.2 (m, 2F), −142.3 ppm (m, 2F). ^{31}P{^{1}H} NMR (121.5 MHz, [D$_8$]toluene, 300 K): δ = 18.5 (dtm, ^{1}J(Rh,P) = 132 Hz, ^{2}J(P,P) = 39 Hz, 1P),14.3 ppm (dd, ^{1}J(Rh,P) = 142 Hz, ^{2}J(P,P) = 39 Hz, 2P).

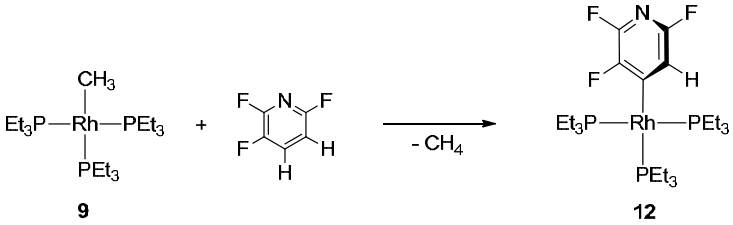
MS (LIFDI, [D$_8$]toluene): m/z = 606 [M]$^{+}$.

Formation of [Rh{4-(2,3,5-C_5F_3HN)}(PEt_3)$_3$] (7) by C–H Activation at [Rh(CH_3)(PEt_3)$_3$] (9)



2,3,5-Trifluoropyridine (6.9 µL, 0.079 mmol) was added to a solution of [Rh(CH_3)(PEt_3)$_3$] (**9**) (0.079 mmol) in [D_8]-toluene (0.8 mL) and the reaction mixture was stirred for 90 min at 70 °C. The $^{31}P^1\{H\}$ spectrum reveals the conversion of the methyl complex **9** into [Rh{4-(2,3,5-C_5F_3HN)}(PEt_3)$_3$] (**7**) and [Rh(*p*-$C_6D_4CD_3$)(PEt_3)$_3$] (95:5).[1b,4] The solution of **7** was *in situ* used for further reactions because of the low solubility of **7** after evaporation of the solvent. For NMR data of **7** see page 11.

Formation of [Rh{4-(2,3,6-C_5F_3HN)}(PEt_3)$_3$] (12)



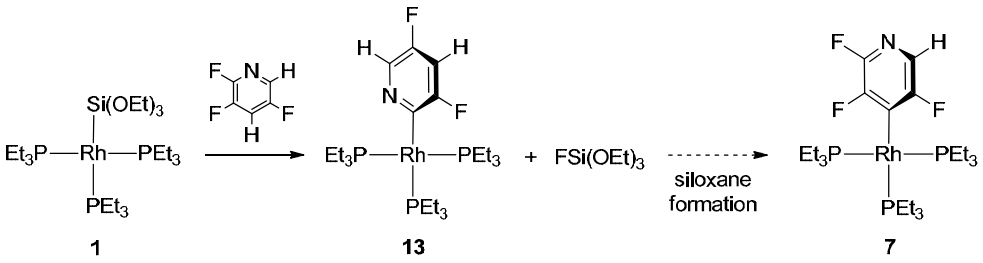
2,3,6-Trifluoropyridine (6.9 µL, 0.079 mmol) was added to a solution of [Rh(CH_3)(PEt_3)$_3$] (**9**) (0.079 mmol) in [D_8]-toluene (0.8 mL) and stirred for 90 min at 70 °C. The $^{31}P^1\{H\}$ spectrum reveals the conversion of the methyl complex **9** into [Rh{4-(2,3,6-C_5F_3HN)}(PEt_3)$_3$] (**12**). As additional product [Rh(*p*-$C_6D_4CD_3$)(PEt_3)$_3$] was observed in a ratio of 98:2.[1b,4] The ratio was determined by integration from the ^1H NMR spectrum. The solution of **12** was *in situ* used for further reactions because of the low solubility of **12** after evaporation of the solvent.

NMR data for **12**: ^1H NMR (300.1 MHz, [D_8]toluene, 300 K): δ = 7.2 (m, 1H, C_5F_3HN), 1.4 (m, q in the $^1H\{^{31}P\}$ NMR spectrum,^3J(H,H) = 7.6 Hz, 6H, PC***H***$_2$CH$_3$), 1.3 (m, q in the $^1H\{^{31}P\}$ NMR spectrum,^3J(H,H) = 7.6 Hz, 12H, PC***H***$_2$CH$_3$), 1.0 (m, t in the $^1H\{^{31}P\}$ NMR spectrum , ^3J(H,H) = 7.6 Hz, 9H, PCH$_2$C***H***$_3$), 0.9 ppm (m, t in the $^1H\{^{31}P\}$ NMR spectrum, ^3J(H,H) = 7.6 Hz, 18 H, PCH$_2$C***H***$_3$). ^{19}F NMR (282.4 MHz, [D_8]toluene, 300 K): δ = −89.7 (m, 1F), −102.6 (m, 1F), −125.8 ppm (m, 1F). $^{31}P\{^1H\}$ NMR (121.5 MHz, [D_8]toluene, 300 K): δ = 18.1 (dtm, ^1J(Rh,P) = 120 Hz, ^2J(P,P) = 39 Hz, 1P), 12.4 ppm (dd, ^1J(Rh,P) = 146 Hz, ^2J(P,P) = 39 Hz, 2P).

General procedure for the treatment of the complexes 7, 10-12 with triethoxyfluorosilane

A solution of the tetrafluorophenyl complexes **10** or **11** in [D_8]-THF (0.027 mmol in 0.25 mL) or a solution of the trifluoropyridyl complexes **7** and **12** in [D_8]-toluene (0.027 mmol in 0.25 mL) was treated with a solution of $FSi(OEt)_3$ (0.027 mmol) in [D_8]-Toluene (0.15 mL, prepared according the procedure which is descripted at page 10). NaOEt (2 mg, 0.03 mmol) was added. The reaction mixtures were monitored by NMR spectroscopy. No reaction of the rhodium complexes with $FSi(OEt)_3$ was observed.

Syntheses of [Rh{2-(3,5-$C_5F_2H_2N$)}(PEt_3)$_3$] (13) and *in situ* fluorination with triethoxyfluorosilane as fluoride source to yield [Rh{4-(2,3,5-C_5F_3HN)}(PEt_3)$_3$] (7)

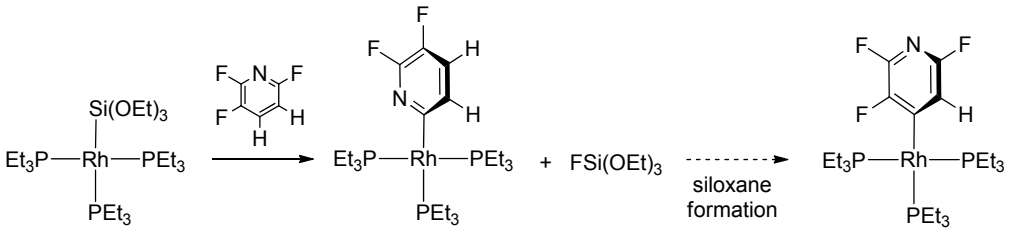


2,3,5-Trifluoropyridine (4.7 µL, 0.053 mmol) was added to a solution of [Rh{$Si(OEt)_3$}(PEt_3)$_3$] (**1**) (0.053 mmol) in [D_8]-toluene (0.3 mL). After 1.5 h the $^{31}P\{^1H\}$ NMR spectrum shows that **1** was fully consumed to give [Rh(2-3,5-$C_5F_2H_2N$)(PEt_3)$_3$] (**13**) and triethoxyfluorosilane as well as small amounts of **7** (by fluorination of **13**). [Rh(2-3,5-$C_5F_2H_2N$)(PEt_3)$_3$] (**13**) was characterized in solution by NMR spectroscopy. The formation of [Rh{4-(2,3,5-C_5F_3HN)}(PEt_3)$_3$] (**7**) from **13** and triethoxyfluorosilane was monitored by $^{31}P\{^1H\}$ and $^{19}F\{^1H\}$ NMR spectroscopy. Complex **7** was generated after 21 hours. Additionally to the generation of **7** and [Rh(2-3,5-$C_5F_2H_2N$)(PEt_3)$_3$] (**13**), the formation of [RhH(PEt_3)$_3$] (**6**) and other rhodium complexes, which were not identified further, was observed according to the $^{31}P\{^1H\}$ NMR spectrum (ratio: 58:18:13:11).

NMR data for **13**: ^1H NMR (300.1 MHz, [D_6]benzene, 300 K): δ = 8.6 (m, d in the $^1H\{^{19}F\}$ NMR spectrum,^3J(H,H) = 2.3 Hz, 1H, $C_5F_2H_2N$), 6.4 (m, ddm in the $^1H\{^{31}P\}$ NMR spectrum, ^3J(H,F) = 12.1 Hz, ^3J(H,H) = 2.3 Hz, 1H, $C_5F_2H_2N$), 1.6 (m, q in the $^1H\{^{31}P\}$ NMR spectrum,^3J(H,H) = 7.5 Hz, 6H, PC***H***$_2$$CH_3$), 1.5 (m, q in the $^1H\{^{31}P\}$ NMR spectrum,^3J(H,H) = 7.5 Hz, 12H, PC***H***$_2$$CH_3$), 1.1 (m, t in the $^1H\{^{31}P\}$ NMR spectrum, ^3J(H,H) = 7.5 Hz, 9H, PCH_2C***H***$_3$), 1.0 ppm (m, t in the $^1H\{^{31}P\}$ NMR spectrum, ^3J(H,H) = 7.5 Hz, 18 H, PCH_2C***H***$_3$); ^{19}F NMR (282.4 MHz, [D_8]toluene, 300 K): δ = −101.9 (s, 1F), −146.1 ppm (d, ^3J(H,F) = 12.1 Hz, s in the $^1H\{^{19}F\}$ NMR spectrum, 1F); $^{31}P\{^1H\}$ NMR (121.5

MHz, [D_8]toluene, 300 K): δ = 20.8 (dtm, ^1J(Rh,P) = 121 Hz, ^2J(P,P) = 37 Hz, 1P), 16.7 ppm (ddm, ^1J(Rh,P) = 155 Hz, ^2J(P,P) = 37 Hz, 2P). For NMR data of **7** see page 11.

Syntheses of [Rh{2-(5,6-$C_5F_2H_2N$)}(PEt_3)$_3$] (14) and *in situ* fluorination with triethoxyfluorosilane as fluoride source to yield [Rh{4-(2,3,6-C_5F_3HN)}(PEt_3)$_3$] (12)



2,3,6-Trifluoropyridine (4.7 µL, 0.053 mmol) was added to a solution of [Rh{$Si(OEt)_3$}(PEt_3)$_3$] (**1**) (0.053 mmol) in [D_8]-toluene (0.3 mL). After 1 h the $^{31}P\{^1H\}$ NMR spectrum shows that **1** was fully consumed to give [Rh{2-(5,6-$C_5F_2H_2N$)}(PEt_3)$_3$] (**14**) and triethoxyfluorosilane as well as small amounts of **12** (by fluorination of **14**). [Rh{2-(5,6-$C_5F_2H_2N$)}(PEt_3)$_3$] (**14**) was characterized in solution by NMR spectroscopy. The formation of [Rh{4-(2,3,6-C_5F_3HN)}(PEt_3)$_3$] (**12**) from **14** was observed by $^{31}P\{^1H\}$, and $^{19}F\{^1H\}$ spectroscopy. After 16 h the $^{31}P\{^1H\}$ NMR spectrum displayed the complexes [Rh{2-(5,6-$C_5F_2H_2N$)}(PEt_3)$_3$] (**14**), [Rh{4-(2,3,6-C_5F_3HN)}(PEt_3)$_3$] (**12**) and [RhH(PEt_3)$_3$] (**6**) and rhodium compounds which could not be further characterized in a ratio of 23:59:18:12.

NMR data for **14**: ^1H NMR (300.1 MHz, [D_6]benzene, 300 K): δ = 6.5 (m, 1H, $C_5F_2H_2N$), 6.0 (m, 1H, $C_5F_2H_2N$), 1.6 (m, q in the $^1H\{^{31}P\}$ NMR spectrum,^3J(H,H) = 7.2 Hz, 6H, PC***H***$_2$CH$_3$), 1.4 (m, q in the $^1H\{^{31}P\}$ NMR spectrum,^3J(H,H) = 7.7 Hz, 12H, PC***H***$_2$CH$_3$), 1.1 (m, t in the $^1H\{^{31}P\}$ NMR spectrum, ^3J(H,H) = 7.7 Hz, 9H, PCH$_2$C***H***$_3$), 1.0 ppm (m, t in the $^1H\{^{31}P\}$ NMR spectrum, ^3J(H,H) = 7.2 Hz, 18 H, PCH$_2$C***H***$_3$). ^{19}F NMR (282.4 MHz, [D_8]toluene, 300 K): δ = −75.6 (d, ^3J(F,F) = 32.5 Hz, 1F), −107.5 ppm (d, ^3J(F,F) = 32.5 Hz, 1F). $^{31}P\{^1H\}$ NMR (121.5 MHz, [D_8]toluene, 300 K): δ = 20.0 (dtm, ^1J(Rh,P) = 119 Hz, ^2J(P,P) = 38 Hz, 1P), 16.2 ppm (ddm, ^1J(Rh,P) = 155 Hz, ^2J(P,P) = 38 Hz, 2P). For the NMR data of **12** see page 14.

Theoretical Methods

The structure calculation of compound **3** was done using the Gaussian 09 (Revision C.01) program package[5] and the B3LYP functional. cc-pVTZ basis sets were employed for all atoms except the carbon and hydrogen atoms of the PEt_3 ligands, which were described with cc-pVDZ basis sets, and rhodium, which was described using a RECP with the associated cc-pVTZ-PP basis set.[6] A frequency calculation was run to identify the obtained structure as a minimum (no negative eigenvalues). Energy was corrected for zero-point energy.

xyz-coordinates for compound **3**:

Rh	0.05140	-0.00887	-0.49304
P	0.19618	-2.35160	-0.88375
P	0.00918	2.37262	-0.58266
C	-0.82361	-2.83903	-2.35028
C	-0.35885	-3.49580	0.46588
C	1.86622	-3.02908	-1.36076
C	-0.59294	3.30212	0.90081
C	-1.03624	2.97419	-2.00184
C	1.68363	3.10278	-0.91390
C	1.79737	4.61149	-1.15983
C	-1.65482	4.37658	-1.93048
C	0.22543	3.05749	2.17290
C	-0.43771	-2.11328	-3.64477
C	-0.44579	-4.99209	0.14040
C	2.81114	-3.40503	-0.21213
H	2.08319	2.54595	-1.77561
H	2.30995	2.81048	-0.05796
H	-1.83804	2.23218	-2.10697
H	-0.39397	2.87607	-2.89400
H	-1.63338	2.98194	1.05644
H	-0.61796	4.37591	0.65756
H	-0.74029	-3.92947	-2.48694
H	-1.86487	-2.61449	-2.07562
H	-1.33994	-3.11752	0.78152
H	0.33034	-3.31794	1.30708
H	2.33729	-2.27367	-2.00681
H	1.68543	-3.91336	-1.99526
H	1.28859	4.91987	-2.08553

H	2.85790	4.89294	-1.26281
H	1.38182	5.20509	-0.33038
H	-2.35768	4.46503	-1.08805
H	-2.22614	4.57591	-2.85209
H	-0.90712	5.17634	-1.82850
H	0.25169	1.98984	2.43164
H	-0.22056	3.60320	3.01957
H	1.26496	3.40776	2.06948
H	-0.50360	-1.02080	-3.52257
H	-1.11366	-2.40604	-4.46410
H	0.58927	-2.35338	-3.96339
H	-0.70776	-5.56064	1.04766
H	0.50467	-5.39985	-0.23753
H	-1.22253	-5.20206	-0.61074
H	2.96571	-2.57320	0.48909
H	3.79738	-3.68615	-0.61446
H	2.43643	-4.26426	0.36475
N	4.76157	0.09865	1.07583
C	2.43942	-0.02074	1.56360
C	2.05050	0.03126	0.23329
C	3.12655	0.11438	-0.63853
C	4.43640	0.14451	-0.19364
C	3.77491	0.01835	1.93564
F	2.90842	0.16781	-1.98391
F	4.10355	-0.03089	3.23353
F	5.44074	0.22355	-1.07758
F	1.51553	-0.12295	2.55344
H	-1.30127	-0.03537	-1.37334
Si	-2.14027	-0.05817	0.24662
O	-2.92502	-1.50141	-0.09313
O	-2.19233	0.12875	1.90570
O	-3.11149	1.20718	-0.24324
C	-4.26973	-1.78790	0.28038
C	-4.59729	-3.23410	-0.04286
C	-4.19887	1.77849	0.47910
C	-5.16951	2.42560	-0.49152
C	-1.75793	-0.80151	2.89248

C	-1.95342	-0.19770	4.27015
H	-4.94860	-1.12421	-0.26435
H	-4.41480	-1.59943	1.34930
H	-4.46796	-3.42930	-1.10779
H	-5.63255	-3.45584	0.22242
H	-3.95063	-3.91504	0.51144
H	-3.81503	2.52341	1.18302
H	-4.70855	1.02018	1.07776
H	-4.67161	3.19659	-1.08006
H	-5.99596	2.88848	0.05116
H	-5.58056	1.68671	-1.18027
H	-0.70649	-1.04648	2.73615
H	-2.33469	-1.72890	2.80416
H	-1.36488	0.71362	4.37427
H	-1.63482	-0.90141	5.04132
H	-3.00205	0.04941	4.44039

Literature

1 a) A. L. Raza, J. A. Panetier, M. Teltewskoi, S. A. Macgregor and T. Braun, *Organometallics* 2013, **32**, 3795; b) P. Zhao, J. F. Hartwig, *Organometallics* **2008**, *27*, 4749; c) M. G. Voronkov and Y. I. Skorik, *Russ Chem Bull* 1964, **13**, 1127.

2 J. Méndez-Vivar and A. Mendoza-Bandala, *Journal of Non-Crystalline Solids* 2000, **261**, 127.

3 T. Braun, D. Noveski, B. Neumann and H. G. Stammler, *Angew. Chem.* 2002, **114**, 2870.

4 R. T. Price, R. A. Andersen, E. L. Muetterties, *Journal of Organometallic Chemistry* 1989, **376**, 407.

5 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, H. P. H. X. Li, A. F. Izmaylov, G. Z. J. Bloino, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, in *Gaussian 09, Revision C.01*, Gaussian, Inc., Wallingford CT, 2010.

6 K. A. Peterson, D. Figgen and H. S. M. Dolg, *J. Chem. Phys.* 2007, **126**, 124101.