Supporting Information

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S–F and S–C Activation of SF₆ and SF₅ Derivatives at Rhodium: Conversion of SF₆ into H₂S**

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Supplementary Information

Experimental Section

All experiments were performed on a Schlenk line under an atmosphere of argon or in an argon-filled dry-box with dioxygen levels below 10 ppm. All solvents were purified and dried by conventional methods and distilled under an atmosphere of argon prior to use. [Rh(µ-H)(dippp)]$_2$ (1), [Rh(µ-F)(dippp)]$_2$ (2) and [Rh(µ-Cl)(dippp)]$_2$ (9) were prepared according to literature procedures.$^{[1]}$ (Pentafluorosulfanyl)benzene, 1-methyl-4-(pentafluorosulfanyl)benzene, thiophenole and HSiEt$_3$ were purchased from Sigma-Aldrich, $p$-thiocresole was obtained from ABCR. Trifluoromethyl sulfur pentafluoride was purchased from Apollo Scientific. SF$_6$ was a gift of Solvay Fluor GmbH. (Pentafluorosulfanyl)benzene and 1-methyl-4-(pentafluorosulfanyl)benzene were distilled under an atmosphere of argon and stored over Molecular Sieve (3 Å) before use. Microanalyses were performed with a HEKAtech Euro EA Elemental Analyzer. The NMR spectra were recorded at 298 K on a Bruker DPX 300 or on a Bruker Avance 400 spectrometer. The $^{19}$F NMR and $^{29}$Si NMR spectra were referenced externally to 85% H$_2$PO$_4$ at $\delta=0$ ppm, to C$_6$F$_6$ at $\delta=-162.9$ ppm and to Si(CH$_3$)$_4$ at $\delta=0$ ppm, respectively. Mass spectra were measured with a Micromass Q-Tof-2 instrument equipped with a Linden LIFDI source (Linden CMS GmbH). GC mass spectra were recorded with an Agilent 6890N gas chromatograph and an Agilent 5973 Network mass selective detector.

Reaction of [Rh(µ-H)(dippp)]$_2$ (1) with PhSF$_6$

In a PFA tube [Rh(µ-H)(dippp)]$_2$ (1) (15.8 mg, 20.8 µmol) was dissolved in cyclohexane-d$_{12}$ (0.25 mL). PhSF$_6$ (0.9 µL, 6.2 µmol) was added to the solution. $^{31}$P$\{^1$H$\}$, $^1$H and $^{19}$F$\{^1$H$\}$ NMR spectra were recorded at room temperature and the reaction mixture was then heated to 50 °C. The reaction was monitored by NMR spectroscopy. After 120 h the $^{31}$P$\{^1$H$\}$, $^1$H and $^{19}$F$\{^1$H$\}$ NMR spectroscopic data revealed a complete conversion of 1 into [Rh(µ-F)(dippp)]$_2$ (2)$^{[19,21]}$ and [Rh$_2$(µ-H)(µ-SPh)(dippp)]$_2$ (3a) which were present in a ratio of 2.5 : 1. The complexes [Rh$_2$(µ-H)(µ-F)(dippp)]$_2$ (4) and [Rh$_2$(µ-H)(µ-H)$_3$(dippp)]$_2$ (5)$^{[18]}$ and HF were observed as intermediates (Figure 1).

Analytical data for [Rh$_2$(µ-H)(µ-F)(dippp)]$_2$ (4): MS (LIFDI, benzene): calcd. for C$_{30}$H$_{49}$FP$_4$Rh$_2$: $m/z$ (%) 778.244; found: 778.265. $^1$H NMR (300 MHz, C$_6$D$_{12}$): $\delta=-10.43$ (m, $^1$J(Rh,H)=26.5 Hz, 1H, RhH) ppm; the signal for the hydrido ligand was assigned by measuring a $^1$H-$^{31}$P-HMBC NMR spectrum; the $^1$J(Rh,H) coupling constant was confirmed from a $^1$H$\{^{31}$P$\}$ NMR spectrum; the signals for the hydrogen atoms of the phosphine ligands could not be assigned because of overlap with the signals for 1, 2, 3a and 5, which are present in the reaction mixture. $^{19}$F$\{^1$H$\}$ NMR (282.4 MHz, C$_6$D$_{12}$): $\delta=-355.6$ ppm (m). $^{31}$P$\{^1$H$\}$ NMR (121.5 MHz, C$_6$D$_{12}$): $\delta=66.9$ (ddm, $^1$J(P,Rh)=193.8 Hz, $^2$J(P,F)=174.2 Hz), 39.3 ppm (m). Analytical data for [Rh$_2$(µ-H)(µ-H)$_3$(dippp)]$_2$ (5)$^{[14]}$: $^1$H NMR (300 MHz, C$_6$D$_{12}$): $\delta=-7.83$ (s, br, RhH), −14.25 ppm (s, br, RhH). $^{31}$P$\{^1$H$\}$ NMR (121.5 MHz, C$_6$D$_{12}$): $\delta=62.7$ (d, br, $^1$J(P,Rh)=105.8 Hz), 57.1 ppm (d, br, $^1$J(P,Rh)=167.3 Hz).
Figure 1. $^{31}$P($^1$H)-NMR-spectra of the complexes 1, 2, 3a, 4 and 5; after 0 h, 24 h, 48 h, 72 h and 120 h reaction time.

Reaction of [Rh($\mu$-H)(dippp)]$_2$ (1) with CH$_3$C$_6$H$_4$SF$_5$

In a PFA tube [Rh($\mu$-H)(dippp)]$_2$ (1) (11.5 mg, 15.1 $\mu$mol) was dissolved in cyclohexane-d$_{12}$ (0.25 mL). CH$_3$C$_6$H$_4$SF$_5$ (1 mg, 4.5 $\mu$mol) was added to the solution. $^{31}$P($^1$H), $^1$H and $^{19}$F($^1$H) NMR spectra were recorded at room temperature and the reaction mixture was then heated to 50 °C. The reaction was monitored by NMR spectroscopy. After 72 h the $^{31}$P($^1$H), $^1$H and $^{19}$F($^1$H) NMR spectroscopic data revealed a complete conversion of 1 into [Rh($\mu$-F)(dippp)]$_2$ (2)\textsuperscript{1b,2} and [Rh$_2$(H)($\mu$-SC$_6$H$_4$CH$_3$)(dippp)]$_2$ (3b) in a ratio of 2.5 : 1. The complexes [Rh$_2$(H)($\mu$-H)$_3$(dippp)]$_2$ (4) and [Rh$_2$(H)($\mu$-H)$_3$(dippp)]$_2$ (5)\textsuperscript{1a} and HF were observed as intermediates.

Reaction of [Rh($\mu$-H)(dippp)]$_2$ (1) with SF$_5$CF$_3$

In a PFA tube [Rh($\mu$-H)(dippp)]$_2$ (1) (12.2 mg, 16.0 $\mu$mol) was dissolved in cyclohexane-d$_{12}$ (0.3 mL). The PFA tube was inserted into a Young NMR tube. The solution was cooled to $-196$ °C and the NMR tube was degassed in vacuo. After warming up to room temperature the reaction mixture was pressurized with gaseous SF$_5$CF$_3$ to 1 atm. The reaction was monitored by NMR spectroscopy. After 48 h at room temperature the $^{31}$P($^1$H), $^1$H and $^{19}$F($^1$H) NMR spectroscopic data revealed a complete conversion of 1 into [Rh($\mu$-F)(dippp)]$_2$ (2)\textsuperscript{1b,2} and [Rh$_2$(H)($\mu$-SCF$_3$)(dippp)]$_2$ (3c) which were present in a ratio of 2.5 : 1. The complexes [Rh$_2$(H)($\mu$-H)($\mu$-F)(dippp)]$_2$...
(4) and [Rh₂(H)(μ-H)₂(dippp)]₂ (5)\(^{1a}\) were observed as intermediates. Analytical data for [Rh₂(μ-H)(μ-SCF₆)](dippp)]₂ (3e): MS (LIFDI, benzene): calcd. for C₃₁H₆₀P₄Rh₂S⁶ [M]⁺: m/z (%) 860.213; found: 860.213. \(^{1}H\) NMR (300 MHz, C₆D₁₂): \(\delta=–11.07\) ppm (m, \(J(Rh,H)=21.7\) Hz, 1H; RhH); the signal for the hydrido ligand was assigned by measuring a \(^{1}H\)–\(^{31}P\) HMBC NMR spectrum; the \(1/2\)(H,H) coupling constant was confirmed from a \(^{1}H\)–\(^{31}P\) NMR spectrum; the signals for the hydrogen atoms of the phosphine ligands could not be assigned because of overlap with the signals for 2, which is present in the reaction mixture. \(^{19}F\)\(^{[1]H}\) NMR (282.4 MHz, C₆D₁₂): \(\delta=–24.8\) ppm (m, br, SCF₆). \(^{31}P\)^\(^{[1]H}\) NMR (121.5 MHz, C₆D₁₂): \(\delta=44.3\) (dm, \(\nu(J(P,Rh)=173.2\) Hz), 38.9 ppm (dm, \(\nu(J(P,Rh)=169.0\) Hz). A correct elemental analysis could not be obtained, because we were not able to separate complex 3c from 2.

Synthesis of [Rh₂(μ-H)(μ-SPh)(dippp)]₂ (3a)

A solution of thiophenole (25 \(µL\), 245 \(µmol\)) in toluene (1 mL) was slowly added at –78 °C to a solution of [Rh₂(μ-H)(dippp)]₂ (1) (183 mg, 241 \(µmol\)) in toluene (4 mL). The reaction mixture was allowed to warm to –40 °C and was stirred for additional 3 h. The volatiles were then removed in vacuo. The crude product of 3a contained a 10 % impurity of [Rh₂(μ-SPh)(dippp)]₂. Pure 3a was obtained by fractional crystallization (two times) of the crude product from a toluene solution at –30 °C to yield orange crystals of 3a which were dried in vacuo. Yield: 134 mg (64%). Elemental analysis (%) calcd. for C₃₆H₆₀P₄Rh₂S⁶: C 49.77, H 8.59, S 6.39; found: C 49.90, H 8.61, S 3.30. \(^{1}H\) NMR (300 MHz, C₆D₁₂): \(\delta=7.74\) (m, 2H; Ph), 6.96 (m, 2H; Ph), 6.89 (m, 1H; Ph), 2.19 (m, 8H; CH), 1.73 (m, br, 4H; CH₂CH₂CH₃), 1.46 (dd, \(\nu(J(H,P)=15.8\) Hz, \(\nu(J(H,H)=7.2\) Hz, 12H; CH₃), 1.25–1.09 (m, 32H; CH₂CH₂CH₃, CH₃), 1.05 (dd, \(\nu(J(H,P)=12.4\) Hz, \(\nu(J(H,H)=6.9\) Hz, 12H; CH₃), –10.14 ppm (m, \(\nu(J(Rh,H)=21.8\) Hz, 1H; RhH); the \(1/2\)(H,H) and \(1/2\)(Rh,H) coupling constants were confirmed from a \(^{1}H\)–\(^{31}P\) NMR spectrum. \(^{31}P\)^\(^{[1]H}\) NMR (121.5 MHz, C₆D₁₂): \(\delta=45.9\) (dm, \(\nu(J(P,Rh)=167.8\) Hz), 38.9 ppm (dm, \(\nu(J(P,Rh)=168.9\) Hz).

Synthesis of [Rh₂(μ-SPh)(dippp)]₂

A solution of thiophenole (18 \(µL\), 177 \(µmol\)) in toluene (1 mL) was slowly added to a solution of [Rh₂(μ-H)(dippp)]₂ (1) (61.3 mg, 81 \(µmol\)) in toluene (1 mL). The reaction mixture was stirred at room temperature for 4 h. The volatiles were then removed in vacuo. The residue was recrystallized from a THF solution at room temperature to yield orange crystals of [Rh₂(μ-SPh)(dippp)]₂ which were dried in vacuo. Yield: 61.4 mg (78%). Elemental analysis (%) calcd. for C₄₂H₇₅P₄Rh₂S₂ (868.74): calc.: C 51.64, H 8.05, S 6.56; found: C 51.98, H 8.06, S 6.11. \(^{1}H\) NMR (300 MHz, C₆D₁₂): \(\delta=8.49\) (m, 4H; Ph), 7.1–7.0 (m, 6H; Ph), 1.93 (m, 8H; CH), 1.29 (dd, \(\nu(J(H,P)=14.3\) Hz, \(\nu(J(H,H)=7.2\) Hz, 24H; CH₃), 1.14 (dd, \(\nu(J(H,P)=11.5\) Hz, \(\nu(J(H,H)=6.9\) Hz, 24H; CH₃), 0.91 (m, 8H; CH₂CH₂CH₂), 0.78 ppm (m, br, 4H; CH₂CH₂CH₂); the \(3/2\)(H,H) coupling constants were confirmed from a \(^{1}H\)–\(^{31}P\) NMR spectrum. \(^{31}P\)^\(^{[1]H}\) NMR (121.5 MHz, C₆D₁₂): \(\delta=35.1\) ppm (dm, \(\nu(J(P,Rh)=165.3\) Hz).
Figure 2. Molecular structure of 3a\(^\text{[3]}\) (ORTEP, ellipsoids are set at a 50% probability). All hydrogen atoms except for the bridging hydride are omitted for clarity. Selected bond lengths [Å] and angles [°]: Rh1–S1 2.3129(10), Rh2–S1 2.3131(11), S1–C1 1.785(2), C1–S1–Rh1 112.32(13), Rh1–S1–Rh2 77.167(15).

Figure 3. Molecular structure of [Rh(µ-SPh)(dippp)]\(^2\)\(^\text{[3]}\) (ORTEP, ellipsoids set at 50% probability). All hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Rh1–P1 2.2220(6), Rh1–P2 2.2244(7), Rh1–S1 2.4232(6), S1–C1 1.785(3), P1–Rh1–P2 94.58(2), P1–Rh1–S1 92.72(2), P2–Rh1–S1 166.25(2), C1–S1–Rh1 101.34(8).

**Synthesis of [Rh\(_2\)(µ-H)(µ-SC\(_6\)H\(_4\)CH\(_3\))(dippp)]\(_2\) (3b)**

A solution of \(p\)-thiocresole (13.4 mg, 108 \(\mu\)mol) in toluene (1 mL) was at \(-78\) °C slowly added to a solution of [Rh(µ-H)(dippp)]\(_2\) (1) (82 mg, 108 \(\mu\)mol) in toluene (4 mL). The reaction mixture was allowed to warm to \(-40\) °C and was stirred for additional 3 h. The volatiles were then removed in vacuo. The residue was recrystallized from a toluene solution at \(-30\) °C to yield orange crystals of 3b which were dried in vacuo. Yield: 134 mg (64%). Elemental analysis (%) calcd. for C\(_{37}\)H\(_{76}\)P\(_4\)Rh\(_2\)S (868.74): calc.: C 50.34, H 8.68, S 3.63; found: C 50.49, H 8.67, S 3.34. \(^1\)H NMR (300 MHz, C\(_6\)D\(_6\)): \(\delta=7.64\) (d, \(^3J(H,H)=7.9\) Hz, 2H; SC\(_6\)H\(_4\)CH\(_3\)), 2.21 (m, 8H; CH), 2.00 (s, 3H; SC\(_6\)H\(_4\)CH\(_3\)), 1.73 (m br, 4H; CH\(_2\)CH\(_2\)CH\(_2\)), 1.48 (dd, \(^3J(H,P)=15.8\) Hz, \(^3J(H,H)=7.2\) Hz, 12H; CH\(_3\)), 1.28-0.99 (m, 32H; CH\(_2\)CH\(_2\)CH\(_2\)), 0.93 (dd, \(^3J(H,P)=14.6\) Hz, \(^3J(H,H)=7.2\) Hz, 12H; CH\(_3\)), 10.07 ppm (m, \(^1J(P,Rh)=21.8\) Hz, 1H; RH); the \(^3J(H,H)\) and \(^1J(Rh,H)\) coupling constants were confirmed from a \(^{31}\)P\\(^{[1]}\)\(_H\) NMR spectrum. \(^{31}\)P\\(^{[1]}\)\(_H\) NMR (121.5 MHz, C\(_6\)D\(_6\)): \(\delta=45.8\) (dm, \(^1J(P,Rh)=167.8\) Hz), 39.0 ppm (dm, \(^1J(P,Rh)=167.1\) Hz).
NMR spectroscopy. Complex $[\text{Rh} \left( \mu \right) \left( \mu - \text{SC}_6\text{H}_5\text{CH}_3 \right) \text{(dippp)}]_2$ (3b)$^{11}$ (ORTEP, ellipsoids set at 50% probability). All hydrogen atoms except for the bridging hydride are omitted for clarity. Selected bond lengths [Å] and angles [°]: $\text{Rh}_1-\text{P}_1$ 2.2222(6), $\text{Rh}_1-\text{P}_2$ 2.2281(5), $\text{Rh}_1-\text{S}_1$ 2.3280(6), $\text{Rh}_1$–$\text{H}_1\text{A}$ 1.75(3), $\text{S}_1$–$\text{C}_1\text{E}$ 1.788(3), $\text{P}_1$–$\text{Rh}_1$–$\text{P}_2$ 96.32(2), $\text{P}_1$–$\text{Rh}_1$–$\text{S}_1$ 168.940(18), $\text{P}_2$–$\text{Rh}_1$–$\text{S}_1$ 94.745(19), $\text{P}_1$–$\text{Rh}_1$–$\text{H}_1\text{A}$ 82.5(14), $\text{P}_2$–$\text{Rh}_1$–$\text{H}_1\text{A}$ 174.2(15), $\text{S}_1$–$\text{Rh}_1$–$\text{H}_1\text{A}$ 86.5(14), $\text{C}_1\text{E}$–$\text{S}_1$–$\text{Rh}_1$ 108.37(8).

**Reaction of $[\text{Rh}(\mu-H)(\text{dippp})]_2$ (1) with PhSF$_3$ in the presence of neohexene**

In a PFA tube $[\text{Rh}(\mu-H)(\text{dippp})]_2$ (1) (26.0 mg, 34.2 μmol) was dissolved in cyclohexane-d$_{12}$ (0.3 mL). Neohexene (42.0 μL, 342.0 μmol) and PhSF$_3$ (1.4 μL, 10.3 μmol) were added to the solution. The reaction mixture was heated to 50 °C and the reaction was monitored by NMR spectroscopy. After 96 h the $^{31}$P[$^1$H], $^1$H and $^{19}$F[$^1$H] NMR spectroscopic data revealed a complete conversion of 1 into $[\text{Rh}(\mu-F)(\text{dippp})]_2$ (2)$^{1b,2}$ and $[\text{Rh}_2(\mu-F)(\mu-SPh)(\text{dippp})]_2$ (6a) which were present in a ratio of 1.5 : 1. HF could be detected by $^1$H and $^{19}$F NMR spectroscopy. Complex $[\text{Rh}_2(\mu-H)(\mu-F)(\text{dippp})]_2$ (4) was observed as intermediate. Analytical data for $[\text{Rh}_2(\mu-F)(\mu-SPh)(\text{dippp})]_2$ (6a): MS (LIFDI, benzene): calcd. for C$_{30}$H$_{35}$FP$_4$Rh$_2$S$_4$ [M]$^+$: m/z (%) 886.248; found: 886.244. $^{19}$F[$^1$H] NMR (282.4 MHz, C$_6$D$_{12}$): δ=−390.8 ppm (m, br). $^{31}$P[$^1$H] NMR (121.5 MHz, C$_6$D$_{12}$): δ=58.4 ppm (m, partially overlapped by the signal for 2), 38.8 ppm (ddm, $^1$J(P,Rh)=169.8 Hz, $^2$J(P,P)=53.4 Hz). The signals of the hydrogen atoms of the phosphine ligands could not be assigned because of overlap with the signals for the hydrogen atoms for complex 2 which was present in the reaction mixture.

**Reaction of $[\text{Rh}(\mu-H)(\text{dippp})]_2$ (1) with CH$_3$C$_6$H$_5$SF$_3$ in the presence of neohexene**

In a PFA tube $[\text{Rh}(\mu-H)(\text{dippp})]_2$ (1) (21.8 mg, 28.7 μmol) was dissolved in cyclohexane-d$_{12}$ (0.3 mL). Neohexene (35.0 μL, 287.0 μmol) and CH$_3$C$_6$H$_5$SF$_3$ (1.9 mg, 8.6 μmol) were added to the solution. The reaction mixture was heated to 50 °C and the reaction was monitored by NMR spectroscopy. After 96 h the $^{31}$P[$^1$H], $^1$H and $^{19}$F[$^1$H] NMR spectroscopic data revealed a complete conversion of 1 into $[\text{Rh}(\mu-F)(\text{dippp})]_2$ (2)$^{1b,2}$ and $[\text{Rh}_2(\mu-F)(\mu-\text{SC}_6\text{H}_5\text{CH}_3)(\text{dippp})]_2$ (6b) which were present in a ratio of 1.5 : 1. HF could be detected by $^1$H and $^{19}$F NMR spectroscopy. Complex $[\text{Rh}_2(\mu-H)(\mu-F)(\text{dippp})]_2$ (4) was observed as intermediate. Analytical data for $[\text{Rh}_2(\mu-F)(\mu-\text{SC}_6\text{H}_5\text{CH}_3)(\text{dippp})]_2$ (6b): MS (LIFDI, benzene): calcd. for C$_{37}$H$_{45}$FP$_4$Rh$_2$S$_4$ [M]$^+$: m/z (%) 900.263; found: 900.250. $^{19}$F[$^1$H] NMR (282.4 MHz, C$_6$D$_{12}$): δ=−380.6 ppm (m br). $^{31}$P[$^1$H] NMR (121.5 MHz, C$_6$D$_{12}$): δ=58.5 ppm (m, partially overlapped by the signal for 2), 38.1 ppm (ddm, $^1$J(P,Rh)=170.3 Hz, $^2$J(P,P)=53.6 Hz).
signals of the hydrogen atoms of the phosphine ligands could not be assigned because of overlap with the signals for the hydrogen atoms for 2 which was present in the reaction mixture.

**Reaction of [Rh(µ-H)(dippp)]₂ (I) with SF₂CF₃ in the presence of neohexene**

In a PFA tube [Rh(µ-H)(dippp)]₂ (I) (21.6 mg, 28.4 µmol) was dissolved in cyclohexane-d₁₂ (0.3 mL) and neohexene (34.9 µL, 284.0 µmol) was added to the solution. The PFA tube was inserted into a Young NMR tube. The reaction mixture was then heated to 50 °C and the reaction was monitored by NMR spectroscopy. After 48 h the ³¹P{¹H}, ¹H and ¹⁹F{¹H} NMR spectroscopic data revealed a complete conversion of 1 into [Rh(µ-F)(dippp)]₂ (2) and [Rh₂(µ-F)(µ-SCF₃)(dippp)]₂ (6c) which were present in a ratio of 1.5 : 1. HF could be detected by ¹H and ¹⁹F NMR spectroscopy. Complex [Rh₂(µ-H)(µ-F)(dippp)]₂ (4) was observed as intermediate. Analytical data for [Rh₂(µ-F)(µ-SCF₃)(dippp)]₂ (6c): MS (LIFDI, benzene): calcd. for C₁₅H₁₁₆F₂₁P₂Rh₄S₄: [M]⁺ m/z (%) 878.204; found: 878.206. ¹⁹F{¹H} NMR (282.4 MHz, C₆D₁₂): δ=−19.6 (m, br, SCF₃), −390.8 ppm (m, br RhF). ³¹P{¹H} NMR (121.5 MHz, C₆D₁₂): δ=56.7 (m, partially overlapped by the signal for 2), 38.9 ppm (ddm, ¹J(P,Rh)=70.3 Hz, ²J(P,P)=56.2 Hz). The signals of the hydrogen atoms of the phosphine ligands could not be assigned because of overlap with the signals for the hydrogen atoms for 2 which was present in the reaction mixture.

**Reaction of [Rh₂(µ-F)(µ-SPh)(dippp)]₂ (6a) with H₂**

In a PFA tube [Rh₂(µ-F)(µ-SPh)(dippp)]₂ (6a) (26.0 mg, 34.2 µmol) was dissolved in cyclohexane-d₁₂ (0.3 mL). Neohexene (42.0 µL, 342.0 µmol) and PhSF₃ (1.4 µL, 10.3 µmol) were added to the solution and the PFA tube was inserted into a Young NMR tube. The reaction mixture was then heated to 50 °C and the reaction was monitored by NMR spectroscopy. After 96 h the ³¹P{¹H}, ¹H and ¹⁹F{¹H} NMR spectroscopic data revealed a complete conversion of 1 into [Rh₂(µ-F)(dippp)]₂ (2) and [Rh₂(µ-F)(µ-SCF₃)(dippp)]₂ (6a) which were present in a ratio of 1.5 : 1. The volatiles were then removed in vacuo and benzene-d₆ (0.3 mL) was added. The solution was cooled to −196 °C, was degassed in vacuo and the NMR tube was pressurized with gaseous SF₂CF₃ to 1 atm. After warming up to room temperature the reaction mixture was heated to 50 °C and the reaction was monitored by NMR spectroscopy. After 24 h the ³¹P{¹H}, ¹H and ¹⁹F{¹H} NMR spectroscopic data revealed a complete conversion of 6a into [Rh₂(µ-H)(µ-SPh)(dippp)]₂ (3a). The formation of HF was confirmed by NMR spectroscopy.

**Reaction of [Rh(µ-H)(dippp)]₂ (I) with PhSF₂ in the presence of HSiEt₃**

In a PFA tube [Rh(µ-H)(dippp)]₂ (I) (25.9 mg, 34.0 µmol) was dissolved in cyclohexane-d₁₂ (0.3 mL). PhSF₃ (4.7 µL, 34.0 µmol) and HSiEt₃ (33 µL, 340 µmol) were added to the solution. The reaction mixture was then heated to 50 °C and the reaction was monitored by NMR spectroscopy. After 120 h the ³¹P{¹H}, ¹H and ¹⁹F{¹H} NMR spectroscopic data revealed a complete conversion of 1 into [Rh₂(µ-H)(µ-SSiEt₃)(dippp)]₂ (8) and [Rh₂(µ-H)(µ-SPh)(dippp)]₂ (3a) which were present in a ratio of 2.5 : 1. The NMR spectroscopic data also revealed the formation of FSiEt₃ and benzene.
Reaction of $[\text{Rh}(\mu\text{-H})(\text{dippp})]_2 \ (1)$ with $\text{CH}_3\text{C}_6\text{H}_4\text{SF}_5$ in the presence of HSiEt$_3$

In a PFA tube $[\text{Rh}(\mu\text{-H})(\text{dippp})]_2 \ (1)$ (17.6 mg, 23.1 $\mu$mol) was dissolved in cyclohexane-d$_{12}$ (0.3 mL). CH$_3$C$_6$H$_4$SF$_5$ (5.0 mg, 23.1 $\mu$mol) and HSiEt$_3$ (37 $\mu$L, 231 $\mu$mol) were added to the solution. The reaction mixture was heated to 50 °C and the reaction was monitored by NMR spectroscopy. After 120 h the $^{31}\text{P}\{^1\text{H}\}$, $^1\text{H}$ and $^{19}\text{F}\{^1\text{H}\}$ NMR spectroscopic data revealed a complete conversion of 1 into $[\text{Rh}_2(\mu\text{-H})(\mu\text{-SSiEt}_3)(\text{dippp})_2] \ (8)$ and $[\text{Rh}_2(\mu\text{-H})(\mu\text{-SCC}_6\text{H}_4\text{CH}_3)(\text{dippp})_2] \ (3b)$ which were present in a ratio of 2.5 : 1. The NMR spectroscopic data also revealed the formation of FSiEt$_3$ and toluene.

Reaction of $[\text{Rh}(\mu\text{-H})(\text{dippp})]_2 \ (1)$ with SF$_5\text{CF}_3$ in the presence of HSiEt$_3$

In a PFA tube $[\text{Rh}(\mu\text{-H})(\text{dippp})]_2 \ (1)$ (18.2 mg, 23.9 $\mu$mol) was dissolved in cyclohexane-d$_{12}$ (0.3 mL). HSiEt$_3$ (38 $\mu$L, 239 $\mu$mol) was added to the solution and the PFA tube was inserted into a Young NMR tube. The solution was cooled to $-196$ °C, the NMR tube was degassed in vacuo and was pressurized with SF$_5\text{CF}_3$ to 1 atm. After warming up to room temperature the reaction mixture was heated to 50 °C and the reaction was monitored by NMR spectroscopy. After 120 h the $^{31}\text{P}\{^1\text{H}\}$, $^1\text{H}$ and $^{19}\text{F}\{^1\text{H}\}$ NMR spectroscopic data revealed a complete conversion of 1 into $[\text{Rh}_2(\mu\text{-H})(\mu\text{-SSiEt}_3)(\text{dippp})_2] \ (8)$ and $[\text{Rh}_2(\mu\text{-H})(\mu\text{-SCF}_3)(\text{dippp})_2] \ (3c)$ which were present in a ratio of 2.5 : 1. The NMR spectroscopic data also revealed the formation of FSiEt$_3$ and trifluoromethane.

Reaction of $[\text{Rh}(\mu\text{-H})(\text{dippp})]_2 \ (1)$ with PhSF$_5$ in the presence of HSiEt$_3$

In a PFA tube $[\text{Rh}(\mu\text{-F})(\text{dippp})]_2 \ (2)$ (27.3 mg, 34.3 $\mu$mol) was dissolved in toluene-d$_8$ (0.35 mL). HSiEt$_3$ (38 $\mu$L, 239 $\mu$mol) was added to the solution. The solution was cooled to $-30$ °C and HSiEt$_3$ (55 $\mu$L, 343 $\mu$mol) was added. The reaction mixture was stored at $-15$ °C. After 20 h the $^1\text{H}$, $^{19}\text{F}$ and $^{31}\text{P}$ NMR spectroscopic data revealed a quantitative conversion of 2 into $[\text{Rh}(\eta^2\text{-HSiEt}_3)(\text{dippp})] \ (7)^{10b}$ and the formation of FSiEt$_3$ was observed. PhSF$_5$ (4.7 $\mu$L, 34.3 $\mu$mol) was added to the reaction mixture. The reaction mixture was heated to 50 °C and the reaction was monitored by NMR spectroscopy. After 72 h the $^{31}\text{P}\{^1\text{H}\}$, $^1\text{H}$ and $^{19}\text{F}\{^1\text{H}\}$ NMR spectroscopic data revealed a complete conversion of 7 into $[\text{Rh}_2(\mu\text{-H})(\mu\text{-SSiEt}_3)(\text{dippp})_2] \ (8)$. The NMR spectroscopic data also revealed the formation of benzene.

Reaction of $[\text{Rh}(\mu\text{-F})(\text{dippp})]_2 \ (2)$ with PhSF$_5$ in the presence of HSiEt$_3$

In a PFA tube $[\text{Rh}(\mu\text{-F})(\text{dippp})]_2 \ (2)$ (28.3 mg, 35.5 $\mu$mol) was dissolved in cyclohexane-d$_{12}$ (0.3 mL). PhSF$_5$ (4.8 $\mu$L, 35.5 $\mu$mol) and HSiEt$_3$ (58 $\mu$L, 355 $\mu$mol) were added to the solution. The reaction mixture was heated to 50 °C and the reaction was monitored by NMR spectroscopy. After 120 h the $^{31}\text{P}\{^1\text{H}\}$, $^1\text{H}$ and $^{19}\text{F}\{^1\text{H}\}$ NMR spectroscopic data revealed a complete conversion of 2 into $[\text{Rh}_2(\mu\text{-H})(\mu\text{-SSiEt}_3)(\text{dippp})_2] \ (8)$. The NMR spectroscopic data also revealed the formation of FSiEt$_3$ and benzene.
Reaction of $[\text{Rh}(\mu-H)(\text{dippp})]_2$ (1) with SF$_6$ in the presence of HSiEt$_3$:

Synthesis $[\text{Rh}_2(\mu-H)(\mu-\text{SSiEt}_3)(\text{dippp})]_2$ (8)

In a PFA tube $[\text{Rh}(\mu-H)(\text{dippp})]_2$ (1) (24.3 mg, 31.9 $\mu$mol) was dissolved in cyclohexane-$d_{12}$ (0.3 mL). HSiEt$_3$ (52.0 $\mu$L, 319.0 $\mu$mol) was added to the solution and the PFA tube was inserted into a Young NMR tube. The solution was cooled to $-196$ °C, the NMR tube was degassed in vacuo, and was pressurized with gaseous SF$_6$ to 1 atm. After warming up to room temperature, the reaction mixture was heated to 50 °C and the reaction was monitored by NMR spectroscopy. After 72 h the $^{31}$P-$^1$H, $^1$H and $^{19}$F-$^1$H NMR spectroscopic data revealed a complete conversion of 1 into $[\text{Rh}_2(\mu-H)(\mu-\text{SSiEt}_3)(\text{dippp})]_2$ (8) together with the formation of FSiEt$_3$.

Alternatively, $[\text{Rh}_2(\mu-H)(\mu-\text{SSiEt}_3)(\text{dippp})]_2$ (8) was synthesized in larger amounts by stirring a mixture of $[\text{Rh}(\mu-H)(\text{dippp})]_2$ (1) (164 mg, 0.216 mmol) and HSiEt$_3$ (690 $\mu$L, 6.5 mmol) in toluene (2 mL) in a PFA tube under 1 atm of SF$_6$ at room temperature. After 10 days the volatiles were removed in vacuo. The residue was washed with 1,1,1,3,3-pentafluorobutane (3 x 4 mL) and dried in vacuo to yield a red solid of 8. Yield: 141 mg (72%).

$^1$H NMR (300 MHz, C$_6$D$_6$): $\delta$=2.17 (m, br, 8H; CH), 1.78 (m, br, 4H; CH$_2$CH$_2$CH$_2$), 1.51 (dd, $^3$J(H,P)=13.8 Hz, $^3$J(H,H)=7.2 Hz, 12H; CH$_3$), 1.35 (dd, $^3$J(H,P)=15.2 Hz, $^3$J(H,H)=7.2 Hz, 12H; CH$_3$), 1.30-1.02 (m, 47H; CH$_2$CH$_2$CH$_2$, CH$_3$, Si(CH$_2$CH$_3$)$_3$), $\sim$11.46 ppm (m, $^1$J(Rh,H)=21.9 Hz, 1H; RhH); the $^3$J(H,H) and $^1$J(Rh,H) coupling constants were confirmed from a $^1$H-$^{29}$Si-HMBC NMR spectrum. $^{31}$P-$^1$H NMR (121.5 MHz, C$_6$D$_6$): $\delta$=41.0 (dm, $^1$J(P,Rh)=172.4 Hz), 36.9 ppm (dm, $^1$J(P,Rh)=176.2 Hz). $^{29}$Si-$^1$H NMR ((59.6 MHz, C$_6$D$_6$): $\delta$=22.1 ppm (m). The $^1$H-$^{29}$Si-HMBC NMR spectrum shows a strong correlation of the $^{29}$Si resonance with the signals for the silicon-bound ethyl groups at $\delta$=1.30-1.02 ppm in the $^1$H domain. Although the compound was spectroscopically pure, satisfactory microanalytical data could despite several attempts not be obtained, because of the extremely high air sensitivity.

Figure 5. Molecular structure of 8[3] (ORTEP, ellipsoids are set at a 50% probability). All hydrogen atoms except for H1 are omitted for clarity. Selected bond lengths [Å] and angles [°]: Rh1–S1 2.3600(5), Rh2–S1 2.3816(5), S1–Si1 2.1586(7), P3–Rh1–S1 167.035(18), P4–Rh1–S1 94.677(18), Rh1–S1–Rh2 75.908(15).
Reaction of $[\text{Rh(H)}(\eta^2-\text{HSiEt}_3)(\text{dippp})](7)$ with SF$_6$ in the presence of HSiEt$_3$

In a PFA tube $[\text{Rh(µ-F)(dippp)}]_2$ (2) (18.9 mg, 23.7 µmol) was dissolved in toluene-d$_8$ (0.3 mL). The solution was cooled to −30 °C and HSiEt$_3$ (38 µL, 237 µmol) was added. The reaction mixture was stored at −15 °C. After 22 h the $^1$H, $^{19}$F and $^{31}$P NMR spectroscopic data revealed a quantitative conversion of 2 into $[\text{Rh(H)}(\eta^2-\text{HSiEt}_3)(\text{dippp})](7)$ and the formation of FSiEt$_3$. The PFA tube was inserted into a Young NMR tube. The reaction mixture was cooled to −196 °C, was degassed in vacuo, and was pressurized with gaseous SF$_6$ to 1 atm. After warming up to room temperature the reaction mixture was heated to 50 °C and the reaction was monitored by NMR spectroscopy. After 48 h $^{31}$P{$^1$H}, $^1$H and $^{19}$F{$^1$H} NMR spectroscopic data revealed complete conversion of 7 into $[\text{Rh}_2(µ-H)(µ-\text{SSiEt}_3)(\text{dippp})]_2$ (8).

Reaction of $[\text{Rh}(µ-F)(\text{dippp})]_2$ (2) with SF$_6$ in the presence of HSiEt$_3$

In a PFA tube $[\text{Rh}(µ-F)(\text{dippp})]_2$ (2) (34.8 mg, 43.7 µmol) was dissolved in cyclohexane-d$_{12}$ (0.3 mL). HSiEt$_3$ (71.0 µL, 437.0 µmol) was added to the solution and the PFA tube was inserted into a Young NMR tube. The solution was cooled to −196 °C, the NMR tube was degassed in vacuo, and was pressurized with gaseous SF$_6$ to 1 atm. After warming up to room temperature the reaction mixture was heated to 50 °C and the reaction was monitored by NMR spectroscopy. After 72 h the $^{31}$P{$^1$H}, $^1$H and $^{19}$F{$^1$H} NMR spectroscopic data revealed a complete conversion of 2 into $[\text{Rh}_2(µ-H)(µ-\text{SSiEt}_3)(\text{dippp})]_2$ (8). The NMR spectroscopic data also revealed the formation of FSiEt$_3$.

Reaction of $[\text{Rh}_2(µ-H)(µ-\text{SSiEt}_3)(\text{dippp})]_2$ (8) with HCl and DCl

In a Young NMR tube $[\text{Rh}_2(µ-H)(µ-\text{SSiEt}_3)(\text{dippp})]_2$ (8) (15.9 mg, 17.5 µmol) was dissolved in benzene-d$_6$. The solution was cooled to −78 °C, a solution of HCl (2 M in Et$_2$O, 35.1 µmol, 18 µL) was added and the reaction mixture was allowed to warm up to room temperature. After 16 h the $^{31}$P NMR spectroscopic data revealed a complete conversion of 8 into $[\text{Rh}(µ-\text{Cl})(\text{dippp})]_2$ (9). The formation of H$_2$, HSiEt$_3$ and H$_2$S was observed. Complex 9 was identified by comparison of the NMR data with literature. ClSiEt$_3$ was identified by GC-MS analysis and by comparison of the $^1$H and $^{29}$Si NMR data by comparison with a pure sample of ClSiEt$_3$. H$_2$S was identified by GC-MS analysis in solution as well as in the gas phase above the reaction mixture.

In an independent reaction 8 (17.0 mg, 18.8 µmol) was treated with a solution of DCl (1 M in Et$_2$O, 86.1 µmol, 86 µL) under the same conditions and D$_2$S was identified by GC-MS analysis in solution as well as in the gas phase above the reaction mixture and by comparison of the $^2$H NMR spectroscopic data with the NMR spectroscopic data of a solution of H$_2$S gas in benzene-d$_6$ ($^1$H NMR (300 MHz, C$_6$D$_6$): δ=0.41 ppm (br s)).

Regeneration of $[\text{Rh}(µ-H)(\text{dippp})]_2$ (1) from $[\text{Rh}(µ-\text{Cl})(\text{dippp})]_2$ (9)

A solution of allylmagnesium bromide (1M in Et$_2$O, 80 µL, 80.0 µmol) was slowly added to a solution of $[\text{Rh}(µ-\text{Cl})(\text{dippp})]_2$ (9) (21.6 mg, 25.5 µmol) in thf-d$_8$ (0.4 mL). After 4 h at room temperature the $^{31}$P NMR
spectroscopic data revealed complete conversion of 9 into [Rh(η⁵-C₅H₅)(dippp)] (10) Complex 10 can be converted into [Rh(μ-H)(dippp)]: (1) by treatment with H₂ following a literature procedure.[1a]

References


[3] Data for X-ray structure analysis: All structures were solved by direct methods and refined with the full-matrix least squares method on F² (SHELXL-97).[1] Orange crystals of 3a were obtained by cooling a toluene solution to ~30 °C. Crystallographic data for 3a: C₆H₅P₃Rh₂S, M = 868.71, crystal dimensions 0.38 x 0.12 x 0.06 mm³, monoclinic; space group P2₁/a; a = 8.8423(2) Å, b = 22.0835(6) Å, c = 11.4253(2) Å, β = 112.2560(14)°, V = 2064.80(8) Å³, Z = 2, ρcalc = 1.397 g cm⁻³; 2θmax = 55.00°, MoKα radiation (λ = 0.71073 Å), T = 100(2) K, 34268 reflections collected, 9482 independent reflections (Rint = 0.0580); STOE IPDS 2θ diffractometer; multiscan absorption correction 2σ (min./max. transmission 0.6961/0.9409), μ = 1.028 mm⁻¹. Final R₁, wR₂ values on all data: 0.0263, 0.0469; R₁, wR₂ values for 8519 reflections with I > 2σ(I): 0.0221, 0.0462; residual electron density +0.361/-0.818 e Å⁻³; the metal bound hydrogen atom was located in the difference Fourier map and refined isotropically. Orange crystals of [Rh(μ-SPh)(dippp)]₃ were obtained by slow evaporation of the solvent from a THF solution stored at room temperature. Crystallographic data: C₆H₅P₃Rh₂S₃R, M = 976.86, crystal dimensions 0.36 x 0.24 x 0.16 mm³, monoclinic; space group P2₁/c; a = 10.6222(4) Å, b = 13.2071(3) Å, c = 17.7829(7) Å, β = 113.595(3)°, V = 2286.17(14) Å³, Z = 2, ρcalc = 1.419 g cm⁻³; 2θmax = 59.32°, MoKα radiation (λ = 0.71073 Å), T = 90(2) K, 21293 reflections collected, 5219 independent reflections (Rint = 0.1437); STOE IPDS 2θ diffractometer; multiscan absorption correction 2σ (min./max. transmission 0.7190/0.8588), μ = 0.981 mm⁻¹. Final R₁, wR₂ values on all data: 0.0327, 0.1317; R₁, wR₂ values for 3975 reflections with I > 2σ(I): 0.0299, 0.1281; residual electron density +1.650/-1.472 e Å⁻³; Orange crystals of 3b were obtained by cooling a toluene solution to ~30 °C. Crystallographic data: C₆H₅P₃Rh₂S, M = 882.74, crystal dimensions 0.36 x 0.32 x 0.25 mm³, orthorhombic; space group Pmn2₁; a = 21.2769(10) Å, b = 8.8769(4) Å, c = 11.2570(6) Å, Z = 2, ρcalc = 1.379 g cm⁻³; 2θmax = 64.42°, MoKα radiation (λ = 0.71073 Å), T = 100(2) K, 32390 reflections collected, 6356 independent reflections (Rint = 0.0402); STOE IPDS 2θ diffractometer; multiscan absorption correction 2σ (min./max. transmission 0.7149/0.7882), μ = 0.999 mm⁻¹. Final R₁, wR₂ values on all data: 0.0296, 0.0530; R₁, wR₂ values for 5937 reflections with I > 2σ(I): 0.0247, 0.0512; residual electron density +0.806/-0.656 e Å⁻³; the metal bound hydrogen atom was located in the difference Fourier map and refined isotropically. Red crystals of 8 were obtained by cooling a n-hexane solution to ~30 °C. Crystallographic data for 8: C₆H₅P₃Rh₂SSi, M = 907.89, crystal dimensions 0.36 x 0.16 x 0.12 mm³, monoclinic; space group P2₁/c; a = 12.6589(3) Å, b = 24.8568(6) Å, c = 18.7621(4) Å, β = 130.566(2)°, V = 4484.77(18) Å³, Z = 4, ρcalc = 1.345 g cm⁻³; 2θmax = 53.34°, MoKα radiation (λ = 0.71073 Å), T = 100(2) K, 30720 reflections collected, 8932 independent reflections (Rint = 0.0440); STOE IPDS 2θ
diffractometer; multiscan absorption correction 2σ (min./max. transmission 0.7204 /0.8920), \( \mu = 0.975 \) mm\(^{-1} \). Final \( R_1, wR_2 \) values on all data: 0.0320, 0.0554; \( R_1, wR_2 \) values for 7698 reflections with \( I_o > 2\sigma(I_o) \): 0.0242, 0.0535; residual electron density +0.675/−0.810 e Å\(^{-3} \). CCDC 957478 (3a), 957481 ([Rh(\( \mu \)-SPh)(dippp)]\( _2 \)), 957479 (3b) and 957480 (8) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif