Supplementary Material (ESI) for Chemical Communications
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Supporting Information for:

Phosphine-Stabilized Silylene Rhodium Complex

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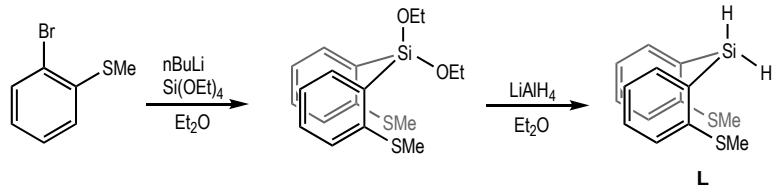
Experimental

All manipulations, unless otherwise stated, were performed under an atmosphere of nitrogen, using standard Schlenk techniques. Glassware was oven dried at 120ºC overnight and flamed under vacuum prior to use. Dry and oxygen free solvents were employed. $[Rh(PPh_3)_3Cl]$[1] and $[NaBAr^F{}_4]$[2] were prepared as previously described. NMR spectra were recorded on Bruker Ultra Shift 500 MHz spectrometer. ^1H and ^{13}C NMR spectra were referenced to the residual solvent signals. ^{31}P NMR spectra were referenced against 85% H_3PO_4 (external) and ^{29}Si NMR spectra were referenced against Me_4Si (TMS). Chemical shifts are quoted in ppm and coupling constants in Hz. Microanalysis was carried out with a LECO TRUSPEC microanalyzer. ESI-MS was recorded on a Bruker MicrOTOF instrument and MALDI-MS was recorded on a Bruker Microflex using terthiophene as matrix.

Synthesis and characterization of L



L

To a Schlenk charged with a solution of 2-bromothioanisole (0.47 mL, 3.51 mmol) in diethyl ether (5 mL) was added n-BuLi (2.63 mL of a 1.6 M solution in hexane, 4.18 mmol) at 0 ºC. The reaction mixture was stirred for 1 hour and $Si(OEt)_4$ was added dropwise (0.40 mL, 1.74 mmol) at -78 ºC. After being warmed to room temperature and stirred for 16 h, the reaction mixture was filtered through silica gel and the solvent was removed under vacuum. The resulting product $[Si(o\text{-}C_6H_4SMe)_2(OEt)_2]$ was recrystallized in a mixture of Et_2O (3 mL) and pentane (6 mL) at -20 ºC. $[Si(o\text{-}C_6H_4SMe)_2(OEt)_2]$ is isolated as a white microcrystalline solid (0.48 g, 76%).

To a Schlenk charged with $[Si(o\text{-}C_6H_4SMe)_2(OEt)_2]$ (80 mg, 0.22 mmol) and $LiAlH_4$ (417 mg, 10.98 mmol), Et_2O (9 mL) was added. The reaction mixture was stirred at room temperature overnight (16 h). After this time the reaction mixture was filtered through silica gel and the solution was evaporated to dryness and the residue washed with pentane (3 x 5 mL) to yield $[Si(o\text{-}C_6H_4SMe)_2H_2]$ (**L**) as a white powder (50 mg, 82%).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.57-7.19 (8H, aromatics), 5.12 (s, 2H, Si-H), 2.43 (s, 6H, S-CH_3).

^{29}Si NMR ($CDCl_3$): *obtained from correlation $^{1}H/^{29}Si$*: δ -42

Microanalysis for $C_{14}H_{16}S_2Si$: Requires: C, 60.82; H, 5.83; S, 23.19. Found: C, 60.71; H, 6.02; S, 22.99

ESI-MS (MeOH): calc. $[M-H]^+$: 275.04; found m/z 275.04

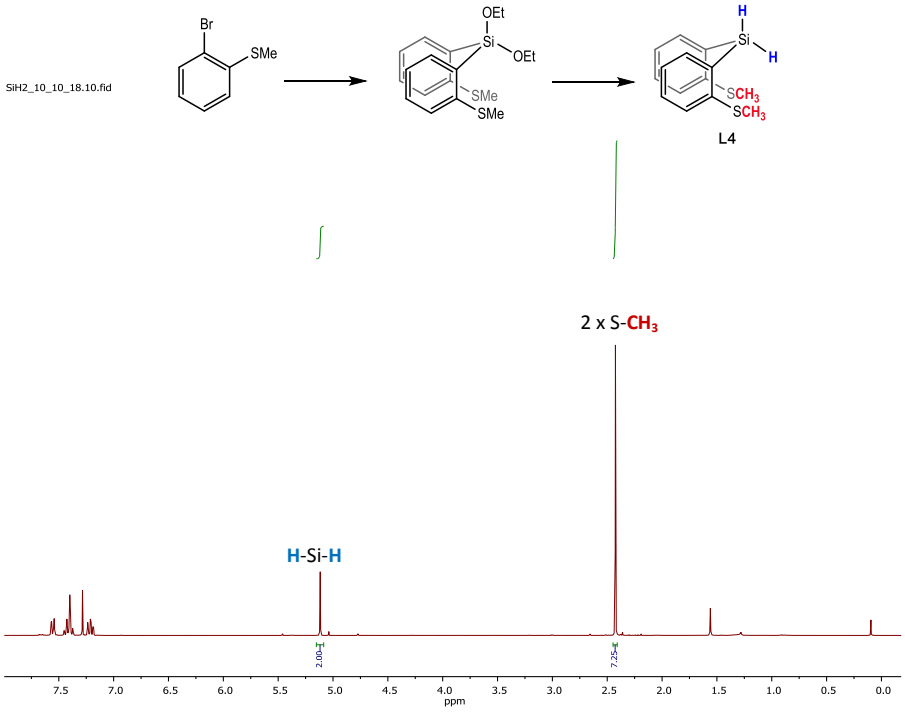


Figure S.1. ^{1}H NMR of **L**.

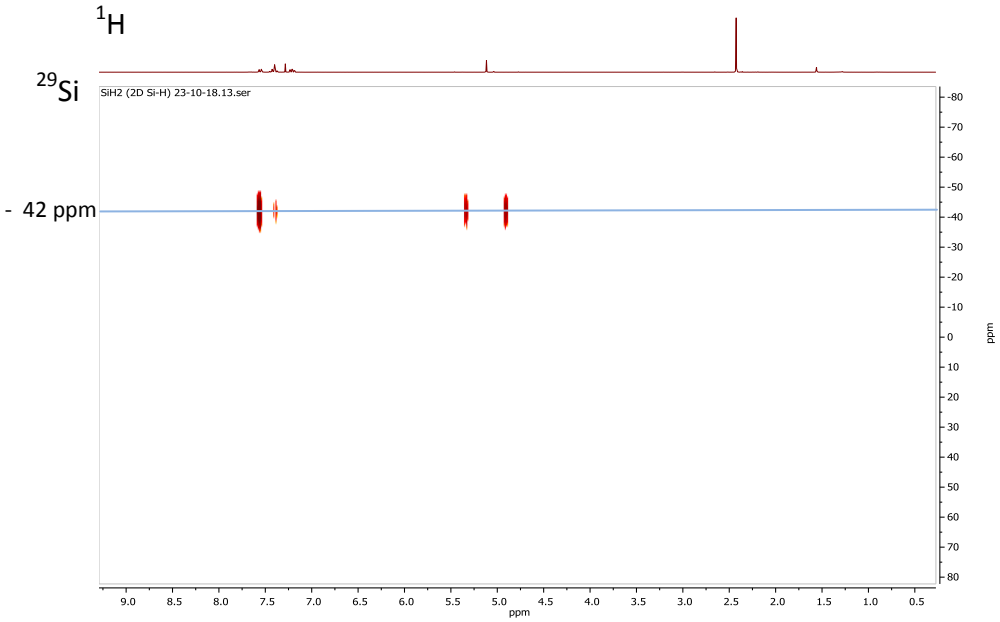


Figure S.2. ^{29}Si/^{1}H correlation for **L**.

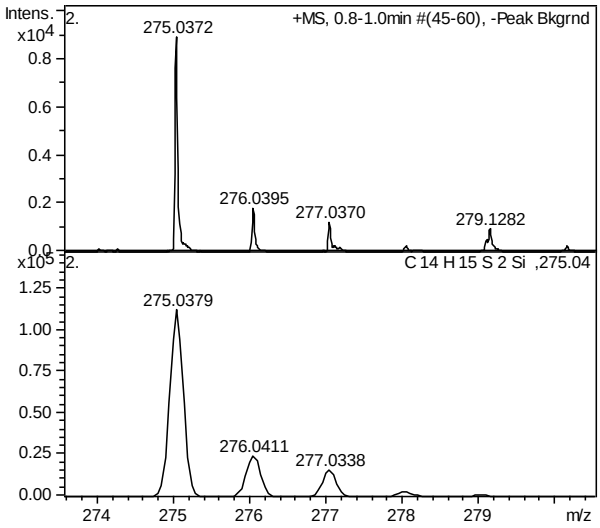
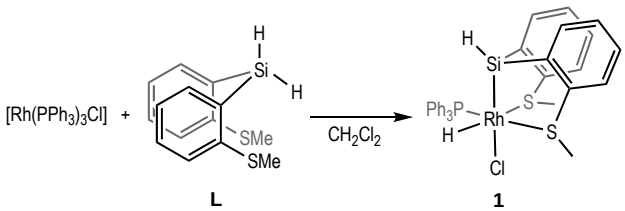


Figure S.3. ESI-MS of **L**.

Synthesis and characterization of 1



To a Schlenk charged with $[Rh(PPh_3)_3Cl]$ (33.5 mg, 0.036 mmol) in CH_2Cl_2 (5 mL), the equimolar amount of ligand $SiH_2(o\text{-}C_6H_4SMe)_2$ (10 mg, 0.036 mmol) was added. The mixture was stirred for 30 minutes and concentrated under vacuum. Addition of 20 mL of pentane gave a pale yellow precipitate that was washed with pentane and dried under vacuum. Yield 20 mg (82%).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.71-7.16 (m, 23H, aromatics), 4.09 (dt, $^2J_{Rh\text{-}H}$ = 8.6, $^3J_{P\text{-}H}$ = $^3J_{H\text{-}H}$ = 2.6 Hz, 1H), 3.27 (s, 3H, S-CH_3), 2.58 (s, 3H, S-CH_3),-12.78 (t, $^1J_{Rh\text{-}H}$ = $^2J_{P\text{-}H}$ = 16.8 Hz, 1H, Rh-H).

^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$): δ 46.5 (d, $^1J_{Rh\text{-}P}$= 138 Hz).

^{29}Si($CDCl_3$): *obtained from correlation $^1H/^{29}Si$*: δ 44

Microanalysis for $C_{32}H_{31}PClRhS_2Si$: Requires: C, 56.76; H, 4.61; S, 9.47. Found: C, 56.98; H, 4.65; S, 9.15

ESI-MS (MeOH): calc. $[M\text{-}Cl]^+$: 641.04; found m/z 641.04

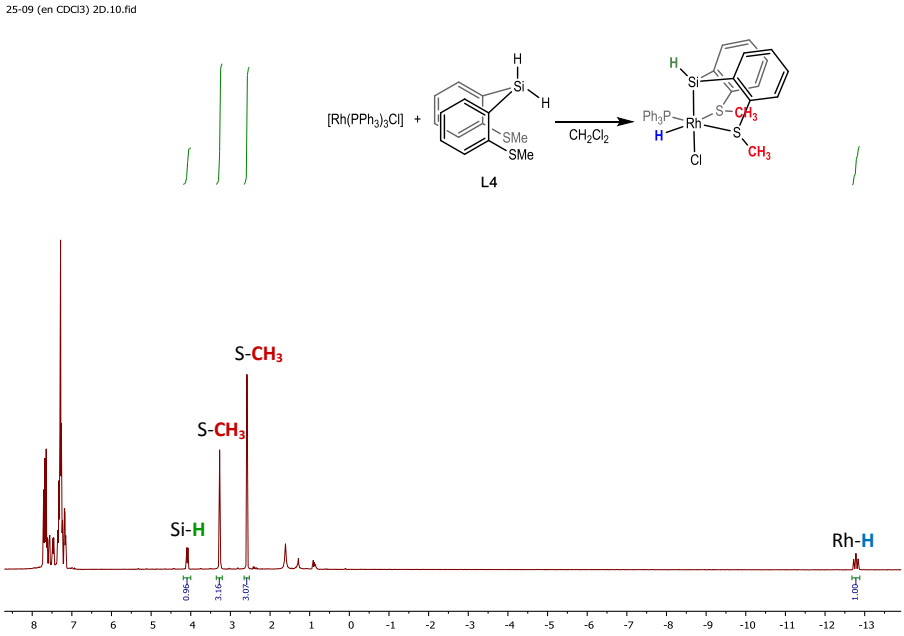


Figure S.4. ^{1}H NMR of **1**.

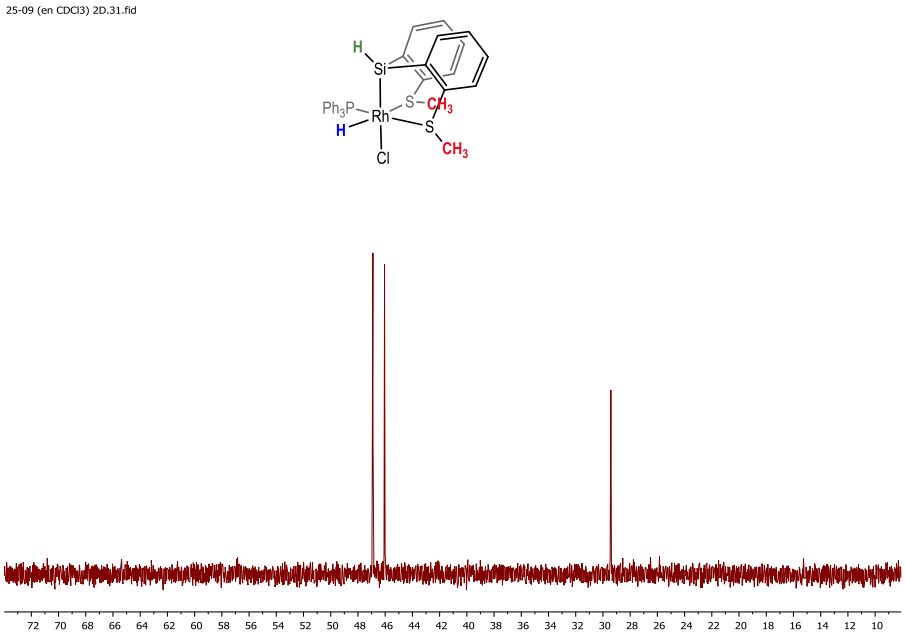


Figure S.5. $^{31}P\{^{1}H\}$ NMR of **1**.

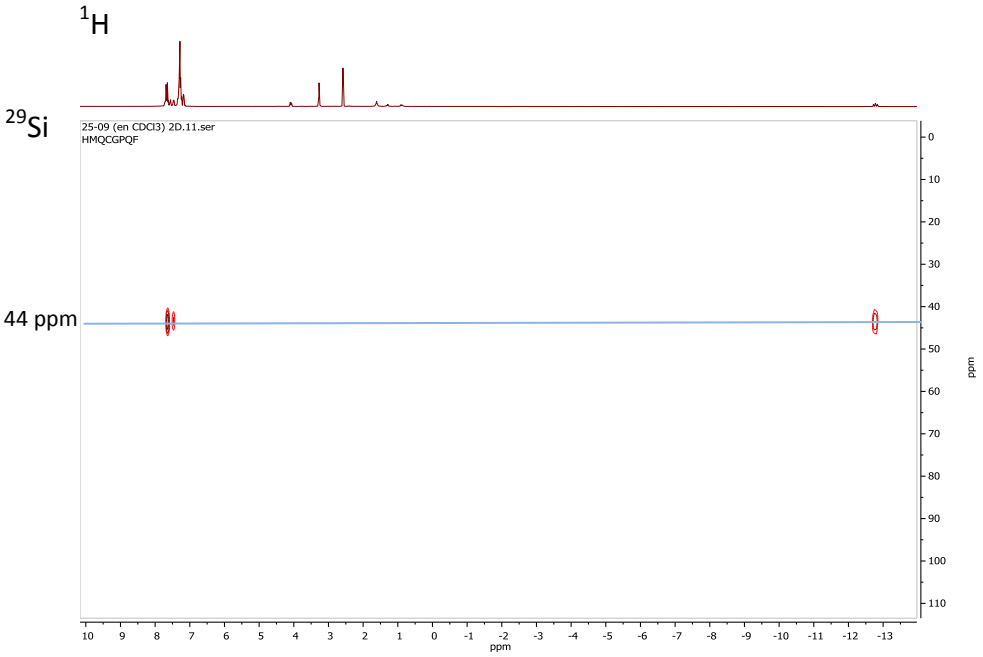


Figure S.6. $^{29}Si/^{1}H$ correlation for **1**.

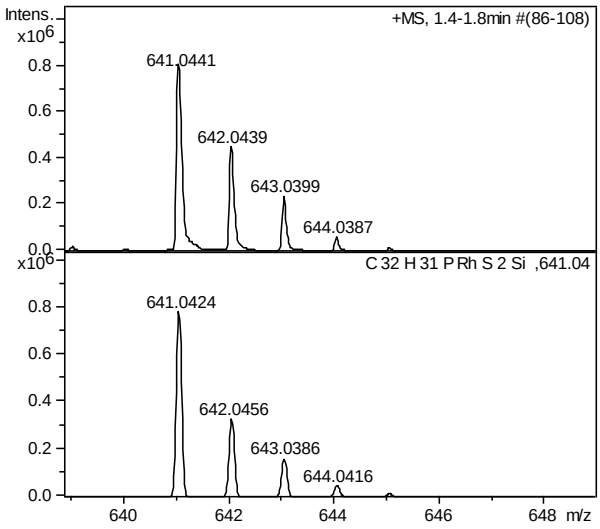
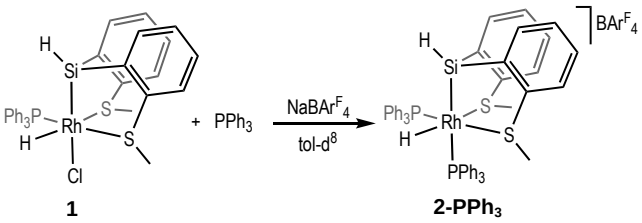


Figure S.7. ESI-MS of **1**.

Reactivity of 1 with PPh_3 and BAr^F_4



1 **2-PPh_3**

To a Young NMR tube charged with **1** (5.2 mg, 0.008 mmol), PPh_3 (4 mg, 0.016 mmol) and $NaBAr^F_4$ (6.8 mg, 0.008 mmol), toluene-d8 (0.5 mL) was added. The reaction was characterized in situ by NMR. The reaction was quantitative (i.e. > 95%) by NMR spectroscopy.

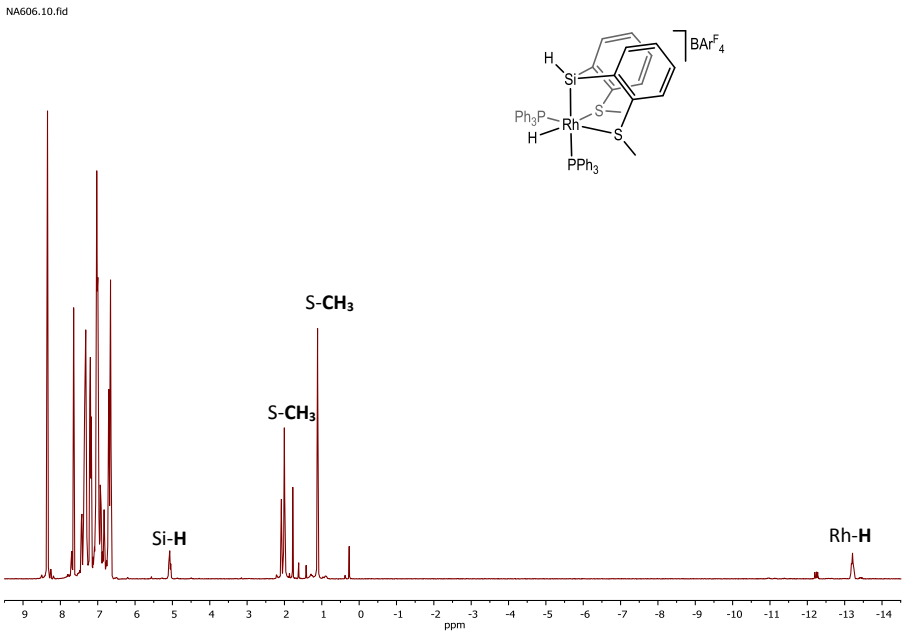


Figure S.8. ^1H NMR of **2-PPh_3**.

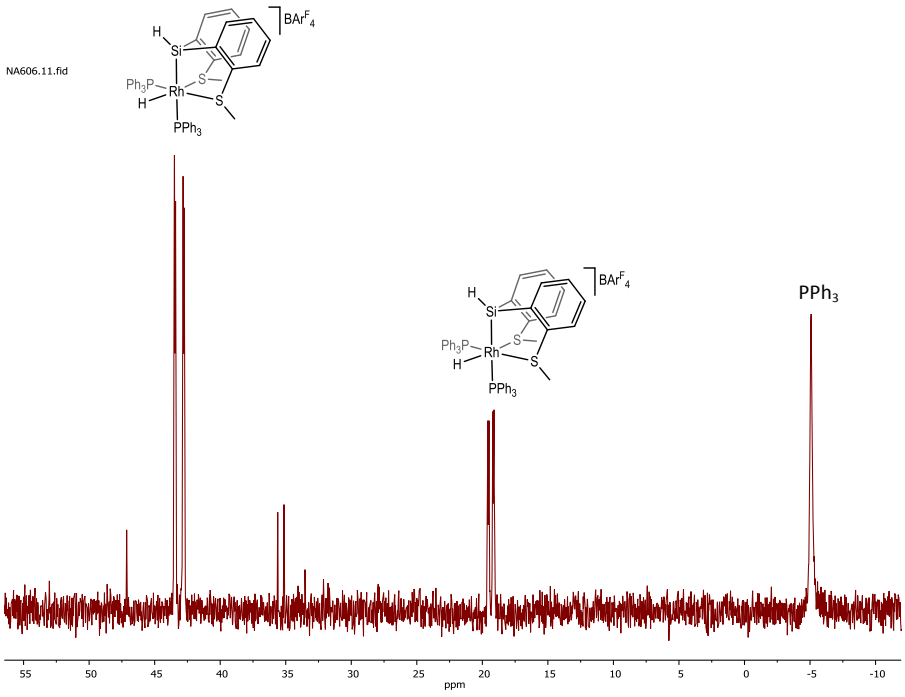
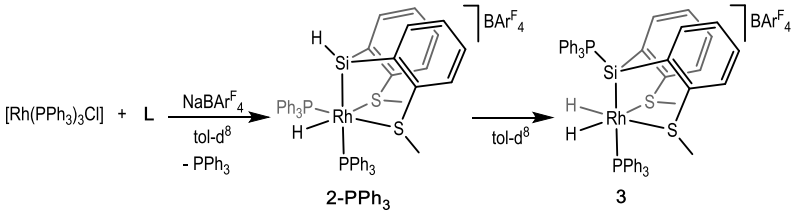


Figure S.9. $^{31}P\{^1H\}$ NMR of **2-PPh$_3$.**

Synthesis and characterization of 2-PPh$_3$ and 3



Synthesis of **2-PPh$_3$:** To a Young NMR tube charged with [Rh(PPh$_3$)$_3$Cl] (10 mg, 0.011 mmol), SiH$_2$(*o*-C$_6$H$_4$SMe)$_2$ (3 mg, 0.011 mmol) and NaBAr$^F_4$ (9.6 mg, 0.011 mmol), toluene-d8 (0.5 mL) was added. Compound **2-PPh$_3$** was characterized in situ by NMR. The reaction was quantitative (i.e. > 95%) by NMR spectroscopy.

^{1}H NMR (500 MHz, toluene-d8): δ 8.34-6.65 (38H, aromatics), 5.07 (t, $^2J_{Rh\text{-}H} = {}^3J_{Ptrans\text{-}H}$ = 13.6 Hz, 1H,Si-H), 2.01 (s, 3H, S-CH$_3$), 1.11 (s, 3H, S-CH$_3$), -13.21 (t, $^1J_{Rh\text{-}H} = {}^2J_{P\text{-}H}$ =13.3 Hz, 1H, Rh-H).

^{31}P{^{1}H} NMR (202 MHz, toluene-d8): δ 43.04 (dd, $^1J_{Rh\text{-}P}$ = 133, $^2J_{P\text{-}P}$ = 19 Hz), 19.26 (dd, $^1J_{Rh\text{-}P}$ = 78, $^2J_{P\text{-}P}$ = 19 Hz).

^{29}Si NMR (toluene-d8): *obtained from correlation $^1H/^{29}Si$*: δ 53

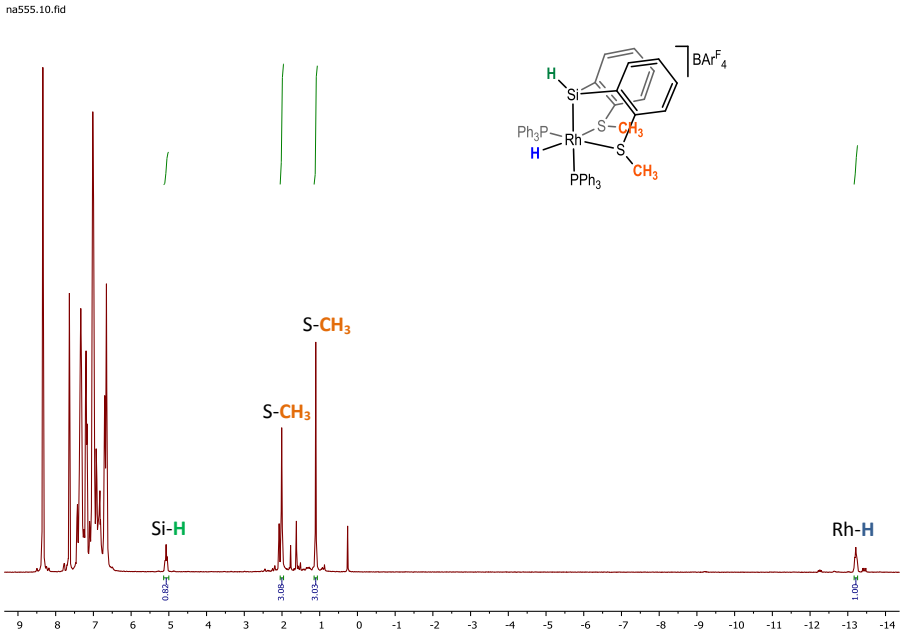


Figure S.10. ^{1}H NMR of **2-PPh$_3$**.

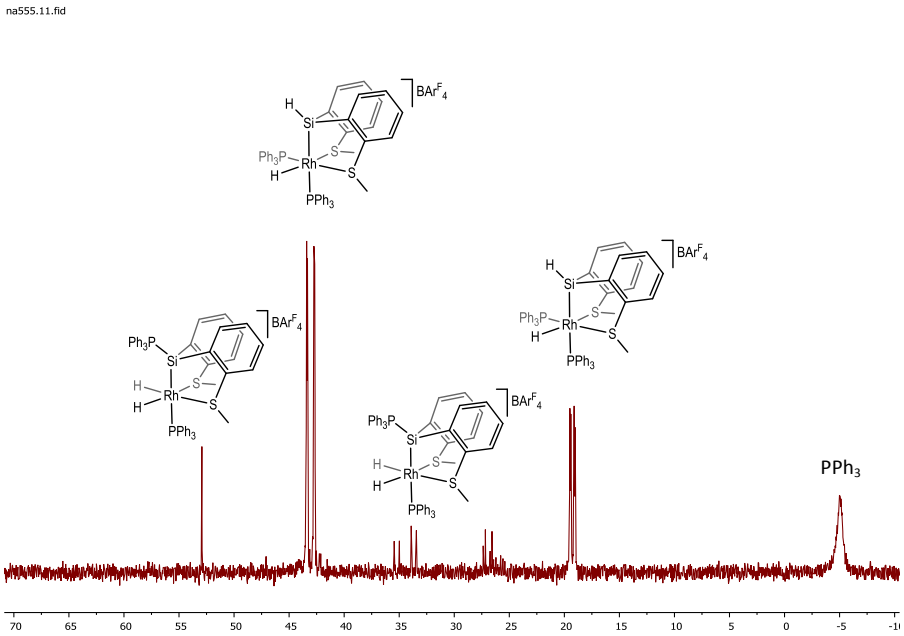


Figure S.11. $^{31}P\{^{1}H\}$ NMR of **2-PPh$_3$**.

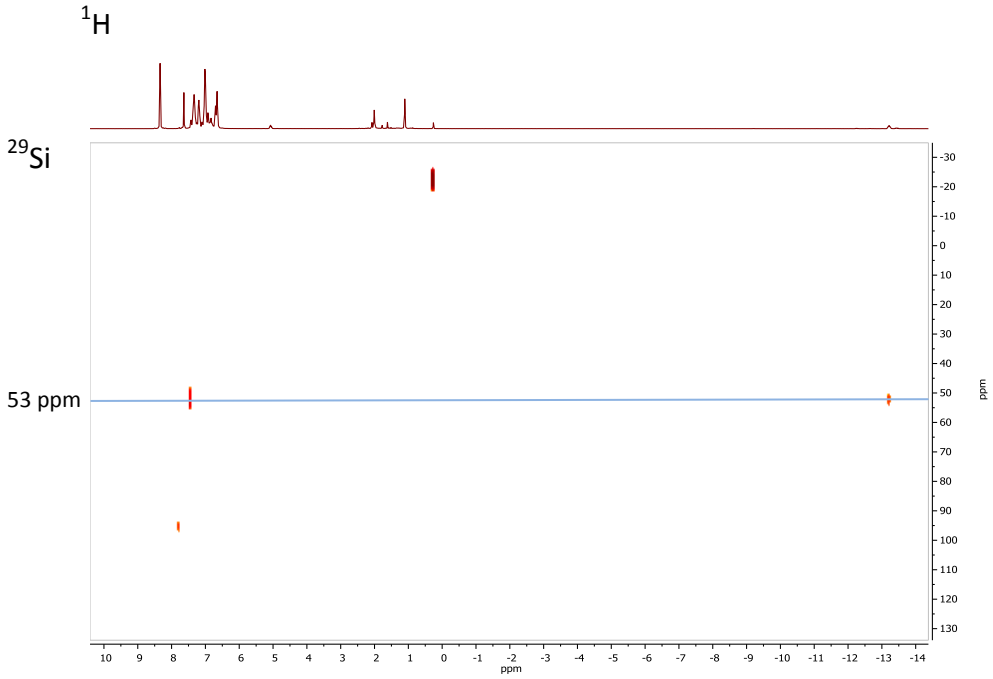


Figure S.12. $^{29}Si/^{1}H$ correlation for **2-PPh$_3$**.

Synthesis of **3:** To a Young NMR tube charged with [Rh(PPh$_3$)$_3$Cl] (10 mg, 0.011 mmol), SiH$_2$(*o*-C$_6$H$_4$SMe)$_2$ (3 mg, 0.011 mmol) and NaBAr$^F_4$ (9.6 mg, 0.011 mmol), toluene-d8 (0.5 mL) was added. The Young NMR tube was shaked during 48 hours. Compound **3** was characterized in situ by NMR. The reaction was almost quantitative (i.e. > 85%) by NMR spectroscopy.

^{1}H NMR (500 MHz, toluene-d8): δ 7.94-7.00 (38H, aromatics), 1.62 (s, 6H, S-CH$_3$), -13.43 (dd, $^{1}J_{Rh-H}$ = 24.9, $^{2}J_{P-H}$ = 14.0 Hz, 2H).

^{13}C{^{1}H} NMR (125 MHz, toluene-d8): δ 162.2 (q, J_{F-C} = 50 Hz, BAr$^F_4$), 135.2 (s, BAr$^F_4$), 129.1 (q, J_{F-C} = 11 Hz, BAr$^F_4$), 125.0 (q, J_{F-C} = 272 Hz, CF$_3$), 117.9 (p, J_{F-C} = 4.1 Hz, BAr$^F_4$), 136.2-121.5 (aromatics), 27.4 (s, 2 x S-CH$_3$).

^{31}P{^{1}H} NMR (202 MHz, toluene-d8): δ 53.09 (s), 33.84 (d, $^{1}J_{Rh-P}$ = 93.6 Hz).

^{29}Si{^{1}H} NMR (99 MHz, toluene-d8): δ 95 (ddd, $^{1}J_{P-Si}$ = 180 Hz, $^{1}J_{Rh-Si}$ = 41 Hz and $^{2}J_{P-Si}$ = 10 Hz).

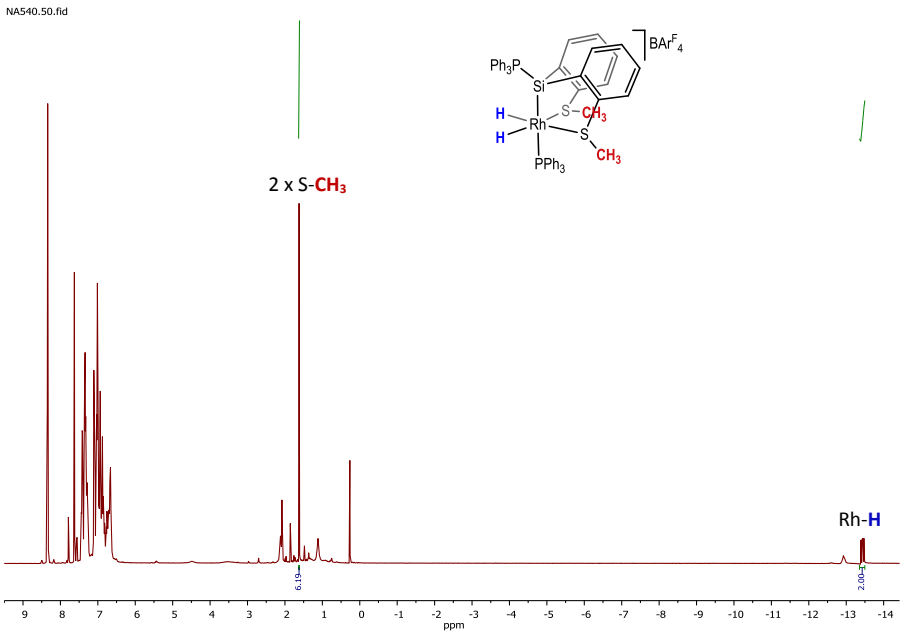


Figure S.13. ^{1}H NMR of **3**.

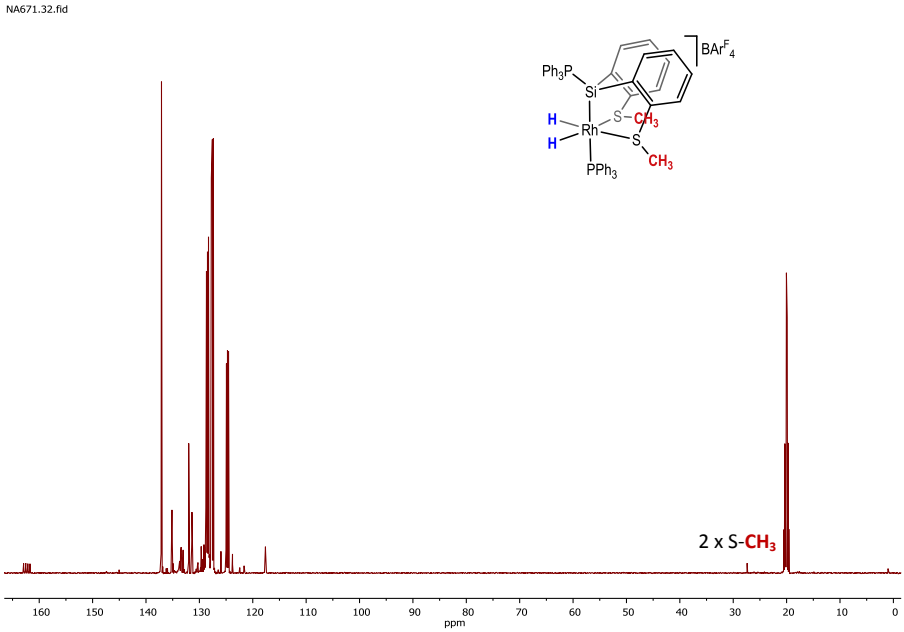


Figure S.14. $^{13}C\{^{1}H\}$ NMR of **3**.

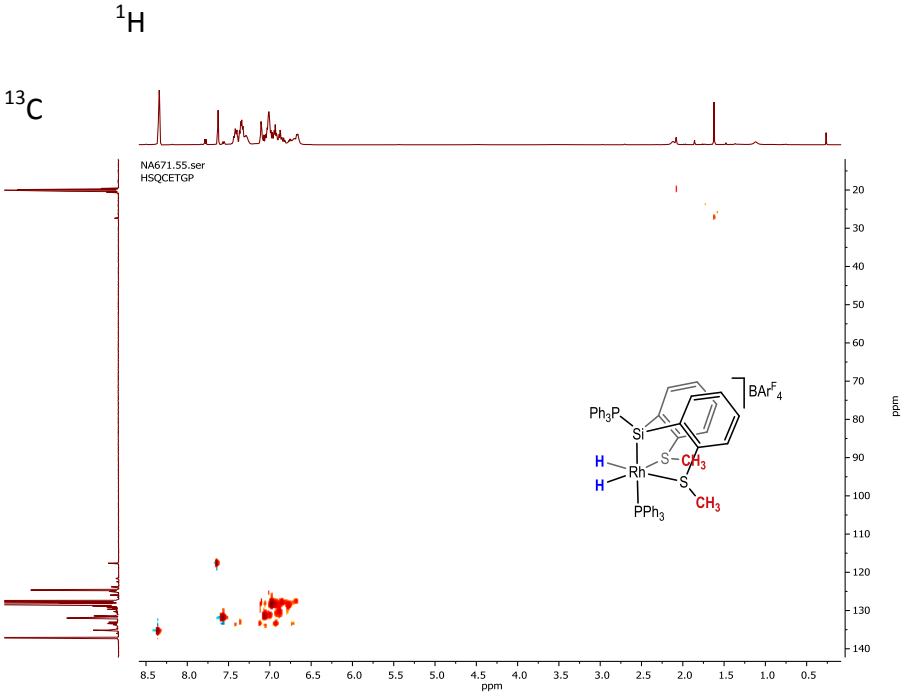


Figure S.15. ^{13}C{^{1}H}/^{1}H correlation for **3**.

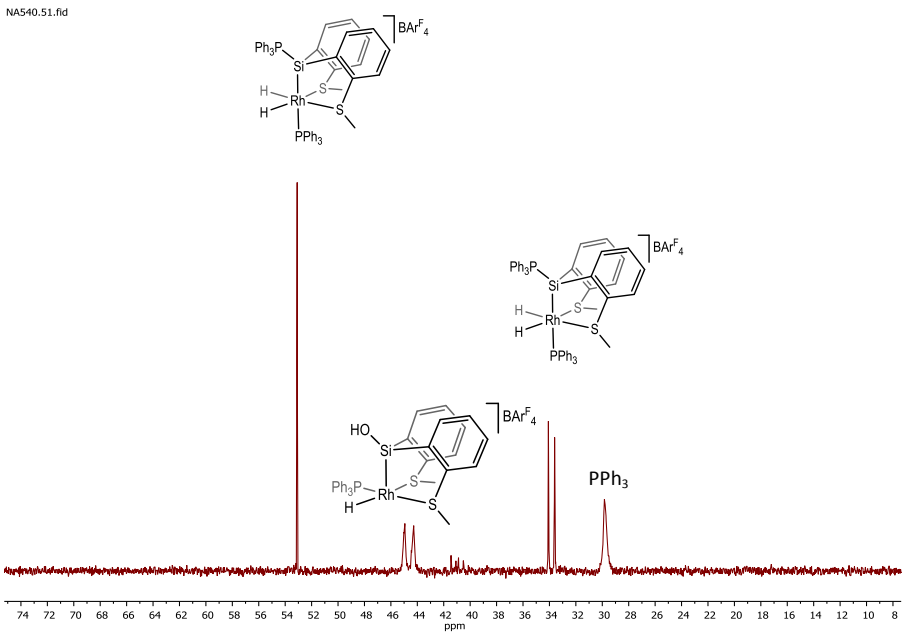


Figure S.16. ^{31}P{^{1}H} NMR of **3**.

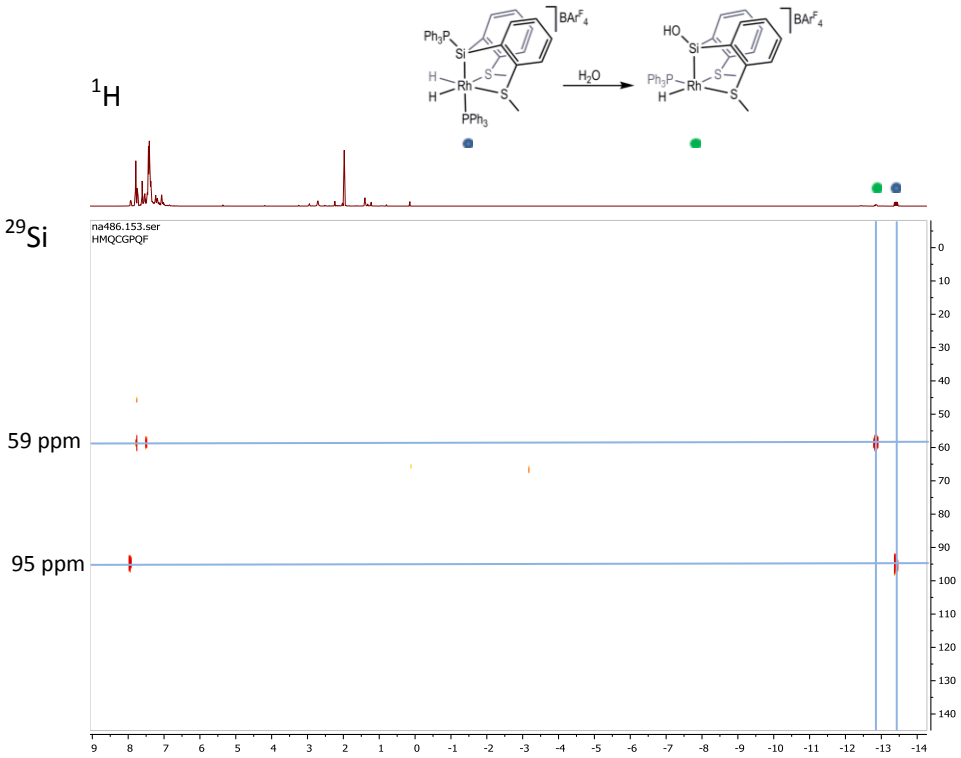


Figure S.17. ^{29}Si/^{1}H correlation for **3**.

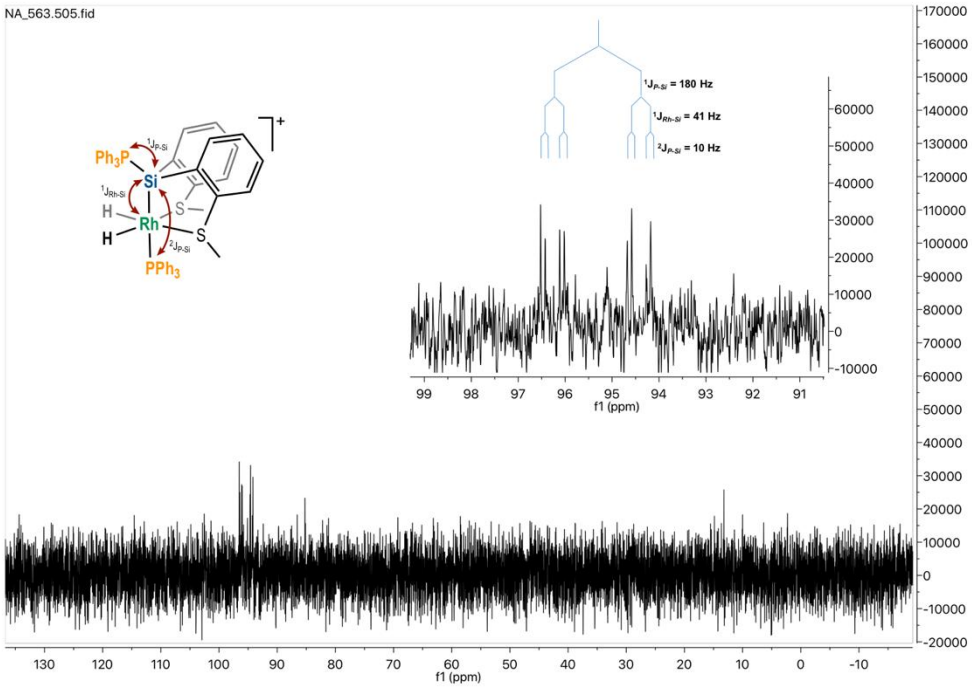


Figure S.18. ^{29}Si{^{1}H} NMR of **3**.

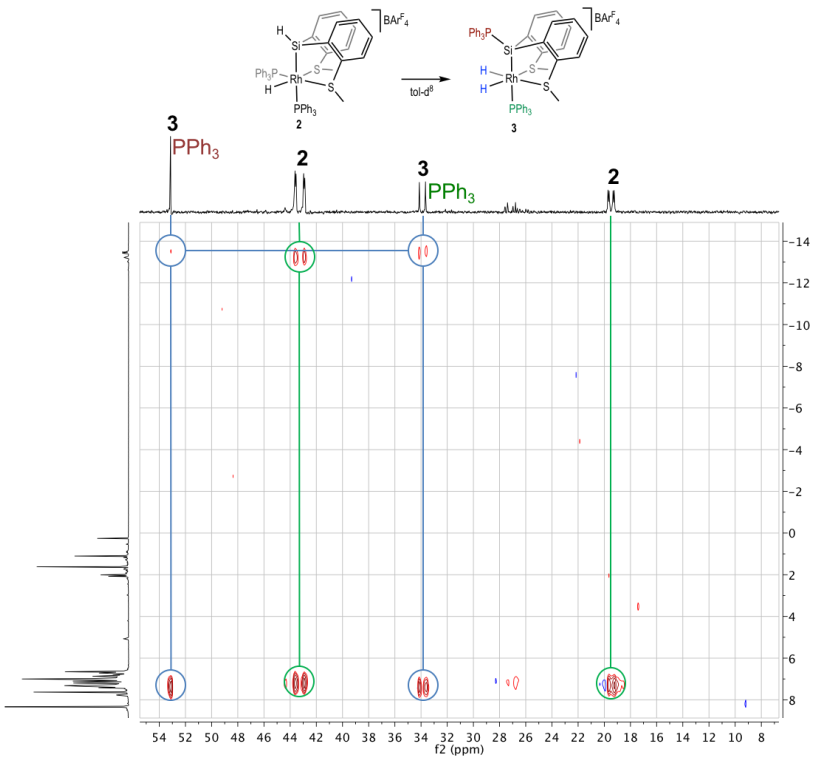


Figure S.19. $^{31}P–^{1}H$ HOESY of **3**.

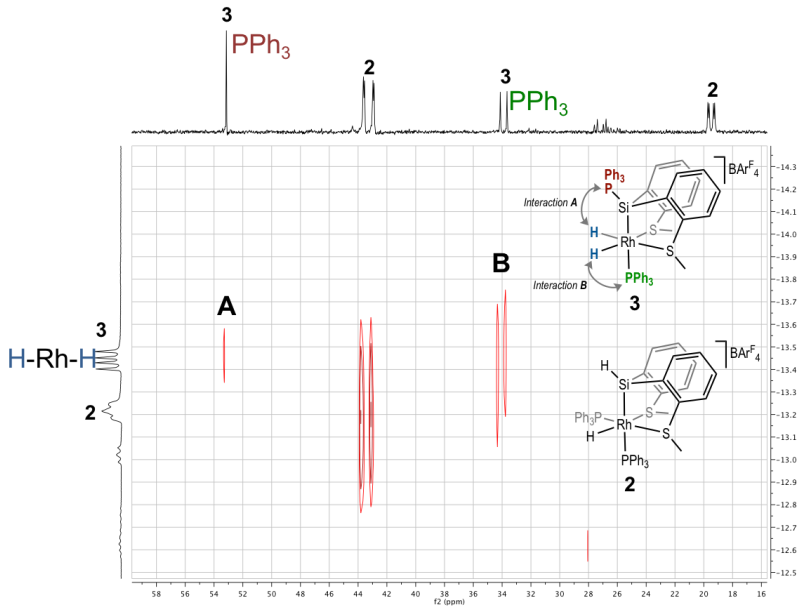


Figure S.20. $^{31}P–^{1}H$ HOESY of **3** (expanded hydride region).

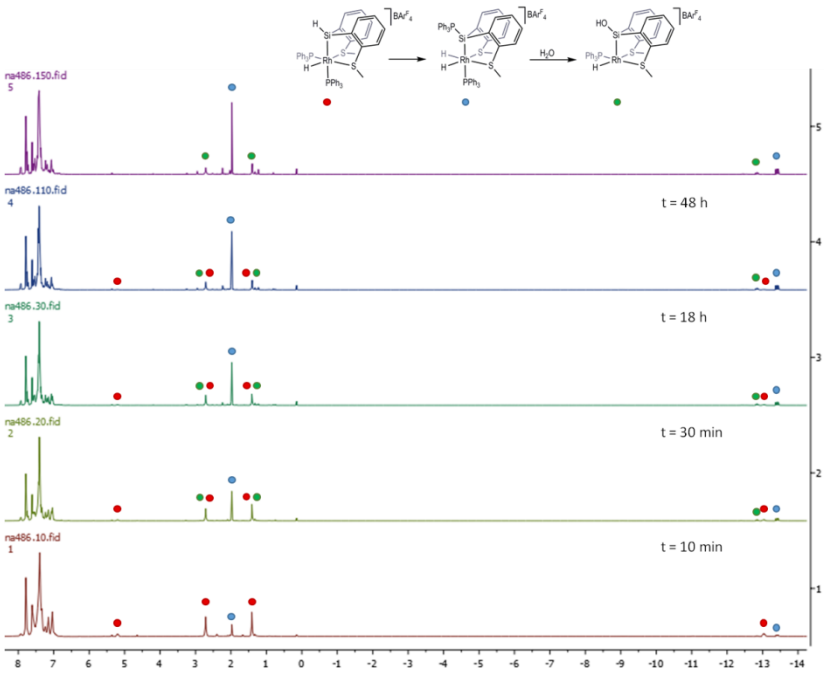


Figure S.21. ^{1}H NMR array of **3**.

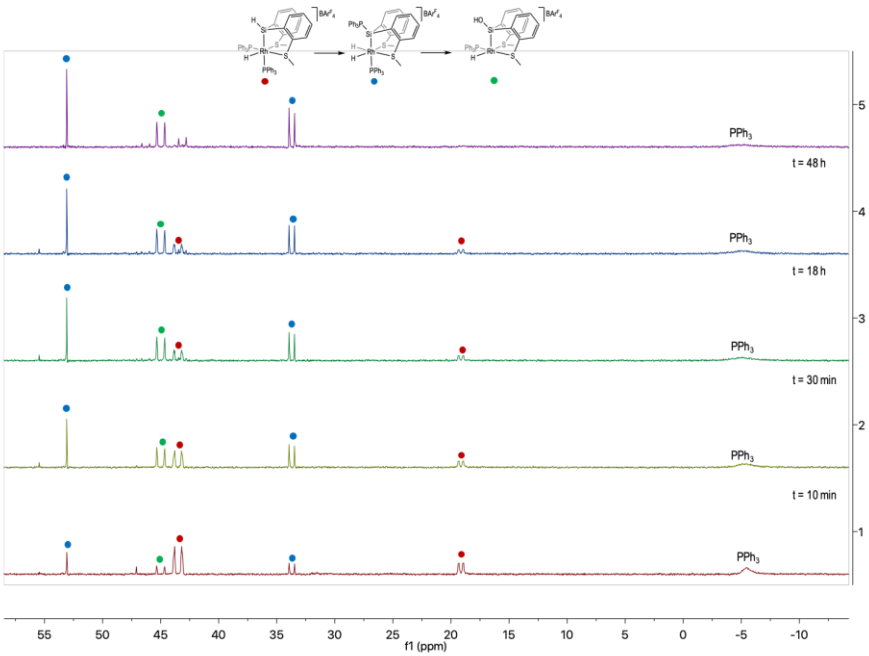
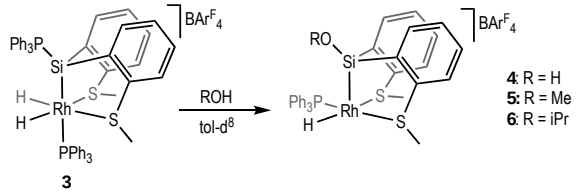


Figure S.22. $^{31}P\{^{1}H\}$ NMR array of **3.**

Synthesis and characterization of 4, 5 and 6



Synthesis and characterization in situ:

To a Young NMR tube charged with [Rh(PPh$_3$)$_3$Cl] (10 mg, 0.011 mmol), SiH$_2$(*o*-C$_6$H$_4$SMe)$_2$ (3 mg, 0.011 mmol) and NaBAr$^F_4$ (9.6 mg, 0.011 mmol), toluene-d^8 (0.5 mL) was added. After 48 hours, the Young NMR tube was opened under nitrogen and ROH was added (R = H, 0.6 μL, 0.033 mmol; R = Me, 1.4 μL, 0.033 mmol; R = iPr, 2.5 μL, 0.033 mmol). Compounds **4**, **5** and **6** were characterized in situ by NMR. The reaction was quantitative in all cases (i.e. > 95%) by NMR spectroscopy. The mixture was filtered off via cannula and concentrated under vacuum and characterized without other purification by MALDI.

Synthesis, isolation and characterization:

To a schlenk tube with young tap charged with [Rh(PPh$_3$)$_3$Cl] (50 mg, 0.054 mmol), SiH$_2$(*o*-C$_6$H$_4$SMe)$_2$ (15 mg, 0.054 mmol) and NaBAr$^F_4$ (48 mg, 0.054 mmol) in 1mL of distilled and deoxygenated toluene, 2 equivalents of ROH was added (R = H, 2 μL, 0.108 mmol; R = Me, 4.4 μL, 0.108 mmol; R = iPr, 8.3 μL, 0.108 mmol). The mixture was stirred 10 minutes, filtered off via cannula to another schlenk and concentrated under vacuum. Addition of 20 mL of pentane gave a yellow pale solid which was dried under vacuum. Yields: compound **4** (59 mg, 72 %), compound **5** (55 mg, 66 %), compound **6** (42 mg, 50 %).

Characterization of **4** (*in situ*):

^{1}H NMR (500 MHz, toluene-d8): δ 8.34-6.60 (23H, aromatics), 2.02 (s, 3H, S-CH$_3$), 1.15 (s, 3H, S-CH$_3$), -12.99 (t, $^1J_{Rh\text{-}H}$ = $^2J_{P\text{-}H}$ = 15.7 Hz, 1H, Rh-H).

^{31}P{^{1}H} NMR (202 MHz, toluene-d8): δ 44.4 (d, $^1J_{Rh\text{-}P}$= 138 Hz).

^{29}Si NMR (toluene-d8): *obtained from correlation ^{1}H/^{29}Si (figure S.13)*: δ 59

MALDI-MS: calc. [M]$^+$: 657.04; found m/z 657.0

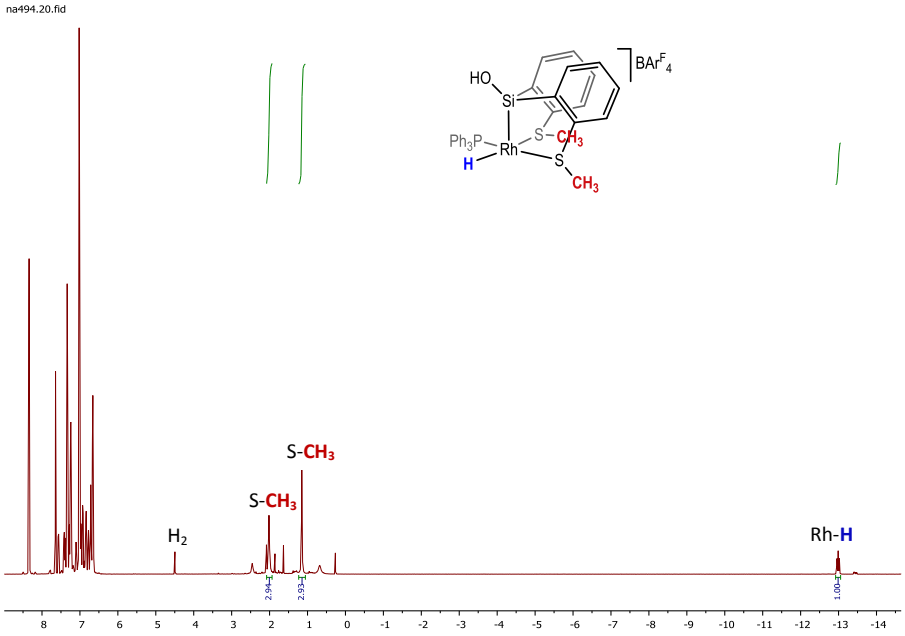


Figure S.23. ^{1}H NMR of **4**.

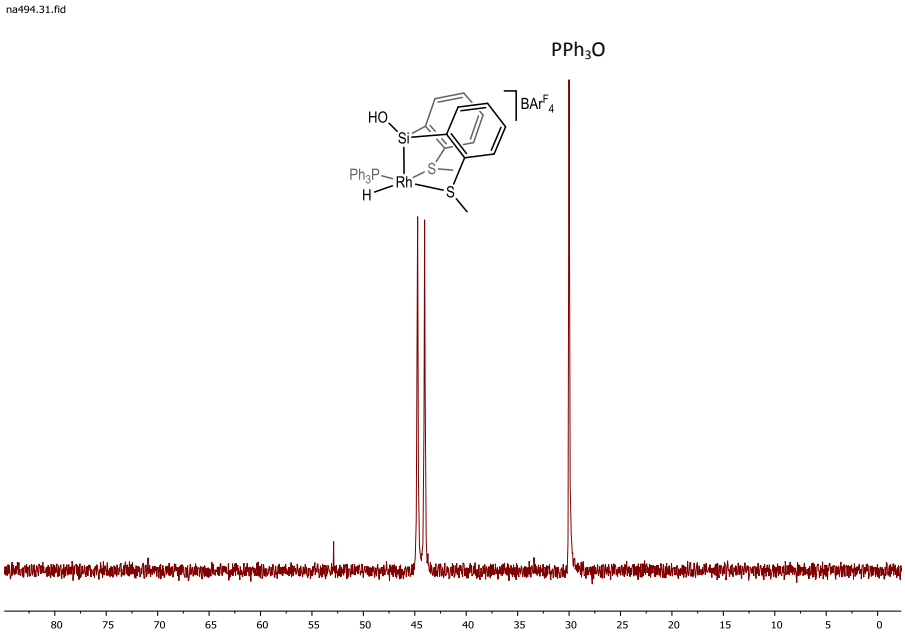


Figure S.24. ^{31}P{^{1}H} NMR of **4**.

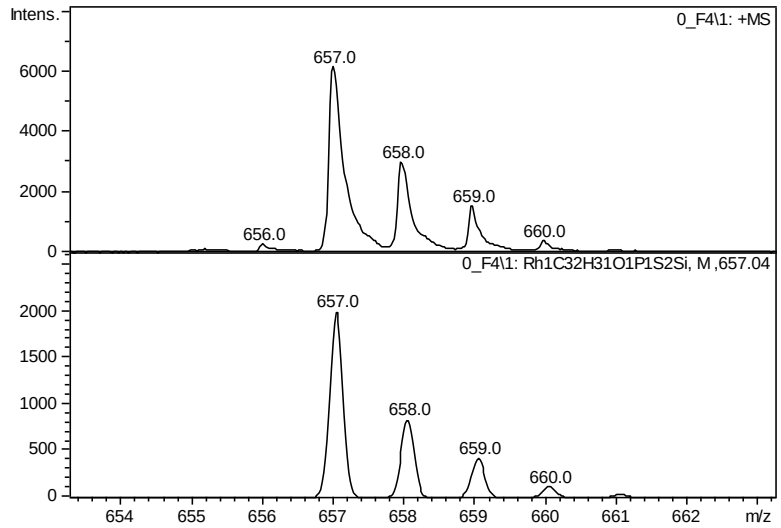


Figure S.25. ESI-MS of **4**.

Characterization of **4** (*isolated*):

^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.75-7.01 (23H, aromatics), 2.69 (s, 3H, S-CH_3), 1.34 (s, 3H, S-CH_3), -12.87 (dd, $^{1}J_{Rh\text{-}H}$ = 17.6, $^{2}J_{P\text{-}H}$ = 13.6, 1H, Rh-H)

^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2): δ 45.4 (d, $^{1}J_{Rh\text{-}P}$= 137 Hz).

^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2): δ 162.2 (q, $J_{F\text{-}C}$ = 50 Hz, BAr^F_4), 135.2 (s, BAr^F_4), 129.1 (q, $J_{F\text{-}C}$ = 11 Hz, BAr^F_4), 125.0 (q, $J_{F\text{-}C}$ = 272 Hz, CF_3), 117.9 (p, $J_{F\text{-}C}$ = 4.1 Hz, BAr^F_4), 134.5-128.9 (aromatics), 33.8 (s, S-CH_3), 24.0 (s, S-CH_3).

Microanalysis for [$C_{64}H_{43}PBF_{24}RhS_2SiO$] + [$PC_{18}H_{15}O$]: Calcd. C 54.74, H 3.25, S 3.56; found C 54.61, H 3.13, S 3.16.

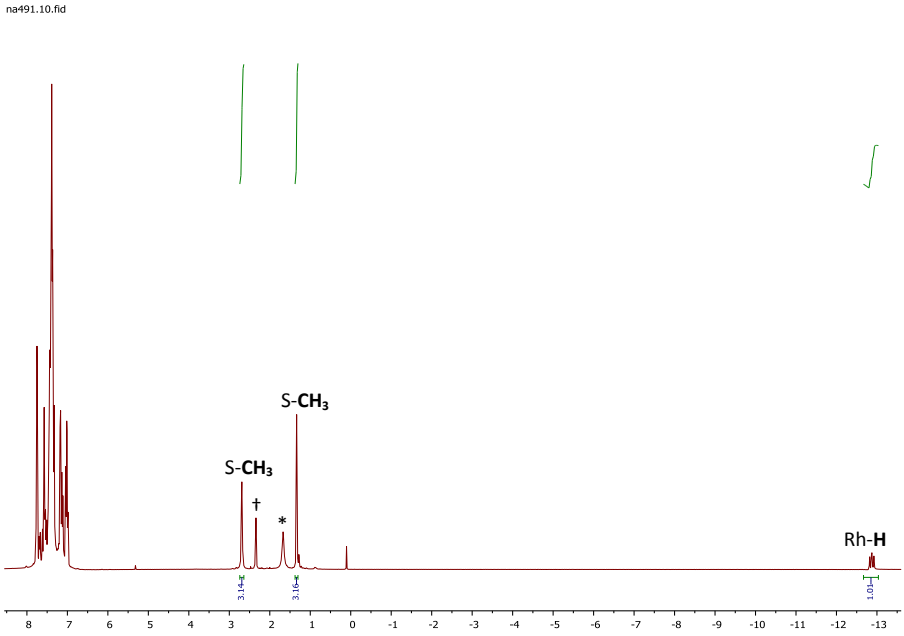


Figure S.26. ^{1}H NMR of **4**. (*water, †acetone)

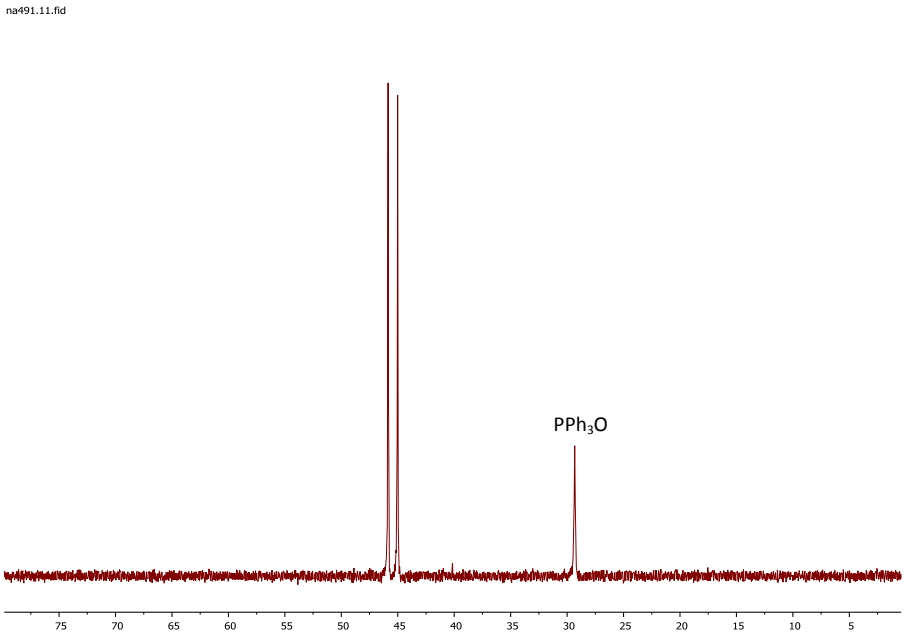


Figure S.27. $^{31}P\{^{1}H\}$ NMR of **4**.

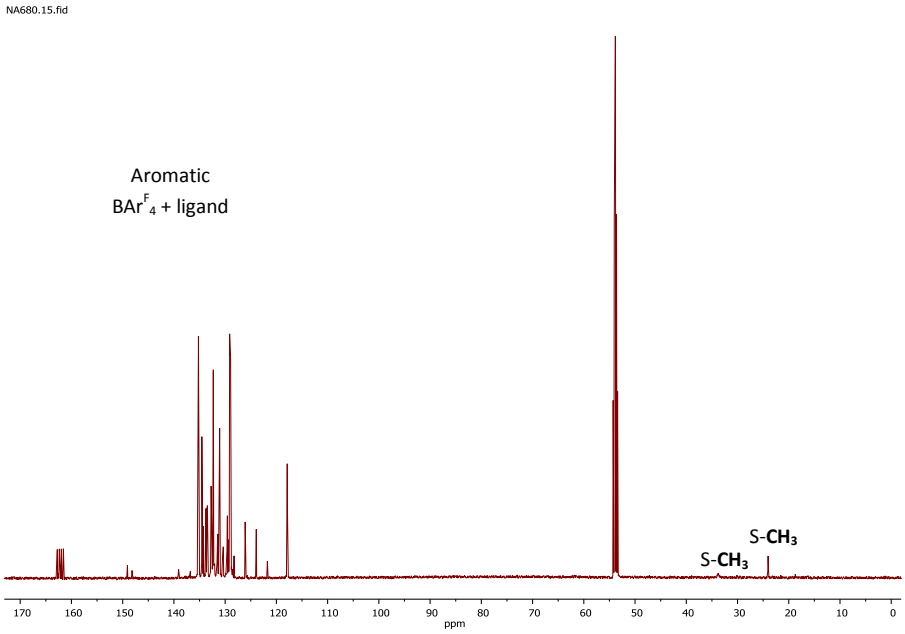


Figure S.28. $^{13}C\{^1H\}$ NMR of **4**.

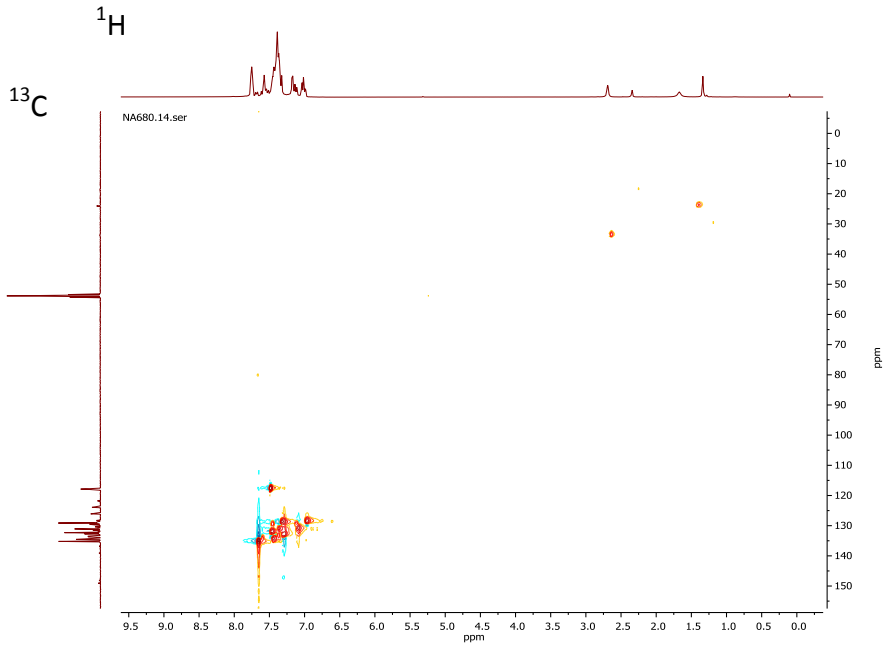


Figure S.29. $^{13}C\{^1H\}/^1H$ correlation for **4**.

Characterization of **5** (in situ):

^{1}H NMR (500 MHz, toluene-d8): δ 3.12 (s, 3H, O-CH_3), 2.35 (s, 3H, S-CH_3), 1.08 (s, 3H, S-CH_3), -12.86 (t, $^{1}J_{Rh\text{-}H}$ = $^{2}J_{P\text{-}H}$ = 15.7 Hz, 1H, Rh-H).

^{31}P{^{1}H} NMR (202 MHz, toluene-d8): δ 44.5(d, $^{1}J_{Rh\text{-}P}$= 137Hz).

^{29}Si NMR (toluene-d8): *obtained from correlation $^{1}H/^{29}Si$*: δ 58

MALDI-MS: calc. $[M]^{+}$: 671.05; found m/z 671.1

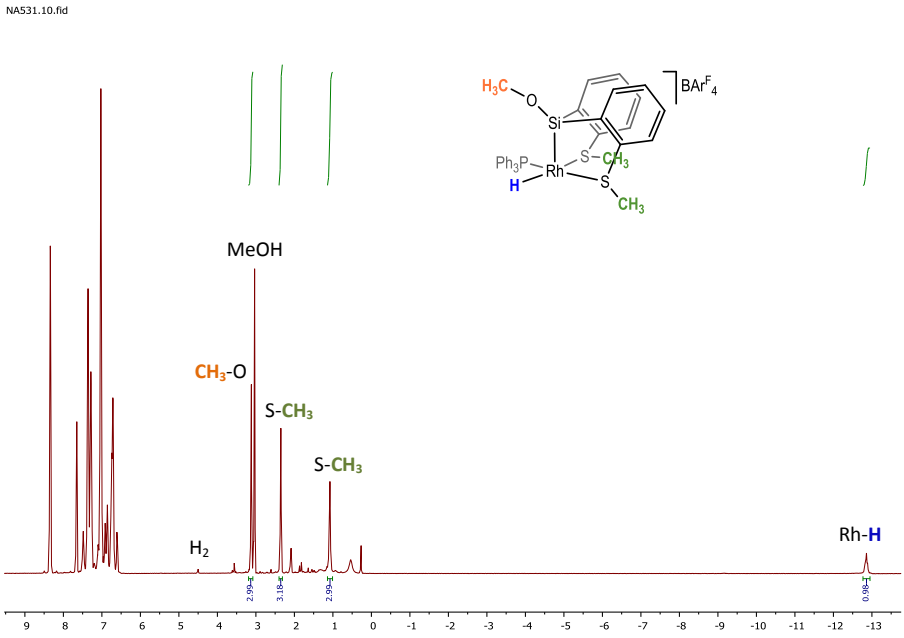


Figure S.30. ^{1}H NMR of **5**.

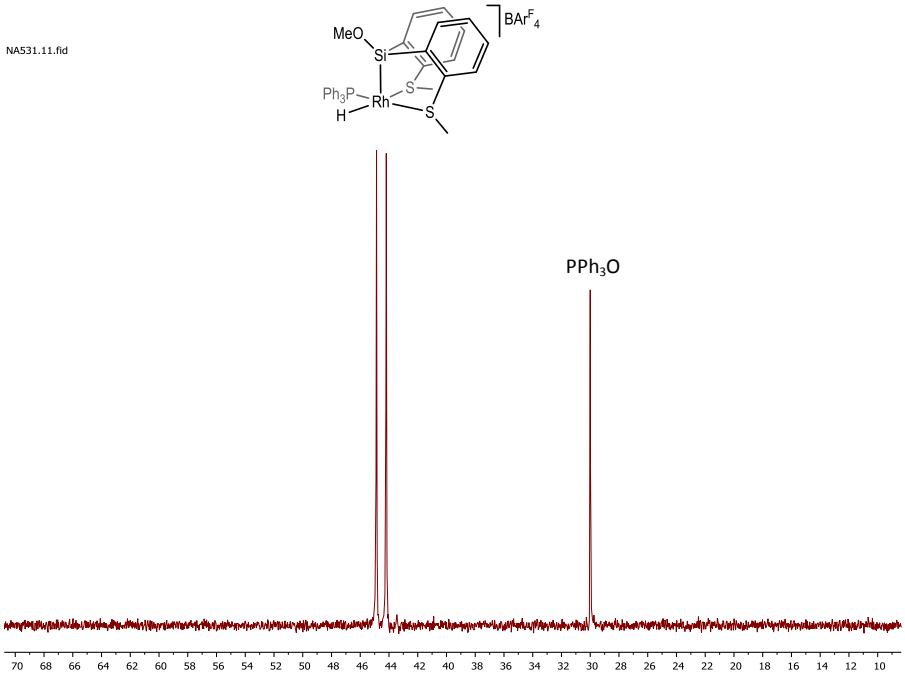


Figure S.31. $^{31}P\{^{1}H\}$ NMR of **5**.

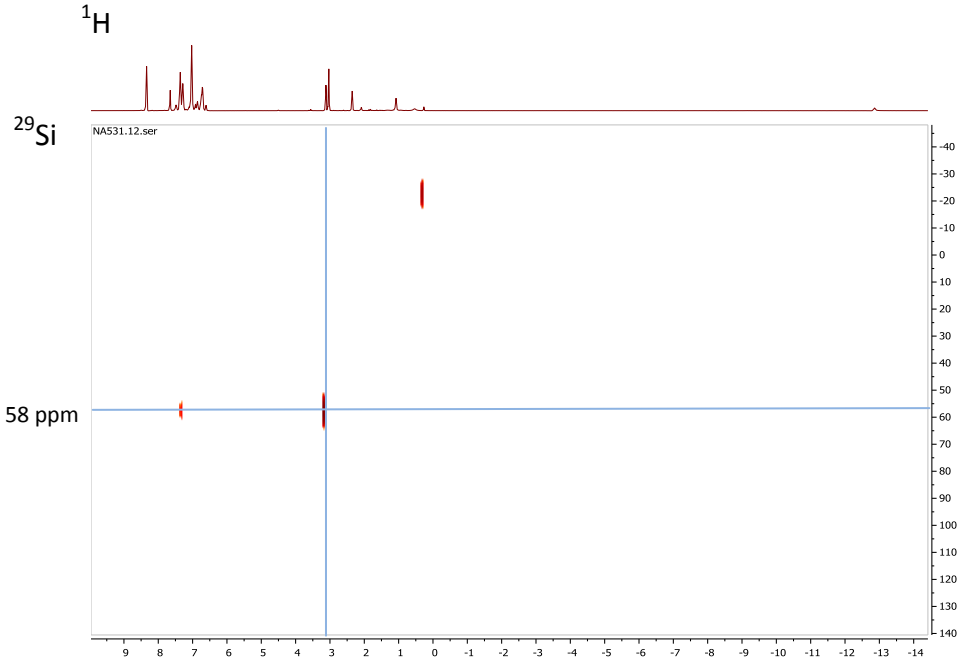


Figure S.32. $^{29}Si/^{1}H$ correlation for **5**.

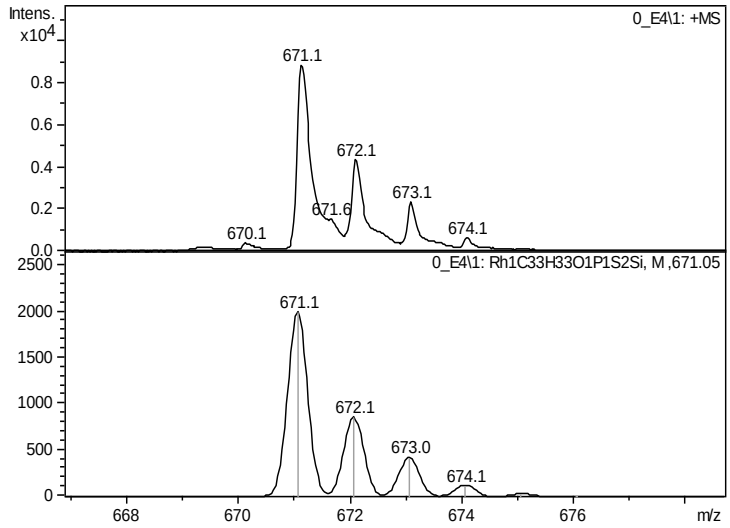


Figure S.33. ESI-MS of **5**.

Characterization of **5** (*isolated*):

^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.79-7.12 (23H, aromatics), 3.23 (s, 3H, O-CH_3), 2.88 (s, 3H, S-CH_3), 1.65 (s, 3H, S-CH_3), -12.35 (t, $^{1}J_{Rh-H}$ = $^{2}J_{P-H}$ = 14.7, 1H, Rh-H).

^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2): δ 44.0 (d, $^{1}J_{Rh-P}$= 139 Hz).

^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2): δ 162.2 (q, J_{F-C} = 50 Hz, BAr^F_4), 135.2 (s, BAr^F_4), 129.8-129.3 (m, BAr^F_4), 125.0 (q, J_{F-C} = 272 Hz, CF_3), 117.9 (p, J_{F-C} = 4.1 Hz, BAr^F_4), 135.2-128.6 (aromatics), 52.2 (s, O-CH_3), 34.8 (s, S-CH_3), 24.0 (s, S-CH_3).

Microanalysis for [$C_{65}H_{45}PBF_{24}RhS_2SiO$] + [$PC_{18}H_{15}O$]: Calcd. C 54.98, H 3.34, S 3.54; found C 54.90, H 3.19, S 3.20.

COMPLETA EN CD2Cl2.10.fid

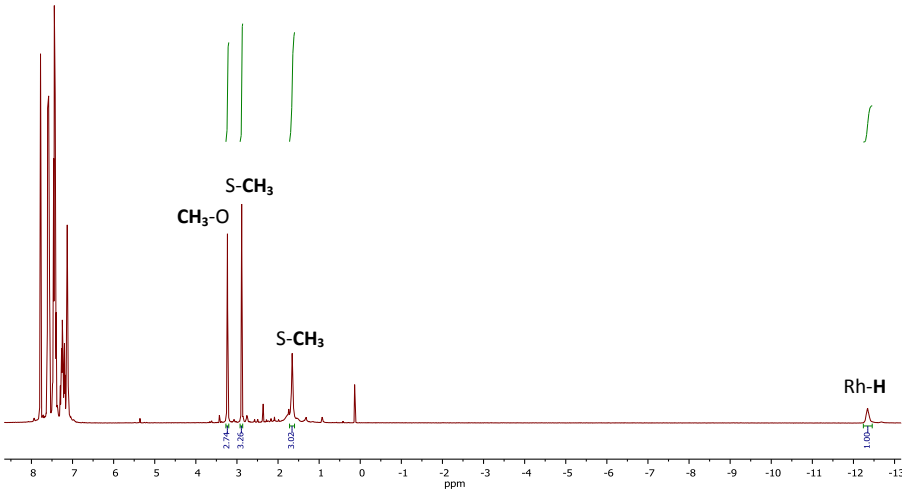


Figure S.34. ^{1}H NMR of **5**.

COMPLETA EN CD2Cl2.11.fid

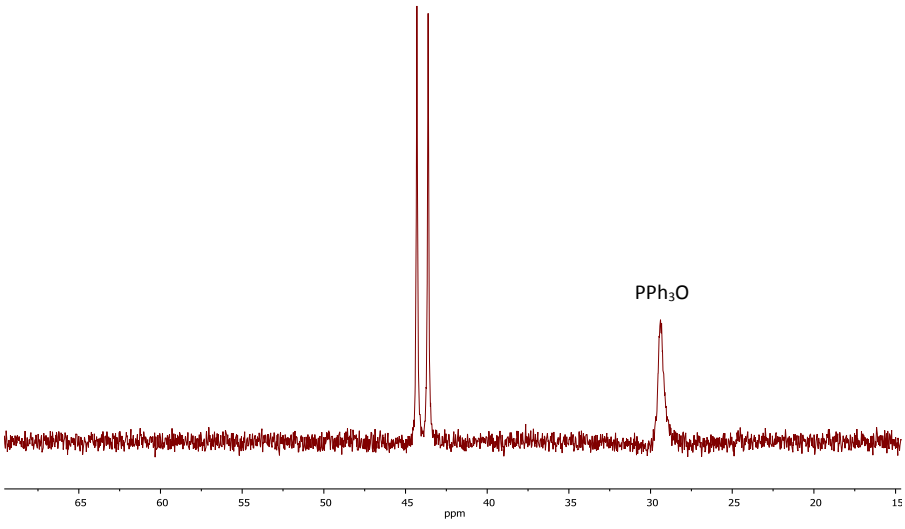


Figure S.35. $^{31}P\{^{1}H\}$ NMR of **5**.

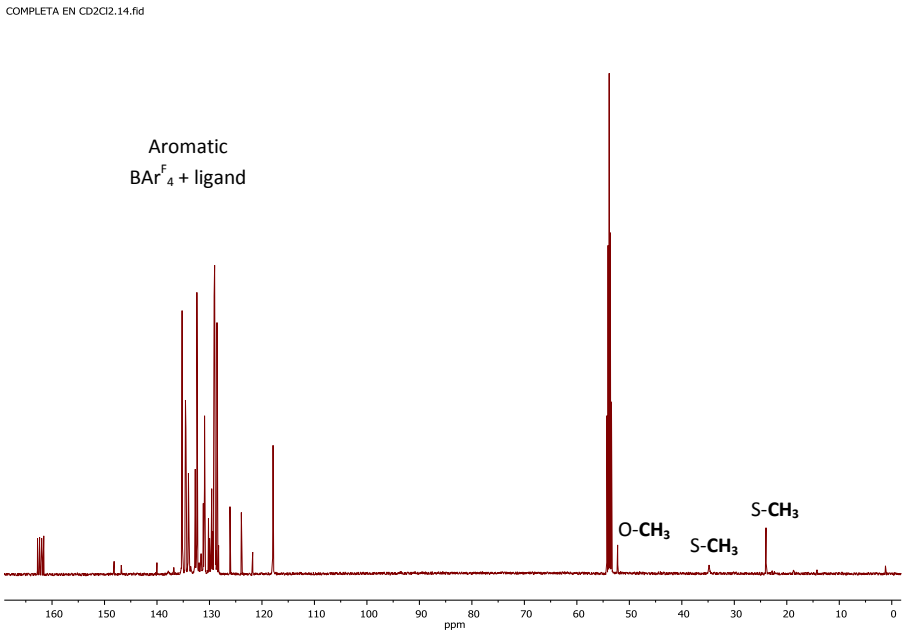


Figure S.36. $^{13}C\{^1H\}$ NMR of **5**.

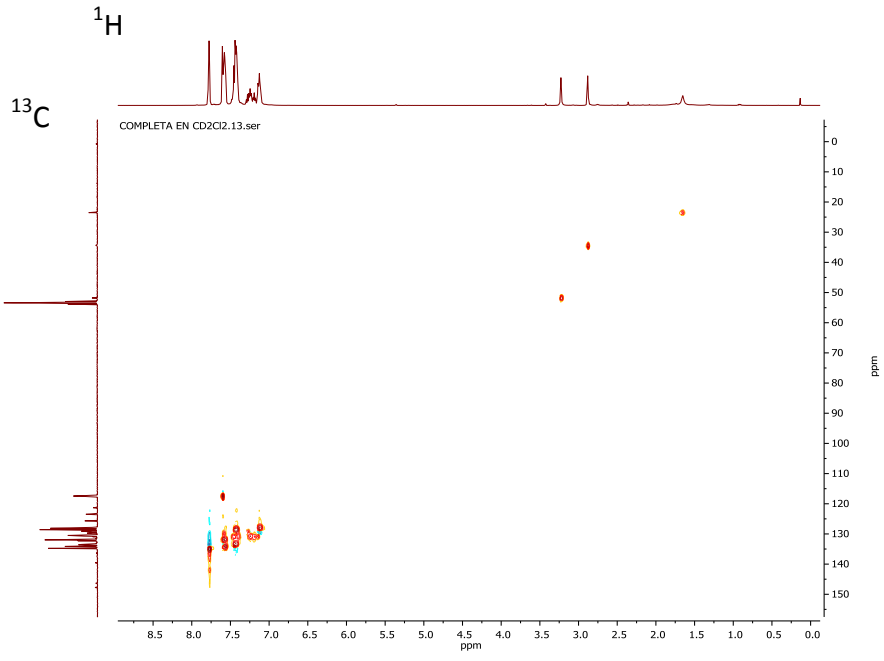


Figure S.37. $^{13}C\{^1H\}/^1H$ correlation for **5**.

Characterization of **6** (in situ):

^{1}H NMR (500 MHz, toluene-d8): δ 4.19 (sept, $^{3}J_{H\text{-}H}$ = 6.1 Hz, 1H,C-H ^{i}PrO), 2.36 (s, 3H,S-CH_3), 0.90 (s, 3H, S-CH_3), 0.83 (6 H, d, $^{3}J_{H\text{-}H}$ = 6.1 Hz, 3H, CH_3 ^{i}PrO), -13.05 (t, $^{1}J_{Rh\text{-}H}$ = $^{2}J_{P\text{-}H}$ = 14.9 Hz, 1H, Rh-H).

^{31}P{^{1}H} NMR (202 MHz, toluene-d8): δ 42.4 (d, $^{1}J_{Rh\text{-}P}$= 137Hz).

^{29}Si NMR (toluene-d8): *obtained from correlation $^{1}H/^{29}Si$*: δ 48

MALDI-MS: calc. $[M]^{+}$: 699.08; found m/z 699.2

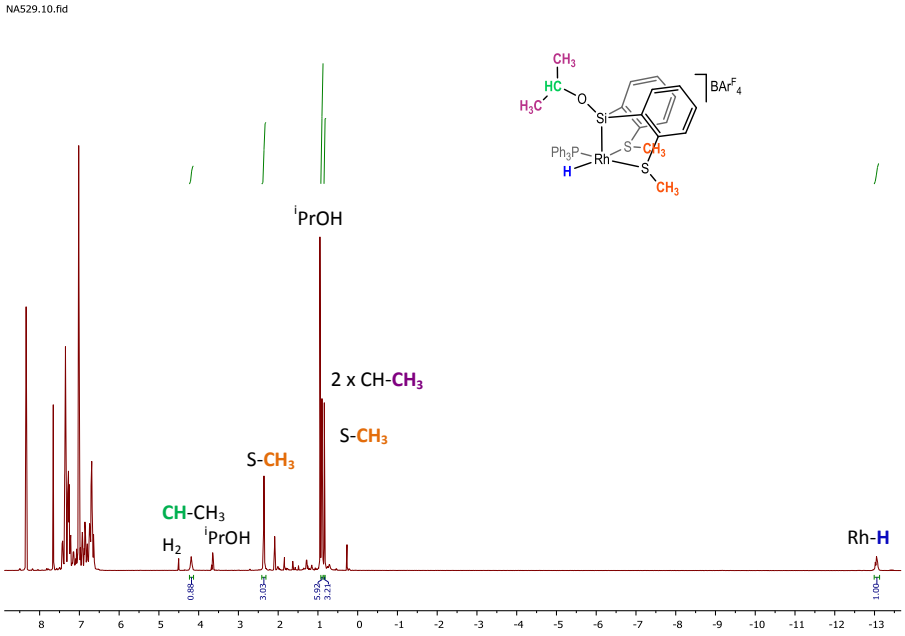


Figure S.38. ^{1}H NMR of **6**.

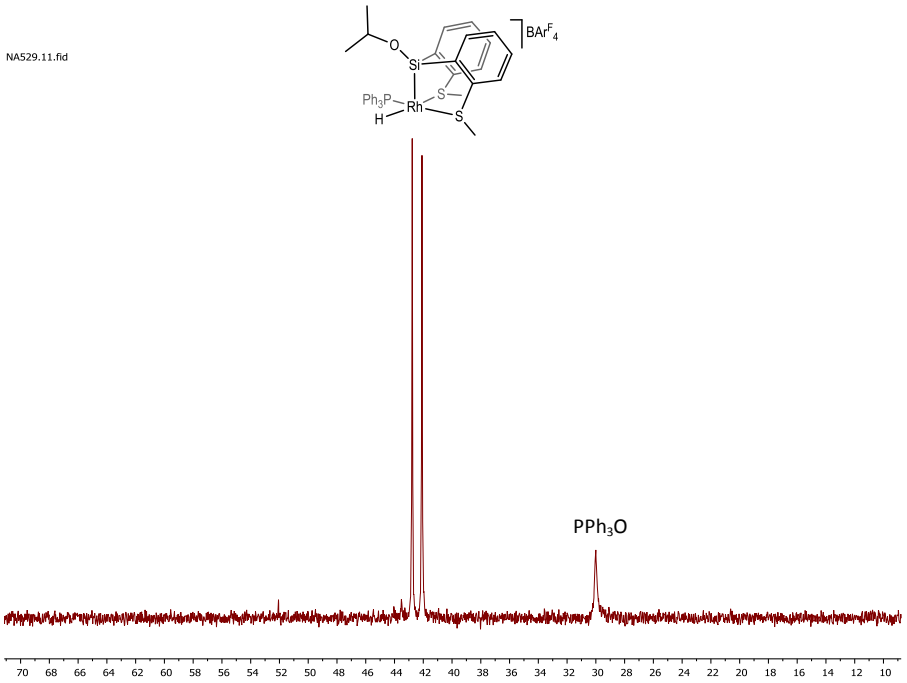


Figure S.39. $^{31}P\{^1H\}$ NMR of **6**.

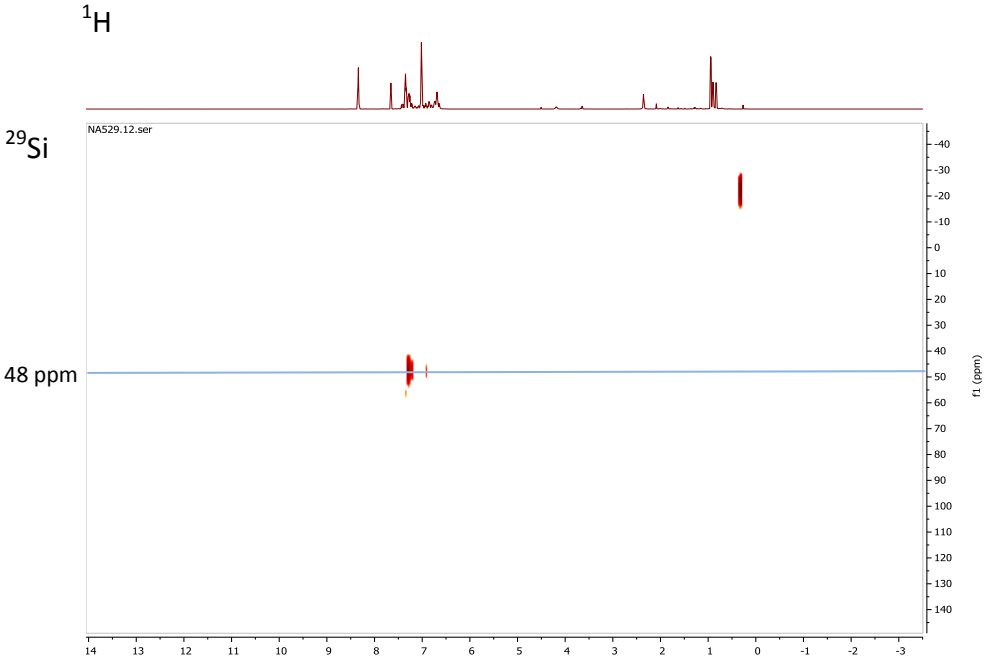


Figure S.40. Correlation $^{29}Si/^1H$ for **6**.

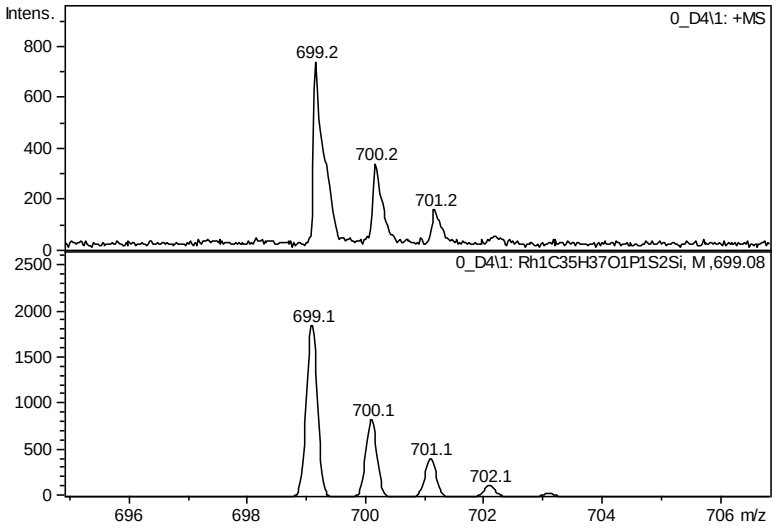


Figure S.41. ESI-MS of **6**.

Characterization of **6** (isolated):

^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.78-7.07 (23H, aromatics), 4.40 (sept, $^{3}J_{H-H}$ = 6.1 Hz, 1H, C-H ^{i}PrO), 2.87 (s, 3H, S-CH_3), 1.35 (s, 3H, S-CH_3), 1.02 (d, $^{3}J_{H-H}$ = 6.1 Hz, 3H, CH_3 ^{i}PrO), 1.00 (d, $^{3}J_{H-H}$ = 6.1 Hz, 3H, CH_3 ^{i}PrO), -12.58 (t, $^{1}J_{Rh-H}$ = $^{2}J_{P-H}$ = 15.2, 1H, Rh-H).

^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2): δ 40.7 (d, $^{1}J_{Rh-P}$= 138 Hz).

^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2): δ 162.2 (q, J_{F-C} = 50 Hz, BAr^F_4), 135.2 (s, BAr^F_4), 129.3-128.8 (m, BAr^F_4), 125.0 (q, J_{F-C} = 272 Hz, CF_3), 117.9 (p, J_{F-C} = 4.1 Hz, BAr^F_4), 135.4-128.5 (aromatics), 69.1 (s, C-H ^{i}PrO), 35.8 (s, S-CH_3), 25.5 (s, 2 x CH_3 ^{i}PrO), 23.8 (S-CH_3).

Microanalysis for [$C_{67}H_{49}PBF_{24}RhS_2SiO$] + [$PC_{18}H_{15}O$]: Calcd. C 55.45, H 3.50, S 3.48; found C 56.04, H 3.15, S 2.70.

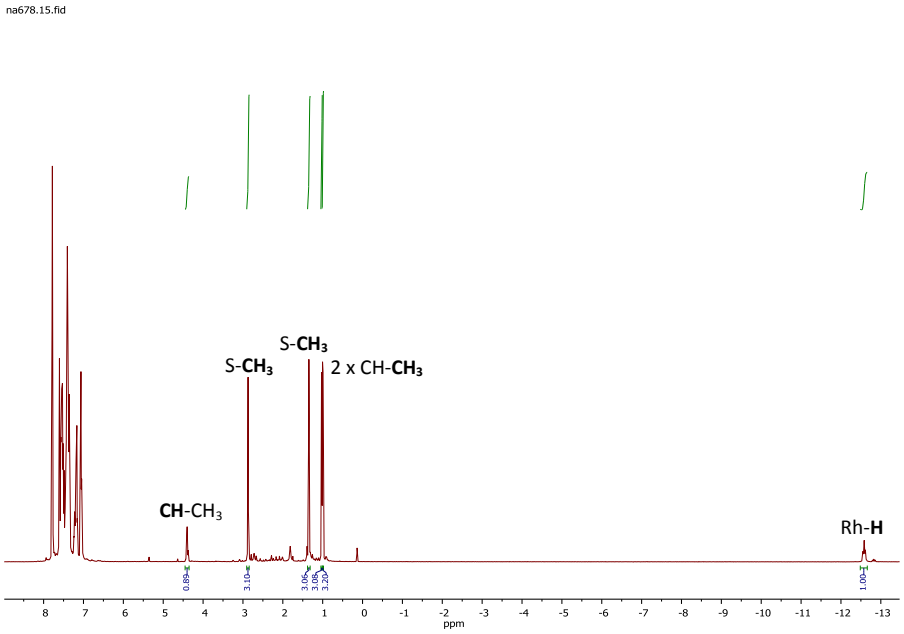


Figure S.42. ^{1}H NMR of **6**.

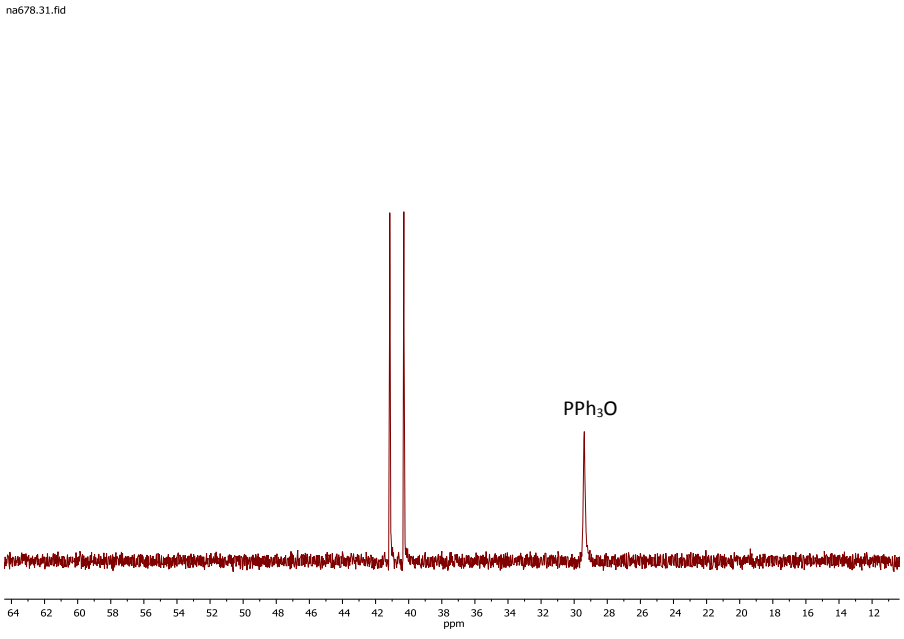


Figure S.43. $^{31}P\{^{1}H\}$ NMR of **6**.

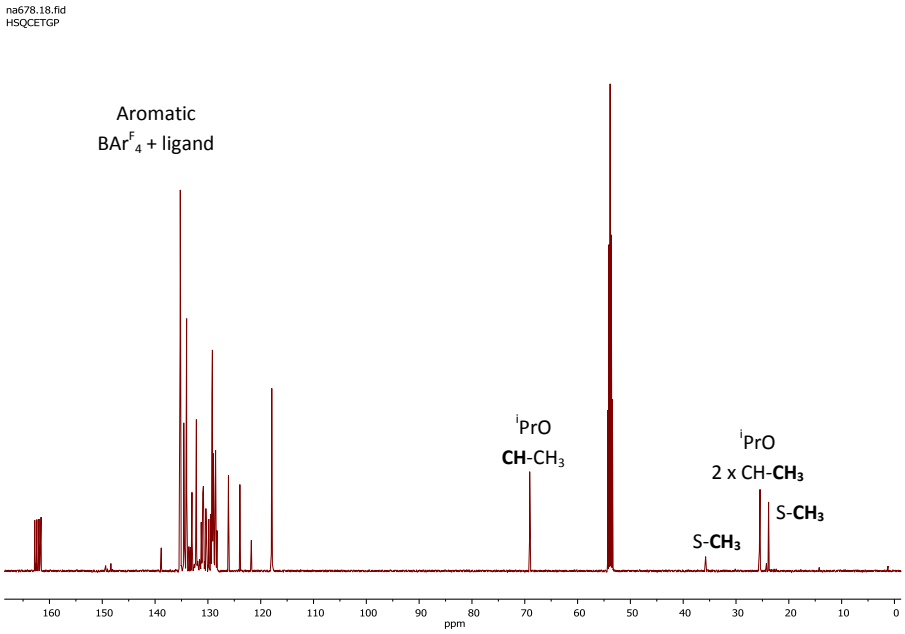


Figure S.44. $^{13}C\{^1H\}$ NMR of **6**.

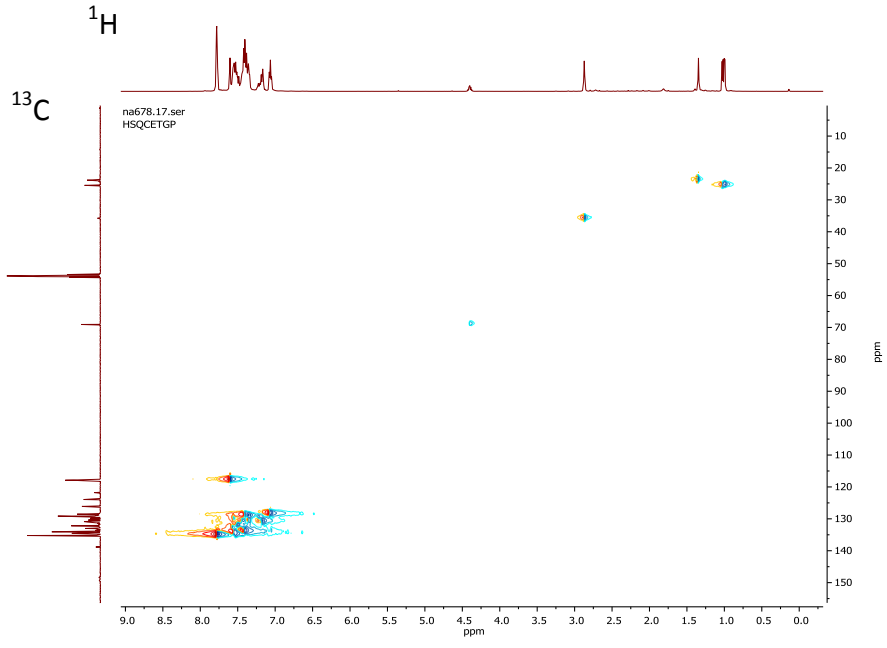
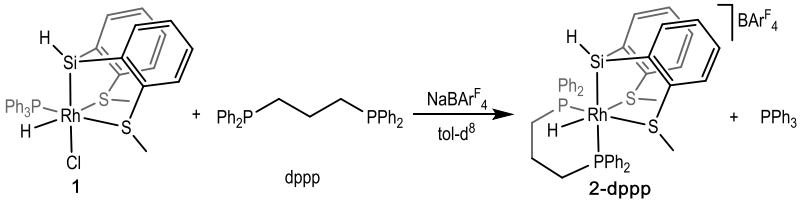


Figure S.45. $^{13}C\{^1H\}/^1H$ correlation for **6**.

Synthesis and characterization of 2-dppp



To a Young NMR tube charged with **1** (9 mg, 0.013 mmol), 1,3-bis(diphenylphosphino)propane (5.5 mg, 0.013 mmol) and $NaBAr^F_4$ (11.8 mg, 0.013 mmol), toluene-d8 (0.5 mL) was added. Compound **2-dppp** was characterized in situ by NMR. The reaction was quantitative (i.e. > 95) by NMR spectroscopy.

^{1}H NMR (500 MHz, toluene-*d*8): δ 5.22 (tt, $^2J_{Rh-H}$ = 11.7, $^3J_{P-H}$ = 3.6 Hz, 1H, Si-H), 2.43 (t, $^2J_{H-H}$ = 12.2, 1H, CH_2 phosphine), 2.29 – 2.14 (m, 1H, CH_2 phosphine), 2.09 – 1.98 (m, 2H, CH_2 phosphine), 1.91 (s, 3H, S-CH_3), 1.74 – 1.58 (m, 1H, CH_2 phosphine), 1.49 (s, 3H, S-CH_3), 1.09 (q, $^2J_{H-H}$ = 12.6 Hz, 1H, CH_2 phosphine), -12.68 (dt, $^1J_{Rh-H}$ = 15.7, $^2J_{P-H}$ = 8.5 Hz, 1H, Rh-H).

^{13}C NMR (126 MHz, toluene-*d*8): δ 162.3 (q, J_{F-C} = 50 Hz, BAr^F_4), 137.1 (s, BAr^F_4), 129.3-128.8 (m, BAr^F_4), 125.0 (q, J_{F-C} = 272 Hz, CF_3), 117.6 (t, J_{F-C} = 4 Hz, BAr^F_4),135.2 – 123.7 (aromatics), 32.5 (s, S-CH_3), 30.0 – 29.3 (m, P-CH_2), 26.7 (d, $^1J_{P-C}$ = 29 Hz, P-CH_2), 23.5 (s, S-CH_3), 17.30 (s, CH_2 phosphine).

^{31}P{^{1}H} NMR (202 MHz, toluene-*d*8): δ 26.2 (dd, $^1J_{Rh-P}$ = 123, $^2J_{P-P}$ = 36 Hz), -0.2 (dd, $^1J_{Rh-P}$ = 80, $^2J_{P-P}$ = 36 Hz).

^{29}Si NMR (toluene-*d*8): *obtained from correlation $^1H/^{29}Si$*: δ 50

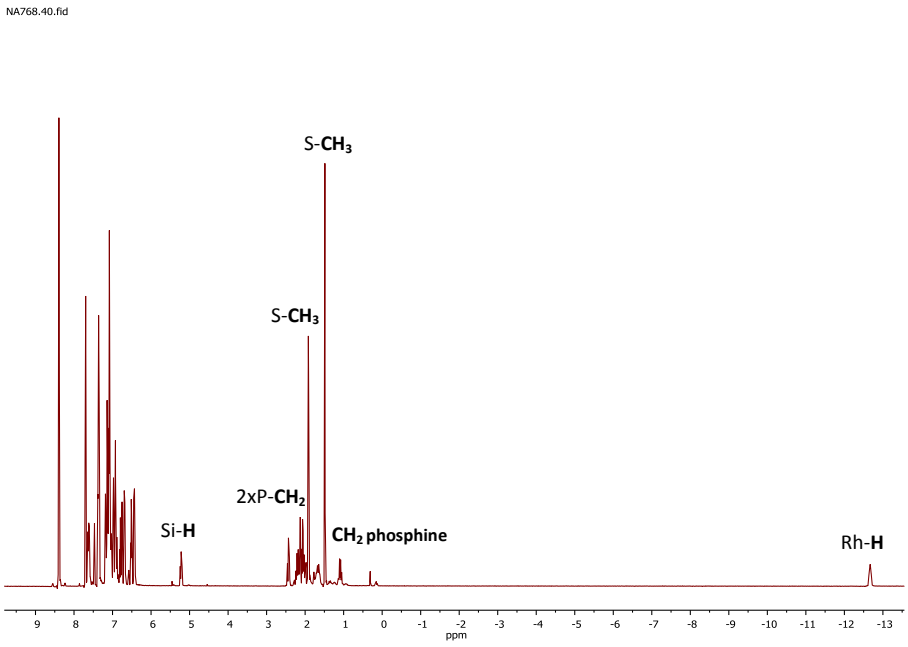


Figure S.46. ^{1}H NMR of **2-dppp**.

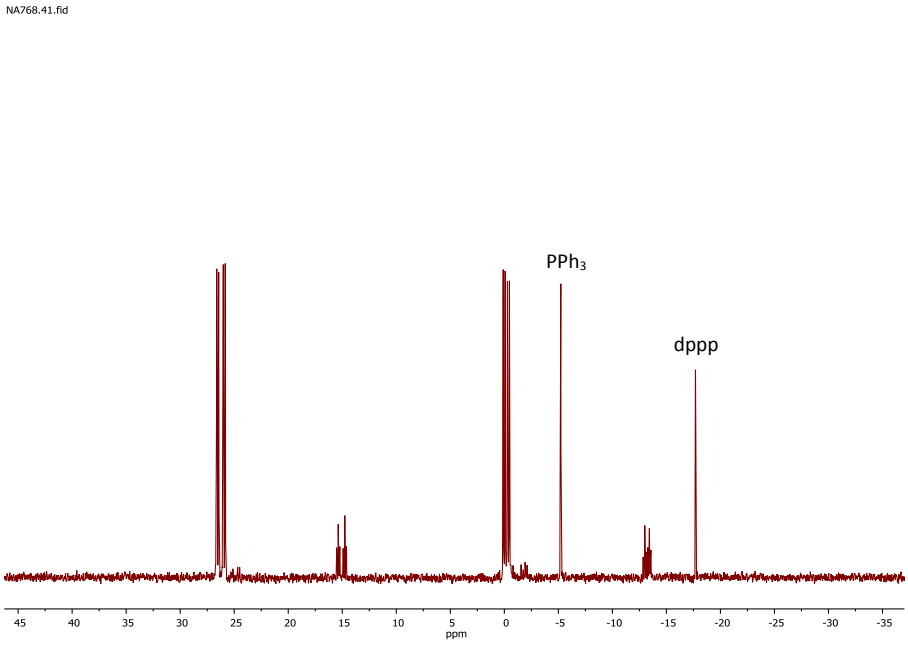


Figure S.47. $^{31}P\{^{1}H\}$ NMR of **2-dppp.**

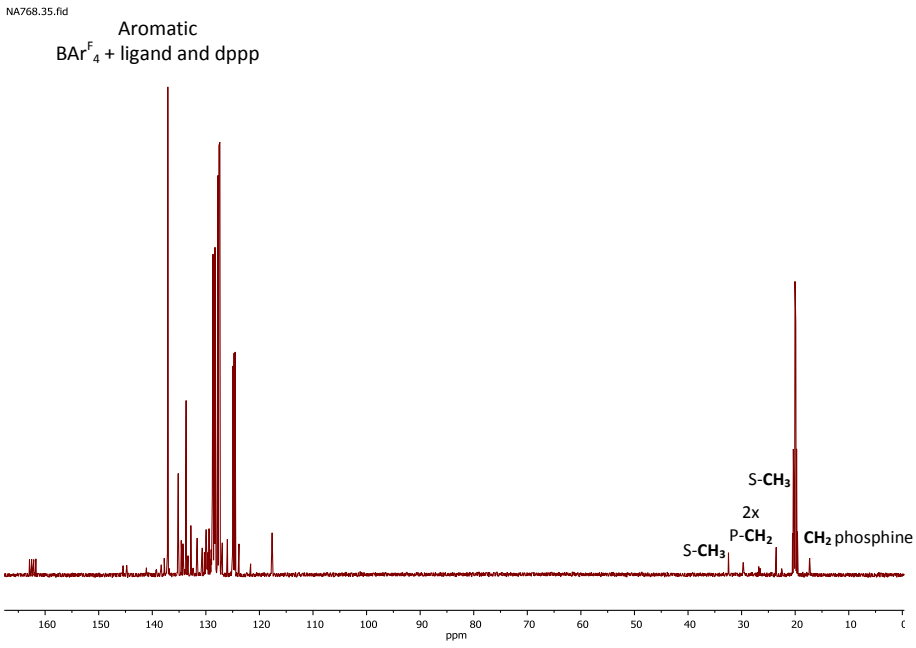


Figure S.48. $^{13}C\{^{1}H\}$ NMR of **2-dppp**.

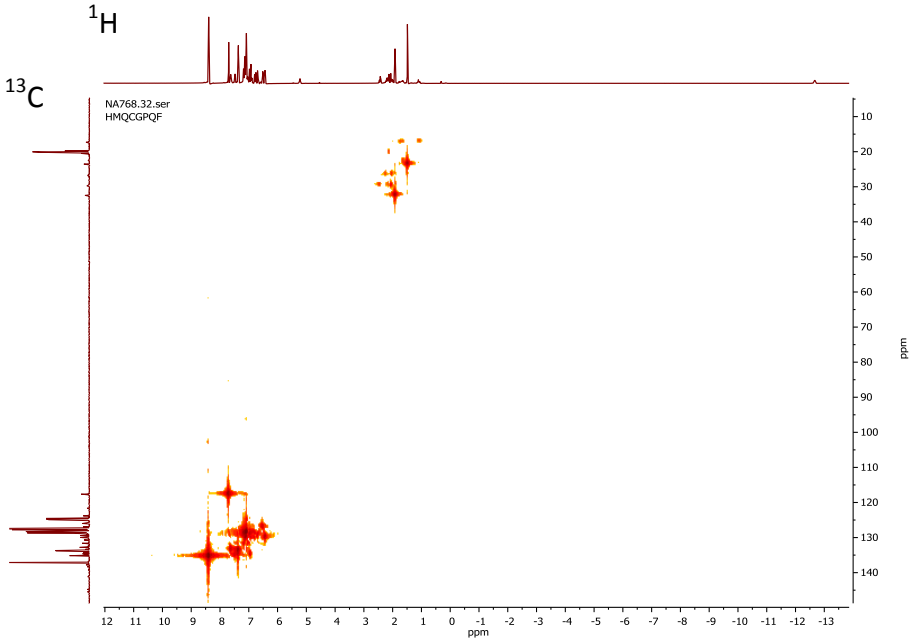


Figure S.49. ^{13}C{^{1}H}/^{1}H correlation for **2-dppp**.

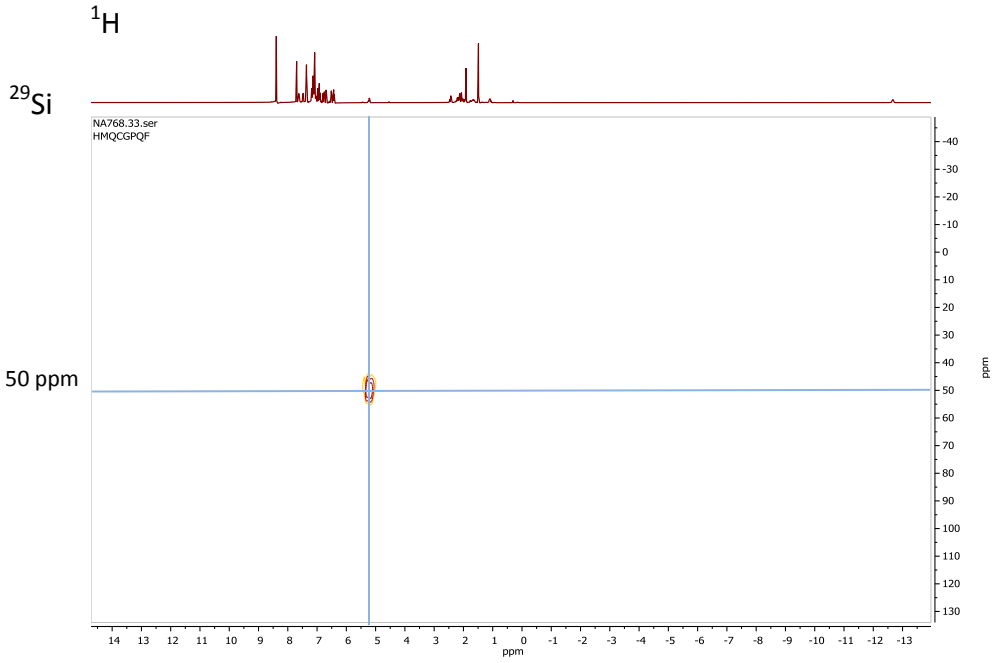


Figure S.50. ^{29}Si/^{1}H correlation for **2-dppp**.

Reactivity of 2-dppp with H_2O

A Young NMR tube charged with **2-dppp** in toluene-d8 (0.5 mL) was opened under air and 4 equivalents of H_2O (1 µL) were added. ^{1}H and $^{31}P\{^{1}H\}$ spectra were obtained before, after 2 hours and after 7 hours of the addition of water.

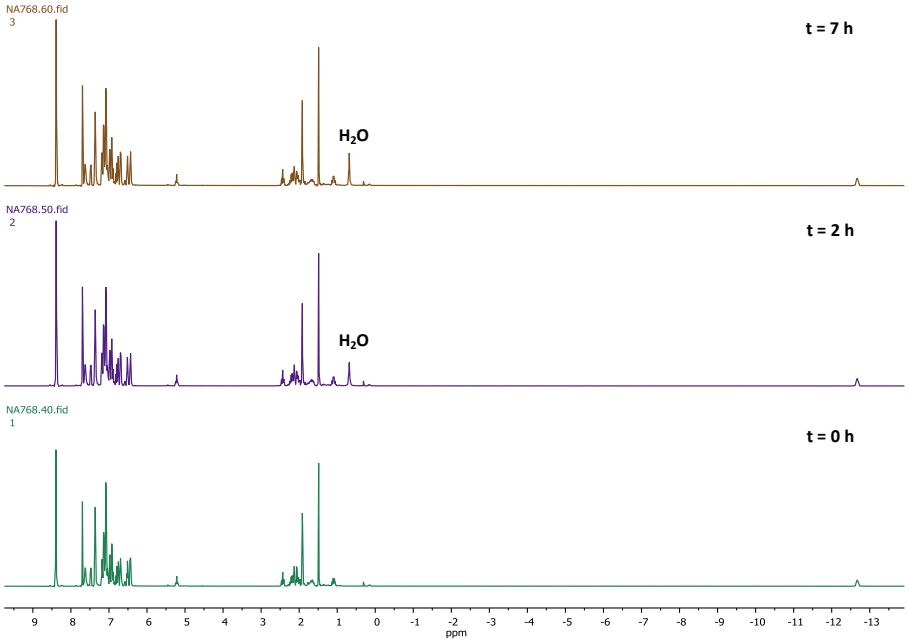


Figure S.51. ^{1}H NMR array of **2-dppp** before (green spectrum) and after (blue and red spectra) water was added.

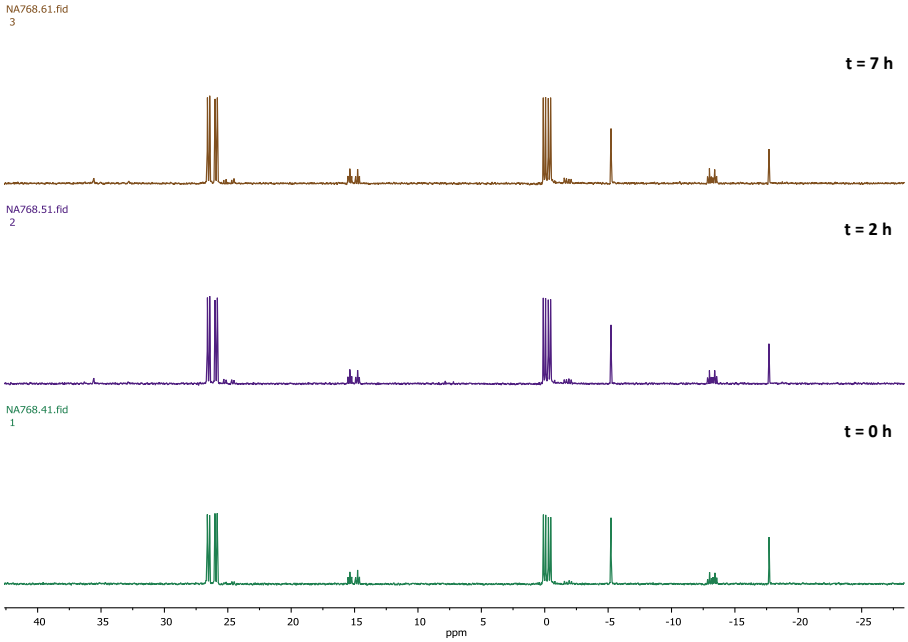
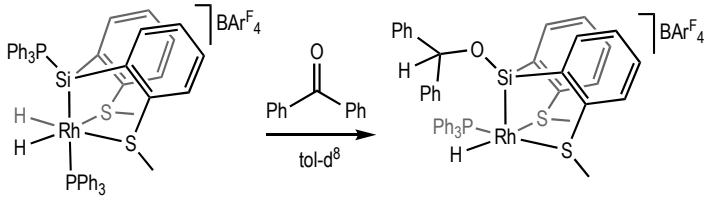


Figure S.52. $^{31}P\{^{1}H\}$ NMR array of **2-dppp** (green spectrum) and after (blue and red spectra) water was added.

Synthesis and characterization of 7



3 **7**

To a Young NMR tube charged with [Rh(PPh$_3$)$_3$Cl] (10 mg, 0.011 mmol), SiH$_2$(*o*-C$_6$H$_4$SMe)$_2$ (3 mg, 0.011 mmol) and NaBAr$^F_4$ (9.6 mg, 0.011 mmol), toluene-d8 (0.5 mL) was added. After 48 hours, the Young NMR tube was opened under nitrogen and benzophenone was added (2 mg, 0.011 mmol). Compound **7** was characterized in situ by NMR. The reaction was almost quantitative (i.e. > 85%) by NMR spectroscopy. The mixture was filtered of via cannula, concentrated under vacuum and characterized by MALDI without other purification.

^{1}H NMR (500 MHz, toluene-*d*8): δ 6.04 (s, 1H, CH), 2.13 (s, 3H, S-CH$_3$), 0.80 (s, 3H, S-CH$_3$), -13.16 (t, $^1J_{Rh\text{-}H}$ = $^2J_{P\text{-}H}$ = 14.5 Hz, 1H, Rh-H).

^{13}C NMR (126 MHz, toluene-*d*8): δ 161.7 (q, $J_{F\text{-}C}$ = 50 Hz, BAr$^F_4$), 136.4 (s, BAr$^F_4$), 129.9 (m, BAr$^F_4$), 124.2 (q, $J_{F\text{-}C}$ = 272 Hz, CF$_3$), 117.0 (p, $J_{F\text{-}C}$ = 4.1 Hz, BAr$^F_4$), 134.5-123.9 (aromatics), 78.82 (s, CH), 32.94 (s, S-CH$_3$), 21.82 (s, S-CH$_3$).

^{31}P{^{1}H} NMR (202 MHz, toluene-*d*8): δ 42.4 (d, $^1J_{Rh\text{-}P}$= 135 Hz).

^{29}Si NMR (toluene-*d*8): *obtained from correlation ^{1}H/^{29}Si*: δ 52

MALDI-MS: calc. [M]$^+$: 823.12; found m/z 823.0

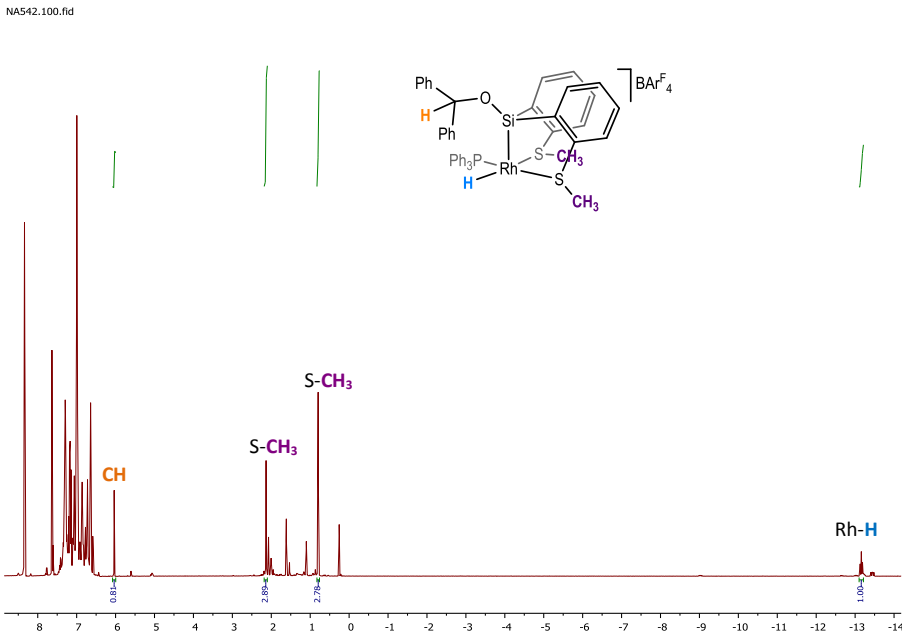


Figure S.53. ^{1}H NMR of **7**.

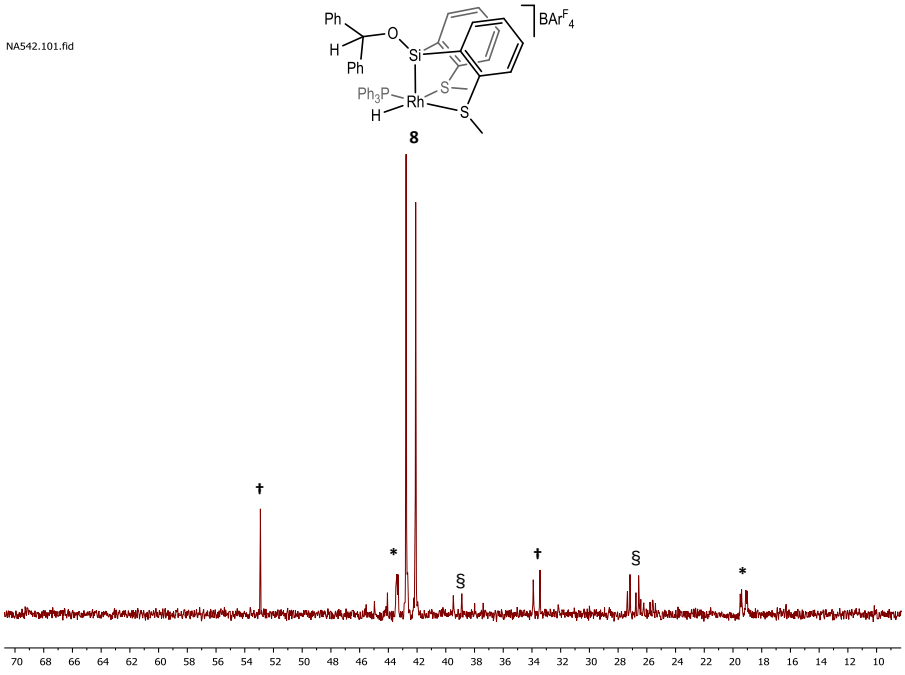


Figure S.54. ^{31}P{^{1}H} NMR of **7**. (***2-PPh$_3$**, †**3**, §unidentified products)

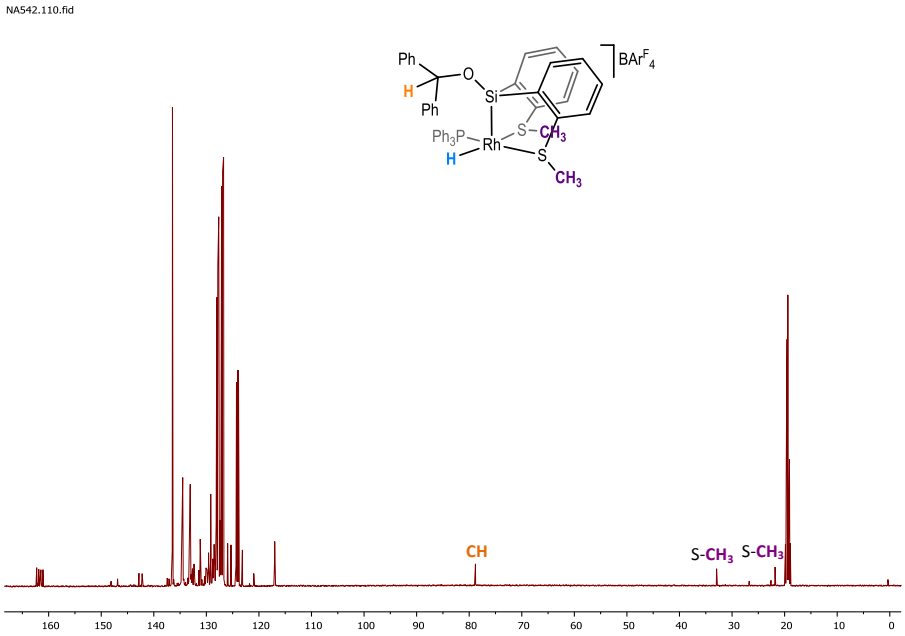


Figure S.55. $^{13}C\{^{1}H\}$ NMR of **7**.

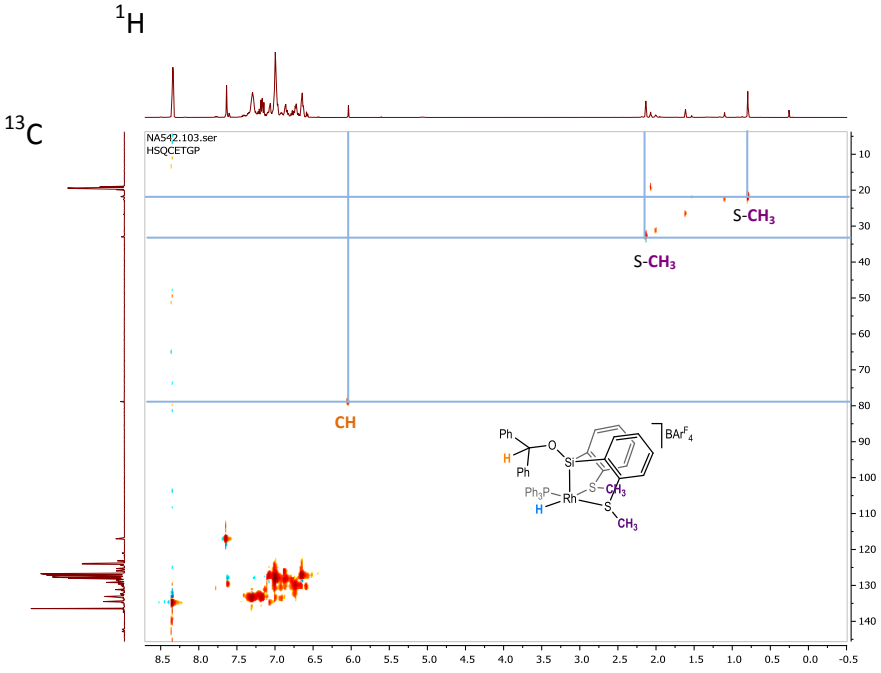


Figure S.56. $^{13}C\{^{1}H\}/^{1}H$ correlation for **7**.

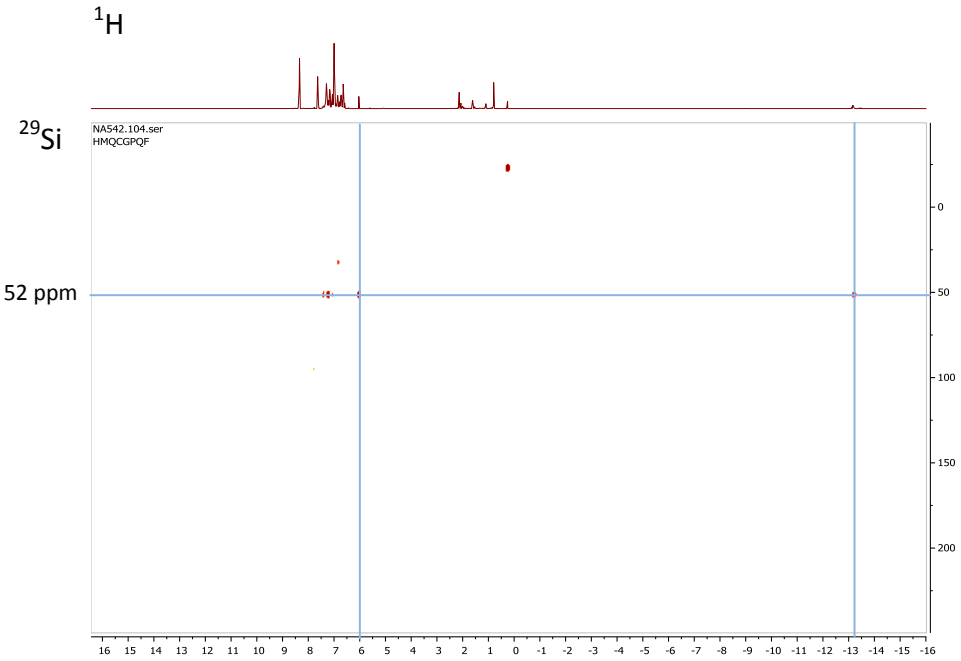


Figure S.57. Correlation $^{29}Si/^{1}H$ for **7.**

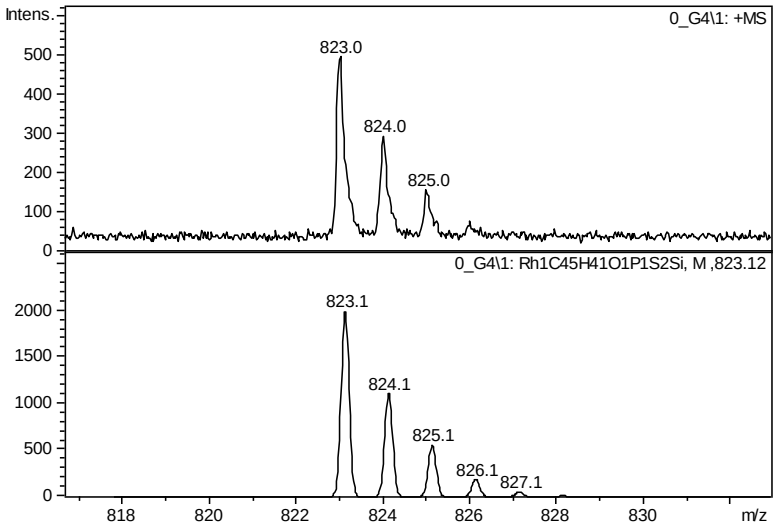


Figure S.58. ESI-MS of **7**.

X-ray Crystallography

Colourless crystal for **1** was mounted on a glass fibre and used for data collection on a Bruker D8 Venture with Photon detector equipped with graphite monochromated MoKα radiation (λ=0.71073 Å). The data reduction were performed with the APEX2[3] software and corrected for absorption using SADABS.[4] Crystal structures were solved by direct methods using the SIR97 program[5] and refined by full-matrix least-squares on F^2 including all reflections using anisotropic displacement parameters by means of the WINGX crystallographic package.[6] Generally, anisotropic temperature factors were assigned to all atoms except for hydrogen atoms, which are riding their parent atoms with an isotropic temperature factor arbitrarily chosen as 1.2 times that of the respective parent. H1 and H01 atoms were located. Final $R(F)$, $wR(F^2)$ and goodness of fit agreement factors, details on the data collection and analysis can be found in Table S1. Selected bond lengths and angles are given in Table S2. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number. CCDC 1899155. Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, U.K. (Fax: +44-1223-335033; e-mail: deposit@ccdc.cam.ac.uk).

Compound	**1**
Formula	$C_{32}H_{31}ClPRhS_2Si$
M	677.11
CCDC	1899155
Crystal System	Monoclinic
Space group	$P2_1/c$
T [K]	100
a [A]	16.1830(7)
b [A]	10.8556(5)
c [A]	21.0205(8)
α [deg]	90
β [deg]	123.025(3)
γ [deg]	90
V [A^3]	3096.2(2)
Z	4
Density [gcm^{-3}]	1.453
μ [mm^{-1}]	0.884
Observed reflections	130618
R_{int}	0.0895
R1 [b] / wR2 [c] [I>2σ(I)]	0.0464 / 0.1210
R1 [b] / wR2 [c] (all data)	0.0549 / 0.1318
GoF	1.173

[a] $S = [\Sigma w(F_0^2 - F_c^2)^2 / (N_{obs} - N_{para}m)]^{1/2}$ [b] $R_1 = \Sigma||F_0|-|F_c|| / \Sigma|F_0|$ [c] $wR_2 = [\Sigma w(F_0^2 - F_c^2)^2 / \Sigma wF_0^2]^{1/2}$

$w = 1/[\sigma^2(F_0^2) + (aP)^2 + bP]$ where $P = (\max(F_0^2,0) + 2F_c^2)/3$

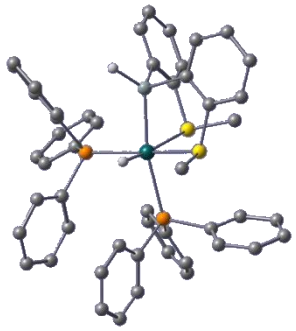
Table S1 Crystallographic data and structure refinement details for all compounds

Bond Distances	Bond Angles
Rh1 P1 2.2712(7)	P1 Rh1 Si1 97.62(3)
Rh1 Si1 2.2731(8)	P1 Rh1 S2 170.00(3)
Rh1 S2 2.3508(7)	Si1 Rh1 S2 86.45(3)
Rh1 S1 2.4400(7)	P1 Rh1 S1 94.03(3)
Rh1 Cl1 2.5245(7)	Si1 Rh1 S1 86.74(3)
Rh1 H01 1.5309	S2 Rh1 S1 95.33(2)
S1 C16 1.793(3)	P1 Rh1 Cl1 93.75(2)
S1 C1 1.812(3)	Si1 Rh1 Cl1 168.47(3)
S2 C5 1.782(3)	S2 Rh1 Cl1 82.63(2)
S2 C2 1.811(3)	S1 Rh1 Cl1 90.58(2)
P1 C29 1.821(3)	P1 Rh1 H01 82.9
P1 C23 1.831(3)	Si1 Rh1 H01 82.0
P1 C17 1.839(3)	S2 Rh1 H01 88.7
	S1 Rh1 H01 167.8
	Cl1 Rh1 H01 101.3

Table S2. Bond distances (Å) and bond angles (º) for compound **1**.

Computational Details

Density functional theory calculations were performed by use of the Gamess[7] 20/apr/2017 (R1).Full geometry optimizations and harmonic analyses were carried out by use of the B3LYP hybrid functional[8] and the DEF2-SVP[9] basis set and the Grimme's empirical dispersion correction DFTD3 V1.2.[10] Single-point energies were computed by use of the B3LYP-D functional DEF2-TZVP.[9]



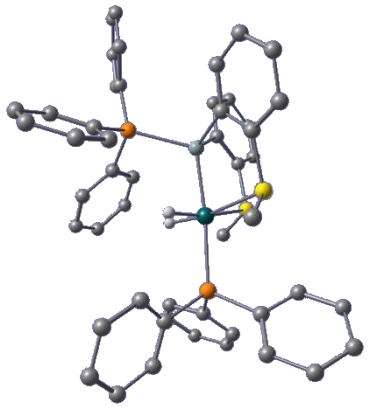
E(B3LYP-D-def2TZVP)=-3811.5262769621

C	2.74377	-1.02475	2.74983
C	0.79035	-3.01738	2.72511
C	0.90388	-3.59419	3.99854
H	1.09095	-2.97033	4.87665
C	0.76384	-4.97697	4.13045
H	0.85368	-5.44077	5.11601
C	0.49419	-5.76335	3.00274
H	0.37694	-6.84488	3.10816
C	0.36658	-5.16636	1.74611
H	0.14298	-5.79351	0.87749
C	0.51463	-3.77637	1.58075
C	-2.39353	-1.62747	2.41238
H	-1.96825	-0.91276	3.12744

H	-3.47448	-1.72877	2.57814
H	-1.89895	-2.60086	2.51653
H	3.25568	-1.59281	1.96309
H	3.04368	-1.37481	3.74656
H	2.95672	0.04693	2.64992
C	-3.16048	-4.69068	-1.76861
C	-1.82710	-4.42162	-1.43947
C	-1.48400	-3.31215	-0.64805
C	-2.52794	-2.47507	-0.21578
C	-3.86693	-2.73009	-0.53362
C	-4.18070	-3.85064	-1.31067
H	-3.40493	-5.55622	-2.38984
H	-1.03879	-5.08202	-1.81326
H	-4.65434	-2.05126	-0.19640
H	-5.22218	-4.05711	-1.56996
C	-0.27161	1.57140	5.75486
C	0.97178	1.88286	5.19905
C	1.11386	2.01355	3.81302
C	0.01075	1.82692	2.96490
C	-1.24060	1.53035	3.53412
C	-1.38065	1.40356	4.91733
H	-0.38165	1.47451	6.83778
H	1.83892	2.03657	5.84660
H	2.08878	2.27641	3.39694
H	-2.11757	1.41550	2.89224
H	-2.36204	1.18060	5.34419
C	3.97623	4.49780	0.70131
C	2.73136	5.10091	0.90893
C	1.57745	4.32026	1.00673
C	1.65367	2.92222	0.89353
C	2.90513	2.32598	0.67077
C	4.05968	3.10829	0.57916
H	4.87742	5.11133	0.62425

H	2.65611	6.18796	0.99484
H	0.61744	4.81395	1.15865
H	2.97029	1.24486	0.53605
H	5.02454	2.62943	0.39509
C	-3.58001	4.22726	-0.18787
C	-3.16493	3.11084	-0.91824
C	-2.03817	2.38674	-0.51414
C	-1.30151	2.77765	0.61514
C	-1.74631	3.88815	1.35988
C	-2.87144	4.60941	0.95731
H	-4.46115	4.79349	-0.50020
H	-3.71975	2.78949	-1.80335
H	-1.74852	1.50672	-1.08434
H	-1.22735	4.18338	2.27444
H	-3.19949	5.47051	1.54505
C	2.89134	-3.54245	-4.25465
C	3.42086	-2.99128	-3.08170
C	2.73699	-1.97497	-2.41541
C	1.52513	-1.47060	-2.92452
C	1.00280	-2.02681	-4.10235
C	1.68035	-3.06237	-4.75668
H	3.41977	-4.34853	-4.76970
H	4.36228	-3.36864	-2.67464
H	3.13940	-1.59204	-1.47445
H	0.06291	-1.66281	-4.51921
H	1.25598	-3.48998	-5.66845
C	-3.05731	0.57914	-4.77646
C	-1.86097	1.25749	-5.03495
C	-0.74778	1.06889	-4.21127
C	-0.82160	0.20142	-3.10540
C	-2.01838	-0.48996	-2.86987
C	-3.13024	-0.30340	-3.69497
H	-3.92515	0.73272	-5.42301

H	-1.79001	1.93729	-5.88787
H	0.17717	1.59964	-4.43942
H	-2.08465	-1.19513	-2.04814
H	-4.05044	-0.85506	-3.48706
C	3.23882	3.68421	-2.77947
C	1.89271	3.79457	-2.42119
C	1.12983	2.64828	-2.19606
C	1.69578	1.36867	-2.33328
C	3.04545	1.26762	-2.70760
C	3.80987	2.41807	-2.92379
H	3.83863	4.58216	-2.94575
H	1.43244	4.77793	-2.30250
H	0.08170	2.76388	-1.92086
H	3.51349	0.29491	-2.85176
H	4.85859	2.31785	-3.21480
Rh	0.38703	-0.57965	0.28557
H	1.91394	-0.51198	0.03862
P	0.19134	1.81860	1.12435
S	0.93268	-1.22357	2.58818
S	-2.12808	-0.97119	0.71579
P	0.63974	-0.12257	-2.01977
Si	0.30226	-2.91941	-0.11223
H	1.17982	-3.66116	-1.05783



E(B3LYP-D-def2TZVP)=-3811.5103080900

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C	2.06452	2.19489	2.01657
C	2.75676	3.16483	2.75669
H	2.37435	3.50036	3.72361
C	3.95086	3.69470	2.26337
H	4.48199	4.45839	2.83718
C	4.47752	3.22880	1.05329
H	5.42322	3.62756	0.67753
C	3.79882	2.24231	0.33576
H	4.23830	1.87182	-0.59398
C	2.57222	1.71929	0.78751
Si	1.56677	0.36519	-0.08069
C	-0.55687	-3.40044	0.75494
H	-1.50302	-3.48601	1.30217
H	-0.75615	-3.09441	-0.27962
H	-0.01810	-4.35627	0.79284
H	-1.43672	2.56670	3.37609
H	-0.01816	3.61416	3.70481
H	-0.64845	3.44240	2.01786
C	4.48497	-2.67459	-0.53183
C	3.80425	-1.46315	-0.66755
C	2.55336	-1.25554	-0.05312
C	2.01154	-2.30262	0.72100

C	2.70742	-3.50919	0.88692
C	3.93461	-3.69857	0.24796
H	5.45028	-2.81825	-1.02383
H	4.25451	-0.66763	-1.26695
H	2.29676	-4.29939	1.52059
H	4.46921	-4.64347	0.37379
C	-2.86762	0.53117	6.33242
C	-3.84629	1.13941	5.54123
C	-3.84247	0.96462	4.15266
C	-2.84980	0.18156	3.53985
C	-1.86185	-0.41882	4.34383
C	-1.87652	-0.25273	5.73038
H	-2.87402	0.67002	7.41660
H	-4.62079	1.75576	6.00510
H	-4.61409	1.44837	3.55094
H	-1.06901	-1.01191	3.88148
H	-1.10463	-0.72794	6.34096
C	-5.87545	2.97063	0.09339
C	-6.28445	1.71892	0.56697
C	-5.33881	0.80212	1.03313
C	-3.97004	1.12705	1.02987
C	-3.56799	2.38157	0.54562
C	-4.51623	3.29920	0.08345
H	-6.61646	3.68668	-0.27132
H	-7.34492	1.45381	0.57330
H	-5.66835	-0.17238	1.40125
H	-2.50562	2.63172	0.51948
H	-4.19071	4.27290	-0.29244
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C	-4.13328	-3.32243	-0.29584
C	-3.62885	-2.06394	0.03060
C	-3.48631	-1.68295	1.37829
C	-3.85561	-2.58201	2.38943

C	-4.34977	-3.85004	2.05662
H	-4.87826	-5.21170	0.46080
H	-4.24184	-3.60771	-1.34572
H	-3.32986	-1.37539	-0.76427
H	-3.75600	-2.30021	3.43984
H	-4.63138	-4.54548	2.85156
P	1.43299	0.89842	-2.36513
C	-1.87706	-2.07003	-3.63983
C	-0.66297	-2.54085	-3.12721
C	0.35196	-1.64309	-2.79326
C	0.16497	-0.26112	-2.98924
C	-1.05429	0.20739	-3.50183
C	-2.06963	-0.69808	-3.82518
H	-2.67408	-2.77388	-3.89273
H	-0.50900	-3.61178	-2.97386
H	1.27384	-2.02105	-2.34644
H	-1.22692	1.27714	-3.63054
H	-3.01777	-0.32494	-4.22005
C	-0.06174	5.20142	-3.16473
C	0.35444	4.38735	-4.22547
C	0.81556	3.09437	-3.97474
C	0.85548	2.60435	-2.65522
C	0.44347	3.42560	-1.59280
C	-0.01263	4.72115	-1.85275
H	-0.41951	6.21494	-3.36292
H	0.32331	4.76252	-5.25135
H	1.14999	2.46752	-4.80549
H	0.47361	3.06133	-0.56611
H	-0.32770	5.35862	-1.02286
C	5.41406	0.49936	-4.70653
C	5.12284	1.65699	-3.97561
C	3.90328	1.77541	-3.30659
C	2.96148	0.72990	-3.36175

C	3.25276	-0.42463	-4.10561
C	4.47617	-0.53497	-4.77424
H	6.36842	0.40896	-5.23111
H	5.84544	2.47555	-3.93063
H	3.67952	2.69072	-2.75354
H	2.52860	-1.23641	-4.17748
H	4.69281	-1.43471	-5.35527
Rh	-0.48469	0.12103	0.88108
H	-0.86430	1.43799	0.14213
P	-2.71826	-0.04260	1.71086
S	0.56376	1.45537	2.73192
H	-0.98505	-0.54676	-0.43250
S	0.42834	-2.11099	1.60201

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