Selective Carbanion–Pyridine Coordination of a Reactive P,N Ligand to Rh

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PROCEDURES AND SPECTROSCOPIC DATA

**General comments:** All reactions and manipulations were carried out under an atmosphere of dry dinitrogen using standard Schlenk techniques or in a glove-box. All solvents were purged with dinitrogen and dried using an MBRAUN Solvent Purification System (SPS). $^1$H, $^{13}$C, $^{31}$P, $^{29}$Si NMR spectra were recorded on Bruker AV 300, Bruker DRX 300, Bruker AV 400 or on a Varian Mercury 300 spectrometer at room temperature unless noted otherwise. Chemical shifts were expressed in positive sign, in parts per million, calibrated to residual $^1$H (5.32 ppm), $^{13}$C (53.84 ppm) solvent signals, 85% H$_3$PO$_4$ and external tetramethylsilane (0 ppm) respectively. Mass spectra were recorded on an AccuTOF LC, JMS-T100LP or an AccuTOF GC v 4g, JMS-T100GCV mass spectrometer. Infrared spectra were recorded with a Bruker Vertex 70v spectrometer. Elemental analyses were carried out by Kolbe Mikroanalytisches Labor, Oberhausen (Germany). (Diphenylphosphino)methyl-6-methyl-pyridine was prepared according to a literature procedure.$^{51}$
2,6-bis((diphenylmethylsilyl)methyl)pyridine A

\[
\begin{align*}
&\text{1) } n\text{-BuLi, TMEDA} \\
&\text{Et}_2\text{O, } -78 \degree \text{C to RT, 5h} \\
\rightarrow &\text{[Si]} \\
&\text{2) } \text{ClSiMePh}_2 \\
&\text{Et}_2\text{O, } -90 \degree \text{C to RT, 48h} \\
\rightarrow &\text{29%}
\end{align*}
\]

This compound was prepared from a slightly modified procedure.\textsuperscript{32}

To a solution of 1,6-dimethylpyridine (7.22 mL, 62.2 mmol) and tetramethylethylenediamine (19.6 mL, 130.6 mmol, 2.1 eq.) in diethylether (200 mL) was added dropwise a solution of \textit{n}-butyl lithium in hexanes (51.6 mL, 2.5 M, 2.07 eq.) at 0 \degree C leading to an intense red solution. The reaction mixture was allowed to warm up to room temperature and was further stirred for 5 h. During this time, the color of the solution turned from red to brownish. The solution thus obtained was added dropwise over 45 min (via an addition funnel) to a -90 \degree C solution of diphenylmethylsilylchloride (27.2 mL, 128.8 mmol, 2.07 eq.) in diethylether (200 mL). The reaction mixture was then allowed to slowly warm up to room temperature and stirred for an additional 48 hours leading to a clear yellow solution and a white precipitate.

After removal of the volatiles under reduced pressure, the solid residue was extracted with diethylether and filtered over a plug of activated neutral alumina. The ether was then removed under reduced pressure giving a yellow oil. After column chromatography on silica gel (eluent Et\(_2\)O / pentane, 20 / 80; Rf = 0.46), the compound was obtained as a white solid that was crystallized at -20 \degree C from a saturated Et\(_2\)O / pentane solution as white crystals with a yield of 35%.

HR-MS (CSI, -30 \degree C): exact mass (monoisotopic) calcd for \([\text{C}_{33}\text{H}_{33}\text{NSi}_2]^+\), \textit{m/z} 499.2152; found 499.2171.

\(^1\text{H} \text{NMR (300 MHz, C}_6\text{D}_6, \delta): 0.53 \text{ (s, 6H, CH}_3\text{), 2.84 \text{ (s, 4H, CH}_2\text{), 6.32 \text{ (d, 2H, }^3\text{J}_\text{HH} = 7.61 \text{ Hz, H}_\text{m-py}), 6.76 \text{ (t, 1H, }^3\text{J}_\text{HH} = 7.61 \text{ Hz, H}_\text{p-py}), 7.14-7.22 \text{ (m, 12H, H}_\text{Ph}), 7.49-7.57 \text{ (m, 8H, H}_\text{Ph}).}

\(^{13}\text{C}(^1\text{H}) \text{NMR (76 MHz, C}_6\text{D}_6, \delta): -3.75 \text{ (s, 2C, CH}_3\text{), 27.9 \text{ (s, 2C, CH}_2\text{), 118.9 \text{ (s, 2C, CH}_\text{m-py}), 128.1 \text{ (s, 8C, CH}_\text{Ph}), 129.5 \text{ (s, 4C, CH}_\text{p-Ph}), 135.2 \text{ (s, 8C, CH}_\text{Ph}), 135.6 \text{ (s, 1C, CH}_\text{p-py}), 137.2 \text{ (s, 4C, CH}_\text{p-Ph}), 159.6 \text{ (s, 2C, C}_\text{o-py}).
Ligand PN$^{12}$

![Diagram of the ligand PN$^{12}$]

To a suspension of A (2.5 g, 5.0 mmol) in diethyl ether (25 mL) was added dropwise a solution of n-Butyl lithium in hexanes (2.0 mL, 2.5 M, 1.0 eq.) at -78 °C. The resulting mixture was then allowed to warm up to room temperature and was stirred for 15 min at room temperature leading to an orange solution. This solution was then cooled down to -78 °C and chlorodiphenylphosphine (0.92 mL, 5.0 mmol, 1 eq.) was added dropwise at this temperature. The reaction mixture was then allowed to warm up to room temperature and was stirred for 15 min. After filtration via Celite, the volatiles were removed under vacuum and the residue was extracted with hexane (2 × 20 mL) and filtered via canula. After removal of the volatiles under reduced pressure, 2 was obtained as a colorless oil with a yield of 94%.

HR-MS (FD, -30 °C): exact mass (monoisotopic) calcd for [C$_{45}$H$_{42}$N$_2$P$_3$Si$_2$]$^+$, m/z 683.25934; found 683.26875.

Anal. Calcd. For C$_{45}$H$_{42}$NPSi$_2$; C, 79.02; H, 6.19; N, 2.05. Found: C, 79.23; H, 6.36; N, 2.11.

$^1$H NMR (300 MHz, CD$_2$Cl$_2$, δ): 0.44 (s, 3H, CH$_3$), 0.50 (s, 3H, CH$_3$), 2.74 (AB spin system, 2H, $^2$J$_{HH}$ = 13.4 Hz, CH$_2$), 4.05 (d, 1H, $^2$J$_{HP}$ = 3.4 Hz, HC$_p$), 6.32 (d, 1H, $^3$J$_{HH}$ = 7.6 Hz, H$_{m-py}$), 6.69 (d, 1H, $^3$J$_{HH}$ = 7.7 Hz, H$_{m-py}$), 6.96 (pseudo-t, 1H, $^3$J$_{HH}$ = 7.7 Hz, H$_{p-py}$), 7.02-7.63 (m, 30H, H$_n$).

$^{13}$C($^1$H) NMR (76 MHz, CD$_2$Cl$_2$, δ): -4.0 (s, 1C, CH$_3$), -3.5 (d, 1C, $^3$J$_{CP}$ = 4.9 Hz, CH$_3$), 27.5 (s, 1C, CH$_3$), 37.4 (d, 1C, $^1$J$_{CP}$ = 33.0 Hz, HC$_p$), 119.2 (d, 1C, $^1$J$_{CP}$ = 1.8 Hz, CH$_{m-py}$), 120.3 (d, 1C, $^1$J$_{CP}$ = 8.5 Hz, CH$_{m-py}$), 127.6 (s, 2C, CH$_{Ph-Si}$), 127.7 (s, 2C, CH$_{Ph-Si}$), 128.1 (s, 2C, CH$_{Ph-Si}$), 128.2 (s, 2C, CH$_{Ph-Si}$), 128.2 (d, 2C, $^1$J$_{CP}$ = 7.2 Hz, CH$_{Ph-p}$), 128.3 (d, 2C, $^2$J$_{CP}$ = 8.0 Hz, CH$_{Ph-p}$), 128.4 (s, 1C, CH$_n$), 129.2 (s, 1C, CH$_{Ph-Si}$), 129.3 (s, 1C, CH$_{Ph-Si}$), 129.4 (s, 1C, CH$_{Ph-Si}$), 129.5 (s, 1C, CH$_{Ph-Si}$), 129.6 (s, 1C, CH$_{Ph-Si}$), 133.5 (d, 2C, $^2$J$_{CP}$ = 20.5 Hz, CH$_{Ph-p}$), 134.8 (d, 2C, $^2$J$_{CP}$ = 22.5 Hz, CH$_{Ph-p}$), 135.1 (s, 2C, CH$_n$), 135.1 (s, 2C, CH$_{Ph}$), 135.4 (d, 2C, $^2$J$_{CP}$ = 1.4 Hz, CH$_{Ph}$), 135.7 (m, 3C, 2CH$_n$ and CH$_{Ph-p}$), 136.2 (d, 1C, $^1$J$_{CP}$ = 2.9 Hz, Si-C$_{quat}$), 136.4 (d, 1C, $^1$J$_{CP}$ = 1.4 Hz, Si-C$_{quat}$), 137.2 (s, 1C, Si-C$_{quat}$), 137.4 (s, 1C, Si-C$_{quat}$), 138.2 (d, 1C, $^1$J$_{CP}$ = 15.3 Hz, P-C$_{quat}$), 139.3 (d, 1C, $^1$J$_{CP}$ = 21.6 Hz, P-C$_{quat}$), 159.6 (s, 1C, C$_{o-py}$), 160.2 (d, 1C, $^1$J$_{CP}$ = 4.4 Hz, C$_{o-py}$).

$^{31}$P($^1$H) NMR (121 MHz, CD$_2$Cl$_2$, δ): -9.7 (s).

$^{29}$Si($^1$H) NMR (60 MHz, CD$_2$Cl$_2$, δ): -8.2 (d, $^2$J$_{SiP}$ = 18.5 Hz, Si$_1$), -7.8 (s, Si$_2$).
n-Butyl lithium in solution in diethyl ether (1.92 mmol, 0.77 mL, 2.5 M, 1 eq.) was added dropwise to a solution of 2-(diphenylphosphino)methyl-6-methylpyridine\textsuperscript{51} (560 mg, 1.92 mmol) in diethyl ether (20 mL) at -78 °C. Then, the resulting yellow solution was allowed to warm up to room temperature and was stirred for an additional 30 minutes at this temperature leading to an orange solution. After cooling down this solution to -78 °C, chloromethyldiphenylsilane (404 µL, 1.92 mmol, 1 eq.) was added dropwise and the reaction mixture was allowed to warm up to room temperature and was further stirred for 1 h at this temperature.

After removal of the volatiles under reduced pressure, the orange residue was extracted with pentane (2 × 10 mL), the extracts were combined and filtered over a plug of neutral alumina that was then washed with pentane (5 mL) affording a clear and colorless solution. This solution was concentrated until saturation and stored at -20 °C overnight leading to the precipitation of the expected compound as a colorless oil with a yield of 23%.

HRMS (FD): exact mass (monoisotopic) calcd for [C\textsubscript{32}H\textsubscript{39}N\textsubscript{2}P\textsubscript{2}Si\textsubscript{2}]\textsuperscript{+}, m/z 487.18851; found 487.18183.

\textsuperscript{1}H NMR (300 MHz, CD\textsubscript{2}Cl\textsubscript{2}, \textit{δ}): 0.45 (s, 3H, CH\textsubscript{3}-Si), 2.32 (s, 3H, CH\textsubscript{3}), 4.03 (d, 1H, \textit{j}\textsubscript{siP} = 3.4 Hz, HC-P), 6.64 (d, 1H, \textit{j}\textsubscript{siH} = 7.6 Hz, CH\textsubscript{m-PY}), 6.77 (d, 1H, \textit{j}\textsubscript{siH} = 7.8 Hz, CH\textsubscript{m-PY}), 7.03-7.50 (m, 21H, H\textsubscript{Ph}).

\textsuperscript{13}C[\textsuperscript{1}H]NMR (76 MHz, CD\textsubscript{2}Cl\textsubscript{2}, \textit{δ}): -3.6 (d, 1C, \textit{j}\textsubscript{CP} = 4.8 Hz, CH\textsubscript{2}-Si), 24.3 (s, 1C, CH\textsubscript{3}), 37.5 (d, 1C, \textit{j}\textsubscript{CP} = 33.3 Hz, P-C(H)-Si), 119.1 (d, 1C, \textit{j}\textsubscript{CP} = 2.0 Hz, CH\textsubscript{m-PY}), 121.2 (d, 1C, \textit{j}\textsubscript{CP} = 7.8 Hz, CH\textsubscript{m-PY}), 127.6 (s, 2C, CH\textsubscript{Ph-Si}), 127.7 (s, 2C, CH\textsubscript{Ph-Si}), 128.1 (d, 2C, \textit{j}\textsubscript{CP} = 7.0 Hz, CH\textsubscript{Ph-P}), 128.4 (d, 2C, \textit{j}\textsubscript{CP} = 7.8 Hz, CH\textsubscript{Ph-P}), 128.5 (s, 1C, CH\textsubscript{Ph}), 129.2 (s, 1C, CH\textsubscript{Ph}), 129.3 (s, 1C, CH\textsubscript{Ph}), 129.3 (s br., 1C, CH\textsubscript{Ph}), 133.6 (d, 2C, \textit{j}\textsubscript{CP} = 20.5 Hz, CH\textsubscript{Ph-P}), 134.7 (d, 2C, \textit{j}\textsubscript{CP} = 22.4 Hz, CH\textsubscript{Ph-P}), 135.3 (d, 2C, \textit{j}\textsubscript{CP} = 1.2 Hz, CH\textsubscript{Ph-P}), 135.7 (d, 2C, \textit{j}\textsubscript{CP} = 1.5 Hz, CH\textsubscript{Ph-Si}), 136.1 (s, 1C, CH\textsubscript{P-P}), 136.3 (d, 1C, \textit{j}\textsubscript{CP} = 2.1 Hz, Si-C\textsubscript{quat.}), 138.0 (d, 1C, \textit{j}\textsubscript{CP} = 14.8 Hz, P-C\textsubscript{quat.}), 138.9 (d, 1C, \textit{j}\textsubscript{CP} = 20.9 Hz, P-C\textsubscript{quat.}), 157.9 (s, 1C, C\textsubscript{P-P}), 160.2 (d, 1C, \textit{j}\textsubscript{CP} = 4.1 Hz, C\textsubscript{P-P}), one quaternary carbon connected to silicon was not observed.

\textsuperscript{31}P[\textsuperscript{1}H] NMR (121 MHz, CD\textsubscript{2}Cl\textsubscript{2}, \textit{δ}): 8.5.

\textsuperscript{29}Si[\textsuperscript{1}H] NMR (60 MHz, CD\textsubscript{2}Cl\textsubscript{2}, \textit{δ}): -8.3 (d, \textit{j}\textsubscript{SiP} = 18.4 Hz).
Complex 1

Dichloromethane (10 mL) was added to a neat mixture of \textbf{PN}^{Si2} (536 mg, 0.78 mmol) and dicarbonyl rhodium(III) chloride dimer (145 mg, 0.37 mmol, 0.475 eq.) at -78 °C and the resulting mixture was allowed to warm up to room temperature under stirring giving an orange solution. The complex was then precipitated as a yellow powder by the addition of pentane (50 mL) and the mother liquor was removed by filtration. The powder was then solubilized in dichloromethane, filtered over Celite and layered with pentane affording the expecting complex as yellow crystals with a yield of 47% (regarding to the rhodium complex). Crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of pentane into a saturated dichloromethane solution of the complex at room temperature.

HR-MS (FD): exact mass (monoisotopic) calcd for [C_{46}H_{24}Cl_{2}O_{3}N_{2}P_{2}S_{2}Rh_{1}]^+, m/z 849.12861; found 849.12866.

Anal. Calcd. for C_{46}H_{24}ClNOPRhSi_{2}: C, 64.97; H, 4.98; N, 1.65. Found: C, 64.97; H, 5.02; N, 1.64.

$^1$H NMR (300 MHz, CD_{2}Cl_{2}, $\delta$): 0.05 (s, 3H, CH$_3$-Si), 1.21 (s, 3H, CH$_3$-Si), 2.97 (d, 1H, $^2$J$_{HH}$ = 13.6 Hz, CH$_2$), 4.42 (d, 1H, $^2$J$_{HP}$ = 15.6 Hz, HC-P), 5.30 (d, 1H, $^2$J$_{HH}$ = 13.6 Hz, CH$_2$), 6.30 (d, 2H, $^2$J$_{HH}$ = 7.8 Hz, H$_p$-py), 6.82 (t, 1H, $^3$J$_{HH}$ = 7.8 Hz, H$_p$-py), 6.94-7.04 (m, 2H, H$_{arom.}$), 7.08-7.18 (m, 2H, H$_{arom.}$), 7.19-7.44 (m, 24H, H$_{arom.}$), 7.53-7.63 (m, 2H, H$_{arom.}$).

$^{13}$C($^1$H) NMR (76 MHz, CD$_2$Cl$_2$, $\delta$): -41.3 (s, 1C, CH$_3$-Si), -2.9 (s, 1C, CH$_3$-Si), 29.5 (s, 1C, CH$_3$), 43.0 (d, 1C, $^1$J$_{CP}$ = 15.5 Hz, P-C(H)-Si), 120.1 (d, 1C, $^1$J$_{CP}$ = 9.4 Hz, CH$_{m-py}$), 123.0 (s, 1C, CH$_{m-py}$), 128.0 (s, 2C, CH$_{Ph-si}$), 128.1-128.3 (m, 6C, CH$_{Ph-si}$), 128.6 (d, 2C, $^1$J$_{CP}$ = 11.2 Hz, CH$_{Ph-p}$), 129.1 (d, $^1$J$_{CP}$ = 10.3 Hz, CH$_{Ph-p}$), 129.6 (dd, 1C, $^1$J$_{CP}$ = 56.6 Hz, J$_{C_{Ph}}$ = 4.5 Hz, P-C$_{quat}$), 129.6 (s, 1C, CH$_{Ph-si}$), 129.7 (s, 1C, CH$_{Ph-si}$), 129.8 (s, 1C, CH$_{Ph-si}$), 130.0 (s, 1C, CH$_{Ph-si}$), 130.4 (d, 1C, $^1$J$_{CP}$ = 2.3 Hz, CH$_{Ph-p}$), 131.8 (d, 2C, $^1$J$_{CP}$ = 11.5 Hz, CH$_{Ph-p}$), 131.8 (d, 1C, $^1$J$_{CP}$ = 2.7 Hz, CH$_{Ph-p}$), 133.5 (s, 1C, Si$_{1}$-C$_{quat}$), 134.1 (d, 1C, $^1$J$_{CP}$ = 40.4 Hz, P-C$_{quat}$), 134.1 (dd, 2C, $^1$J$_{CP}$ = 12.6 Hz, J$_{C_{Ph}}$ = 1.7 Hz, CH$_{Ph-p}$), 134.9 (s, 2C, CH$_{Ph-si}$), 135.0 (d, 1C, $^1$J$_{CP}$ = 4.9 Hz, Si$_{1}$-C$_{quat}$), 135.1 (s, 2C, CH$_{Ph-si}$), 135.3 (s, 2C, CH$_{Ph-si}$), 135.4 (s, 2C, CH$_{Ph-si}$), 136.1 (s, 1C, CH$_{Ph-p}$), 162.1 (d, 1C, $^1$J$_{CP}$ = 3.2 Hz, C$_{C-py}$), 165.8 (s, 1C, C$_{C-py}$), 190.4 (dd, 1C, J$_{C_{Ph}}$ = 74.4 Hz, $^1$J$_{C_{Ph}}$ = 13.8 Hz, CO).

$^{31}$P($^1$H) NMR (121 MHz, CD$_2$Cl$_2$, $\delta$): 67.6 (d, $^1$J$_{PPh}$ = 167.6 Hz).

$^{29}$Si($^1$H) NMR (79 MHz, CD$_2$Cl$_2$, $\delta$): -7.0 (s), -6.7 (s br.).

$\text{IR (KBr) mode cm}^{-1}$: v 1987 (s, CO).
Complex 1'

Dichloromethane (5 mL) was added to a neat mixture of $\text{PN}^{\text{Si}}$ (218 mg, 0.45 mmol) and dicarbonylrhodium(I) chloride dimer (86.9 mg, 0.22 mmol, 0.5 eq.) at -78 °C under stirring and the resulting mixture was allowed to warm up to room temperature giving an orange solution. The complex was then precipitated as a yellow powder by the addition of pentane (20 mL) and the mother liquor was removed by filtration. The powder was then solubilized in dichloromethane (6 mL), filtered via canula and layered with pentane (16 mL) affording the expecting complex as a solvate of dichloromethane (orange crystals, yield = 63%). Crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of pentane into a saturated dichloromethane solution of the complex at room temperature.

HR-MS (FD): exact mass (monoisotopic) calcd for $[\text{C}_{33}\text{H}_{30}\text{N}_1\text{P}_1\text{Rh}_1\text{Si}_1\text{CO}]^+$, m/z 625.06287; found 625.09933.

Anal. Calcd. for $[\text{C}_{33}\text{H}_{30}\text{ClNOPRhSi+CH}_2\text{Cl}_2]$: C, 55.26; H, 4.36; N, 1.90. Found: C, 55.48; H, 4.30; N, 1.98.

$^1\text{H}$ NMR (300 MHz, CD$_2$Cl$_2$, δ): 0.18 (s, 3H, CH$_3$-Si), 3.04 (s, 3H, CH$_3$-py), 4.42 (d br., 1H, $^3J_{Hp}$ = 15.0 Hz, CH-P), 6.40 (d, 1H, $^3J_{HH}$ = 9.0 Hz, H$_m$-py), 6.84 (d, 1H, $^3J_{HH}$ = 9.0 Hz, H$_m$-py), 6.97 – 7.08 (m, 2H, H$_\text{arom.}$), 7.09 – 7.48 (m, 17H, H$_\text{arom.}$), 7.50 – 7.61 (m, 2H, H$_\text{arom.}$).

$^{13}\text{C}^{{}^1\text{H}}$ NMR (75 MHz, CD$_2$Cl$_2$, δ): -2.7 (s, 1C, CH$_3$-Si), 27.9 (s, 1C, CH$_{30-py}$), 43.9 (d, 1C, $^1J_{CP}$ = 15.8 Hz, P-C(H)-Si), 121.4 (d, 1C, $J_{CP}$ = 9.0 Hz, CH$_{m-py}$), 123.0 (s, 1C, CH$_{m-py}$), 128.2 (s, 2C, CH$_{Ph-Si}$), 128.7 (d, 2C, $J_{CP}$ = 11.3 Hz, CH$_{Ph-p}$), 128.9 (d, 2C, $J_{CP}$ = 10.5 Hz, CH$_{Ph-p}$), 129.5 (dd, 1C, $J_{CP}$ = 56.5 Hz, $J_{CRh}$ = 4.5 Hz, P-C$_\text{quat.}$), 129.9 (s, 1C, CH$_{Ph-Si}$), 130.1 (s, 1C, CH$_{Ph-Si}$), 130.7 (d, 1C, $J_{CP}$ = 2.3 Hz, CH$_{Ph-p}$), 131.7 (d, 1C, $J_{CP}$ = 3.0 Hz, CH$_{Ph-p}$), 132.6 (d br., 2C, $J_{CP}$ = 12.0 Hz, CH$_{Ph-p}$), 133.5 (dd, 2C, $J_{CP}$ = 15.0 Hz, $J_{CPh} = 1.5$ Hz, CH$_{Ph-p}$), 133.7 (s, 1C, Si-C$_\text{quat.}$), 134.2 (d, 1C, $J_{CP}$ = 39.8 Hz, P-C$_\text{quat.}$), 134.9 (d, 1C, $^3J_{CP}$ = 5.3 Hz, Si-C$_\text{quat.}$), 135.2 (s, 2C, CH$_{Ph-Si}$), 135.4 (s, 2C, CH$_{Ph-Si}$), 138.0 (s, 1C, CH$_{p-py}$), 162.6 (dd, 1C, $J_{CP}$ = 3.8 Hz, $J_{CPh} = 0.8$ Hz, CO$_{p-py}$), 163.4 (s, 1C, CO$_{p-py}$), 190.5 (dd, 1C, $J_{CRh} = 74.3$ Hz, $J_{CP}$ = 13.5 Hz, CO).

$^{31}\text{P}^{{}^1\text{H}}$ NMR (121 MHz, CD$_2$Cl$_2$, δ): 70.1 (d, $^1J_{RP}$ = 164.6 Hz).

$^{29}\text{Si}^{{}^1\text{H}}$ NMR (60 MHz, CD$_2$Cl$_2$, δ): -7.3 (d, $^2J_{PP}$ = 3.0 Hz).

$\text{PN}^{\text{Si}}$
Dimeric complex 2

Tetrahydrofuran (13 mL) was added to a mixture of 1 (186.5 mg, 0.22 mmol) and sodium azide (90.0 mg, 1.38 mmol, 6.3 eq.) in a Schlenk kept away from light and the resulting suspension was stirred at room temperature for 4 days leading to a brown reaction mixture. The $^{31}$P{$_1$H} NMR analysis of the crude mixture showed the disappearance of the starting material and the formation of a new species resonating at $\delta$47.2 ppm in THF.

The crude mixture was filtered over Celite, slightly concentrated (to 10 mL) and pentane (20 mL) was added leading to the precipitation of a yellow powder. After elimination of the mother liquor by filtration, the powder was solubilized in tetrahydrofuran (5 mL) and the solution was filtered in order to get a very limpid solution. This solution was layered with pentane (13 mL) affording 2 as yellow crystals (containing 2 molecules of THF per complex) with a yield of 37%.

Anal. Calcd. for [C$_{66}$H$_{58}$N$_2$P$_2$O$_2$Rh$_2$Si$_2$+2THF]: C, 64.44; H, 5.41; N,2.03. Found: C, 64.62; H, 5.58; N, 2.07.

$^1$H NMR (300 MHz, THF-$d_8$, $\delta$): 0.30 (s, 6H, CH$_3$-Si), 2.33 (br., 2H, HC-P), 2.65 (AB spin system, 4H, $^2$J$_{HH}$ = 15.0 Hz, CH$_2$), 6.36 (d, 2H, $^1$J$_{HH}$ = 6.0 Hz, CH$_{Py}$), 6.41 (d, 2H, $^1$J$_{HH}$ = 9.0 Hz, CH$_{Py}$), 7.08-7.38 (m, 24H, H$_{arom}$), 7.39-7.48 (m, 4H, H$_{arom}$), 7.50-7.61 (m, 2H, H$_{arom}$), 7.73-7.84 (m, 2H, H$_{arom}$).

$^{13}$C{$_1$H}: Due to the very low resolution of the spectrum, the attribution was not possible.

$^{31}$P{$_1$H} NMR (121 MHz, THF-$d_8$, $\delta$): 45.7.

$^{29}$Si{$_1$H} NMR (79 MHz, THF-$d_8$, $\delta$): -9.3(s).

IR (ATR, cm$^{-1}$): $\nu$ 1947 (s; CO).
**Isomerisation of 2 into 3**

**Method 1**

Tetrahydrofuran (5.0 mL) was added to a mixture of 2 (360 mg, 0.290 mmol) and diphenylamine (46.9 mg, 0.277 mmol, 0.95 eq.) in a young valve suitable for reactions under pressure. The resulting suspension was heated up to 90 °C during 48 h leading to a dark red solution (NMR yield = 46 %, internal standard dichloroethane). After removal of the volatiles under reduced pressure, the residue was extracted with diethylether (5 mL), filtered and concentrated until saturation. Placing this solution at -20 °C afforded a dark red mixture of 2 and HNPh₂ (1 / 0.69), yield = 16 %.

Crystals suitable for X-ray diffraction were obtained from slow evaporation of a saturated diethyl ether solution at room temperature, the crystal lattice contains one molecule of diphenylamine.

**Method 2**

An NMR tube containing a solution of 2 (20 mg, 14.5 μmol) and trimethylamine (2.0 μL, 14.5 μmol, 1 eq.) in THF-d₈ was heated at 90 °C. Monitoring of the reaction by ^1H NMR spectroscopy showed complete conversion after 25 h with a yield of 66%. The yield was determined by ^1H NMR spectroscopy by integration of the resonance signal of one Si-Me group relative to the Me group of toluene as an internal standard (V_tol = 2 μL, D1 relaxation time = 10s).

HR-MS (CSI, -43 °C): exact mass (monoisotopic) calcd for [C₆₆H₅₈N₂O₂P₂Si₂Rh₂+H]^+, 1235.1700; found 1235.1696.

**NMR Characterization**
$^1$H NMR (300 MHz, CD$_2$Cl$_2$, $\delta$): 0.5 (s, 3H, CH$_3$-Si($\beta$)), 0.58 (s, 3H, CH$_3$-Si($\alpha$)), 2.70 [AB system $\Delta$V$_{AB}$ = 13.4 Hz: 2.68 (1H, $^3$J$_{HH}$ = 12.9 Hz, Si-CH$_2$($\alpha$)), 2.72 (1H, $^3$J$_{HH}$ = 12.9 Hz, Si-CH$_2$($\alpha$))], 2.81 (d, 1H, $^3$J$_{HH}$ = 13.9 Hz, CH$_2$-Si($\beta$)), 4.02 (d, 1H, $^3$J$_{HH}$ = 13.9 Hz, CH$_2$-Si($\beta$)), 4.22 (dd, 1H, $^3$J$_{HH}$ = 12.0 Hz, $^3$J$_{HP}$ = 12.0 Hz, CH$_2$-P($\beta$)), 4.75 (pseudo-dt, 1H, $^3$J$_{PH}$ = 4.3 Hz, $^3$J$_{PH}$ = 4.3 Hz, $^3$J$_{HH}$ = 2.7 Hz, HC-Rh), 5.13 (dd, 1H, $^3$J$_{HH}$ = 12.0 Hz, $^3$J$_{PH}$ = 6.3 Hz, CH$_2$-P($\beta$)), 5.65 (d, 1H, $^3$J$_{HH}$ = 7.9 Hz, CH$_3$-py($\beta$)), 5.98 (d, 1H, $^3$J$_{HH}$ = 7.9 Hz, CH$_3$-py($\alpha$)), 6.58 (d, 1H, $^3$J$_{HH}$ = 7.9 Hz, CH$_3$-py($\beta$)), 6.64 (d, 1H, $^3$J$_{HH}$ = 7.8 Hz, CH$_3$-py($\beta$)), 7.03-7.61 (m, 37H, H$_{arom}$), 7.78 (m, 2H, H$_{arom}$), 8.04 (m, 2H, H$_{arom}$).

$^{13}$C($^1$H) NMR (76 MHz, CD$_2$Cl$_2$, $\delta$): -4.1 (s, 1C, CH$_3$-Si), -3.5 (s, 1C, CH$_3$-Si), 28.7 (s, 1C, CH$_2$-Si($\beta$)), 41.1 (br., 1C, HC-Rh), 45.5 (d br., 1C, $^1$J$_{PC}$ = 21.0 Hz, CH$_2$-P($\beta$)), 117.2 (s br., 1C, CH$_3$-py($\alpha$)), 122.8 (s br., 1C, CH$_3$-py($\beta$)), 123.9 (s br., 1C, CH$_3$-py($\beta$)), 127.8 (d, 2C, $^1$J$_{PC}$ = 11.4 Hz, CH$_3$-py($\beta$)), 127.9 (s, 2C, CH$_3$-py($\beta$)), 128.0 (d br., 2C, $^1$J$_{PC}$ = 10.6 Hz, CH$_3$-py($\beta$)), 128.1 (s, 2C, CH$_3$-py($\beta$)), 128.4 (s, 2C, CH$_3$-py($\beta$)), 128.5 (s, 2C, CH$_3$-py($\beta$)), 128.6 (d, 2C, $^1$J$_{PC}$ = 8.8 Hz, CH$_3$-py($\beta$)), 128.7 (d, 2C, $^1$J$_{PC}$ = 9.5 Hz, CH$_3$-py($\beta$)), 129.1 (s br., 1C, CH$_3$-py($\beta$)), 129.3 (s, 1C, CH$_3$-py($\beta$)), 129.4 (d, 1C, $^1$J$_{PC}$ = 2.5 Hz, CH$_3$-py($\beta$)), 129.5 (s, 1C, CH$_3$-py($\beta$)), 129.8 (s, 1C, CH$_3$-py($\beta$)), 130.1 (s, 1C, CH$_3$-py($\beta$)), 130.2 (s br., 1C, CH$_3$), 130.3 (d, 2C, $^1$J$_{PC}$ = 10.2 Hz, CH$_3$-py($\beta$)), 130.9 (d, 1C, $^1$J$_{PC}$ = 2.0 Hz, CH$_3$-py($\beta$)), 132.9 (d, 2C, $^1$J$_{PC}$ = 10.9 Hz, CH$_3$-py($\beta$)), 134.5 (dd, 2C, $^1$J$_{PC}$ = 10.2 Hz, $^1$J$_{HH}$ = 1.5 Hz, CH$_3$-py($\beta$)), 134.7 (s, 2C, CH$_3$-py($\beta$)), 135.1 (s, 2C, CH$_3$-py($\beta$)), 135.3 (s, 2C, CH$_3$-py($\beta$)), 135.4 (s, 2C, CH$_3$-py($\beta$)), 136.3 (d br., 2C, $^1$J$_{PC}$ = 15.1 Hz, CH$_3$-py($\beta$)), 136.3 (s, 1C, CH$_3$-py($\beta$)), 136.4 (d br., $^1$J$_{PC}$ = 64.6 Hz, CH$_3$-py($\beta$)), 133.0 (s, 1C, CH$_3$-py($\beta$)), 137.2 (s, 1C, CH$_3$-py($\beta$)), 137.4 (d, 1C, $^1$J$_{PC}$ = 1.5 Hz, CH$_3$-py($\beta$)), 143.1 (dd, $^1$J$_{PC}$ = 41.0 Hz, $^1$J$_{HH}$ = 1.4 Hz, CH$_3$-py($\beta$)), 151.9 (br., 1C, CH$_3$-py($\beta$)), 153.7 (s, 1C, CH$_3$-py($\beta$)), 157.5 (d, 1C, $^1$J$_{PC}$ = 4.1 Hz, CH$_3$-py($\beta$)), 163.0 (d, 1C, $^1$J$_{PC}$ = 2.0 Hz, CH$_3$-py($\beta$)), 163.8 (s, 1C, CH$_3$-py($\beta$)), 191.4-193.1 (br., 2C, CO). The carbon connected to rhodium in meta position of the N-heterocycle was not observed.

$^{31}$P($^1$H) NMR (121 MHz, CD$_2$Cl$_2$, $\delta$): 17.9 (ddd, $^1$J$_{RP}$ = 124.1 Hz, $J = 17.2$ Hz, $J = 4.5$ Hz), 34.3 (ddd, $^1$J$_{RP}$ = 164.6 Hz, $J = 17.2$ Hz, $J = 4.5$ Hz).

$^{29}$Si($^1$H) NMR (79 MHz, CD$_2$Cl$_2$, $\delta$): -8.2 (br., Si($\alpha$) and Si($\beta$)), detected by means of a 2D HSQC [$^1$H,$^2$Si] experiment.
NMR SPECTRA

NMR spectra of A

[Si] — [Si]

[Si] = SiPh₂Me

Figure S1. ¹H NMR spectrum of A (300 MHz, 20 °C) in C₆D₆

Figure S2. ¹H NMR spectrum of A (300 MHz, 20 °C) in C₆D₆ aromatic region
Figure S3. $^{13}\text{C}[^1\text{H}]$ NMR spectrum of A (76 MHz, 20 °C) in C$_6$D$_6$

Figure S4. $^{13}\text{C}[^1\text{H}]$ NMR spectrum of A (76 MHz, 20 °C) in C$_6$D$_6$, aromatic region
NMR spectra of $\text{PN}^{\text{Si2}}$

![Image](image-url)

Figure S5. $^{31}\text{P}^{[\text{H}]}$ NMR spectrum of $\text{PN}^{\text{Si2}}$ (121 MHz, 20 °C) in CD$_2$Cl$_2$

![Image](image-url)

Figure S6. $^1\text{H}$ NMR spectrum of $\text{PN}^{\text{Si2}}$ (300 MHz, 20 °C) in CD$_2$Cl$_2$
Figure S7. $^1$H NMR spectrum of $\text{PN}^{\text{Si2}}$ (300 MHz, 20 °C) in CD$_2$Cl$_2$, aliphatic region

Figure S8. $^1$H NMR spectrum of $\text{PN}^{\text{Si2}}$ (300 MHz, 20 °C) in CD$_2$Cl$_2$, aromatic region
Figure S9. $^{13}\text{C}[^1\text{H}] \text{NMR}$ spectrum of $\text{PN}^{\text{Si2}}$ (76 MHz, 20 °C) in CD$_2$Cl$_2$

Figure S10. $^{13}\text{C}[^1\text{H}] \text{NMR}$ spectrum of $\text{PN}^{\text{Si2}}$ (76 MHz, 20 °C) in CD$_2$Cl$_2$, zoom Si-CH$_3$ region
Figure S11. $^{13}$C($^1$H) NMR spectrum of $\text{PN}^{\text{Si}_2}$ (76 MHz, 20 °C) in CD$_2$Cl$_2$, aliphatic region

Figure S12. $^{13}$C($^1$H) NMR spectrum of $\text{PN}^{\text{Si}_2}$ (76 MHz, 20 °C) in CD$_2$Cl$_2$, aromatic zoom 1
Figure S13. $^{13}$C($^1$H) NMR spectrum of $\text{PN}^{\text{Si2}}$ (76 MHz, 20 °C) in CD$_2$Cl$_2$, aromatic zoom 2

Figure S14. $^{13}$C($^1$H) NMR spectrum of $\text{PN}^{\text{Si2}}$ (76 MHz, 20 °C) in CD$_2$Cl$_2$, aromatic zoom 3
Figure S15. $^{13}$C[$^1$H] NMR spectrum of PN$_{Si2}$ (76 MHz, 20 °C) in CD$_2$Cl$_2$, aromatic zoom 4

Figure S16. $^{29}$Si[$^1$H] NMR spectrum of PN$_{Si2}$ (60 MHz, 20 °C) in CD$_2$Cl$_2$
NMR spectra of $\text{PN}^\text{Si}$

$\text{[Si]} - \text{Ph}$

$\text{[Si]} = \text{SiPh}_2\text{Me}$

Figure S17. $^{31}\text{P}^\text{1H}$ NMR spectrum of $\text{PN}^\text{Si}$ (121 MHz, 20 °C) in CD$_2$Cl$_2$
Figure S18. $^1$H NMR spectrum of PN$^{30}$Si (300 MHz, 20 °C) in CD$_2$Cl$_2$

Figure S19. $^{13}$C($^1$H) NMR spectrum of PN$^{30}$Si (76 MHz, 20 °C) in CD$_2$Cl$_2$
Figure S20. $^{13}$C$\text{[}^1\text{H}]$ NMR spectrum of PN$^{\text{H}}$ (76 MHz, 20 °C) in CD$_2$Cl$_2$, aliphatic region

Figure S21. $^{13}$C$\text{[}^1\text{H}]$ NMR spectrum of PN$^{\text{H}}$ (76 MHz, 20 °C) in CD$_2$Cl$_2$, aromatic region zoom 1
Figure S22. $^{13}$C($^1$H) NMR spectrum of PN$^\text{II}$ (76 MHz, 20 °C) in CD$_2$Cl$_2$, aromatic region zoom 2

Figure S23. $^{13}$C($^1$H) NMR spectrum of PN$^\text{II}$ (76 MHz, 20 °C) in CD$_2$Cl$_2$, aromatic region zoom 3
Figure S24. $^{29}\text{Si}^{1}\text{H}$ NMR spectrum of PN$^\text{Si}$ (60 MHz, 20 °C) in CD$_2$Cl$_2$
NMR spectra of 1

Figure S25. $^{31}\text{P}$$^1\text{H}$ NMR spectrum of 1 (121 MHz, 20 °C) in CD$_2$Cl$_2$

Figure S26. $^1\text{H}$ NMR spectrum of 1 (300 MHz, 20 °C) in CD$_2$Cl$_2$
Figure S27. $^{13}$C($^1$H) NMR spectrum of 1 (76 MHz, 20 °C) in CD$_2$Cl$_2$

Figure S28. $^{13}$C($^1$H) NMR spectrum of 1 (76 MHz, 20 °C) in CD$_2$Cl$_2$, aliphatic region
Figure S29. $^{13}$C($^1$H) NMR spectrum of 1 (76 MHz, 20 °C) in CD$_2$Cl$_2$, aromatic region zoom 1

Figure S30. $^{13}$C($^1$H) NMR spectrum of 1 (76 MHz, 20 °C) in CD$_2$Cl$_2$, aromatic region zoom 2
Figure S31. $^{13}$C($^1$H) NMR spectrum of 1 (76 MHz, 20 °C) in CD$_2$Cl$_2$, aromatic region zoom 3

Figure S32. $^{13}$C($^1$H) NMR spectrum of 1 (76 MHz, 20 °C) in CD$_2$Cl$_2$, aromatic region zoom 4
Figure S33. $^{13}$C($^1$H) NMR spectrum of 1 (76 MHz, 20 °C) in CD$_2$Cl$_2$, aromatic region zoom 5

Figure S34. $^{29}$Si($^1$H) NMR spectrum of 1 (60 MHz, 20 °C) in CD$_2$Cl$_2$
NMR spectra of 1'

Figure S35. $^{31}$P{$^1$H} NMR spectrum of 1' (121 MHz, 20 °C) in CD$_2$Cl$_2$
Figure S36. $^1$H NMR spectrum of 1' (300 MHz, 20 °C) in CD$_2$Cl$_2$

Figure S37. $^1$H NMR spectrum of 1' (300 MHz, 20 °C) in CD$_2$Cl$_2$, zoom
Figure S38. $^{13}$C($^1$H) NMR spectrum of 1' (76 MHz, 20 °C) in CD$_2$Cl$_2$

Figure S39. $^{13}$C($^1$H) NMR spectrum of 1' (76 MHz, 20 °C) in CD$_2$Cl$_2$, aliphatic region
Figure S40. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 1' (76 MHz, 20 °C) in CD$_2$Cl$_2$, aromatic region zoom 1

Figure S41. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 1' (76 MHz, 20 °C) in CD$_2$Cl$_2$, aromatic region zoom 2
Figure S42. $^{13}$C($^1$H) NMR spectrum of 1' (76 MHz, 20 °C) in CD$_2$Cl$_2$, aromatic region zoom 3

Figure S43. $^{13}$C($^1$H) NMR spectrum of 1' (76 MHz, 20 °C) in CD$_2$Cl$_2$, aromatic region zoom 4
Figure S44. $^{13}$C($^1$H) NMR spectrum of 1' (76 MHz, 20 °C) in CD$_2$Cl$_2$, aromatic region zoom 5

Figure S45. $^{29}$Si($^1$H) NMR spectrum of 1' (60 MHz, 20 °C) in CD$_2$Cl$_2$
Figure S46. $^{31}$P{$^1$H} NMR spectrum of 2 (121 MHz, 20 °C) in THF-$d_8$
Figure S47. $^1$H NMR spectrum of 2 (300 MHz, 20 °C) in THF-$d_8$

Figure S48. $^1$H NMR spectrum of 2 (300 MHz, 20 °C) in THF-$d_8$, aliphatic region
Figure S49. $^1$H NMR spectrum of 2 (300 MHz, 20 °C) in THF-$d_8$, aromatic region

Figure S50. $^{29}$Si($^1$H) NMR spectrum of 2 (60 MHz, 20 °C) in THF-$d_8$
Figure S51. $^{31}\text{P}$$\{	ext{H}\}$ NMR spectrum of 3 (121 MHz, 20 °C) in CD$_2$Cl$_2$
Figure S52. $^1$H NMR spectrum of 3 (300 MHz, 20 °C) in CD$_2$Cl$_2$

*Attributed based on COSY ($^1$H,$^1$H) NMR spectroscopy (correlation with meta-H J and K)

Figure S53. $^1$H NMR spectrum of 3 (300 MHz, 20 °C) in CD$_2$Cl$_2$, aliphatic region
Figure S54. $^1$H NMR spectrum of 3 (300 MHz, 20 °C) in CD$_2$Cl$_2$, olefinic region

*Resonance signal attributed to the N-H proton of diphenylamine

Figure S55. $^1$H NMR spectrum of 3 (300 MHz, 20 °C) in CD$_2$Cl$_2$, aromatic region

*Resonance signal attributed to aromatic protons of diphenylamine
Figure S56. Stacked \(^1\text{H}\) NMR and \(^1\text{H}\{^{31}\text{P}\}\) NMR spectra of 3 (300 MHz, 20 °C) in CD\(_2\)Cl\(_2\), olefinic region.

Figure S57. COSY \((^{1}\text{H},^{1}\text{H})\) NMR spectrum of 3 (300 MHz, 20 °C) in CD\(_2\)Cl\(_2\).

Figure S58. $^{13}$C($^1$H) NMR spectrum of 3 (76 MHz, 20 °C) in CD$_2$Cl$_2$

Figure S59. $^{13}$C($^1$H) NMR spectrum of 3 (76 MHz, 20 °C) in CD$_2$Cl$_2$, aliphatic region

* impurity
*Resonance signal attributed to the aromatic CH carbons of diphenylamine

*Resonance signal attributed to the aromatic CH carbons of diphenylamine
Figure S62. $^{13}$C($^1$H) NMR spectrum of 3 (76 MHz, 20 °C) in CD$_2$Cl$_2$, aromatic region 3

*Resonance signal attributed to the aromatic C$_{ipso-Ph}$ carbons of diphenylamine

Figure S63. $^{13}$C($^1$H) NMR spectrum of 3 (76 MHz, 20 °C) in CD$_2$Cl$_2$, aromatic region 4

*Resonance signal attributed to the aromatic C$_{ipso-Ph}$ carbons of diphenylamine
Figure S64. Stacked $^{13}\text{C}(^1\text{H})$ and $^{13}\text{C}(^1\text{H}, ^{31}\text{P})$ NMR spectra of 3 (76 MHz, 20 °C) in CD$_2$Cl$_2$, aliphatic region

Figure S65. Stacked $^{13}\text{C}(^1\text{H})$ and $^{13}\text{C}(^1\text{H}, ^{31}\text{P})$ NMR spectra of 3 (76 MHz, 20 °C) in CD$_2$Cl$_2$, aromatic region 1. *Resonance signal attributed to the aromatic CH carbons of diphenylamine
Figure S66. Stacked $^{13}\text{C}({}^1\text{H})$ and $^{13}\text{C}({}^1\text{H},{}^{31}\text{P})$ NMR spectra of 3 (76 MHz, 20 °C) in CD$_2$Cl$_2$, aromatic region 2

*Resonance signal attributed to the aromatic CH carbons of diphenylamine
Figure S67. Stacked $^{13}\text{C}({}^1\text{H})$ and $^{13}\text{C}({}^1\text{H}, {}^{31}\text{P})$ NMR spectra of 3 (76 MHz, 20 °C) in CD$_2$Cl$_2$, aromatic region 3
Figure S68. Stacked $^{13}\text{C}^{1\text{H}}$ and $^{13}\text{C}^{1\text{H},31\text{P}}$ NMR spectra of 3 (76 MHz, 20 °C) in CD$_2$Cl$_2$, aromatic region 4
Figure S69. Stacked $^{13}\text{C}(^1\text{H})$ and $^{13}\text{C}(^1\text{H}, ^{31}\text{P})$ NMR spectra of 3 (76 MHz, 20 °C) in CD$_2$Cl$_2$, CO region
Figure S70. Stacked $^{13}\text{C}\{^1\text{H}\}$, $^{13}\text{C}\{^1\text{H},^{31}\text{P}\}$ and $^{13}\text{C}\{^1\text{H}\}$ jmod NMR spectra of 3 (76 MHz, 20 °C) in CD$_2$Cl$_2$, aliphatic region
Figure S71. Stacked $^{13}$C($^1$H), $^{13}$C($^1$H, $^{31}$P) and $^{13}$C($^1$H) jmod NMR spectra of 3 (76 MHz, 20 °C) in CD$_2$Cl$_2$, aromatic region 1.
Figure S72. Stacked $^{13}$C($^1$H), $^{13}$C($^1$H,$^{31}$P) and $^{13}$C($^1$H) jmod NMR spectra of 3 (76 MHz, 20 °C) in CD$_2$Cl$_2$, aromatic region 2
Figure S73. HSQC ($^1$H,$^{13}$C) NMR spectrum of 3 (300 MHz, 20 °C) in CD$_2$Cl$_2$

Figure S74. HSQC ($^1$H,$^{13}$C) NMR spectrum of 3 (300 MHz, 20 °C) in CD$_2$Cl$_2$, aliphatic region
Figure S75. HSQC ($^1$H,$^{13}$C) NMR spectrum of 3 (300 MHz, 20 °C) in CD$_2$Cl$_2$, aromatic region

Figure S76. HMBC ($^1$H,$^{29}$Si) NMR spectrum of 3 (300 MHz, 20 °C) in CD$_2$Cl$_2$
Reaction of complex 1 with silver(I) hexafluoroantimonate

![Chemical structure of complex 1 and silver(I) hexafluoroantimonate](image)

Figure S77. $^{31}$P($^1$H) NMR spectrum of 1 / AgSbF$_6$ (121 MHz, 20 °C) in CD$_2$Cl$_2$
Figure S78. $^1$H NMR spectrum of $1 / \text{AgSbF}_6$ (300 MHz, 20 °C) in CD$_2$Cl$_2$

Figure S79. Stacked $^1$H NMR spectrum of $1$ (bottom) and $^1$H NMR spectrum of $1 / \text{AgSbF}_6$ (top) (300 MHz, 20 °C) in CD$_2$Cl$_2$
Small Molecule X-ray Crystallography

Complexes 1 and 2: All reflections intensities were measured on a Bruker D8 Quest Eco diffractometer equipped with a Triumph monochromator (\( \lambda = 0.71073 \) Å) and a CMOS Photon 50 detector at a temperature of 150(2) K. Intensity data were integrated with the Bruker APEX2 software.\(^5\) Absorption correction and scaling was performed with SADABS.\(^6\) The structures were solved using intrinsic phasing with the program SHELXT.\(^3\) Least-squares refinement was performed with SHELXL-2013\(^8\) against \( F^2 \) of all reflections. Non-hydrogen atoms were refined with anisotropic displacement parameters. The H atoms were placed at calculated positions using the instructions AFIX 13, AFIX 43 or AFIX 137 with isotropic displacement parameters having values 1.2 or 1.5 times \( U_{eq} \) of the attached C atoms.

Complex 3: All reflection intensities were measured at 110(2) using a Super Nova diffractometer (equipped with Atlas detector) with Mo K\( \alpha \) radiation (\( \lambda = 0.71073 \) Å) under the program CrysAlisPro (Version 1.171.36.32, Agilent Technologies, 2013 or Version 1.171.38.41, Rigaku OD, 2015). The same program was used to refine the cell dimensions and for data reduction. The structure was solved with the program SHELXS-2014/7 (Sheldrick, 2015) and was refined on \( F^2 \) with SHELXL-2014/7.\(^9\) Numerical absorption correction based on gaussian integration or analytical numeric absorption correction over a multifaceted crystal model was applied using CrysAlisPro. The temperature of the data collection was controlled using the system Cryojet (manufactured by Oxford Instruments). The H atoms were placed at calculated positions (unless otherwise specified) using the instructions AFIX 43, AFIX 123, AFIX 137 or AFIX 147 with isotropic displacement parameters having values 1.2 or 1.5 \( U_{eq} \) of the attached C or O atoms.

The CCDC 1590066, 1590067 and 1589141 reference numbers 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.

Complex 1: The structure is mostly ordered except for one phenyl group, which is disordered over two orientations. The occupancy factor of the major component of the disorder refines to 0.778(11). \( \text{C}_{46}\text{H}_{42}\text{ClNOPRhSi}_2 \), \( \text{Fw} = 850.32 \), yellow needle, 0.90x0.40x0.10 mm, monoclinic, \( P2_1/c \) (No: 14), \( a = 12.8772(5) \), \( b = 19.2512(7) \), \( c = 16.9684(6) \) Å, \( b = 97.166(2)^\circ \), \( V = 4173.6(3) \) Å\(^3\), \( Z = 4 \), \( D_x = 1.353 \) g/cm\(^3\), \( \mu = 0.604 \) mm\(^-1\). 72197 Reflections were measured up to a resolution of (sin \( \theta/\lambda \))\(_{max} \) = 0.65. 9567 Reflections were unique (\( R_{int} = 0.0715 \)), of which 7528 were observed \(|I > 2\sigma (I)| \). 526 Parameters were refined with 198 restraints. R1/wR2 \(|I > 2\sigma (I)| \): 0.0314/0.0678. R1/wR2 \[all refl.\]: 0.0523/0.0802. \( S = 1.089 \). Residual electron density between -0.68 and 0.72 e/Å\(^3\). CCDC 1590066.

Complex 2: The structure is mostly ordered except for one phenyl group and one lattice THF solvent molecule, which are both disordered over two orientations. The occupancy factors of the major components of the disorder refine to 0.608(11) and 0.786(8), respectively. Additionally, the asymmetric unit contains one very disordered lattice THF solvent molecule whose contribution has been removed from the final refinement using the Squeeze Procedure.\(^7\) \( \text{C}_{66}\text{H}_{58}\text{N}_2\text{O}_2\text{P}_2\text{Rh}_2\text{Si}_2\text{C}_4\text{H}_8\text{O} \), \( \text{Fw} = 1307.19 \), small orange block, 0.90x0.60x0.40 mm, triclinic, \( P-1 \) (No: 2), \( a = 14.6478(6) \), \( b = 15.3121(6) \), \( c = 17.7858(7) \) Å, \( \alpha = 67.193(2) \), \( \beta = 87.432(3) \), \( \gamma = 62.658(2)^\circ \), \( V = 4222.9(2) \) Å\(^3\), \( Z = 2 \), \( D_x = 1.347 \) g/cm\(^3\), \( \mu = 0.646 \) mm\(^-1\). 57289 Reflections were measured up to a resolution of (sin \( \theta/\lambda \))\(_{max} \) = 0.60. 11342 Reflections were unique (\( R_{int} = 0.1088 \)), of which 7543 were observed.
S58 Parameters were refined with 368 restraints. R1/wR2 [I > 2σ(I)]: 0.0402/0.0776. R1/wR2 [all refl.]: 0.0848/0.0926. S = 0.999. Residual electron density between -0.53 and 1.12 e Å$^{-3}$. CCDC 1590067.

**Complex 3:** C$_{44}$H$_{64}$Cl$_2$N$_4$O$_2$Ru, Fw = 852.96, small orange block, 0.09×0.06×0.04 mm, triclinic, P-1 (No: 2), a = 8.5758(3), b = 9.5568(3), c = 14.6431(5) Å, α = 88.457(3), β = 84.548(3), γ = 66.688(3)$^\circ$, V = 1097.07(7) Å$^3$, Z = 1, D$_x$ = 1.291 g/cm$^3$, μ = 4.309 mm$^{-1}$. 14305 Reflections were measured up to a resolution of (sin θ/λ)$_{\text{max}}$ = 0.616. 4291 Reflections were unique (R$_{\text{int}}$ = 0.037), of which 3966 were observed [I > 2σ(I)]. 290 Parameters were refined with 123 restraints. R1/wR2 [I > 2σ(I)]: 0.0325/0.0792. R1/wR2 [all refl.]: 0.0364/0.0816. S = 1.046. Residual electron density between -0.63 and 0.82 e Å$^{-3}$. CCDC 1589141.

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Figure S80 X-ray structure of complex 1
Figure S81 X-ray structure of complex 1’
DFT Calculations

Density functional calculations were performed at the ωB97X-D\(^{15}\) level of theory using Gaussian09, revision D.01.\(^{[59]}\) Geometry optimizations were performed using the DEF2TZVP basis set\(^{[310]}\) and frequency calculations have been performed to ensure minima on the potential energy surface. NICS values\(^{[511]}\) have been calculated using the GIAO method\(^{[512]}\) at the B3LYP/6-31G(d,p) level\(^{[513][514]}\)

The interaction energy of the Rh(CO)Cl fragment at the different coordination modes of I and 2\(^\text{M}\) has been determined with respect to the ligand in the geometry of the complexes. The Topological Analysis of the Electron Density\(^{[515]}\) has been performed using ADF\(^{[516]}\) at the ωB97X-D/TZ2P level including relativistic effects with the Zero Order Regular Approximation (Zora).\(^{[517]}\)

Phenyl groups have been replaced by methyl groups to keep the computation time manageable.

### Free Ligand

| Atom | X      | Y      | Z      |
|------|--------|--------|--------|
| H    | 2.99901315 | 0.98852467 | 0.52965623 |
| C    | 3.62181878 | 0.40010088 | 0.40648418 |
| H    | 4.30650812 | 2.76838503 | 0.60967364 |
| H    | 4.38578495 | 4.0645278 | 4.21187993 |
| H    | 4.35136759 | 2.50737058 | 0.91849704 |
| H    | 2.99901315 | 2.65737977 | 0.20779125 |

### 1Me

| Atom | X      | Y      | Z      |
|------|--------|--------|--------|
| H    | 2.0117833 | 0.5970931 | 0.52842715 |
| C    | 1.4239504  | 0.17784458 | 0.87371802 |
| H    | 0.87368005 | 0.22486239 | 0.88440975 |
| C    | 1.57891556 | -1.77463399 | 0.73157966 |
| H    | 0.98943595 | -2.48352832 | 0.23550022 |
| H    | 0.87368005 | -1.12766618 | 1.25856540 |
| H    | 2.23352488 | -2.25640767 | 1.46317479 |
| C    | -2.27509176 | -2.16784831 | 0.48032341 |
| H    | -1.31719156 | -1.91298919 | 0.02574589 |
| H    | -2.15282677 | -2.20890679 | 1.56443060 |
| C    | -2.60712555 | -1.35179539 | 0.13057988 |
| C    | -3.33920799 | -0.97463646 | 1.78495897 |
| C    | -2.30569434 | -0.76181070 | 0.02616294 |
| C    | -3.61714631 | -1.97425215 | 1.21449181 |
| C    | -3.99670872 | -0.24518463 | 2.25747930 |
| C    | 3.70453382 | 0.40010088 | 0.46648418 |
| H    | 4.38578495 | -0.14586986 | 1.60862961 |
| H    | 4.30508018 | 0.98852467 | -0.29136323 |
| H    | 3.16245586 | 1.09738315 | 1.06212776 |
| C    | 3.62181878 | -1.94119308 | 1.54605770 |
| H    | 4.21187993 | -1.38785333 | -2.28141944 |
| H    | 4.31536759 | -2.50737058 | -0.91849704 |
| H    | 2.99901315 | -2.65737977 | -0.20779125 |

E[total]= -1155.63345031 au, NICS=+0.335
E[0]=-1155.61704589 au
E[2^\text{M}]=-1155.58156959 au

\[ E(tot) = -1155.63345031 \text{ au}, \text{ NICS}=+0.335 \]
\[ E[0]= -1155.61704589 \text{ au} \]
\[ E[2^\text{M}]=-1155.58156959 \text{ au} \]
CP: -1.781227 -2.230958 0.738876

\[
\begin{align*}
Rho &= 0.1772379E+00 \\
|\text{GRAD}(Rho)| &= 0.6236114E-15 \\
\text{GRAD}(Rho)_x &= -0.1571031E-15 \\
\text{GRAD}(Rho)_y &= -0.5866687E-15 \\
\text{GRAD}(Rho)_z &= 0.1415261E-15 \\
\text{Laplacian} &= 0.5316842E+00 \\
\left[-\frac{1}{4}\text{Del}^2(Rho)\right] &= -0.1329210E+00 \\
\text{Diamond} &= 0.8996025E+00 \\
\text{Metallicity} &= 0.6843931E+01 \\
\text{Ellipticity} &= 0.2032277E-01
\end{align*}
\]

CP # 92 (Rh2-C26)
(RANK,SIGNATURE): (3, -1)
CP: 1.242119 -1.599956 -0.656677

\[
\begin{align*}
Rho &= 0.9680949E+01 \\
|\text{GRAD}(Rho)| &= 0.2124174E-13 \\
\text{GRAD}(Rho)_x &= -0.1167690E-13 \\
\text{GRAD}(Rho)_y &= 0.1564267E-13 \\
\text{GRAD}(Rho)_z &= 0.8376652E-14 \\
\text{Laplacian} &= 0.1648259E+00 \\
\left[-\frac{1}{4}\text{Del}^2(Rho)\right] &= -0.4120649E+00 \\
\text{Diamond} &= 0.1475841E+00 \\
\text{Metallicity} &= 0.8533310E+01 \\
\text{Ellipticity} &= 0.2365653E+00
\end{align*}
\]

CP # 141 (Rh2-C29)
(RANK,SIGNATURE): (3, -1)
CP: -0.816106 -0.535895 -0.155230

\[
\begin{align*}
Rho &= 0.7425806E+01 \\
|\text{GRAD}(Rho)| &= 0.3483873E-15 \\
\text{GRAD}(Rho)_x &= -0.8431418E-16 \\
\text{GRAD}(Rho)_y &= -0.2950539E-15 \\
\text{GRAD}(Rho)_z &= 0.1551887E-15 \\
\text{Laplacian} &= 0.1731208E+00 \\
\left[-\frac{1}{4}\text{Del}^2(Rho)\right] &= -0.4328021E+01 \\
\text{Diamond} &= 0.9227472E+01 \\
\text{Metallicity} &= 0.5221996E+01 \\
\text{Ellipticity} &= 0.5445488E+00
\end{align*}
\]
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