

SUPPLEMENTARY INFORMATION for:

**‘Hemilabile’ Silyl Pincer Ligation: Platinum Group PSiN Complexes and
Triple C-H Activation to Form a (PSiC)Ru Carbene Complex**

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Experimental Section

General Considerations. All experiments were conducted under argon or nitrogen in an MBraun glovebox or using standard Schlenk techniques. Tetrahydrofuran and diethyl ether were distilled from Na/benzophenone ketyl; while benzene, toluene, and pentane were purified over one activated alumina column and one column packed with activated Q-5. All purified solvents were stored over 4 Å molecular sieves. Benzene-*d*₆ and toluene-*d*₈ were degassed via three freeze-pump-thaw cycles and stored over 4 Å molecular sieves. The compound (2-BrC₆H₄)P^tBu₂ was prepared according to a literature procedure.^{S1} All other reagents were purchased from Strem or Aldrich and used without further purification. Unless otherwise stated, ¹H, ¹³C, ³¹P NMR, ²⁹Si characterization data were collected at 300K on a Bruker AV-500 spectrometer operating at 500.1, 125.8, 202.5, and 99.4 MHz (respectively) with chemical shifts reported in parts per million downfield of SiMe₄ (for ¹H, ¹³C, and ²⁹Si) or 85% H₃PO₄ in D₂O (for ³¹P). Variable-temperature NMR data were collected on a Bruker AC-250 spectrometer. ¹H and ¹³C NMR chemical shift assignments are based on data obtained from ¹³C-DEPTQ, ¹H-¹H COSY, ¹H-¹³C HSQC, and ¹H-¹³C HMBC NMR experiments. In some cases, fewer than expected unique ¹³C NMR resonances were observed, despite prolonged acquisition times. ²⁹Si NMR assignments are based on ¹H-²⁹Si HMQC and ¹H-²⁹Si HMBC experiments. Elemental analyses were performed by Columbia Analytical Services of Tucson, Arizona and Midwest Microlab of Indianapolis, Indiana. Infrared spectra were recorded as thin films between NaCl plates using a Bruker VECTOR 22 FT-IR spectrometer at a resolution of 4 cm⁻¹.

C₆H₄(NMe₂)SiMeHCl. A solution of 2-bromo-N,N-dimethylaniline (5.00 g, 25.0 mmol) in ca. 75 mL THF was added dropwise to flask containing Mg turnings (0.91 g, 37.5 mmol) and the reaction mixture was subsequently heated for 18 hours at 75 °C. The resulting brown solution was allowed to cool to room temperature and was then added drop-wise to a solution of Cl₂SiMeH (14.34 g, 125 mmol) in ca. 50 mL of THF at -78 °C. A color change to orange was observed. The reaction mixture was allowed to warm to room temperature and stir for 18 h, at which point the volatile components were

removed *in vacuo*, and the residue was extracted with benzene (ca. 30 mL). The benzene extract was filtered through Celite and the benzene was subsequently removed *in vacuo* to yield a red oil. This oil was then distilled under reduced pressure to afford $C_6H_4(NMe_2)SiMeHCl$ (bp = 39° C, <0.1 mm Hg) as a colorless oil (2.34 g, 47%). 1H NMR (500 MHz, benzene- d_6): δ 7.89 (m, 1 H, H_{arom}), 7.15 (m, 1 H, H_{arom}), 7.06 (m, 1 H, H_{arom}), 6.84 (m, 1 H, H_{arom}), 5.55 (m, 1 H, Si- H), 2.20 (s, 6H, NMe_2), 0.60 (d, 3 H, $J = 3$ Hz, SiMe). $^{13}C\{^1H\}$ NMR (125.8 MHz, benzene- d_6): δ 160.65 (C_{arom}), 136.6 (CH_{arom}), 133.9 (C_{arom}), 132.9 (CH_{arom}), 127.3 (CH_{arom}), 121.4 (CH_{arom}), 46.6 (NMe_2), 2.4 (SiMe). ^{29}Si NMR (99.4 MHz, benzene- d_6): δ -21.0 ppm.

(^tBu-PSiN-Me)H (1). nBuLi (1.6 M in hexanes, 0.69 mL, 1.1 mmol) was added to a cold (-78 °C) solution of (2-Br C_6H_4)P^tBu₂ (0.33 g, 1.1 mmol) in ca. 5 mL of pentane. The reaction mixture was allowed to warm to room temperature and after stirring for 2 h the volatile components were removed *in vacuo*. The remaining beige solid was dissolved in ca. 3 mL of THF and cooled to -30 °C. The cold THF solution was added drop-wise to a pre-cooled (-30 °C) solution of $C_6H_4NMe_2SiMeHCl$ (0.22 g, 1.1 mmol) in ca. 3 mL of THF. The reaction mixture was allowed to warm to room temperature and stir for 2 h. The volatile components were removed *in vacuo*, and the residue was extracted with ca. 10 mL of benzene. The benzene extracts were filtered through Celite and the filtrate solution was dried *in vacuo* to yield **1** as a pale yellow oil (0.33 g, 78%). 1H NMR (500 MHz, benzene- d_6): δ 7.81 (m, 1 H, H_{arom}), 7.70 (m, 1 H, H_{arom}), 7.65 (m, 1 H, H_{arom}), 7.22 (m, 1 H, H_{arom}), 7.15 – 7.13 (overlapping resonances, 2 H, H_{arom}), 7.08 (m, 1 H, H_{arom}), 6.99 (m, 1 H, H_{arom}), 5.87 (m, 1 H, Si- H), 2.34 (s, 6 H, NMe_2), 1.16 (d, 9 H, $PCMe_3$, $^3J_{PH} = 11$ Hz), 1.10 (d, 9 H, $PCMe_3$, $^3J_{PH} = 11$ Hz), 0.83 (d, 3 H, SiMe, $^3J_{HP} = 4$ Hz). $^{13}C\{^1H\}$ NMR (125.8 MHz, benzene- d_6): δ 161.6 (C_{arom}), 149.1 (d, C_{arom} , $J_{CP} = 51$ Hz), 144.7 (d, C_{arom} , $J_{CP} = 21$ Hz), 138.7 (CH_{arom}), 137.2 (d, CH_{arom} , $J_{CP} = 17$ Hz), 136.6 (C_{arom}), 135.1 (CH_{arom}), 131.5 (CH_{arom}), 128.9 (CH_{arom}), 128.6 (CH_{arom}), 125.3 (CH_{arom}), 121.5 (CH_{arom}), 46.6 (NMe_2), 33.6 (d, $PCMe_3$, $J_{CP} = 8$ Hz), 33.4 (d, $PCMe_3$, $J_{CP} = 8$ Hz), 31.5 – 31.3 (overlapping resonances, $PCMe_3$), -1.6 (d, SiMe,

$J_{\text{CP}} = 10 \text{ Hz}$). $^{31}\text{P}\{^1\text{H}\}$ NMR (202.5 MHz, benzene- d_6): δ 23.2. ^{29}Si NMR (99.4 MHz, benzene- d_6): δ -24.4 ppm ($^1J_{\text{SiH}} = 205 \text{ Hz}$). IR (cm^{-1}): 2128 (br, m, Si-H). Anal. Calcd for $\text{C}_{23}\text{H}_{36}\text{NPSi}$: C, 71.64; H, 9.41; N, 3.63. Found: C, 71.23; H, 9.18; N, 3.50.

κ^3 -(^tBu-PSiN-Me)PdBr (2). A solution of **1** (0.22 g, 0.57 mmol) and NEt_3 (0.095 mL, 0.68 mmol) in ca. 5 mL of benzene was added to a slurry of PdBr_2 (0.15 g, 0.57 mmol) in ca. 5 mL of benzene. The resulting reaction mixture was allowed to stir at room temperature for 18 h. The pale yellow solution was filtered through Celite and the volatile components were removed *in vacuo*. The residue was triturated with pentane ($3 \times 2 \text{ mL}$) and dried *in vacuo* to yield **2** as a pale yellow solid (0.28 g, 86 % yield). ^1H NMR (500 MHz, benzene- d_6): δ 7.67 – 7.63 (overlapping resonances, 2 H, H_{arom}), 7.54 (m, 1 H, H_{arom}), 7.20-7.17 (overlapping resonances, 2 H, H_{arom}), 7.09 – 7.03 (overlapping resonances, 3 H, H_{arom}), 6.96 (d, 1 H, $J = 7 \text{ Hz}$, H_{arom}), 3.17 (br s, 6 H, NMe_2), 1.43 (d, 9 H, PCMe_3 , $^3J_{\text{PH}} = 14 \text{ Hz}$), 1.32 (d, 9 H, PCMe_3 , $^3J_{\text{PH}} = 14 \text{ Hz}$), 0.59 (s, 3 H, SiMe). $^{13}\text{C}\{^1\text{H}\}$ NMR (300 K, 125.8 MHz, benzene- d_6): δ 162.0 (C_{arom}), 140.8 (C_{arom}), 133.9 (CH_{arom}), 133.5 (d, CH_{arom} , $J_{\text{CP}} = 24 \text{ Hz}$), 133.2 (CH_{arom}), 131.1 (CH_{arom}), 130.8 (CH_{arom}), 128.9 (CH_{arom}), 127.6 (CH_{arom}), 122.0 (CH_{arom}), 52.0 (NMe), 37.6 (CMe_3), 38.0 (CMe_3), 31.9 (d, CMe_3 , $J_{\text{CP}} = 5 \text{ Hz}$), 31.1 (d, CMe_3 , $J_{\text{CP}} = 5 \text{ Hz}$), 7.5 (SiMe). $^{31}\text{P}\{^1\text{H}\}$ NMR (202.5 MHz, benzene- d_6): δ 99.4. ^{29}Si NMR (99.4 MHz, benzene- d_6): δ 54.0. Anal. Calcd for $\text{C}_{23}\text{H}_{35}\text{BrNPPdSi}$: C, 48.39; H, 6.18; N, 2.45. Found: C, 48.05; H, 6.33; N, 2.29.

κ^3 -(^tBu-PSiN-Me)PtCl (3). $(\text{COD})\text{PtCl}_2$ (0.13 g, 0.36 mmol) was added to a solution of **1** (0.14 g, 0.36 mmol) and NEt_3 (0.060 mL, 0.43 mmol) in ca. 5 mL of benzene. The resulting reaction mixture was heated at $75 \text{ }^\circ\text{C}$ for 48 h. The solution was subsequently filtered through Celite and the volatile components were removed *in vacuo*. The residue was triturated with pentane ($3 \times 2 \text{ mL}$) and dried *in vacuo* to yield **3** as an off white solid (0.15 g, 68%). ^1H NMR (500 MHz, benzene- d_6): δ 7.82 (d, 1 H, $J = 7 \text{ Hz}$, H_{arom}), 7.72 (m, 1 H, H_{arom}), 7.60 (m, 1 H, H_{arom}), 7.17 (m, 1 H, H_{arom}), 7.06 – 7.03 (overlapping resonances, 2 H, H_{arom}), 6.92 (m, 1 H, H_{arom}), 6.90 (d, 1H, $J = 7 \text{ Hz}$, H_{arom}), 3.22 (br s, 6 H, NMe_2), 1.40

(d, 18 H, $PCMe_3$, $^3J_{PH} = 14$ Hz), 0.52 (s, 3 H, $SiMe$). $^{13}C\{^1H\}$ NMR (300 K, 125.8 MHz, benzene- d_6): δ 133.5 (CH_{arom}), 133.1 (d, CH_{arom} , $J_{CP} = 19$ Hz), 132.9 (CH_{arom}), 130.6 (CH_{arom}), 130.5 (CH_{arom}), 128.7 (CH_{arom}), 127.9 (CH_{arom}), 121.8 (CH_{arom}), 36.8 (CMe_3), 31.5 (CMe_3), 30.8 (CMe_3), 8.69 ($SiMe$). $^{31}P\{^1H\}$ NMR (202.5 MHz, benzene- d_6): δ 74.7 (s with Pt satellites, $^1J_{PPt} = 4804$ Hz) ^{29}Si NMR (99.4 MHz, benzene- d_6): δ 24.9. Anal. Calcd for $C_{23}H_{35}NPPtClSi$: C, 44.91; H, 5.76; N, 2.28. Found: C, 44.82; H, 6.12, N, 1.93.

κ^3 -(t -Bu- $PSiN$ -Me)Pd(OTf) (4). AgOTf (0.027 g, 0.11 mmol) was added to a solution of **2** (0.060 g, 0.11 mmol) in ca. 5 mL of benzene. The resulting reaction mixture was allowed to stir at room temperature for 30 minutes. The solution was subsequently filtered through Celite and the volatile components were removed *in vacuo*. The residue was triturated with pentane (3×2 mL) and dried *in vacuo* to yield **4** as a pale yellow solid (0.063 g, 89%). 1H NMR (500 MHz, benzene- d_6): δ 7.52 (d, 1 H, H_{arom} , $J = 7$ Hz), 7.43 (m, 1 H, H_{arom}), 7.38 (m, 1 H, H_{arom}), 7.14 (m, 1 H, H_{arom}), 7.02 (m, 1 H, H_{arom}), 6.96 (m, 1 H, H_{arom}), 6.87 (d, 1 H, H_{arom} , $J = 8$ Hz), 3.13 (s, 3 H, NMe), 3.03 (s, 3 H, NMe), 1.26 (d, 9 H, $PCMe_3$, $^3J_{PH} = 15$ Hz), 1.15 (d, 9 H, $PCMe_3$, $^3J_{PH} = 15$ Hz), 0.43 (d, 3 H, $SiMe$, $J = 2$ Hz). $^{13}C\{^1H\}$ NMR (125.8 MHz, benzene- d_6): δ 161.5 (C_{arom}), 139.0 (C_{arom}), 133.4 – 133.2 (overlapping resonances, CH_{arom}), 132.6 (CH_{arom}), 131.7 (CH_{arom}), 131.1 (CH_{arom}), 129.6 (CH_{arom}), 121.5 (CH_{arom}), 49.6 (NMe), 37.5 (CMe_3), 36.4 (CMe_3), 31.2 (CMe_3), 30.6 (CMe_3), 6.93 ($SiMe$). $^{31}P\{^1H\}$ NMR (202.5 MHz, benzene- d_6): δ 92.4. ^{29}Si NMR (99.4 MHz, benzene- d_6): δ 53.3. Anal. Calcd for $C_{24}H_{35}NPPdSiO_3SF_3$: C, 45.03; H, 5.51; N, 2.19. Found: C, 44.87; H, 5.94, N, 2.12. A single crystal of **4**· $0.5C_6H_6$ suitable for X-ray diffraction analysis was grown from a concentrated benzene solution.

κ^3 -(t -Bu- $PSiN$ -Me)Pt(OTf) (5). AgOTf (0.022 g, 0.086 mmol) was added to a solution of **3** (0.053 g, 0.086 mmol) in ca. 5 mL of benzene. The resulting reaction mixture was allowed to stir at room temperature for 30 minutes. The solution was subsequently filtered through Celite and the volatile components were removed *in vacuo*. The residue was triturated with pentane (3×2 mL) and dried *in*

vacuo to yield **4** as a pale yellow solid (0.050 g, 80%). ^1H NMR (500 MHz, benzene- d_6): δ 7.61 (d, 1 H, H_{arom} , $J = 7$ Hz), 7.50 (m, 1 H, H_{arom}), 7.43 (m, 1 H, H_{arom}), 7.12 (m, 1 H, H_{arom}) 7.04 - 6.94 (overlapping resonances, 3 H, H_{arom}), 6.87 (d, 1 H, H_{arom} , $J = 8$ Hz), 3.19 (d, 6 H, NMe , $J = 2$ Hz), 3.17 (d, 6 H, NMe , $J = 2$ Hz), 1.30 (d, 9 H, PCMe_3 , $^3J_{\text{PH}} = 15$ Hz), 1.22 (d, 9 H, PCMe_3 , $^3J_{\text{PH}} = 15$ Hz), 0.39 (s, 3 H, SiMe). $^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz, benzene- d_6): δ 162.1 (C_{arom}), 150.5 (C_{arom}), 142.1 (d, C_{arom} , $J_{\text{CP}} = 55$ Hz). 138.0 (C_{arom}), 133.1 (d, CH_{arom} , $J_{\text{CP}} = 5$ Hz), 132.8 (d, CH_{arom} , $J_{\text{CP}} = 18$ Hz), 132.2 (CH_{arom}), 131.4 (CH_{arom}), 130.8 (CH_{arom}), 129.1 (d, CH_{arom} , $J_{\text{CP}} = 7$ Hz), 128.9 (CH_{arom}), 121.3 (CH_{arom}), 53.6 (NMe), 50.2 (NMe), 36.7 (CMe_3), 35.2 (CMe_3), 31.2 (d, CMe_3 , $J_{\text{CP}} = 5$ Hz), 30.5 (d, CMe_3 , $J_{\text{CP}} = 5$ Hz), 6.0 (SiMe). $^{31}\text{P}\{^1\text{H}\}$ NMR (202.5 MHz, benzene- d_6): δ 70.8 (s with Pt satellites, $^1J_{\text{PP}} = 4611$ Hz). ^{29}Si NMR (99.4 MHz, benzene- d_6): δ 14.6. Anal. Calcd for $\text{C}_{24}\text{H}_{35}\text{NPPtSiO}_3\text{SF}_3$: C, 39.56; H, 4.84; N, 1.92. Found: C, 39.19; H, 4.97, N, 2.06.

κ^2 -(t -Bu- PSiN-Me)PdBr(PMe_3) (6**).** A solution of **2** (0.10 g, 0.18 mmol) in ca. 5 mL of benzene was treated with PMe_3 (0.04 mL, 0.39 mmol). The reaction mixture was allowed to stand at room temperature for 10 minutes. The volatile components of the reaction mixture were subsequently removed *in vacuo*. The residue was triturated with pentane (3×2 mL) and dried *in vacuo* to yield **6** as a pale yellow solid (0.10 g, 93%). ^1H NMR (500 MHz, benzene- d_6): δ 7.90 (d, 1 H, H_{arom} , $J = 7$ Hz), 7.66 (m, 1 H, H_{arom}), 7.50 (d, 1 H, H_{arom} , $J = 7$ Hz), 7.18 (m, 1 H, H_{arom}), 7.07 - 6.96 (overlapping resonances, 4 H, H_{arom}), 2.29 (s, 6 H, NMe_2), 1.60 (d, 9 H, PCMe_3 , $^3J_{\text{PH}} = 14$ Hz), 1.49 (d, 9 H, PCMe_3 , $^3J_{\text{PH}} = 14$ Hz), 1.20 (d, 9 H, $J = 9$ Hz, PMe_3), 0.81 (s, 3 H, SiMe). $^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz, benzene- d_6): δ 160.4 (C_{arom}), 138.5 (CH_{arom}), 134.3 (d, CH_{arom} , $J_{\text{CP}} = 39$ Hz), 133.8 (CH_{arom}), 131.0 (CH_{arom}), 130.3 (CH_{arom}), 127.6 (d, CH_{arom} , $J_{\text{CP}} = 7$ Hz), 125.3 (CH_{arom}), 122.8 (CH_{arom}), 47.4 (NMe_2), 37.5 (CMe_3), 32.3 (d, CMe_3 , $J_{\text{CP}} = 6$ Hz), 31.8 (d, CMe_3 , $J_{\text{CP}} = 6$ Hz), 17.0 (d, PMe_3 , $J_{\text{CP}} = 28$ Hz), 6.6 (SiMe). $^{31}\text{P}\{^1\text{H}\}$ NMR (202.5 MHz, benzene- d_6): δ 95.2 (d, 1 P, $P^t\text{Bu}_2$, $^2J_{\text{PP}} = 347$ Hz), -20.4 (d, 1 P, PMe_3 , $^2J_{\text{PP}}$

= 347 Hz). ^{29}Si NMR (99.4 MHz, benzene- d_6): δ 30.3. Anal. Calcd for $\text{C}_{26}\text{H}_{44}\text{BrNP}_2\text{PdSi}$: C, 48.27; H, 6.85; N, 2.16. Found: C, 48.06; H, 6.87, N, 1.85.

κ^2 -($t\text{Bu-PSiN-Me}$)PtCl(PMe $_3$) (7). A solution of **3** (0.070 g, 0.11 mmol) in ca. 5 mL of benzene was treated with PMe $_3$ (0.02 mL, 0.24 mmol). The reaction mixture was allowed to stand at room temperature for 10 minutes. The volatile components of the reaction mixture were subsequently removed *in vacuo*. The residue was triturated with pentane (3 \times 2 mL) and dried *in vacuo* to yield **7** as a pale yellow solid (0.021 g, 28%). ^1H NMR (500 MHz, benzene- d_6): δ 8.09 (d, 1 H, H_{arom} , $J = 7$ Hz), 7.69 - 7.67 (overlapping resonances, 2 H, H_{arom}), 7.19 (m, 1 H, H_{arom} , $J = 7$ Hz), 7.10-7.05 (overlapping resonances, 3 H, H_{arom}), 6.98 (m, 1 H, H_{arom} , $J = 7$ Hz), 2.37 (s, 6 H, NMe $_2$), 1.61 (d, 9 H, PCMe $_3$, $^3J_{\text{PH}} = 14$ Hz), 1.50 (d, 9 H, PCMe $_3$, $^3J_{\text{PH}} = 14$ Hz), 1.23 (dd, 9 H, PMe $_3$, $^2J_{\text{HP}} = 10$ Hz, $^4J_{\text{HP}} = 2$ Hz), 0.95 (s with Pt satellites, 3 H, SiMe, $^3J_{\text{HPt}} = 9$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz, benzene- d_6): δ 161.4 (C_{arom}), 141.3 (C_{arom}), 139.3 (CH_{arom}), 134.6 (CH_{arom}), 133.5 (CH_{arom}), 131.2 (CH_{arom}), 130.7 (CH_{arom}), 127.3 (CH_{arom}), 125.1 (CH_{arom}), 122.6 (CH_{arom}), 47.5 (NMe $_2$), 38.9 (CMe $_3$), 38.7 (CMe $_3$), 32.2 (d, CMe $_3$, $J_{\text{CP}} = 6$ Hz), 31.4 (d, CMe $_3$, $J_{\text{CP}} = 6$ Hz), 15.4 (d, PMe $_3$, $J_{\text{CP}} = 36$ Hz), 6.7 (SiMe). $^{31}\text{P}\{^1\text{H}\}$ NMR (202.5 MHz, benzene- d_6): δ 88.9 (d with Pt satellites, 1 P, P $t\text{Bu}_2$, $^2J_{\text{PP}} = 381$ Hz, $^1J_{\text{PP}} = 3013$ Hz), -11.4 (d with Pt satellites, 1 P, PMe $_3$, $^2J_{\text{PP}} = 381$ Hz, $^1J_{\text{PP}} = 2692$ Hz). ^{29}Si NMR (99.4 MHz, benzene- d_6): δ 6.5. $\text{C}_{26}\text{H}_{44}\text{ClNP}_2\text{PtSi}$: C, 45.18; H, 6.42; N, 2.03. Found: C, 44.82; H, 6.51, N, 2.37. A single crystal of **7** suitable for X-ray diffraction analysis was grown from benzene solution at room temperature.

κ^3 -($t\text{Bu-PSiN-Me}$)Rh(H)Cl (8). A room temperature solution of **1** (0.28 g, 0.73 mmol) in ca. 5 mL of benzene was added to a solution of [(1,5-COD)RhCl] $_2$ (0.18 g, 0.37 mmol) in ca. 5 mL of benzene. An immediate color change from orange to yellow was observed. The reaction mixture was allowed to stir at room temperature for 18 h, and the volatile components were subsequently removed *in vacuo*. The residue was triturated with pentane (2 \times 2 mL) and dried *in vacuo* to yield **8** as a yellow solid (0.36 g, 94%). ^1H NMR (300 K, benzene- d_6): δ 7.75 (d, 1 H, H_{arom} , $J = 7$ Hz), 7.62 (m, 1 H,

H_{arom}), 7.46 (m, 1 H, H_{arom}), 7.15 (m, 1 H, H_{arom}), 7.02 – 6.98 (overlapping resonances, 3 H, H_{arom}), 6.92 (m, 1 H, H_{arom}), 3.06 (s, 3 H, *NMe*), 2.96 (s, 3 H, *NMe*), 1.48 (d, 9 H, *PCMe*₃, $^3J_{\text{PH}} = 12$ Hz), 1.29 (d, 9 H, *PCMe*₃, $^3J_{\text{PH}} = 12$ Hz), 0.93 (s, 3 H, *SiMe*), -20.18 (dd, 1 H, *RhH*, $^1J_{\text{RhH}} = 30$ Hz, $^2J_{\text{PH}} = 21$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz, benzene-*d*₆): δ 165.3 (C_{arom}), 155.4 (d, C_{arom} , $J_{\text{CP}} = 40$ Hz), 146.3 (d, C_{arom} , $J_{\text{CP}} = 49$ Hz), 144.8 (C_{arom}), 132.5 (CH_{arom}), 132.3 (CH_{arom}), 131.8 (CH_{arom}), 129.3 – 129.6 (overlapping resonances, CH_{arom}), 127.2 (CH_{arom}), 127.0 (CH_{arom}), 119.5 (CH_{arom}), 54.9 (*NMe*), 47.7 (*NMe*), 37.0 (d, *PCMe*₃, $J_{\text{CP}} = 14$ Hz), 36.8 (*PCMe*₃, $J_{\text{CP}} = 20$ Hz), 32.1 (*CMe*₃), 30.1 (*CMe*₃), 7.1 (*SiMe*). $^{31}\text{P}\{^1\text{H}\}$ NMR (202.5 MHz, benzene-*d*₆): δ 101.0 (d, $^1J_{\text{PRh}} = 164$ Hz). ^{29}Si NMR (99.4 MHz, benzene-*d*₆): δ 45.8. IR (cm^{-1}): 2115 (br, m, *Rh-H*). Anal. Calcd for $\text{C}_{23}\text{H}_{36}\text{ClNPRhSi}$: C, 52.82; H, 6.93; N, 2.67. Found: C, 52.52; H, 6.73; N, 2.59. A single crystal of **8** suitable for X-ray diffraction analysis was grown from benzene solution at room temperature.

κ^3 -(*t*-Bu-*PSiN-Me*)*Ir(H)Cl* (**9**). A room temperature solution of **1** (0.26 g, 0.67 mmol) in ca. 5 mL of benzene was added to a solution of [(1,5-COD)*IrCl*]₂ (0.23 g, 0.34 mmol) in ca. 5 mL of benzene. An immediate color change from orange to yellow was observed. The reaction mixture was allowed to stir at room temperature for 18 h, and the volatile components were subsequently removed *in vacuo*. The residue was triturated with pentane (2 × 2 mL) and dried *in vacuo* to yield **9** as a yellow solid (0.41 g, 99%). ^1H NMR (500 MHz, benzene-*d*₆): δ 7.83 (d, 1 H, H_{arom} , $J = 7$ Hz), 7.68 (m, 1 H, H_{arom}), 7.54 (m, 1 H, H_{arom}), 7.12 (m, 1 H, H_{arom}), 6.99 – 6.94 (overlapping resonances, 3 H, H_{arom}), 6.90 (m, 1 H, H_{arom}), 3.17 (s, 3 H, *NMe*), 2.94 (s, 3 H, *NMe*), 1.47 (d, 9 H, *PCMe*₃, $^3J_{\text{PH}} = 14$ Hz), 1.30 (d, 9 H, *PCMe*₃, $^3J_{\text{PH}} = 14$ Hz), 0.79 (s, 3 H, *SiMe*), -25.00 (d, 1 H, *IrH*, $^2J_{\text{PH}} = 20$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz, benzene-*d*₆): δ 166.5 (C_{arom}), 156.0 (d, C_{arom} , $J_{\text{CP}} = 29$ Hz), 148.5 (d, C_{arom} , $J_{\text{CP}} = 55$ Hz), 145.9 (C_{arom}), 132.3 (CH_{arom}), 132.0 (CH_{arom}), 131.7 (CH_{arom}), 129.2 (CH_{arom}), 129.0 (CH_{arom}), 126.8 - 127.0 (overlapping resonances, CH_{arom}), 118.9 (CH_{arom}), 54.9 (*NMe*), 47.7 (*NMe*), 37.0 (d, *PCMe*₃, $J = 14$ Hz), 36.8 (d, *PCMe*₃, $J = 20$ Hz), 32.1 (*CMe*₃), 30.1 (*CMe*₃), 7.1 (*SiMe*). $^{31}\text{P}\{^1\text{H}\}$ NMR (202.5 MHz,

benzene-*d*₆): δ 62.6. ²⁹Si NMR (99.4 MHz, benzene-*d*₆): δ 3.0. IR (cm⁻¹): 2229 (br, m, Ir-H). C₂₃H₃₆ClNPIrSi: C, 45.04; H, 5.92; N, 2.28. Found: C, 45.32; H, 6.12, N, 2.44. A single crystal of **9** suitable for X-ray diffraction analysis was grown from benzene solution at room temperature.

κ^2 -(^tBu-PSiN-Me)Rh(H)Cl(PMe₃) (**10**). A solution of **8** (0.14 g, 0.27 mmol) in ca. 5 mL of benzene was treated with PMe₃ (0.028 mL, 0.27 mmol). The reaction mixture was allowed to stand at room temperature for 20 minutes. The volatile components of the reaction mixture were subsequently removed *in vacuo*. The residue was triturated with pentane (3 × 2 mL) and dried *in vacuo* to yield to yield **10** as a pale yellow solid (0.13 g, 80%). ¹H NMR (500 MHz, benzene-*d*₆): δ 7.72 (d, 1 H, *H*_{arom}, *J* = 7 Hz), 7.60 (m, 1 H, *H*_{arom}), 7.23 (m, 1 H, *H*_{arom}), 7.15 (m, 1 H, *H*_{arom}), 7.11 – 7.03 (overlapping resonances, 2 H, *H*_{arom}), 6.92 – 6.99 (overlapping resonances, 2 H, *H*_{arom}), 1.97 (s, 6 H, NMe₂), 1.54 (apparent t, 18 H, PCMe₃, ³*J*_{PH} = 13 Hz), 1.29 (s, 3 H, SiMe), 0.95 (d, 9 H, PMe₃, ³*J*_{PH} = 8 Hz), -16.8 (m, 1 H, RhH). ¹³C{¹H} NMR (125.8 MHz, benzene-*d*₆): δ 160.7 (*C*_{arom}), 152.5 (*C*_{arom}), 142.5 (*C*_{arom}), 139.9 (*C*_{arom}), 136.8 (*CH*_{arom}), 134.0 (*CH*_{arom}), 132.8 (*CH*_{arom}), 131.5 (*CH*_{arom}), 129.5 (*CH*_{arom}), 126.7 (*CH*_{arom}), 126.1 (*CH*_{arom}), 124.2 (*CH*_{arom}), 45.9 (NMe₂), 37.0 (PCMe₃), 36.3 (PCMe₃), 31.8 (PCMe₃), 31.4 (PCMe₃), 15.6 (d, PMe₃, ¹*J*_{PC} = 28 Hz), 5.0 (SiMe). ³¹P{¹H} NMR (202.5 MHz, benzene-*d*₆): δ 88.4 (dd, 1 P, ^tBu₂, ²*J*_{PP} = 356 Hz, ¹*J*_{PRh} = 123 Hz), -4.88 (dd, 1 P, PMe₃, ²*J*_{PP} = 356 Hz, ¹*J*_{PRh} = 123 Hz). ²⁹Si NMR (99.4 MHz, benzene-*d*₆): δ 30.0. IR (cm⁻¹): 2091 (br, m, Rh-H). Anal. Calcd for C₂₆H₄₅ClNP₂RhSi: C, 52.04; H, 7.56; N, 2.33. Found: C, 52.47; H, 7.37; N, 2.06. A single crystal of **10** suitable for X-ray diffraction analysis was grown from benzene solution at room temperature.

κ^3 -(^tBu-PSiCH=)Ru(η^3 -C₈H₁₃) (**11**). A room temperature solution of **1** (0.40 g, 1.0 mmol) in ca. 5 mL of THF was added to a solution of (1,5-COD)Ru(2-methylallyl)₂ (0.33 g, 1.0 mmol) in ca. 5 mL of THF. The reaction mixture was heated at 85 °C for 18 h and the volatile components of the reaction mixture were subsequently removed *in vacuo*. The residue was triturated with pentane (5 × 3 mL) and dried *in vacuo* to yield **11** as a beige solid (0.37 g, 62%). ¹H NMR (500 MHz, benzene-*d*₆):

δ 13.11 (s, 1 H, Ru=CH), 7.96 (d, 1 H, H_{arom} , $J = 7$ Hz), 7.67 (m, 1 H, H_{arom}), 7.55 (d, 1 H, H_{arom} , $J = 7$ Hz), 7.27 (m, 1 H, H_{arom}), 7.21 (m, 1 H, H_{arom}), 6.93 – 6.90 (overlapping resonances, 2 H, H_{arom}), 6.72 (d, 1 H, H_{arom} , $J = 8$ Hz), 4.81 (m, 1 H, H_{C8H13}), 4.13 (m, 1 H, H_{C8H13}), 3.61 (m, 1 H, H_{C8H13}), 2.82 (s, 3 H, NMe), 2.26 - 2.41 (overlapping resonances, 2 H, H_{C8H13}), 1.94 (m, 1 H, H_{C8H13}), 1.68 (m, 1 H, H_{C8H13}), 1.56 (m, 2 H, H_{C8H13}) 1.47 (d, 9 H, PCMe₃, $^3J_{\text{PH}} = 12$ Hz), 1.30 – 1.40 (overlapping resonances, 4 H, H_{C8H13}), 1.17 (br s, 9 H, PCMe₃), 0.51 (s, 3 H, SiMe). $^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz, benzene-*d*₆): δ 250.8 (Ru=CH), 162.2 (d, C_{arom} , $J_{\text{CP}} = 49$ Hz), 151.0 (C_{arom}), 145.1 (d, C_{arom} , $^2J_{\text{CP}} = 37$ Hz), 134.2 (CH_{arom}), 132.8 (d, CH_{arom} , $^2J_{\text{CP}} = 18$ Hz), 132.4 (C_{arom}), 131.9 (CH_{arom}), 129.3 (CH_{arom}), 128.9 (CH_{arom}), 125.1 (CH_{arom}), 123.7 (CH_{arom}), 116.7 (CH_{arom}), 101.3 (CH_{C8H13}), 71.9 (CH_{C8H13}), 56.0 (CH_{C8H13}), 48.9 (NMe), 37.7 (CH_2 C_{8H13}), 36.7 (d, PCMe₃, $^1J_{\text{CP}} = 10$ Hz), 35.4 (d, PCMe₃, $^1J_{\text{CP}} = 6$ Hz), 33.1 (CH_2 C_{8H13}), 32.0 (PCMe₃), 30.9 (CH_2 C_{8H13}), 30.8 (CH_2 C_{8H13}), 23.8 (CH_2 C_{8H13}), 2.4 (SiMe). $^{31}\text{P}\{^1\text{H}\}$ NMR (202.5 MHz, benzene-*d*₆): δ 105.7. ^{29}Si NMR (99.4 MHz, benzene-*d*₆): δ 44.3. Anal. Calcd for C₃₁H₄₆NPRuSi: C, 62.81; H, 7.82; N, 2.36. Found: C, 62.75; H, 7.49; N, 2.33. A single crystal of **11** suitable for X-ray diffraction analysis was grown from benzene solution at room temperature.

κ^3 -(^tBu-PSiCH₂-)Ru(η^6 -C₆H₆) (**13**). A thick walled Schlenk tube fitted with a resealable Teflon stopcock was charged with a solution of **11** (0.13 g, 0.22 mmol) in ca. 5 mL of benzene. The reaction mixture was degassed via three freeze-pump-thaw cycles and H₂ (ca. 1atm) was introduced. The reaction mixture was allowed to stir at 75 °C for 72 h and the volatile components of the reaction mixture were subsequently removed *in vacuo*. The residue was triturated with pentane (5 × 3 mL) and dried *in vacuo* to yield **13** as a tan solid (0.066 g, 53%). ^1H NMR (500 MHz, benzene-*d*₆): δ 8.25 (d, 1 H, H_{arom} , $J = 7$ Hz), 8.06 (d, 1 H, H_{arom} , $J = 7$ Hz), 7.52 (m, 1 H, H_{arom}), 7.39 (m, 1 H, H_{arom}), 7.08 (m, 1 H, H_{arom}), 7.01 – 6.90 (overlapping resonances, 2 H, H_{arom}), 6.48 (d, 1 H, H_{arom} , $J = 8$ Hz), 4.90 (s, 6 H, η^6 -C₆H₆), 4.58 (m, 1 H, RuCH₂), 2.65 (s, 3 H, NMe), 1.92 (m, 1 H, RuCH₂), 1.24 (d, 9 H, PCMe₃, $^3J_{\text{PH}} = 12$ Hz), 1.19 (s, 3 H, SiMe), 0.92 (d, 9 H, PCMe₃, $^3J_{\text{PH}} = 12$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz, benzene-

d_6): δ 160.3 (d, C_{arom} , $J_{\text{CP}} = 42$ Hz), 154.0 (C_{arom}), 139.7 (d, C_{arom} , $J_{\text{CP}} = 40$ Hz), 136.0 (CH_{arom}), 135.5 (d, CH_{arom} , $^2J_{\text{CP}} = 18$ Hz), 133.1 (CH_{arom}), 129.5 (CH_{arom}), 129.2 (CH_{arom}), 127.6 (C_{arom}), 126.0 (CH_{arom}), 114.2 (CH_{arom}), 110.4 (CH_{arom}), 88.9 ($\eta^6\text{-C}_6\text{H}_6$), 42.5 (NMe), 38.9 (d, PCMe_3 , $^1J_{\text{CP}} = 18$ Hz), 37.4 (d, PCMe_3 , $^1J_{\text{CP}} = 9$ Hz), 35.8 (d, RuCH_2 , $^2J_{\text{CP}} = 11$ Hz), 33.7 (CMe_3), 30.8 (CMe_3), 8.3 (SiMe). $^{31}\text{P}\{^1\text{H}\}$ NMR (202.5 MHz, benzene- d_6): δ 108.4. ^{29}Si NMR (99.4 MHz, benzene- d_6): δ 33.4. Anal. Calcd for $\text{C}_{29}\text{H}_{40}\text{NPRuSi}$: C, 61.89; H, 7.16; N, 2.49. Found: C, 61.56; H, 6.94; N, 2.40. A single crystal of **13** suitable for X-ray diffraction analysis was grown from benzene solution at room temperature.

(S1) H. Fang, Y.-K. Choe, Y. Li and S. Shimada, *Chem. Asian J.* 2011, **6**, 2512.

Crystallographic Solution and Refinement Details for **4·0.5C₆H₆**, **7**, **8**, **9**, **10**, **11**, and **13**.

Crystallographic data for each of **4·0.5C₆H₆**, **7**, **8**, **9**, **10**, **11**, and **13** were obtained at 173(±2)K on a Bruker D8/APEX II CCD diffractometer using a graphite-monochromated Mo K α ($\lambda = 0.71073 \text{ \AA}$) radiation, employing a sample that was mounted in inert oil and transferred to a cold gas stream on the diffractometer. Programs for diffractometer operation, data collection, and data reduction (including SAINT) were supplied by Bruker. Gaussian integration (face-indexed) was employed as the absorption correction method in each case. All structures were solved by use of the Patterson search/structure expansion and were refined by use of full-matrix least-squares procedures (on F^2) with R_1 based on $F_o^2 \geq 2\sigma(F_o^2)$ and wR_2 based on $F_o^2 \geq -3\sigma(F_o^2)$. During the structure solution process for **4·0.5C₆H₆** half an equivalent of disordered benzene was located in the asymmetric unit. The benzene carbon atoms (C1S-C3S) were modeled isotropically over two positions with occupancies of 0.5. Disorder involving the *P*^{*t*}*Bu*₂ substituents was also identified. The ^{*t*}Bu group carbon atoms (C31-C38) were modeled anisotropically over two positions with occupancy factors of 0.5. Anisotropic displacement parameters were employed for all remaining non-hydrogen atoms. The atomic coordinates and isotropic displacement parameter for the hydrido ligands in **8**, **9**, and **10** were freely refined. Otherwise, all hydrogen atoms were added at calculated positions and refined by use of a riding model employing isotropic displacement parameters based on the isotropic displacement parameter of the attached atom. Additional crystallographic information is provided in Table S1 and in the deposited CIF.

Table S1. Crystallographic Data for **4·0.5C₆H₆**, **7**, **8**, **9**, **10**, **11**, and **13**.

	4·0.5C₆H₆	7	8	9	10	11	13
Empirical formula	C ₂₇ H ₃₈ F ₃ NO ₃ PPdS	C ₂₆ H ₄₄ NP ₂ BrPtSi	C ₂₃ H ₃₆ ClRhNPSi	C ₂₃ H ₃₆ ClIrNPSi	C ₂₆ H ₂₅ ClRhNP ₂ Si	C ₃₁ H ₄₆ NPRuSi	C ₂₉ H ₄₀ NPRuSi
Formula weight	679.10	691.19	523.95	613.24	600.02	592.82	562.75
Crystal dimensions	0.45 x 0.36 x 0.20	0.37 x 0.23 x 0.17	0.34 x 0.30 x 0.27	0.33 x 0.18 x 0.15	0.41 x 0.34 x 0.29	0.35 x 0.25 x 0.14	0.47 x 0.27 x 0.15
Crystal system	orthorhombic	orthorhombic	monoclinic	monoclinic	triclinic	triclinic	monoclinic
Space group	<i>Pbca</i>	<i>Pbca</i>	<i>P2₁/c</i>	<i>P2₁/c</i>	<i>P$\bar{1}$</i>	<i>P$\bar{1}$</i>	<i>P2₁/c</i>
<i>a</i> (Å)	14.8703 (6)	18.097 (3)	15.8620 (4)	15.8428 (16)	8.5552 (6)	9.3387 (3)	10.3542 (5)
<i>b</i> (Å)	15.7929 (7)	16.248 (2)	10.3058 (9)	10.3414 (11)	9.9074 (7)	10.1491 (3)	16.6143 (8)
<i>c</i> (Å)	26.5312 (7)	19.608 (3)	16.0399 (10)	16.0067 (16)	18.9079 (13)	15.4308 (5)	15.3008 (8)
<i>α</i> (deg)	90	90	90	90	93.9595 (7)	91.6768 (4)	90
<i>β</i> (deg)	90	90	113.0811 (2)	112.8869 (10)	100.2991 (7)	90.8227 (4)	94.3988 (5)
<i>γ</i> (deg)	90	90	90	90	106.6562 (7)	99.6424 (3)	90
<i>V</i> (Å ³)	6230.7 (3)	5765.4 (14)	2412.16 (10)	2416.0 (4)	1489.85 (18)	1440.97 (8)	2624.4 (2)
<i>Z</i>	8	8	4	4	2	2	4
<i>ρ</i> _{calcd} (g cm ⁻³)	1.448	1.593	1.443	1.686	1.338	1.366	1.424
<i>μ</i> (mm ⁻¹)	0.798	5.128	0.944	5.762	0.825	0.661	0.722
Range of transmission	0.8534–0.7132	0.4743–0.2555	0.7859–0.7402	0.4746–0.2522	0.7941–0.7290	0.9102–0.8283	0.8988–0.7259
2θ limit (deg)	55.06	55.20	55.02	55.02	55.02	54.98	55.00
	-19 ≤ <i>h</i> ≤ 19	-23 ≤ <i>h</i> ≤ 23	-20 ≤ <i>h</i> ≤ 20	-20 ≤ <i>h</i> ≤ 20	-11 ≤ <i>h</i> ≤ 11	-12 ≤ <i>h</i> ≤ 12	-13 ≤ <i>h</i> ≤ 13
	-20 ≤ <i>k</i> ≤ 20	-21 ≤ <i>k</i> ≤ 21	-13 ≤ <i>k</i> ≤ 13	-13 ≤ <i>k</i> ≤ 13	-12 ≤ <i>k</i> ≤ 12	-13 ≤ <i>k</i> ≤ 13	-21 ≤ <i>k</i> ≤ 21
	-34 ≤ <i>l</i> ≤ 34	-25 ≤ <i>l</i> ≤ 25	-20 ≤ <i>l</i> ≤ 20	-20 ≤ <i>l</i> ≤ 20	-24 ≤ <i>l</i> ≤ 24	-20 ≤ <i>l</i> ≤ 20	-19 ≤ <i>l</i> ≤ 19
Total data collected	52762	48604	21050	20958	13114	12772	23253
Independent reflections	7180	6654	5548	5559	6763	6561	6037
<i>R</i> _{int}	0.0241	0.0359	0.0113	0.0162	0.0115	0.0120	0.0127
Observed reflections	6450	5930	5351	5254	6418	6135	5727
Data/restraints/parameters	7180 / 0 / 412	6654 / 0 / 289	5548 / 0 / 207	5559 / 0 / 257	6763 / 0 / 293	6561 / 0 / 317	6037 / 0 / 299
Goodness-of-fit	1.056	1.116	1.045	1.037	1.057	1.034	1.047
<i>R</i> ₁ [<i>F</i> _o ² ≥ 2σ(<i>F</i> _o ²)]	0.0208	0.0241	0.0197	0.0161	0.0204	0.0224	0.0195
<i>wR</i> ₂ [<i>F</i> _o ² ≥ -3σ(<i>F</i> _o ²)]	0.0556	0.0543	0.0574	0.0415	0.0618	0.0608	0.0537
Largest peak, hole (eÅ ⁻³)	0.447, -0.321	1.049, -1.263	0.673, -0.497	0.945, -0.514	1.048, -0.430	0.493, -0.258	0.559, -0.334

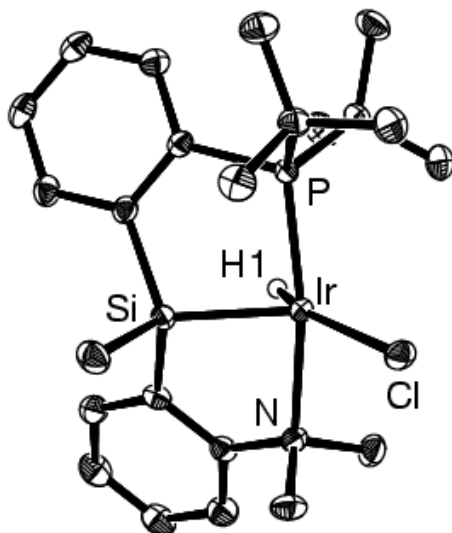


Fig. S1 ORTEP diagram for **9** shown with 50% ellipsoids. Selected H-atoms have been omitted for clarity. Bond lengths (Å) and angles (°): Ir-Si 2.2355(6), Ir-P 2.2380(5), Ir-N 2.2318(18), Ir-Cl 2.4261(6), P-Ir-N 164.84(5), Si-Ir-H1 71.0(12), Cl-Ir-Si 131.38(2).

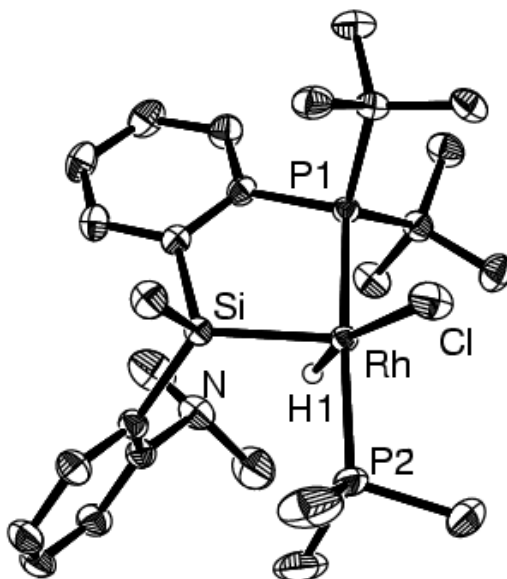
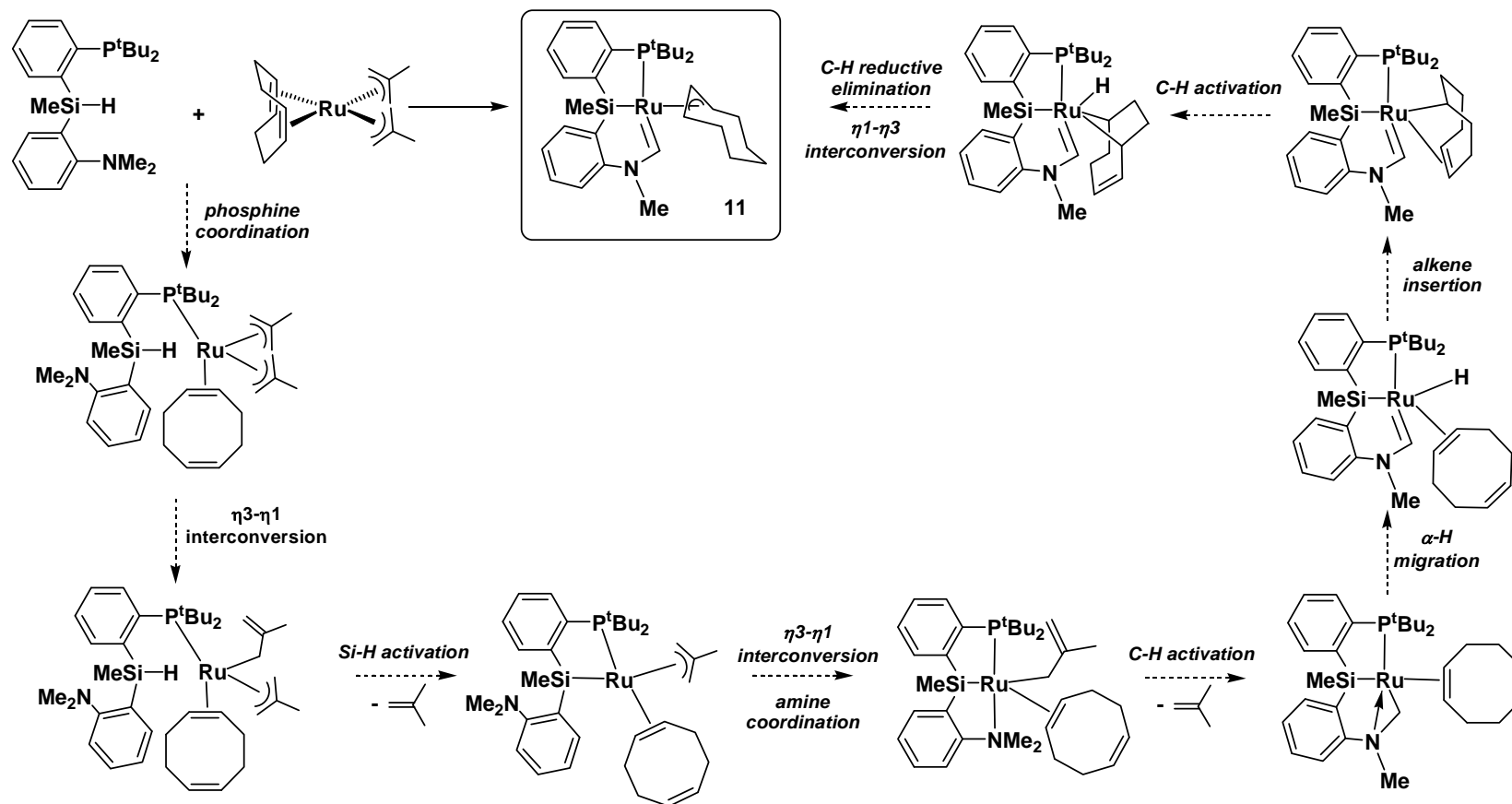


Fig. S2 ORTEP diagram for **10** shown with 50% ellipsoids. Selected H-atoms have been omitted for clarity. Bond lengths (Å) and angles (°): Rh-Si 2.2584(4), Rh-P1 2.3463(4), Rh-P2 2.3031(4), Rh-Cl 2.4300(4), P1-Rh-P2 169.676(15), Si-Rh-Cl 125.470(17), Si-Rh-H1 67.1(8).



Scheme S1 One possible mechanism for the formation of 11.