

SUPPORTING INFORMATION for:

Rhodium and Iridium Amido Complexes Supported by Silyl Pincer

Ligation: Ammonia N-H Bond Activation by a [PSiP]Ir Complex

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Experimental Section

General Considerations. All experiments were conducted under nitrogen in an MBraun glovebox or using standard Schlenk techniques. Dry, oxygen-free solvents were used unless otherwise indicated. All non-deuterated solvents were deoxygenated and dried by sparging with nitrogen and subsequent passage through a double-column solvent purification system purchased from MBraun Inc. Tetrahydrofuran and diethyl ether were purified over two activated alumina columns, 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 cyclohexane-*d*₁₂ were degassed via three freeze-pump-thaw cycles and stored over 4 Å molecular sieves. The compounds [Cy-PSiP]Rh(H)Cl,^{S1} [Cy-PSiP]Ir(H)Cl,^{S1} Me₃SiCH₂Li,^{S2} and PhCH₂K^{S3} were prepared according to literature procedures. Anhydrous ammonia and ethylene were purchased from Air Liquide Canada and used as received. All other reagents were purchased from Aldrich and used without further purification. Unless otherwise stated, ¹H, ¹³C, ³¹P NMR, ¹⁵N, and ²⁹Si characterization data were collected at 300K on a Bruker AV-500 spectrometer operating at 500.1, 125.8, 202.5, 50.7 and 99.4 MHz (respectively) with chemical shifts reported in parts per million downfield of SiMe₄ (for ¹H, ¹³C, and ²⁹Si), MeNO₂ (for ¹⁵N), or 85% H₃PO₄ in D₂O (for ³¹P). 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. ²⁹Si NMR assignments are based on ¹H-²⁹Si HMQC and ¹H-²⁹Si HMBC experiments. ¹⁵N NMR assignments are based on ¹H-¹⁵N HMQC experiments. In some cases, fewer than expected unique ¹³C NMR resonances were observed, despite prolonged acquisition times. Elemental analyses were performed by Canadian Microanalytical Service Ltd. of Delta, British Columbia, Canada and by Columbia Analytical Services of Tucson, Arizona. Infrared spectra were recorded as Nujol mulls between NaCl plates using a Bruker VECTOR 22 FT-IR spectrometer at a resolution of 4 cm⁻¹.

[Cy-PSiP]Rh(H)(NHPH) (1). A solution of LiNHPH (0.011 g, 0.110 mmol) in ca. 5 mL of

THF was added dropwise via pipette to a solution of [Cy-PSiP]Rh(H)Cl (0.080 g, 0.110 mmol) in ca. 5 mL of THF at room temperature. An immediate color change from light yellow to red was observed. The reaction mixture was evaporated to dryness, and the remaining residue was extracted with ca. 10 mL of benzene. The benzene extract was filtered through Celite and the filtrate was dried under vacuum. The remaining solid residue was triturated with pentane (3 × 5 mL) to afford **1** as a red-orange solid (0.077 g, 89%). ¹H NMR (500 MHz, benzene-*d*₆): δ 7.97 (d, 2 H, *J* = 7 Hz, *H*_{arom}), 7.40 (m, 2 H, *H*_{arom}), 7.25 – 7.21 (overlapping resonances, 4 H, *H*_{arom}), 7.14 (t, 2 H, *J* = 7 Hz, *H*_{arom}), 6.94 (d, 2 H, *J* = 7 Hz, *NPh*_{ortho}), 6.69 (t, 1 H, *J* = 7 Hz, *NPh*_{para}), 4.57 (s, 1 H, *NH*), 2.48 (m, 2 H, PCy), 2.37 (m, 2 H, PCy), 2.23 (m, 4 H, PCy), 1.95 – 1.11 (overlapping resonances, 34 H, PCy), 0.90 (m, 2 H, PCy), 0.87 (s, 3 H, SiMe), -16.86 (apparent q, 1 H, ²*J*_{HP} ~ ¹*J*_{HRh} = 16 Hz, RhH). ¹³C{¹H} NMR (125.8 MHz, benzene-*d*₆): δ 164.0 (*C*_{arom}), 157.5 (m, *C*_{arom}), 142.0 (m, *C*_{arom}), 131.6 (apparent t, *J* = 10 Hz, CH_{arom}), 130.0 (CH_{arom}), 128.9 (CH_{arom}), 128.4 (CH_{arom}), 127.5 (CH_{arom}), 118.2 (*NPh*_{ortho}), 112.8 (*NPh*_{para}), 35.3 (apparent t, *J* = 12 Hz, CH_{Cy}), 33.7 (apparent t, *J* = 9 Hz, CH_{Cy}), 30.8 (CH_{2Cy}), 30.2 (CH_{2Cy}), 29.7 (CH_{2Cy}), 27.6 (CH_{2Cy}), 27.2 – 26.9 (overlapping resonances, CH_{2Cy}), 26.2 (CH_{2Cy}), 8.9 (SiMe). ³¹P{¹H} NMR (202.5 MHz, benzene-*d*₆): δ 59.6 (d, ¹*J*_{PRh} = 122 Hz). ²⁹Si NMR (99.4 MHz, benzene-*d*₆): δ 44.0. ¹⁵N NMR (50.7 MHz, benzene-*d*₆): δ -275.9. IR (Nujol, cm⁻¹): 3340 (br, w, N-H), 2019 (m, Rh-H). Anal. Calcd for C₄₃H₆₂RhNP₂Si: C, 65.72; H, 7.95; N, 1.78. Found: C, 65.41; H, 7.82; N, 1.62. X-Ray quality crystals of **1** were grown from a concentrated Et₂O/THF solution at -30 °C.}}}

[Cy-PSiP]Rh(H)[NH(2,6-Me₂C₆H₃)] (2). A solution of LiNH(2,6-Me₂C₆H₃) (0.014 g, 0.110 mmol) in ca. 5 mL of THF was added dropwise via pipette to a solution of [Cy-PSiP]Rh(H)Cl (0.080 g, 0.110 mmol) in ca. 5 mL of THF at room temperature. An immediate color change from light yellow to red-orange was observed. The reaction mixture was evaporated to dryness, and the remaining residue was extracted with ca. 10 mL of benzene. The benzene extract was filtered through Celite and

the filtrate was dried under vacuum. The remaining solid residue was triturated with pentane (3×5 mL) to afford **2** as an orange solid (0.077 g, 84%). ^1H NMR (500 MHz, benzene- d_6): δ 7.98 (d, 2 H, $J = 7$ Hz, H_{arom}), 7.42 (m, 2 H, H_{arom}), 7.23 (t, 2 H, $J = 7$ Hz, H_{arom}), 7.17 (br s, 2 H, H_{arom}), 7.13 (t, 2 H, $J = 7$ Hz, H_{arom}), 6.36 (t, 1 H, $J = 7$ Hz, H_{arom}), 3.28 (s, 1 H, NH), 2.63 (br s, 3 H, 2,6- $\text{Me}_2\text{C}_6\text{H}_3$), 2.42 (br s, 3 H, 2,6- $\text{Me}_2\text{C}_6\text{H}_3$), 2.33 – 2.09 (overlapping resonances, 8 H, PCy), 1.84 – 1.10 (overlapping resonances, 34 H, PCy), 0.97 (m, 2 H, PCy), 0.92 (s, 3 H, SiMe), -17.27 (apparent q, 1 H, $^2J_{\text{HP}} \sim ^1J_{\text{HRh}} = 17$ Hz, RhH). $^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz, benzene- d_6): δ 163.8 (C_{arom}), 157.8 (m, C_{arom}), 143.1 (m, C_{arom}), 132.4 (apparent t, $J = 9$ Hz, CH_{arom}), 130.4 (CH_{arom}), 129.6 (CH_{arom}), 127.9 (CH_{arom}), 112.5 (CH_{arom}), 36.6 (apparent t, $J = 12$ Hz, CH_{Cy}), 35.5 (apparent t, $J = 8$ Hz, CH_{Cy}), 30.9 (CH_2Cy), 30.5 (CH_2Cy), 30.1 (CH_2Cy), 28.3 (CH_2Cy), 27.9 – 27.5 (overlapping resonances, CH_2Cy), 26.9 (CH_2Cy), 20.8 (br, 2,6- $\text{Me}_2\text{C}_6\text{H}_3$), 19.9 (br, 2,6- $\text{Me}_2\text{C}_6\text{H}_3$), 8.9 (SiMe). $^{31}\text{P}\{^1\text{H}\}$ NMR (202.5 MHz, benzene- d_6): δ 57.3 (d, $^1J_{\text{PRh}} = 129$ Hz). ^{29}Si NMR (99.4 MHz, benzene- d_6): δ 43.9. ^{15}N NMR (50.7 MHz, benzene- d_6): δ -293.0. IR (Nujol, cm^{-1}): 3359 (br, w, N-H), 1999 (m, Rh-H). Anal. Calcd for $\text{C}_{45}\text{H}_{66}\text{RhNP}_2\text{Si}$: C, 66.40; H, 8.17; N, 1.72. Found: C, 66.05; H, 7.81; N, 1.68.

[Cy-PSiP]Ir(H)(NHPH) (3). Method 1: A solution of LiNHPH (0.010 g, 0.098 mmol) in ca. 5 mL of THF was added dropwise via pipette to a solution of [Cy-PSiP]Ir(H)Cl (0.080 g, 0.098 mmol) in ca. 5 mL of THF at room temperature. An immediate color change from yellow to red was observed. The reaction mixture was evaporated to dryness, and the remaining residue was extracted with ca. 10 mL of benzene. The benzene extract was filtered through Celite and the filtrate was dried under vacuum. The remaining solid residue was triturated with pentane (3×5 mL) to afford **3** as a red solid (0.069 g, 80%). **Method 2 – NMR-scale:** A solution of $\text{Me}_3\text{SiCH}_2\text{Li}$ (0.0011 g, 0.012 mmol) in ca. 0.4 mL of cyclohexane- d_{12} was added to a solution of [Cy-PSiP]Ir(H)Cl (0.010 g, 0.012 mmol) in ca. 0.4 mL of cyclohexane- d_{12} . An immediate color change from yellow to orange was observed. The reaction mixture was analyzed by ^1H and ^{31}P NMR spectroscopy to confirm the complete consumption

of [Cy-PSiP]Ir(H)Cl and the formation of 1 equiv. of Me₄Si. Aniline (1.1 μL, 0.0011 g, 0.012 mmol) was added to the reaction mixture, and the solution was heated at 65 °C for 16 h, at which point ¹H and ³¹P NMR analysis of the reaction mixture indicated the quantitative formation of **3**. **Method 2 – preparative-scale:** A solution of Me₃SiCH₂Li (0.0046 g, 0.049 mmol) in ca. 2 mL of cyclohexane was added to a solution of [Cy-PSiP]Ir(H)Cl (0.040 g, 0.049 mmol) in ca. 5 mL of cyclohexane. An immediate color change from yellow to orange was observed. An aliquot of the reaction mixture was analyzed by ¹H and ³¹P NMR spectroscopy to confirm the complete consumption of [Cy-PSiP]Ir(H)Cl and the formation of 1 equiv. of Me₄Si. Aniline (4.5 μL, 0.0046 g, 0.049 mmol) was added to the reaction mixture, and the solution was heated at 65 °C for 16 h, at which point ¹H and ³¹P NMR analysis of the reaction mixture indicated the quantitative formation of **3**. The reaction mixture was evaporated to dryness, and the remaining residue was extracted with ca. 10 mL of benzene. The benzene extract was filtered through Celite and the filtrate was dried under vacuum. The remaining solid residue was triturated with pentane (3 × 5 mL) to afford **3** as a red solid (0.041 g, 96%). **Method 3:** A solution of Me₃SiCH₂Li (0.0011 g, 0.012 mmol) in ca. 0.4 mL of benzene-*d*₆ was added to a solution of [Cy-PSiP]Ir(H)Cl (0.010 g, 0.012 mmol) in ca. 0.4 mL of benzene-*d*₆. An immediate color change from yellow to orange was observed. The reaction mixture was analyzed by ¹H and ³¹P NMR spectroscopy to confirm the complete consumption of [Cy-PSiP]Ir(H)Cl and the formation of 1 equiv. of Me₄Si. Aniline (22.0 μL, 0.022 g, 0.240 mmol) was added to the reaction mixture, and the solution was heated at 65 °C for 70 h, at which point ¹H and ³¹P NMR analysis of the reaction mixture indicated the quantitative formation of **3**. ¹H NMR (500 MHz, benzene-*d*₆): δ 8.10 (d, 2 H, *J* = 7 Hz, *H*_{arom}), 7.44 (m, 2 H, *H*_{arom}), 7.26 – 7.17 (overlapping resonances, 6 H, *H*_{arom}), 7.11 (t, 2 H, *J* = 7 Hz, *H*_{arom}), 6.90 (br t, 1 H, ³*J*_{HP} = 4 Hz, *NH*), 6.84 (t, 1 H, *J* = 7 Hz, *H*_{arom}), 2.61 (m, 2 H, PCy), 2.47 (br t, 2 H, *J* = 12 Hz, PCy), 2.32 (br d, 2 H, *J* = 13 Hz, PCy), 2.07 – 1.10 (overlapping resonances, 34 H, PCy), 0.89 (s, 3 H, SiMe), 0.77 (m, 4 H, PCy), -21.16 (t, 1 H, ²*J*_{HP} = 17 Hz, IrH). ¹H NMR (500 MHz, cyclohexane-*d*₁₂): δ

7.99 (d, 2 H, $J = 7$ Hz, H_{arom}), 7.47 (m, 2 H, H_{arom}), 7.21 (t, 2 H, $J = 7$ Hz, H_{arom}), 7.12 (t, 2 H, $J = 7$ Hz, H_{arom}), 6.91 (t, 2 H, $J = 7$ Hz, H_{arom}), 6.75 (d, 2 H, $J = 7$ Hz, H_{arom}), 6.55 – 6.52 (overlapping resonances, 2 H, $H_{\text{arom}} + \text{NH}$), 2.64 (m, 2 H, PCy), 2.33 (br t, 2 H, $J = 12$ Hz, PCy), 2.09 (br d, 2 H, $J = 12$ Hz, PCy), 2.04 – 0.88 (overlapping resonances, 36 H, PCy), 0.59 (m, 2 H, PCy), 0.41 (s, 3 H, SiMe), -21.22 (t, 1 H, $^2J_{\text{HP}} = 17$ Hz, IrH). $^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz, benzene- d_6): δ 165.0 (C_{arom}), 159.3 (m, C_{arom}), 144.4 (m, C_{arom}), 132.4 (apparent t, $J = 9$ Hz, CH_{arom}), 130.9 (CH_{arom}), 129.5 (CH_{arom}), 129.1 (CH_{arom}), 127.3 (CH_{arom}), 121.7 (CH_{arom}), 117.9 (CH_{arom}), 35.5 (apparent t, $J = 16$ Hz, CH_{Cy}), 33.5 (apparent t, $J = 11$ Hz, CH_{Cy}), 31.0 ($\text{CH}_{2\text{Cy}}$), 30.8 ($\text{CH}_{2\text{Cy}}$), 30.6 ($\text{CH}_{2\text{Cy}}$), 28.5 ($\text{CH}_{2\text{Cy}}$), 28.2 ($\text{CH}_{2\text{Cy}}$), 27.8 – 27.6 (overlapping resonances, $\text{CH}_{2\text{Cy}}$), 27.1 ($\text{CH}_{2\text{Cy}}$), 6.2 (SiMe). $^{31}\text{P}\{^1\text{H}\}$ NMR (202.5 MHz, benzene- d_6): δ 55.1. $^{31}\text{P}\{^1\text{H}\}$ NMR (202.5 MHz, cyclohexane- d_{12}): δ 55.3. ^{29}Si NMR (99.4 MHz, benzene- d_6): δ 13.3. ^{15}N NMR (50.7 MHz, benzene- d_6): δ -260.8. IR (Nujol, cm^{-1}): 3371 (br, w, N-H), 2134 (m, Ir-H). Anal. Calcd for $\text{C}_{43}\text{H}_{62}\text{IrNP}_2\text{Si}$: C, 59.01; H, 7.14; N, 1.60. Found: C, 59.38; H, 7.22; N, 1.48. X-Ray quality crystals of **3**·OEt₂ were grown from a concentrated Et₂O solution at -30 °C.

[Cy-PSiP]Ir(H)[NH(2,6-Me₂C₆H₃)] (4). Method 1: A solution of LiNH(2,6-Me₂C₆H₃) (0.019 g, 0.150 mmol) in ca. 5 mL of THF was added dropwise via pipette to a solution of [Cy-PSiP]Ir(H)Cl (0.123 g, 0.150 mmol) in ca. 5 mL of THF at room temperature. An immediate color change from yellow to orange was observed. The reaction mixture was evaporated to dryness, and the remaining residue was extracted with ca. 10 mL of benzene. The benzene extract was filtered through Celite and the filtrate was dried under vacuum. The remaining solid residue was triturated with pentane (3 × 5 mL) to afford **4** as an orange solid (0.118 g, 87%). **Method 2:** A solution of Me₃SiCH₂Li (0.0011 g, 0.012 mmol) in ca. 0.4 mL of cyclohexane- d_{12} was added to a solution of [Cy-PSiP]Ir(H)Cl (0.010 g, 0.012 mmol) in ca. 0.4 mL of cyclohexane- d_{12} . An immediate color change from yellow to orange was observed. The reaction mixture was analyzed by ^1H and ^{31}P NMR spectroscopy to confirm the complete consumption of [Cy-PSiP]Ir(H)Cl and the formation of 1 equiv.

of Me₄Si. Neat H₂N(2,6-Me₂C₆H₃) (29.5 μL, 0.029 g, 0.240 mmol) was added to the reaction mixture, and the solution was heated at 65 °C for 72 h, at which point ¹H and ³¹P NMR analysis of the reaction mixture indicated the quantitative formation of **4**. ¹H NMR (500 MHz, benzene-*d*₆): δ 8.13 (d, 2 H, *J* = 7 Hz, *H*_{arom}), 7.45 (m, 2 H, *H*_{arom}), 7.24 – 7.18 (overlapping resonances, 4 H, *H*_{arom}), 7.12 (t, 2 H, *J* = 7 Hz, *H*_{arom}), 6.89 (t, 1 H, *J* = 7 Hz, *H*_{arom}), 5.98 (br t, 1 H, ³*J*_{HP} = 5 Hz, *NH*), 2.67 (s, 3 H, 2,6-*Me*₂C₆H₃), 2.59 (s, 3 H, 2,6-*Me*₂C₆H₃), 2.50 (br t, 2 H, *J* = 12 Hz, PCy), 2.30 (br d, 2 H, *J* = 13 Hz, PCy), 1.96 – 1.12 (overlapping resonances, 38 H, PCy), 0.94 (s, 3 H, *SiMe*), 0.69 (m, 2 H, PCy), -21.94 (t, 1 H, ²*J*_{HP} = 16 Hz, *IrH*). ¹³C{¹H} NMR (125.8 MHz, benzene-*d*₆): δ 162.9 (*C*_{arom}), 159.7 (apparent t, *J* = 21 Hz, *C*_{arom}), 144.9 (apparent t, *J* = 28 Hz, *C*_{arom}), 132.8 (apparent t, *J* = 21 Hz, *C*_{arom}), 132.4 (apparent t, *J* = 9 Hz, *CH*_{arom}), 131.2 (*C*_{arom}), 130.4 (*CH*_{arom}), 129.2 (*CH*_{arom}), 127.2 (*CH*_{arom}), 120.0 (*CH*_{arom}), 35.3 (apparent t, *J* = 16 Hz, *CH*_{Cy}), 34.0 (apparent t, *J* = 11 Hz, *CH*_{Cy}), 30.6 (*CH*₂Cy), 30.3 (*CH*₂Cy), 29.5 (*CH*₂Cy), 28.2 (*CH*₂Cy), 28.1 (*CH*₂Cy), 27.7 (*CH*₂Cy), 27.5 – 27.3 (overlapping resonances, *CH*₂Cy), 26.9 (*CH*₂Cy), 21.0 (2,6-*Me*₂C₆H₃), 20.9 (2,6-*Me*₂C₆H₃), 5.0 (*SiMe*). ³¹P{¹H} NMR (202.5 MHz, benzene-*d*₆): δ 52.8. ²⁹Si NMR (99.4 MHz, benzene-*d*₆): δ 12.1. ¹⁵N NMR (50.7 MHz, benzene-*d*₆): δ -265.0. IR (Nujol, cm⁻¹): 3377 (br, w, N-H), 2116 (m, Ir-H). Anal. Calcd for C₄₅H₆₆IrNP₂Si: C, 59.84; H, 7.36; N, 1.55. Found: C, 59.44; H, 7.49; N, 1.43. X-Ray quality crystals of **4** were grown from a concentrated pentane/THF solution at -30 °C.

[Cy-PSiP]Ir(H)(NH₂) (5). Method 1: A slurry of LiNH₂ (0.006 g, 0.261 mmol) in ca. 5 mL of THF was added dropwise via pipette to a solution of [Cy-PSiP]Ir(H)Cl (0.040 g, 0.049 mmol) in ca. 5 mL of THF at room temperature. The yellow reaction mixture was transferred to a resealable thick-walled glass vessel containing a magnetic stir bar and equipped with a Teflon stopcock and was heated at 65 °C for 12 h, over the course of which a color change to orange was observed. The reaction mixture was cooled to room temperature and evaporated to dryness, and the remaining residue was extracted with ca. 10 mL of benzene. The benzene extract was filtered through Celite and the filtrate

was dried under vacuum. The remaining solid residue was triturated with pentane (3×5 mL) to afford **5** as a yellow solid (0.036 g, 92%). **Method 2 – NMR scale:** A solution of $\text{Me}_3\text{SiCH}_2\text{Li}$ (0.0017 g, 0.018 mmol) in ca. 0.4 mL of cyclohexane- d_{12} was added to a solution of $[\text{Cy-PSiP}]\text{Ir}(\text{H})\text{Cl}$ (0.015 g, 0.018 mmol) in ca. 0.4 mL of cyclohexane- d_{12} . An immediate color change from yellow to orange was observed. The reaction mixture was analyzed by ^1H and ^{31}P NMR spectroscopy to confirm the complete consumption of $[\text{Cy-PSiP}]\text{Ir}(\text{H})\text{Cl}$ and the formation of 1 equiv. of Me_4Si . The reaction mixture was then filtered through Celite to remove LiCl , and was transferred to a J-Young NMR tube. The solution was degassed via three freeze-pump-thaw cycles, and an atmosphere of anhydrous ammonia was introduced. The reaction mixture was heated at $65\text{ }^\circ\text{C}$ for 14 h. Analysis of the reaction mixture by ^1H and ^{31}P NMR spectroscopy confirmed the formation of **5** (72%) as well as unidentified side-products at $\delta\text{ }^{31}\text{P}$ 97.0 (5%), 94.1 (5%) and 37.9 - 36.6 (18%). **Method 2 – preparative scale:** A solution of $\text{Me}_3\text{SiCH}_2\text{Li}$ (0.0069 g, 0.073 mmol) in ca. 2 mL of cyclohexane- d_{12} was added to a solution of $[\text{Cy-PSiP}]\text{Ir}(\text{H})\text{Cl}$ (0.060 g, 0.073 mmol) in ca. 5 mL of cyclohexane- d_{12} . An immediate color change from yellow to orange was observed. An aliquot of the reaction mixture was analyzed by ^1H and ^{31}P NMR spectroscopy to confirm the complete consumption of $[\text{Cy-PSiP}]\text{Ir}(\text{H})\text{Cl}$ and the formation of 1 equiv. of Me_4Si . The reaction mixture was then filtered through Celite to remove LiCl , and was transferred to a resealable thick-walled glass vessel equipped with a Teflon stopcock. The solution was degassed via three freeze-pump-thaw cycles, and an atmosphere of anhydrous ammonia was introduced. The reaction mixture was heated at $65\text{ }^\circ\text{C}$ for 14 h. The reaction mixture was cooled to room temperature and evaporated to dryness, and the remaining residue was washed with ca. 2 mL of cold ($-30\text{ }^\circ\text{C}$) pentane, then dried in vacuo to afford **5** as a yellow solid (0.040 g, 69%). **Method 3:** A solution of $\text{Me}_3\text{SiCH}_2\text{Li}$ (0.0023 g, 0.024 mmol) in ca. 0.4 mL of benzene- d_6 was added to a solution of $[\text{Cy-PSiP}]\text{Ir}(\text{H})\text{Cl}$ (0.020 g, 0.024 mmol) in ca. 0.4 mL of benzene- d_6 . An immediate color change from yellow to orange was observed. The reaction mixture was analyzed by ^1H and ^{31}P NMR

spectroscopy to confirm the complete consumption of [Cy-PSiP]Ir(H)Cl and the formation of 1 equiv. of Me₄Si. The reaction mixture was then filtered through Celite to remove LiCl, and was transferred to a J-Young NMR tube. The solution was degassed via three freeze-pump-thaw cycles, and an atmosphere of anhydrous ammonia was introduced. The reaction mixture was heated at 65 °C for 144 h. Analysis of the reaction mixture by ¹H and ³¹P NMR spectroscopy confirmed the formation of **5** (45%) as well as [Cy-PSiP]Ir(D)(Ph-*d*₅) (δ ³¹P 56.8, 20%) and unidentified side-products at δ ³¹P 95.6 (10%), 94.1 (10%) and 37.3 (15%). ¹H NMR (500 MHz, benzene-*d*₆): δ 8.16 (d, 2 H, *J* = 7 Hz, *H*_{arom}), 7.49 (m, 2 H, *H*_{arom}), 7.24 (t, 2 H, *J* = 7 Hz, *H*_{arom}), 7.12 (t, 2 H, *J* = 7 Hz, *H*_{arom}), 5.03 (br t, 2 H, ³*J*_{HP} = 6 Hz, *NH*₂), 2.61 (br d, 2 H, *J* = 12 Hz, PCy), 2.47 (br t, 2 H, *J* = 11 Hz, PCH), 2.20 (br t, 2 H, *J* = 12 Hz, PCH), 2.11 (m, 2 H, PCy), 1.94 (m, 4 H, PCy), 1.84 (br d, 2 H, *J* = 12 Hz, PCy), 1.67 – 1.05 (overlapping resonances, 26 H, PCy), 0.97 (m, 2 H, PCy), 0.94 (s, 3 H, SiMe), 0.82 (m, 2 H, PCy), -20.13 (t, 1 H, ²*J*_{HP} = 15 Hz, IrH). ¹H NMR (500 MHz, cyclohexane-*d*₁₂): δ 7.98 (d, 2 H, *J* = 7 Hz, *H*_{arom}), 7.47 (m, 2 H, *H*_{arom}), 7.19 (t, 2 H, *J* = 7 Hz, *H*_{arom}), 7.10 (t, 2 H, *J* = 7 Hz, *H*_{arom}), 4.58 (br s, 2 H, *NH*₂) 2.45 (br m, 2 H, PCy), 2.35 (br d, 2 H, *J* = 11 Hz, PCy), 2.18 – 1.02 (overlapping resonances, 38 H, PCy), 0.82 (m, 2 H, PCy), 0.44 (s, 3 H, SiMe), -20.34 (t, 1 H, ²*J*_{HP} = 15 Hz, IrH). ¹³C{¹H} NMR (125.8 MHz, benzene-*d*₆): δ 161.0 (m, *C*_{arom}), 144.4 (m, *C*_{arom}), 132.0 (apparent t, *J* = 9 Hz, *CH*_{arom}), 130.4 (*CH*_{arom}), 128.8 (*CH*_{arom}), 126.6 (*CH*_{arom}), 34.2 – 33.9 (overlapping resonances, *CH*_{Cy}), 30.3 (*CH*_{2Cy}), 30.2 (*CH*_{2Cy}), 29.2 (*CH*_{2Cy}), 28.0 (*CH*_{2Cy}), 27.7 – 26.9 (overlapping resonances, *CH*_{2Cy}), 26.5 (*CH*_{2Cy}), 6.0 (SiMe). ³¹P{¹H} NMR (202.5 MHz, benzene-*d*₆): δ 55.5. ³¹P{¹H} NMR (202.5 MHz, cyclohexane-*d*₁₂): δ 55.7. ²⁹Si NMR (99.4 MHz, benzene-*d*₆): δ 14.6. ¹⁵N NMR (50.7 MHz, benzene-*d*₆): δ -309.8. IR (Nujol, cm⁻¹): 3418 (w, N-H), 3340 (w, N-H), 2129 (m, M-H). Anal. Calcd for C₃₇H₅₈IrNP₂Si: C, 55.61; H, 7.32; N, 1.75. Found: C, 55.30; H, 7.18; N, 1.38.

Generation of [Cy-PSiP]Ir(H)(NH₂)(PMe₃) (5•PMe₃). A room temperature solution of **5** (0.015 g, 0.019 mmol) in ca. 0.8 mL of benzene-*d*₆ was treated with PMe₃ (2.0 μL, 0.0015 g, 0.019

mmol). The reaction mixture was transferred to an NMR tube and analyzed by use of NMR techniques, which confirmed the quantitative consumption of **5** and the clean formation of putative **5•PMe₃**. Attempts to isolate **5•PMe₃** by removing the volatile components in vacuo resulted in reformation of **5**, as indicated by ¹H and ³¹P NMR spectroscopy of the residue. ¹H NMR (500 MHz, benzene-*d*₆): δ 8.27 (d, 2 H, *J* = 7 Hz, *H*_{arom}), 7.38 (m, 2 H, *H*_{arom}), 7.22 (t, 2 H, *H*_{arom}), 7.09 (t, 2 H, *H*_{arom}), 3.13 (m, 2 H, PCy), 2.88 (br m, 2 H, PCy), 2.13 – 1.06 (overlapping resonances, 43 H, PCy + *PMe*₃; *PMe*₃ at 1.61 ppm, d, ²*J*_{HP} = 6 Hz), 1.01 (s, 3 H, SiMe), 0.71 (m, 4 H, PCy), 0.46 (m, 2 H, PCy), -1.38 (br s, 2 H, NH₂), -13.77 (dt, 1 H, ²*J*_{HPcis} = 22 Hz, ²*J*_{HPtrans} = 127 Hz, IrH) ¹³C {¹H} NMR (125.8 MHz, benzene-*d*₆): δ 160.5 (m, C_{arom}), 146.4 (m, C_{arom}), 133.2 (apparent t, *J* = 9 Hz, CH_{arom}), 129.2 (CH_{arom}), 128.2 (CH_{arom}), 126.7 (CH_{arom}), 37.1 (apparent t, *J* = 10 Hz, CH_{Cy}), 35.6 (apparent t, *J* = 14 Hz, CH_{Cy}), 29.9 (CH_{2Cy}), 29.4 (CH_{2Cy}), 28.9 (CH_{2Cy}), 28.4 – 26.3 (overlapping resonances, CH_{2Cy}), 19.4 (br d, ¹*J*_{CP} = 27 Hz, *PMe*₃), 5.8 (SiMe). ³¹P {¹H} NMR (202.5 MHz, benzene-*d*₆): δ 28.9 (br s, 2 P, *PSiP*), -55.7 (br s, 1 P, *PMe*₃). ²⁹Si NMR (99.4 MHz, benzene-*d*₆): δ 22.9.

Generation of [CyPSiP]Rh(NH₂Ph) (6). A solution of Me₃SiCH₂Li (0.0020 g, 0.021 mmol) in ca. 0.4 mL of cyclohexane-*d*₁₂ was added to a solution of [Cy-PSiP]Rh(H)Cl (0.015 g, 0.021 mmol) in ca. 0.4 mL of cyclohexane-*d*₁₂. An immediate color change from yellow to red-orange was observed. The reaction mixture was analyzed by ¹H and ³¹P NMR spectroscopy to confirm the complete consumption of [Cy-PSiP]Rh(H)Cl and the formation of 1 equiv. of Me₄Si. Aniline (38.3 μL, 0.039 g, 0.420 mmol) was added to the reaction mixture, and the solution was subsequently analyzed by use of NMR techniques, which confirmed the clean formation of putative **6**. The coordinated aniline in **6** was readily displaced in vacuo, precluding the isolation of this compound. Moreover, the presence of excess aniline in the in situ generated solution of **6** precluded the comprehensive assignment of ¹H and ¹³C NMR resonances for this complex. ¹H NMR (500 MHz, cyclohexane-*d*₁₂): δ 7.99 (d, 2 H, *J* = 7 Hz, *H*_{arom}), 7.38 (br m, 2 H, *H*_{arom}), 7.21 (m, 2 H, *H*_{arom}), 7.12 (m, 2 H, *H*_{arom}), 2.26 –

0.79 (overlapping resonances, 44 H, PCy), 0.40 (s, 3 H, SiMe). $^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz, cyclohexane- d_{12}): δ 132.0 (CH_{arom}), 128.2 (CH_{arom}), 126.5 (CH_{arom}), 40.2 (CH_{Cy}), 38.6 (CH_{Cy}), 31.8 ($\text{CH}_{2\text{Cy}}$), 31.3 ($\text{CH}_{2\text{Cy}}$), 30.5 ($\text{CH}_{2\text{Cy}}$), 29.7 ($\text{CH}_{2\text{Cy}}$), 28.0 – 26.6 (overlapping resonances, $\text{CH}_{2\text{Cy}}$), 8.9 (SiMe). $^{31}\text{P}\{^1\text{H}\}$ NMR (202.5 MHz, cyclohexane- d_{12}): δ 54.7 (d, $^1J_{\text{PRh}} = 182$ Hz). ^{29}Si NMR (99.4 MHz, cyclohexane- d_{12}): δ 59.3.

Generation of [CyPSiP]Rh(NH₃) (7). A solution of Me₃SiCH₂Li (0.0020 g, 0.021 mmol) in ca. 0.4 mL of cyclohexane- d_{12} was added to a solution of [Cy-PSiP]Rh(H)Cl (0.015 g, 0.021 mmol) in ca. 0.4 mL of cyclohexane- d_{12} . An immediate color change from yellow to red-orange was observed. The reaction mixture was analyzed by ^1H and ^{31}P NMR spectroscopy to confirm the complete consumption of [Cy-PSiP]Rh(H)Cl and the formation of 1 equiv. of Me₄Si. The reaction mixture was then filtered through Celite to remove LiCl, and was transferred to a J-Young NMR tube. The solution was degassed via three freeze-pump-thaw cycles, and an atmosphere of anhydrous ammonia was introduced, resulting in a color change to light orange. The reaction mixture was subsequently analyzed by use of NMR techniques, which confirmed the clean formation of putative 7. The coordinated ammine in 7 was readily displaced in vacuo, precluding the isolation of this compound. Moreover, the presence of excess ammonia in the in situ generated solution of 7 prevented the unequivocal assignment of the RhNH₃ ^1H NMR resonance for this complex. ^1H NMR (500 MHz, cyclohexane- d_{12}): δ 7.98 (d, 2 H, $J = 7$ Hz, H_{arom}), 7.37 (m, 2 H, H_{arom}), 7.18 (t, 2 H, $J = 7$ Hz, H_{arom}), 7.10 (t, 2 H, $J = 7$ Hz, H_{arom}), 2.22 (br m, 2 H, PCy), 2.14 (br m, 4 H, PCy), 2.03 (t, 2 H, $J = 12$ Hz, PCy), 1.80 – 1.09 (overlapping resonances, 36 H, PCy), 0.26 (s, 3 H, SiMe). $^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz, cyclohexane- d_{12}): δ 162.0 (m, C_{arom}), 146.6 (m, C_{arom}), 132.4 (apparent t, $J = 12$ Hz, CH_{arom}), 129.2 (CH_{arom}), 128.4 (CH_{arom}), 126.9 (CH_{arom}), 41.7 (apparent t, $J = 7$ Hz, CH_{Cy}), 41.0 (apparent t, $J = 8$ Hz, CH_{Cy}), 32.7 ($\text{CH}_{2\text{Cy}}$), 30.9 ($\text{CH}_{2\text{Cy}}$), 28.5 – 28.2 (overlapping resonances, $\text{CH}_{2\text{Cy}}$), 27.7 ($\text{CH}_{2\text{Cy}}$),

27.4 (CH_2Cy), 8.9 (*SiMe*). $^{31}\text{P}\{^1\text{H}\}$ NMR (202.5 MHz, cyclohexane- d_{12}): δ 54.4 (d, $^1J_{\text{PRh}} = 180$ Hz). ^{29}Si NMR (99.4 MHz, cyclohexane- d_{12}): δ 60.8.

[CyPSiP]Ir(C_2H_4) (8). A solution of [Cy-PSiP]Ir(H)Cl (0.100 g, 0.122 mmol) in ca. 10 mL of cyclohexane was treated with $\text{Me}_3\text{SiCH}_2\text{Li}$ (0.012 g, 0.122 mmol). The resulting orange solution was transferred to a resealable thick-walled glass vessel equipped with a Teflon stopcock and was degassed by three freeze-pump-thaw cycles. The vessel was then charged with ca. 1 atm ethylene gas, and the resulting reaction mixture was heated at 65 °C for 16 h. The volatile components were subsequently removed under vacuum, the residue was extracted with ca. 10 mL of cyclohexane, and the extract was filtered through Celite. The filtrate was dried in vacuo, and the remaining residue was triturated with pentane (3×5 mL) to afford **8** as an orange powder (0.088 g, 89%). ^1H NMR (500 MHz, benzene- d_6): δ 8.24 (d, 2 H, $J = 7$ Hz, H_{arom}), 7.52 (m, 2 H, H_{arom}), 7.32 (t, 2 H, $J = 7$ Hz, H_{arom}), 7.18 (t, 2 H, $J = 7$ Hz, H_{arom}), 2.68 (s, 4 H, C_2H_4), 2.59 (m, 4 H, PCy), 2.05 – 1.98 (overlapping resonances, 6 H, PCy), 1.73 – 1.04 (overlapping resonances, 30 H, PCy), 0.88 – 0.79 (overlapping resonances, 7 H, PCy + *SiMe*; *SiMe* at 0.86 ppm). $^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz, benzene- d_6): δ 160.1 (m, C_{arom}), 145.4 (m, C_{arom}), 132.8 (apparent t, $J = 12$ Hz, CH_{arom}), 130.0 (CH_{arom}), 129.6 (CH_{arom}), 127.3 (CH_{arom}), 41.0 (apparent t, $J = 14$ Hz, CH_{Cy}), 37.1 (C_2H_4), 36.4 (apparent t, $J = 16$ Hz, CH_{Cy}), 30.9 (CH_2Cy), 30.4 (CH_2Cy), 29.8 (CH_2Cy), 29.6 (CH_2Cy), 28.6 – 27.2 (overlapping resonances, CH_2Cy), 6.4 (*SiMe*). $^{31}\text{P}\{^1\text{H}\}$ NMR (202.5 MHz, benzene- d_6): δ 65.4. ^{29}Si NMR (99.4 MHz, benzene- d_6): δ 60.1. Anal. Calcd for $\text{C}_{39}\text{H}_{59}\text{P}_2\text{IrSi}$: C, 57.82; H, 7.34. Found: C, 57.58; H, 7.28.

[CyPSiP]Ir(PMe_3) (9). A solution of [Cy-PSiP]Ir(H)Cl (0.050 g, 0.061 mmol) in ca. 10 mL of benzene was treated with $\text{Me}_3\text{SiCH}_2\text{Li}$ (0.006 g, 0.061 mmol). The reaction mixture was subsequently treated with PMe_3 (6.3 μL , 0.005 g, 0.061 mmol), and allowed to stand at room temperature for 20 minutes, over the course of which the solution turned dark red in color. The reaction mixture was filtered through Celite and the filtrate solution was evaporated to dryness. The remaining residue was

trituated with pentane (3×5 mL) to afford **9** as a dark red solid (0.040 g, 77%). ^1H NMR (500 MHz, benzene- d_6): δ 8.41 (d, 2 H, $J = 7$ Hz, H_{arom}), 7.60 (m, 2 H, H_{arom}), 7.36 (t, 2 H, $J = 7$ Hz, H_{arom}), 7.23 (t, 2 H, $J = 7$ Hz, H_{arom}), 2.68 (m, 2 H, PCy), 2.22 (br d, 2 H, $J = 13$ Hz, PCy), 2.11 – 1.12 (overlapping resonances, 49 H, PCy + PMe_3 ; PMe_3 at 1.53 ppm, d, $^2J_{\text{HP}} = 6$ Hz), 0.95 (s, 3 H, SiMe). $^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz, benzene- d_6): δ 160.8 (m, C_{arom}), 147.8 (m, C_{arom}), 133.1 (apparent t, $J = 11$ Hz, CH_{arom}), 130.2 (CH_{arom}), 129.5 (CH_{arom}), 126.9 (CH_{arom}), 42.2 (apparent t, $J = 10$ Hz, CH_{Cy}), 37.7 (apparent t, $J = 15$ Hz, CH_{Cy}), 31.9 (CH_2Cy), 31.0 (CH_2Cy), 30.1 – 27.0 (overlapping resonances, CH_2Cy), 25.2 (d, $^1J_{\text{CP}} = 20$ Hz, PMe_3), 8.7 (SiMe). $^{31}\text{P}\{^1\text{H}\}$ NMR (202.5 MHz, benzene- d_6): δ 70.6 (d, $^2J_{\text{PP}} = 7$ Hz, Cy-PSiP), -21.2 (t, $^2J_{\text{PP}} = 7$ Hz, PMe_3). ^{29}Si NMR (99.4 MHz, benzene- d_6): δ 68.0. Anal. Calcd for $\text{C}_{40}\text{H}_{64}\text{P}_3\text{IrSi}$: C, 55.98; H, 7.52. Found: C, 55.57; H, 7.27.

[CyPSiP]Rh(PMe₃) (10). Method 1: A solution of [Cy-PSiP]Rh(H)Cl (0.060 g, 0.082 mmol) in ca. 7 mL of THF was treated with PMe_3 (8.5 μL , 0.006 g, 0.082 mmol), and the resulting reaction mixture was allowed to stir at room temperature for ca. 30 min. A solution of PhCH_2K (0.011 g, 0.082 mmol) in ca. 3 mL of THF was then added to the reaction mixture at room temperature. A color change to dark red was observed. The volatile components of the reaction mixture were removed under vacuum and the remaining residue was extracted with ca. 10 mL of benzene. The benzene extract was filtered through Celite and evaporated to dryness. The residue was washed with 3×5 mL of pentane and dried in vacuo to afford **10** as a red solid (0.035 g, 56%). **Method 2:** A solution of $\text{Me}_3\text{SiCH}_2\text{Li}$ (0.0013 g, 0.014 mmol) in ca. 0.4 mL of cyclohexane- d_{12} was added to a solution of [Cy-PSiP]Rh(H)Cl (0.010 g, 0.014 mmol) in ca. 0.4 mL of cyclohexane- d_{12} . An immediate color change from yellow to red-orange was observed. The reaction mixture was analyzed by ^1H and ^{31}P NMR spectroscopy to confirm the complete consumption of [Cy-PSiP]Rh(H)Cl and the formation of 1 equiv. of Me_4Si . Neat PMe_3 (1.4 μL , 0.0011 g, 0.014 mmol) was added to the reaction mixture, resulting in an immediate color change to dark red. At this point ^1H and ^{31}P NMR analysis of the reaction mixture

indicated the quantitative formation of **10**. ^1H NMR (500 MHz, benzene- d_6): δ 8.34 (d, 2 H, $J = 7$ Hz, H_{arom}), 7.58 (d, 2 H, $J = 7$ Hz, H_{arom}), 7.36 (t, 2 H, $J = 7$ Hz, H_{arom}), 7.24 (t, 2 H, $J = 7$ Hz, H_{arom}), 2.45 (m, 2 H, PCy), 2.17 – 1.09 (overlapping resonances, 49 H, PCy + PMe_3 ; PMe_3 at 1.38 ppm, d, $^2J_{\text{HP}} = 3$ Hz), 0.91 (s, 3 H, SiMe), 0.86 (m, 2 H, PCy). $^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz, benzene- d_6): δ 160.8 (m, C_{arom}), 147.2 (m, C_{arom}), 133.0 (apparent t, $J = 12$ Hz, CH_{arom}), 130.3 (CH_{arom}), 129.3 (CH_{arom}), 126.9 (CH_{arom}), 41.1 (apparent t, $J = 7$ Hz, CH_{Cy}), 37.6 (apparent t, $J = 11$ Hz, CH_{Cy}), 32.4 (CH_2Cy), 31.3 (CH_2Cy), 30.9 (CH_2Cy), 29.6 (CH_2Cy), 28.7 (CH_2Cy), 27.8 – 27.5 (overlapping resonances, CH_2Cy), 27.1 (CH_2Cy), 23.5 (d, $^1J_{\text{CP}} = 12$ Hz, PMe_3), 9.6 (SiMe). $^{31}\text{P}\{^1\text{H}\}$ NMR (202.5 MHz, benzene- d_6): δ 70.8 (dd, 2 P, $^1J_{\text{PRh}} = 166$ Hz, $^2J_{\text{PP}} = 22$ Hz, Cy-PSiP), -33.1 (dt, 1 P, $^1J_{\text{PRh}} = 128$ Hz, $^2J_{\text{PP}} = 22$ Hz, PMe_3). ^{29}Si NMR (99.4 MHz, benzene- d_6): δ 69.7. Anal. Calcd for $\text{C}_{40}\text{H}_{64}\text{P}_3\text{RhSi}$: C, 62.49; H, 8.39. Found: C, 62.24; H, 8.18. X-Ray quality crystals of **10** were grown from a concentrated benzene solution at room temperature.

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Crystallographic Solution and Refinement Details for **1**, **3·OEt₂**, **4** and **10**.

Crystallographic data for each of **1**, **3·OEt₂**, **4** and **10** were obtained at 193(±2) K on a Bruker D8/APEX II CCD diffractometer using a graphite-monochromated Mo $K\alpha$ ($\lambda = 0.71073$ Å) 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 $F_o^2 \geq -3\sigma(F_o^2)$. Anisotropic displacement parameters were employed throughout for the non-hydrogen atoms. During the structure solution process for **3·OEt₂** an equiv. of Et₂O was located in the asymmetric unit. Disorder involving this solvent molecule and the N-*Ph* group was identified during refinement. The non-hydrogen atoms of the disordered Et₂O solvate were refined over two positions, where O1S and C1S - C4S were refined with an occupancy factor of 0.65, while O2S and C5S - C8S were refined with an occupancy factor of 0.35. Distances involving analogous pairs of atoms within the solvent diethyl ether molecule were constrained to be equal (within 0.03 Å) during refinement: d(O1S–C1S) = d(O2S–C5S); d(O1S–C3S) = d(O2S–C7S); d(C1S–C2S) = d(C5S–C6S); d(C3S–C4S) = d(C7S–C8S); d(O1S···C2S) = d(O2S···C6S); d(O1S···C4S) = d(O2S···C8S); d(C1S···C3S) = d(C5S···C7S). The carbon atoms of the N-*Ph* group in **3·OEt₂** were refined over two positions, where C2A – C7A were refined with an occupancy factor of 0.65, while C2B – C7B were refined with an occupancy factor of 0.35. The N–C2A and N–C2B distances within the HNPh ligand were constrained to be equal (within 0.01 Å) during refinement. The Rh-*H* in **1** and the Ir-*H* in **4** were each located in the difference map and refined with the restraint that in each case the M-*H* distance was fixed at 1.55 Å, thereby allowing for the determination of the hydride isotropic thermal parameter. In the final refinement cycles, this distance restraint was removed; the previously determined hydride thermal parameter was retained and the hydride position was refined by use of a riding model in which the hydride positional changes matched those of the attached metal center. For **3·OEt₂** the Ir-*H* was not located in the difference map. Instead, an initial Ir-*H* position similar to that found in **4** was selected, and in the subsequent refinement cycles the Ir-H distance was fixed (1.55 Å) and the other parameters (X-Ir-H angles, Ir-*H* thermal parameter) were allowed to vary. The Ir-*H* position in **3·OEt₂** following refinement in this manner was similar to that found in **4**. The N-*H* in **1**, **3·OEt₂** and **4** were each

located in the difference map and refined with the restraint that in each case the N-H distance was fixed at 0.88 Å. 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 **1**, **3·OEt₂**, **4**, and **10**.

	1	3·OEt₂	4	10
Empirical formula	C ₄₃ H ₆₂ NP ₂ RhSi	C ₄₇ H ₇₂ IrNOP ₂ Si	C ₄₅ H ₆₆ IrNP ₂ Si	C ₄₀ H ₆₄ P ₃ RhSi
Formula weight	785.88	949.29	903.22	768.82
Crystal dimensions	0.24 × 0.23 × 0.06	0.38 × 0.26 × 0.14	0.26 × 0.18 × 0.12	0.45 × 0.25 × 0.19
Crystal system	monoclinic	orthorhombic	monoclinic	monoclinic
Space group	<i>P2₁/c</i>	<i>Pbca</i>	<i>P2₁/n</i>	<i>P2₁/c</i>
<i>a</i> (Å)	11.7712 (19)	18.8460 (6)	12.0501 (6)	11.9620 (6)
<i>b</i> (Å)	17.415 (3)	17.5996 (5)	19.8548 (10)	18.5340 (9)
<i>c</i> (Å)	20.937 (3)	27.5460 (8)	17.7790 (9)	18.7300 (10)
<i>α</i> (deg)	90	90	90	90
<i>β</i> (deg)	105.739 (2)	90	91.6341 (7)	103.2047 (6)
<i>γ</i> (deg)	90	90	90	90
<i>V</i> (Å ³)	4131.1 (11)	9136.5 (5)	4251.9 (4)	4042.7 (4)
<i>Z</i>	4	8	4	4
<i>ρ</i> _{calcd} (g cm ⁻³)	1.264	1.380	1.411	1.263
<i>μ</i> (mm ⁻¹)	0.549	3.053	3.275	0.597
Range of transmission	0.9657–0.8776	0.6816–0.3916	0.6947–0.4820	0.8966–0.7738
2 <i>θ</i> limit (deg)	50.76	55.06	54.86	55.04
	-13 ≤ <i>h</i> ≤ 14	-24 ≤ <i>h</i> ≤ 24	-15 ≤ <i>h</i> ≤ 15	-15 ≤ <i>h</i> ≤ 15
	-21 ≤ <i>k</i> ≤ 21	-22 ≤ <i>k</i> ≤ 22	-25 ≤ <i>k</i> ≤ 25	-23 ≤ <i>k</i> ≤ 24
	-25 ≤ <i>l</i> ≤ 25	-35 ≤ <i>l</i> ≤ 35	-22 ≤ <i>l</i> ≤ 23	-24 ≤ <i>l</i> ≤ 24
Total data collected	25644	76763	36901	35047
Independent reflections	7558	10506	9694	9291
<i>R</i> _{int}	0.0974	0.0353	0.0380	0.0248
Observed reflections	4460	8132	8035	8142
Data/restraints/parameters	7558 / 0 / 434	10506 / 8 / 575	9694 / 0 / 454	9291 / 0 / 406
Goodness-of-fit	1.009	1.088	1.043	1.038
<i>R</i> ₁ [<i>F</i> _o ² ≥ 2σ(<i>F</i> _o ²)]	0.0519	0.0236	0.0262	0.0264
<i>wR</i> ₂ [<i>F</i> _o ² ≥ -3σ(<i>F</i> _o ²)]	0.1241	0.0618	0.0610	0.0693
Largest peak, hole (eÅ ⁻³)	0.869, -0.600	1.048, -0.430	1.210, -0.533	1.131, -0.483

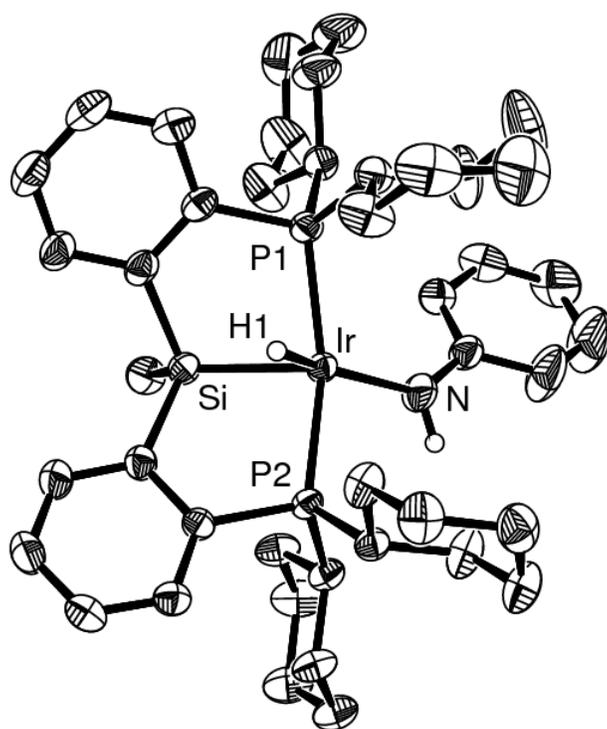


Figure S1. The crystallographically determined structure of **3·OEt₂**, shown with 50% probability ellipsoids. Selected hydrogen atoms, the diethyl ether solvate, and the minor disorder component of the *N-Ph* group have been omitted for clarity. Selected interatomic distances (Å) and angles (°) for **3·OEt₂**: Ir-N 2.056(2); Ir-P1 2.3112(7); Ir-P2 2.2939(7); Ir-Si 22.2833(8); P1-Ir-P2 158.06(3); N-Ir-H1 154.4; N-Ir-Si 137.35(8); Si-Ir-H1 67.5.