SUPPLEMENTARY INFORMATION for:

Room Temperature Benzene C-H Activation by a New [PSiP]Ir Pincer Complex

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Contents:

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, cyclohexane-d_{12}, and methylcyclohexane-d_{14} were degassed via three freeze-pump-thaw cycles and stored over 4 Å molecular sieves. The compounds $[Rh(COE)_2Cl]_2$ and $[Ir(COE)_2Cl]_2$ (COE = η^2-cyclooctene) were purchased from Strem and used as received. The compound 2-$Cy_2PC_6H_4Br$[S1] was prepared according to literature procedures. PhLi was purchased from Aldrich as a 1.8 M solution in di-*n*-butyl ether, dried in vacuo, and used as a solid reagent. All other reagents were purchased from Aldrich and used without further purification. Unless otherwise stated, ^{1}H, ^{13}C, ^{31}P NMR, and ^{29}Si 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 $SiMe_4$ (for ^{1}H, ^{13}C, and ^{29}Si) or 85% H_3PO_4 in D_2O (for ^{31}P). Variable-temperature NMR data were collected on a Bruker AC-250 spectrometer. ^{1}H and ^{13}C NMR chemical shift assignments are based on data obtained from ^{13}C-DEPTQ, ^{1}H-^{1}H COSY, ^{1}H-^{13}C HSQC, and ^{1}H-^{13}C HMBC NMR experiments. ^{29}Si NMR assignments are based on ^{1}H-^{29}Si HMQC and ^{1}H-^{29}Si HMBC experiments. ^{1}H-^{29}Si coupling constants were determined by the use of ^{1}H-coupled ^{1}H-^{29}Si HMQC and ^{1}H-^{29}Si HMBC experiments. In some cases, fewer than expected unique ^{13}C NMR resonances were observed, despite prolonged acquisition times. Elemental analyses were performed by Canadian Microanalytical Service Ltd. of Delta, British Columbia, Canada.

(2-$Cy_2PC_6H_4$)$_2$SiHMe ([CyPSiP]H, 1). A stirring solution of 2-$Cy_2PC_6H_4Br$ (3.0 g, 8.5 mmol) in ca. 60 mL of pentane was cooled to -78 °C. ^{n}BuLi (5.3 mL, 1.6 M in hexanes, 8.5 mmol) was added dropwise to this solution, resulting in a red-orange colored solution. The resulting solution was allowed to warm to room temperature over the course of 3 h, over the course of which a white precipitate was observed and the solution became yellow-orange in color. The mixture was once again cooled to -78 °C and Cl_2SiHMe (0.44 mL, 4.3 mmol) was added via syringe. The resulting pale yellow-orange colored reaction mixture was allowed to warm to room temperature and continue stirring for an additional 14 h at room temperature. The volatile components were then removed in vacuo and the remaining residue was extracted into ca. 20 mL of benzene. The benzene extracts were filtered through Celite and the benzene was removed in vacuo to afford a yellow solid that was triturated with pentane (2 × 5 mL) to give **1** (1.73 g, 69%) as a pale yellow colored solid. ^{1}H NMR (500 MHz, benzene-d_6): δ 7.77 (m, 2 H, H_{arom}), 7.45 (m, 2 H, H_{arom}), 7.21 – 7.14 (4 H, H_{arom}), 6.28 (m, 1 H, Si*H*), 1.98 – 1.84 (8 H, P*Cy*), 1.72 (apparent br t, 4 H, P*Cy*), 1.60 – 1.52 (12 H, P*Cy*), 1.39 – 1.03 (20 H, P*Cy*), 0.96 (d, 3 H, Si*Me*, $^{3}J_{\mathrm{HH}}$ = 4 Hz). ^{13}C{^{1}H} NMR (125.8 MHz, benzene-d_6): δ 147.6 (d, C_{arom}, J_{CP} = 46 Hz), 144.2 (d, $\mathrm{C}_{\mathrm{arom}}$, J_{CP} = 17 Hz), 138.0 (d, $C\mathrm{H}_{\mathrm{arom}}$, J_{CP} = 15 Hz), 132.7 ($C\mathrm{H}_{\mathrm{arom}}$), 129.1 ($C\mathrm{H}_{\mathrm{arom}}$), 36.1 (d, $C\mathrm{H}_{\mathrm{Cy}}$, J_{CP} = 36 Hz), 36.0 (d, $C\mathrm{H}_{\mathrm{Cy}}$, J_{CP} = 36 Hz), 31.4 (apparent t, $C\mathrm{H}_{2\mathrm{Cy}}$, J = 16 Hz), 30.8 (d, $C\mathrm{H}_{2\mathrm{Cy}}$, J_{CP} = 11 Hz), 30.5 (d, $C\mathrm{H}_{2\mathrm{Cy}}$, J_{CP} = 10 Hz), 27.9 – 27.8 ($C\mathrm{H}_{2\mathrm{Cy}}$), 27.2 (d, $C\mathrm{H}_{2\mathrm{Cy}}$, J_{CP} = 8 Hz), -1.1 (t, Si*Me*, J_{CP} = 9 Hz). ^{31}P{^{1}H} NMR (202.5 MHz, benzene-d_6): δ -8.0. ^{29}Si NMR (99.4 MHz, benzene-d_6): δ -24.2 ($^{1}J_{\mathrm{SiH}}$ = 210 Hz).

[CyPSiP]RhHCl (2). A solution of **1** (0.20 g, 0.34 mmol) in 5 mL of THF was added to a slurry of $[Rh(COE)_2Cl]_2$ (0.12 g, 0.17 mmol) in 5 mL of THF at room temperature. The resulting orange colored solution was transferred to a thick walled Schlenk tube fitted with a Teflon stopcock. The reaction mixture was heated at 75 °C for 40 h. The volatile components were then removed in vacuo and the remaining residue was washed with cold pentane (3 × 3 mL). The residue was dried in vacuo to give **2** (0.21 g, 85%) as a bright yellow solid. ^{1}H NMR (500 MHz, benzene-d_6): δ 7.95 (d, 2

H, *H*$_{\text{arom}}$, *J* = 7 Hz), 7.38 (m, 2 H, *H*$_{\text{arom}}$), 7.23 (t, 2 H, *H*$_{\text{arom}}$, *J* = 7 Hz), 7.14 (m, 2 H, *H*$_{\text{arom}}$), 2.86 (m, 2 H, P*Cy*), 2.60 (br d, 2 H, P*Cy*), 2.38 – 2.28 (4 H, P*Cy*), 1.95 (m, 2 H, P*Cy*), 1.85 – 1.77 (4 H, P*Cy*), 1.65 – 0.95 (30 H, P*Cy*), 0.92 (s, 3 H, Si*Me*), -18.80 (dt, 1H, Rh*H*, $^{1}J_{\text{HRh}}$ = 27 Hz, $^{2}J_{\text{HP}}$ = 13 Hz). ^{13}C{^{1}H} NMR (125.8 MHz, benzene-d_6): δ 158.3 (apparent t, *C*$_{\text{arom}}$, *J* = 23 Hz), 142.1 (apparent t, *C*$_{\text{arom}}$, *J* = 23 Hz), 132.4 (apparent t, *C*H$_{\text{arom}}$, *J* = 10 Hz), 131.3 (*C*H$_{\text{arom}}$), 129.8 (*C*H$_{\text{arom}}$), 128.0 (*C*H$_{\text{arom}}$), 35.4 (apparent t, *C*H$_{\text{Cy}}$, *J* = 12 Hz), 34.9 (apparent t, *C*H$_{\text{Cy}}$, *J* = 10 Hz), 31.1 – 31.0 (*C*H$_{2\text{Cy}}$), 30.2 (*C*H$_{2\text{Cy}}$), 28.1 (*C*H$_{2\text{Cy}}$), 27.9 – 27.5 (*C*H$_{2\text{Cy}}$), 27.4 (*C*H$_{2\text{Cy}}$), 26.7 (*C*H$_{2\text{Cy}}$), 9.2 (Si*Me*). ^{31}P{^{1}H} NMR (202.5 MHz, benzene-d_6): δ 59.8 (d, $^{1}J_{\text{PRh}}$ = 118 Hz). ^{29}Si NMR (99.4 MHz, benzene-d_6): δ 42.5 ($^{2}J_{\text{SiH}}$ = 3 Hz). Anal. Calcd for $C_{37}H_{56}ClP_2RhSi$: C, 60.94; H, 7.74. Found: C, 60.75; H, 7.62. A single crystal of **2·(OEt$_2$)$_2$** suitable for X-ray diffraction analysis was grown from THF/diethyl ether at -30 °C.

[CyPSiP]IrHCl (3). A solution of **1** (0.27 g, 0.46 mmol) in 5 mL of THF was added to a slurry of $[Ir(COE)_2Cl]_2$ (0.21 g, 0.23 mmol) in 5 mL of THF at room temperature. The resulting orange colored solution was transferred to a thick walled Schlenk tube fitted with a Teflon stopcock. The reaction mixture was heated at 75 °C for 40 h. The volatile components were then removed in vacuo and the remaining residue was washed with cold pentane (3 × 3 mL). The residue was dried in vacuo to give **3** (0.28 g, 75%) as a bright yellow solid. ^{1}H NMR (500 MHz, benzene-d_6): δ 8.01 (d, 2 H, *H*$_{\text{arom}}$, *J* = 7 Hz), 7.40 (m, 2 H, *H*$_{\text{arom}}$), 7.21 (t, 2 H, *H*$_{\text{arom}}$, *J* = 7 Hz), 7.11 (t, 2 H, *H*$_{\text{arom}}$, *J* = 7 Hz), 2.98 (m, 2 H, P*Cy*), 2.68 (m, 2 H, P*Cy*), 2.59 (br d, 2 H, P*Cy*), 2.26 (br d, 2 H, P*Cy*), 1.95 – 0.82 (36 H, P*Cy*), 0.82 (s, 3 H, Si*Me*), -23.79 (t, 1H, Ir*H*, $^{2}J_{\text{HP}}$ = 14 Hz). ^{13}C{^{1}H} NMR (125.8 MHz, benzene-d_6): δ 158.3 (apparent t, *C*$_{\text{arom}}$, *J* = 23 Hz), 142.1 (apparent t, *C*$_{\text{arom}}$, *J* = 23 Hz), 132.4 (apparent t, *C*H$_{\text{arom}}$, *J* = 10 Hz), 131.3 (*C*H$_{\text{arom}}$), 129.8 (*C*H$_{\text{arom}}$), 128.0 (*C*H$_{\text{arom}}$), 35.4 (apparent t, *C*H$_{\text{Cy}}$, *J* = 12 Hz), 34.9 (apparent t, *C*H$_{\text{Cy}}$, *J* = 10 Hz), 31.1 – 31.0 (*C*H$_{2\text{Cy}}$), 30.2 (*C*H$_{2\text{Cy}}$), 28.1 (*C*H$_{2\text{Cy}}$), 27.9 – 27.5 (*C*H$_{2\text{Cy}}$), 27.4 (*C*H$_{2\text{Cy}}$), 26.7 (*C*H$_{2\text{Cy}}$), 9.2 (Si*Me*). ^{31}P{^{1}H} NMR (202.5 MHz, benzene-d_6): δ 61.1. ^{29}Si NMR

(99.4 MHz, benzene-d_6): δ 7.7 ($^2J_{SiH}$ = 3 Hz). Anal. Calcd for $C_{37}H_{56}ClP_2IrSi$: C, 54.29; H, 6.90. Found: C, 54.40; H, 7.16. A single crystal of **3·(OEt₂)₂** suitable for X-ray diffraction analysis was grown from THF/diethyl ether at -30 °C.

Generation of [CyPSiP]IrH(Ph) (4). Method 1: In the glove box, solid PhLi (0.002 g, 0.020 mmol) was added to a room temperature solution of **3** (0.016 g, 0.020 mmol) in cyclohexane-d_{12} solution. An immediate color change from bright yellow to orange was observed. The reaction mixture was immediately transferred to an NMR tube and analyzed by use of NMR techniques, which confirmed the quantitative consumption of **3** and the clean formation of **4**. Compound **4** was also generated in a similar fashion in benzene-d_6 solution; **4** was converted to **4**-d_6 upon standing in benzene-d_6 solution for 14 h at room temperature or upon heating in benzene-d_6 solution at 70 °C for 1 h. Attempts to isolate **4** by filtering the reaction mixture through Celite (to remove LiCl) and removing the volatile components in vacuo resulted in the partial degradation of **4**, as indicated by ^{1}H and ^{31}P NMR spectroscopy of the isolated material. Efforts to isolate pure **4** by crystallization from the reaction mixture were also unsuccessful. **Method 2**: In the glove box, MeLi (6.5 μl, 1.6 M in Et_2O, 0.010 mmol) was added via syringe to a room temperature solution of **3** (0.009 g, 0.010 mmol) in 0.7 mL of benzene. An immediate color change from bright yellow to orange was observed. The reaction mixture was transferred to an NMR tube, and analyzed by use of NMR techniques. ^{31}P NMR spectroscopy of the reaction mixture upon addition of MeLi indicated the quantitative consumption of **3**, accompanied by the formation of **4** and an intermediate Ir-H species **5** (δ ^{31}P = 59.6; δ ^{1}H Ir*H* = -14.53, t, $^2J_{PH}$ = 15 Hz, observed in an analogous reaction conducted in benzene-d_6), which we tentatively assign as [Cy-PSiP]IrH(Me). The ratio of **4**:**5** after a reaction time of ten minutes was ca. 1:4; the clean conversion of **5** to **4** over the course of an hour at room temperature was observed (^{31}P NMR). Compound **4**-d_6 was generated in a similar fashion in benzene-d_6 solution. ^{1}H NMR (500 MHz, benzene-d_6): δ 8.00 (d, 2 H, H_{arom}, J = 7 Hz), 7.70 (d, 2 H, Ir*Ph*, J = 7 Hz), 7.44 – 7.40 (4 H, Ir*Ph*

+ H_{arom}), 7.20 (t, 2 H, H_{arom}, J = 7 Hz), 7.13 (m, 2 H, H_{arom}), 7.01 (t, 1 H, Ir*Ph*, J = 7 Hz), 2.60 (m, 2 H, P*Cy*), 2.25 – 2.11 (4 H, P*Cy*), 1.82 – 0.83 (38 H, P*Cy*), 0.82 (s, 3 H, Si*Me*), -11.75 (t, 1H, Ir*H*, $^2J_{\mathrm{HP}}$ = 17 Hz). ^{1}H NMR (500 MHz, cyclohexane-d_{12}): δ 7.93 (m, 2 H, H_{arom}), 7.46 (m, 2H, H_{arom}), 7.24 – 7.15 (6 H, H_{arom} + Ir*Ph*), 7.02 (m, 2 H, Ir*Ph*), 6.61 (m, 1 H, Ir*Ph*), 2.66 (m, 2 H, P*Cy*), 2.14 (m, 4 H, P*Cy*), 1.96 – 0.65 (38 H, P*Cy*), 0.49 (s, 3 H, Si*Me*), -12.01 (t, 1 H, Ir*H*, $^2J_{\mathrm{HP}}$ = 16 Hz). ^{13}C{^{1}H} NMR (125.8 MHz, benzene-d_6): δ 181.3 (C_{arom}, Ir*Ph*), 158.5 (apparent t, C_{arom}, J = 21 Hz), 144.4 (apparent t, C_{arom}, J = 27 Hz), 137.2 (br, $C\mathrm{H}_{\mathrm{arom}}$, Ir*Ph*) 131.7 (apparent t, $C\mathrm{H}_{\mathrm{arom}}$, J = 9 Hz), 130.2 ($C\mathrm{H}_{\mathrm{arom}}$), 129.1 ($C\mathrm{H}_{\mathrm{arom}}$), 127.5 ($C\mathrm{H}_{\mathrm{arom}}$), 127.3 ($C\mathrm{H}_{\mathrm{arom}}$, Ir*Ph*), 121.1 ($C\mathrm{H}_{\mathrm{arom}}$, Ir*Ph*), 38.3 (apparent t, $C\mathrm{H}_{\mathrm{Cy}}$, J = 13 Hz), 37.7 (apparent t, $C\mathrm{H}_{\mathrm{Cy}}$, J = 15 Hz), 31.9 ($C\mathrm{H}_{2\mathrm{Cy}}$), 30.8 ($C\mathrm{H}_{2\mathrm{Cy}}$), 28.7 ($C\mathrm{H}_{2\mathrm{Cy}}$), 28.3 ($C\mathrm{H}_{2\mathrm{Cy}}$), 27.8 – 27.3 ($C\mathrm{H}_{2\mathrm{Cy}}$), 26.6 ($C\mathrm{H}_{2\mathrm{Cy}}$), 6.0 (Si*Me*). ^{13}C{^{1}H} NMR (125.8 MHz, cyclohexane-d_{12}): δ 180.3 ($\mathrm{C}_{\mathrm{arom}}$, Ir*Ph*), 158.8 (apparent t, C_{arom}, J = 21 Hz), 144.3 (apparent t, C_{arom}, J = 27 Hz), 136.7 (br, $C\mathrm{H}_{\mathrm{arom}}$, Ir*Ph*), 131.6 (apparent t, $C\mathrm{H}_{\mathrm{arom}}$, J = 9 Hz), 129.9 ($C\mathrm{H}_{\mathrm{arom}}$), 128.7 ($C\mathrm{H}_{\mathrm{arom}}$), 127.1 ($C\mathrm{H}_{\mathrm{arom}}$), 127.0 ($C\mathrm{H}_{\mathrm{arom}}$, Ir*Ph*), 120.8 ($C\mathrm{H}_{\mathrm{arom}}$, Ir*Ph*), 38.5 (apparent t, $C\mathrm{H}_{\mathrm{Cy}}$, J = 13 Hz), 38.0 (apparent t, $C\mathrm{H}_{\mathrm{Cy}}$, J = 14 Hz), 32.0 ($C\mathrm{H}_{2\mathrm{Cy}}$), 30.8 ($C\mathrm{H}_{2\mathrm{Cy}}$), 28.8 ($C\mathrm{H}_{2\mathrm{Cy}}$), 28.4 ($C\mathrm{H}_{2\mathrm{Cy}}$), 28.1 – 27.4 ($C\mathrm{H}_{2\mathrm{Cy}}$), 5.8 (Si*Me*). ^{31}P{^{1}H} NMR (202.5 MHz, benzene-d_6): δ 56.9 (the same shift was observed for **4**-d_6). ^{31}P{^{1}H} NMR (202.5 MHz, cyclohexane-d_{12}): δ 57.2. ^{29}Si NMR (99.4 MHz, benzene-d_6): δ 4.9. ^{29}Si NMR (99.4 MHz, cyclohexane-d_{12}): δ 5.1.

(S1) M. Murata and S. L. Buchwald, *Tetrahedron* 2004, **60**, 7397.

Crystallographic Solution and Refinement Details for **2·(OEt$_2$)$_2$** and **3·(OEt$_2$)$_2$**.

Crystallographic data for each of **2·(OEt$_2$)$_2$** and **3·(OEt$_2$)$_2$** were obtained at 193(±2) K on a Bruker PLATFORM/SMART 1000 CCD diffractometer using a graphite-monochromated Mo Kα (λ = 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. SADABS (Bruker) was employed as the absorption correction method. For **2·(OEt$_2$)$_2$** the structure was solved by use of direct methods, while for **3·(OEt$_2$)$_2$** the structure was solved by use of the Patterson search/structure expansion. Both structures 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 $F_o^2 \geq -3\sigma(F_o^2)$. Each of **2·(OEt$_2$)$_2$** and **3·(OEt$_2$)$_2$** feature crystallographically imposed mirror symmetry (containing Rh or Ir, Si, Cl, C(1), and H1), such that the asymmetric unit contains half of a formula unit of **2** or **3** along with two half-occupied diethyl ether solvates. Anisotropic displacement parameters were employed throughout for the non-hydrogen atoms. The Rh-*H* in **2·(OEt$_2$)$_2$** and the Ir-*H* in **3·(OEt$_2$)$_2$** were each located in the difference map and refined; while no restraints were imposed on the Rh-*H*, the Ir-*H* distance was fixed at 1.55 Å (based on the mean Ir-H distance found in the Cambridge Structural Database; 334 structures with $R_1 < 0.05$). 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 the deposited CIF (see CCDC 693922 for **2·(OEt$_2$)$_2$** and CCDC 693921 for **3·(OEt$_2$)$_2$**).

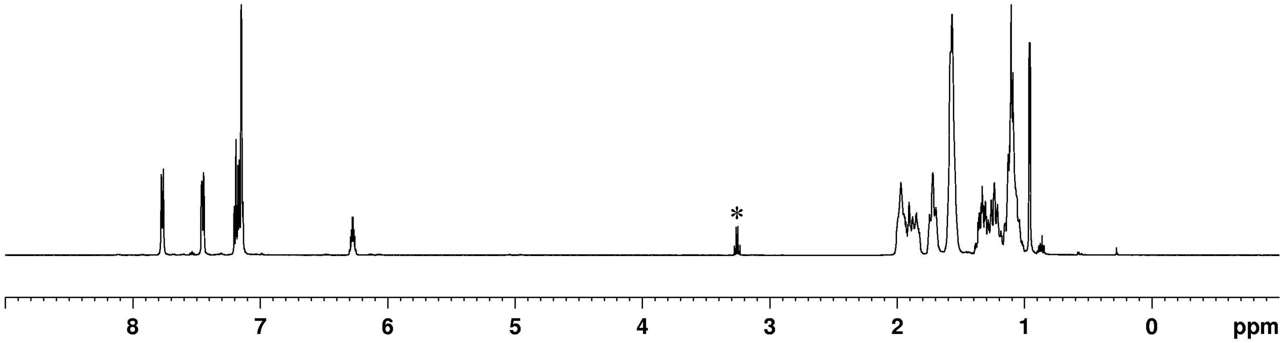

Figure S1. ^{1}H NMR spectrum (benzene-d_6) of [Cy-PSiP]H (**1**). A resonance associated with trace diethyl ether is indicated with an asterisk (*).

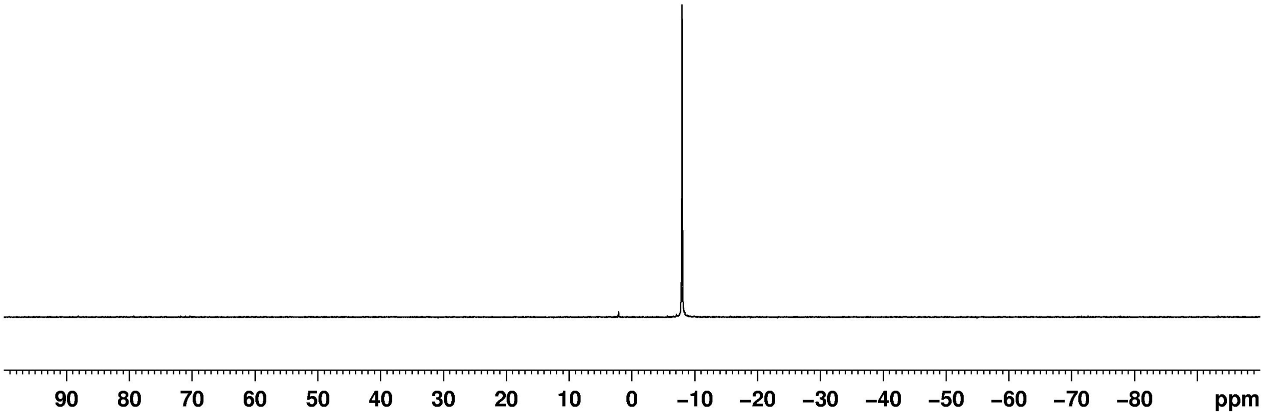

Figure S2. ^{31}P{^{1}H} NMR spectrum (benzene-d_6) of [Cy-PSiP]H (**1**).

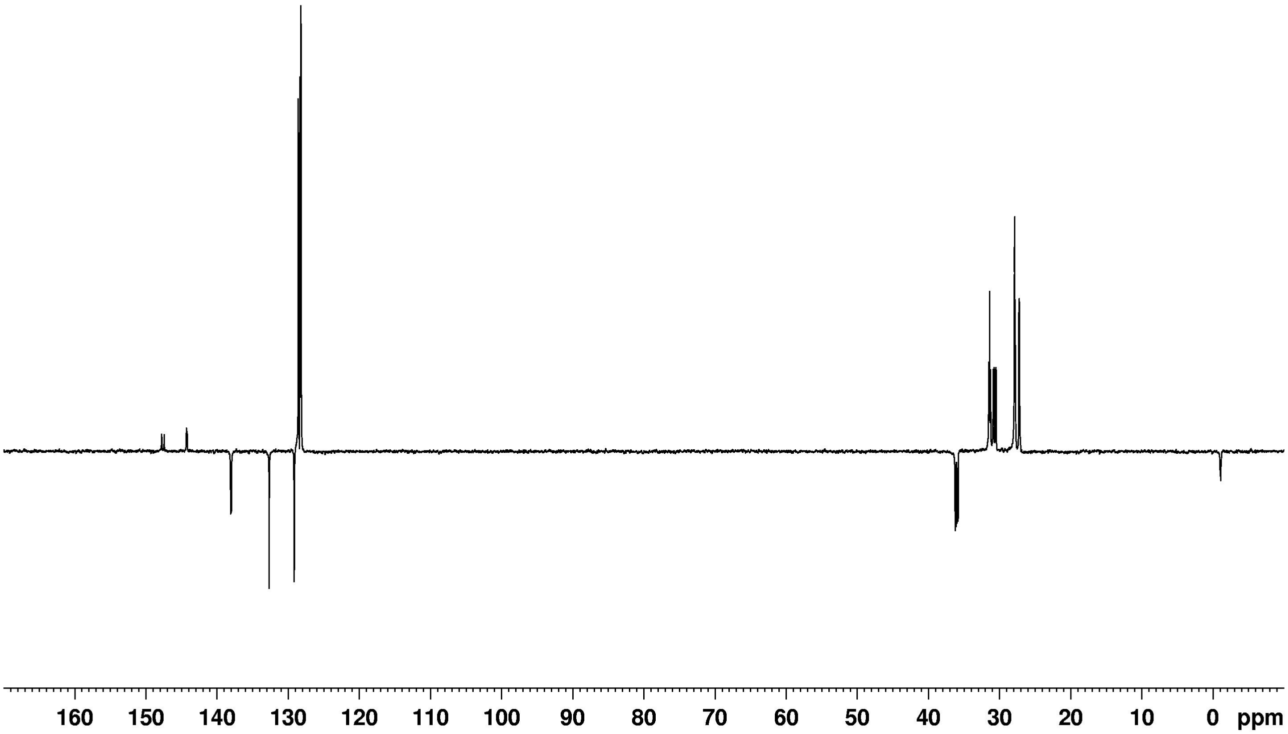

Figure S3. ^{13}C DEPTQ NMR spectrum (benzene-d_6) of [Cy-PSiP]H (**1**); CH and CH_3 resonances are negatively phased, while C and CH_2 resonances are positively phased.

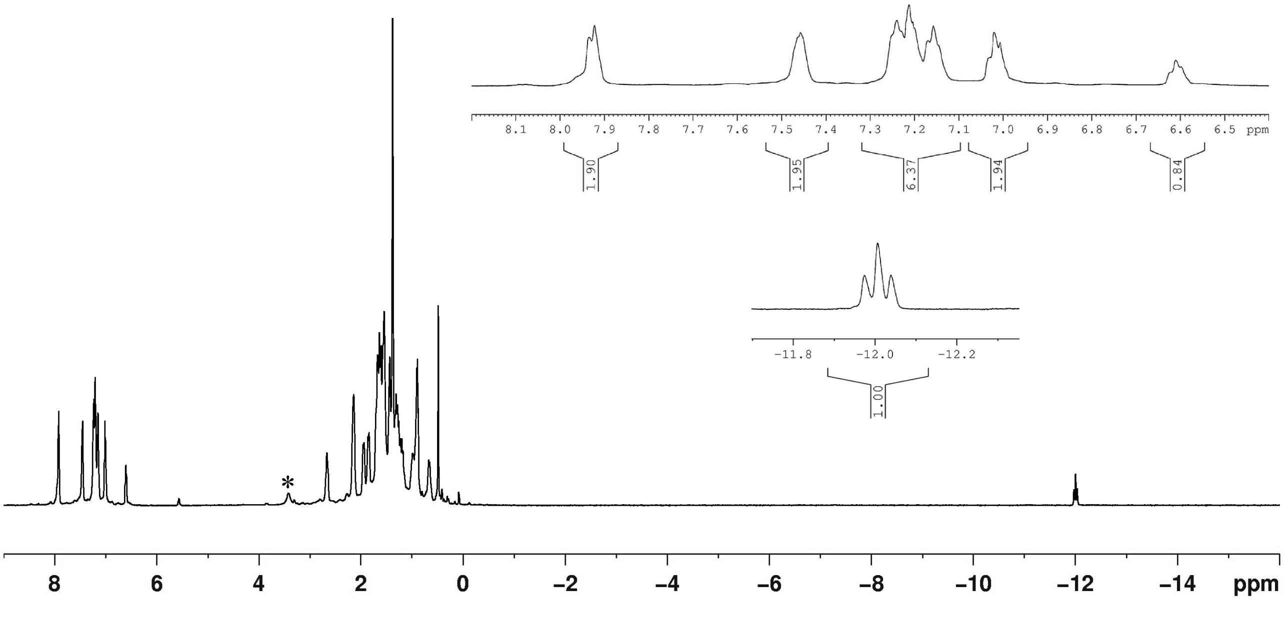

Figure S4. ^{1}H NMR spectrum (cyclohexane-d_{12}) of [Cy-PSiP]IrH(Ph) (**4**). A resonance associated with trace di-*n*-butyl ether is indicated with an asterisk (*).

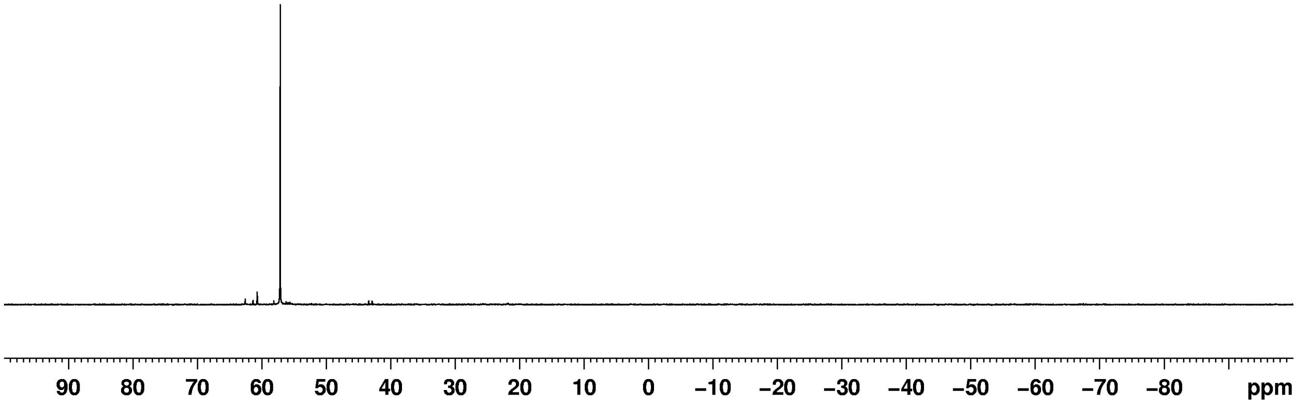

Figure S5. $^{31}P\{^1H\}$ NMR spectrum (cyclohexane-d_{12}) of [Cy-PSiP]IrH(Ph) (**4**).

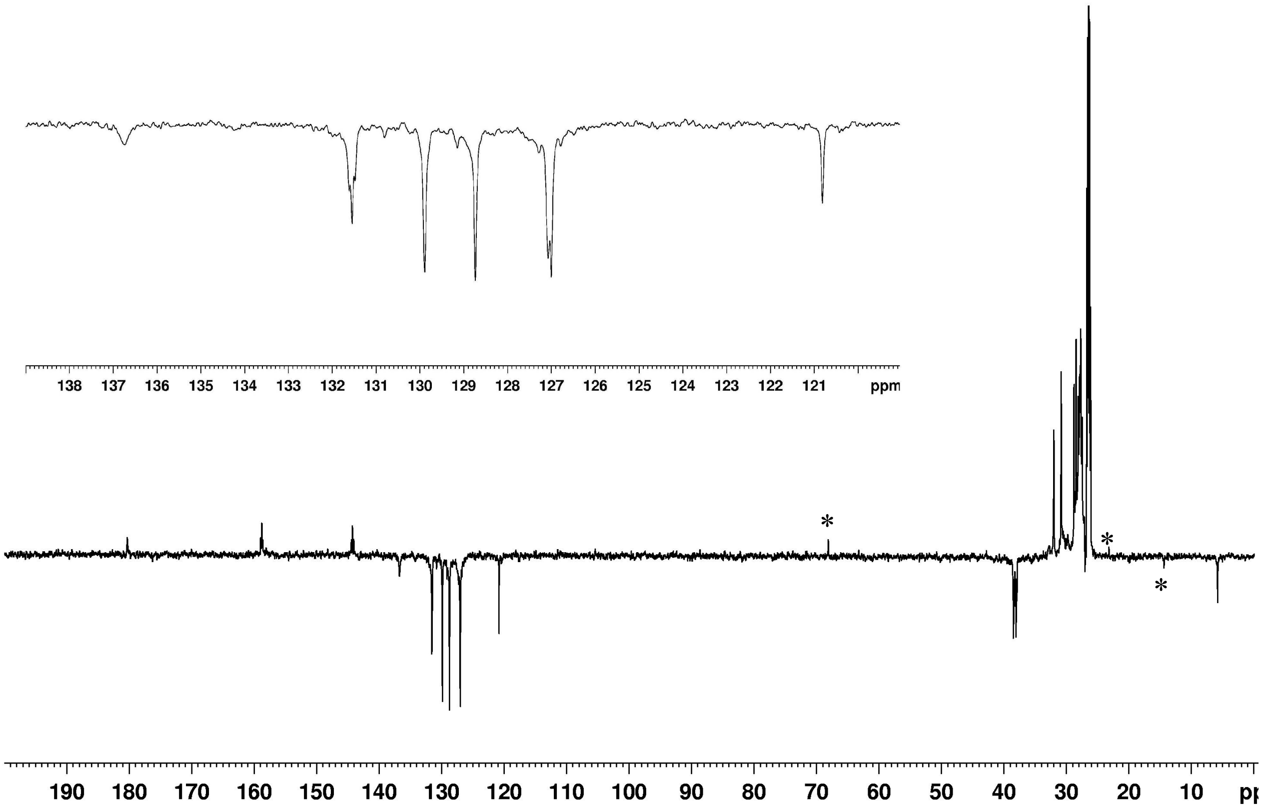

Figure S6. ^{13}C DEPTQ NMR spectrum (cyclohexane-d_{12}) of [Cy-PSiP]IrH(Ph) (**4**); CH and CH_3 resonances are negatively phased, while C and CH_2 resonances are positively phased. Resonances associated with trace di-*n*-butyl ether is indicated with an asterisk (*).

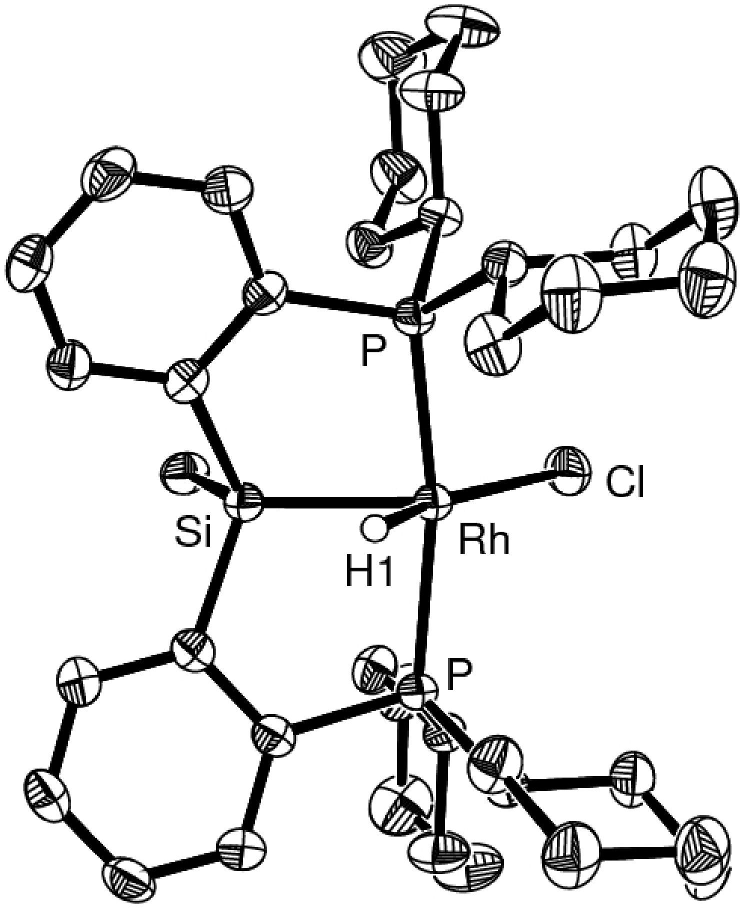

Figure S7. The crystallographically determined structure of **2·(OEt$_2$)$_2$**, shown with 50% probability ellipsoids. Selected hydrogen atoms and the diethyl ether solvates have been omitted for clarity.