

SUPPLEMENTARY INFORMATION for:

Reactivity of a Coordinatively Unsaturated Cp*Ru(κ^2 -P,O) Complex

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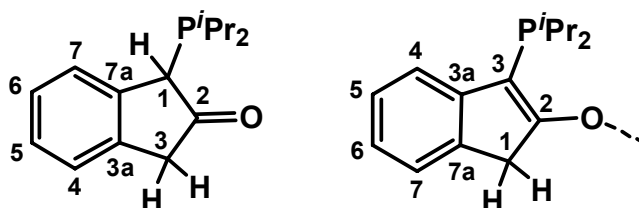
Experimental Section

General Considerations. All manipulations were conducted in the absence of oxygen and water under an atmosphere of dinitrogen, either by use of standard Schlenk methods or within an mBraun glovebox apparatus, utilizing glassware that was oven-dried (130 °C) and evacuated while hot prior to use.

Celite[®] (Aldrich) was oven-dried for 5 d and then evacuated for 24 h prior to use. The non-deuterated solvents dichloromethane, benzene, and pentane were deoxygenated and dried by sparging with dinitrogen gas, followed by passage through a double-column solvent purification system purchased from mBraun Inc. Dichloromethane was purified over two alumina-packed columns, while benzene and pentane were purified over one alumina-packed column and one column packed with copper-Q5 reactant. Benzene-*d*₆ and toluene-*d*₈ (Cambridge Isotopes) were degassed by using three repeated freeze-pump-thaw cycles and then dried over 4 Å molecular sieves for 24 h prior to use. All solvents used within the glovebox were stored over activated 4 Å molecular sieves. Both [Cp*RuCl]₄^{S1} and 1-diisopropylphosphino-2-indanone^{S2} were prepared using literature procedures, and were dried in vacuo for 24 h prior to use. NaN(SiMe₃)₂ (Aldrich) was dried in vacuo for 24 h prior to use. Hydrogen (99.999%, UHP Grade) and carbon monoxide gases (99.5%, chemically pure grade) were obtained from Air Liquide and were used as received. Whereas PhCN (Aldrich) was degassed by sparging with dinitrogen gas, PhSiH₃ (Strem) was degassed by using three repeated freeze-pump-thaw cycles, and Ph₂SiH₂ (Gelest, shipped under argon) was not degassed, each of these reagents was dried over 4 Å molecular sieves for 24 h prior to use. Variable-temperature NMR experiments were conducted on a Bruker AC-250 spectrometer. Unless otherwise stated, ¹H, ¹³C, ²⁹Si and ³¹P NMR characterization data were collected at 300K on a Bruker AV-500 spectrometer operating at 500.1, 125.8, 99.4 and 202.5 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). ¹H and ¹³C NMR chemical shift assignments are based on data obtained from ¹³C-DEPT, ¹H-¹H COSY, ¹H-¹³C HSQC, and ¹H-¹³C HMBC NMR experiments.

^{29}Si NMR chemical shift assignments are given on the basis of data obtained from ^1H - ^{29}Si HMQC (^1H -coupled experiments were employed in the determination of $^1J_{\text{SiH}}$ values) as well as ^1H - ^{29}Si HMBC ($J_{\text{SiH}}^{\text{S3}}$ experiments were employed in the determination of $^nJ_{\text{SiH}}$ values for $n > 1$) experiments. IR data were collected on a Bruker VECTOR 22 FT-IR instrument. Raman data were collected on powdered samples (sealed in glass capillaries under dry dinitrogen) using a Bruker RFS 100 FT-Raman spectrometer. Elemental analyses were performed by Canadian Microanalytical Service Ltd., Delta, British Columbia, Canada.

Atomic Numbering Scheme Employed:



Synthesis of (κ^2 -*P,O*-1-diisopropylphosphino-2-indanone) Cp^*RuCl . To a glass vial containing a magnetically stirred suspension of $[\text{Cp}^*\text{RuCl}]_4$ (0.72 g, 0.66 mmol) in CH_2Cl_2 (4 mL) was added a solution of 1-diisopropylphosphino-2-indanone (0.66 g, 2.66 mmol) in CH_2Cl_2 (4 mL) all at once via Pasteur pipette. The addition caused an immediate color change of the suspension from dark brown to dark red. The vial was then sealed with a PTFE-lined cap and the solution was stirred magnetically for 45 min. ^{31}P NMR data collected on an aliquot of this solution indicated the quantitative formation of the target complex. The CH_2Cl_2 solvent was then removed in vacuo, yielding an oily dark red solid. The solid was then triturated with pentane (1.5 mL) and the pentane was removed in vacuo. The residue was then washed with pentane (2 x 3 mL) and dried in vacuo to yield (κ^2 -*P,O*-1-diisopropylphosphino-2-indanone) Cp^*RuCl as an analytically pure orange-pink powder (1.32 g, 2.55 mmol, 96 %). Anal. Calcd. for $\text{C}_{25}\text{H}_{36}\text{POClRu}$: C 57.74; H 6.98; N 0.00. Found: C 57.93; H 6.68; N < 0.3. ^1H NMR (C_6D_6): δ 7.03-6.91 (m, 3H, aryl-Hs), 6.62 (d, $^3J_{\text{HH}} = 7.0$ Hz, 1H, C4-H or C7-H), 5.27 (d,

$^2J_{\text{PH}} = 12.0$ Hz, 1H, $^i\text{Pr}_2\text{PC-H}$), 2.85 (m, 1H, C(H_a)(H_b)), 2.64 (m, 1H, C(H_a)(H_b)), 2.57 (m, 1H, P(CHMe $_a$ Me $_b$)), 1.96 (m, 1H, P(CHMe $_c$ Me $_d$)), 1.77 (d, $J = 1.5$ Hz, 15H, C $_5$ Me $_5$), 1.69 (d of d, $^3J_{\text{PH}} = 13.0$ Hz, $^3J_{\text{HH}} = 7.5$ Hz, 3H, P(CHMe $_a$ Me $_b$)), 1.32 (d of d, $^3J_{\text{PH}} = 17.5$ Hz, $^3J_{\text{HH}} = 7.0$ Hz, 3H, P(CHMe $_a$ Me $_b$)), 0.86 (d of d, $^3J_{\text{PH}} = 14.0$ Hz, $^3J_{\text{HH}} = 7.0$ Hz, 3H, P(CHMe $_c$ Me $_d$)), 0.58 (d of d, $^3J_{\text{PH}} = 12.0$ Hz, $^3J_{\text{HH}} = 7.0$ Hz, 3H P(CHMe $_c$ Me $_d$)); $^{13}\text{C}\{^1\text{H}\}$ (C $_6$ D $_6$): δ 226.2 (m, C2), 138.5 (d, $J = 8.1$ Hz, C3a or C7a), 137.8 (d, $J = 3.3$ Hz, C7a or C3a), 127.3 (C5 or C6), 127.0 (aryl-CH), 125.4 (C4 or C7), 124.8 (aryl-CH), 79.8 (C $_5$ Me $_5$), 60.8 ($^i\text{Pr}_2\text{PC-H}$), 41.6 (CH $_2$), 27.5 (d, $^1J_{\text{PC}} = 11.2$ Hz, P(CHMe $_c$ Me $_d$)), 26.4 (d, $^1J_{\text{PC}} = 16.3$ Hz, P(CHMe $_a$ Me $_b$)), 21.6 (P(CHMe $_a$ Me $_b$)), 20.9 (d, $^2J_{\text{PC}} = 9.7$ Hz, P(CHMe $_a$ Me $_b$)), 18.2 (d, $^2J_{\text{PC}} = 4.8$ Hz, P(CHMe $_c$ Me $_d$)), 17.6 (P(CHMe $_c$ Me $_d$)), 11.3 (C $_5$ Me $_5$); $^{31}\text{P}\{^1\text{H}\}$ NMR (C $_6$ D $_6$): δ 100.5. Slow evaporation of a concentrated benzene solution of (κ^2 -*P,O*-1-diisopropylphosphino-2-indanone)Cp**Ru*Cl produced a crystal (benzene hemisolvate) suitable for X-ray diffraction analysis.

Synthesis of $\mathbf{1a_2}(\mu\text{-N}_2)$. To a glass vial containing a magnetically stirred deep red suspension of (κ^2 -*P,O*-1-diisopropylphosphino-2-indanone)Cp**Ru*Cl (0.10 g, 0.19 mmol) in benzene (8 mL), was added solid NaN(SiMe $_3$) $_2$ (0.037 g, 0.20 mmol) all at once. The vial was sealed with a PTFE-lined cap and magnetic stirring was initiated. Over the course of several seconds, the reaction mixture became dark green. After 45 min, ^{31}P NMR data collected on an aliquot of this crude reaction mixture indicated the quantitative formation of $\mathbf{1a_2}(\mu\text{-N}_2)$. The solution was filtered through Celite and the benzene solvent and other volatile materials were removed in vacuo, yielding an oily dark green solid. The residue was triturated with pentane (2 x 1 mL), after which the pentane was removed in vacuo. Pentane (2 x 3 mL) was then added to wash the solid, and the dark green supernatant solution was removed carefully via Pasteur pipette, leaving a greenish-brown solid. Analysis of ^{31}P NMR data collected on the pentane washings indicated relatively minor amounts of $\mathbf{1a_2}(\mu\text{-N}_2)$ and as such these washings were discarded. The residue was dried in vacuo, yielding $\mathbf{1a_2}(\mu\text{-N}_2)$ as a greenish-beige powder (0.074 g, 0.074 mmol, 78 %). Anal. Calcd. for C $_{50}$ H $_{70}$ P $_2$ O $_2$ N $_2$ Ru $_2$: C 60.32; H 7.09; N 2.82. Found: C 60.34; H 7.10; N 2.10.

The somewhat low % N value determined for **1a₂·(μ-N₂)** is in keeping with some other Ru dinitrogen complexes.^{S4} ¹H NMR (500.1 MHz, 300K, C₆D₆, *under dinitrogen*): δ 7.38-6.80 (broad m, 4H, aryl-Hs), 3.35-3.17 (broad m, 2H, CH₂), 2.62-2.38 (broad m, 2H, P(CHMe₂)₂), 1.71-0.93 (broad m, 27H, C₅Me₅ and P(CHMe₂)₂). ³¹P{¹H} NMR (202.5 MHz, 300K, C₆D₆, *under dinitrogen*): δ 50.1 (Δν_{1/2} = 213 Hz). ¹H NMR (250.1 MHz, 300K, toluene-*d*₈, *degassed sample*): δ 7.43-6.80 (broad m, 4H, aryl-Hs), 3.28-3.05 (broad m, 2H, CH₂), 2.77-0.53 (broad m, 29H, P(CHMe₂)₂ and C₅Me₅ and P(CHMe₂)₂); ³¹P{¹H} NMR (101.3 MHz, 300K, toluene-*d*₈, *degassed sample*): δ 44.9 (Δν_{1/2} = 240 Hz). No useful information could be derived from the ¹³C NMR spectrum of **1a₂·(μ-N₂)** (125.8 MHz, 300K, C₆D₆, *under dinitrogen*). Raman (cm⁻¹) ν(N₂): 2042. Layering of a C₆D₆ solution of **1a₂·(μ-N₂)** with pentane and slow evaporation of the resultant mixture over the course of approximately two weeks produced a crystal suitable for X-ray diffraction analysis.

Variable-temperature behavior of 1a₂·(μ-N₂). For samples of **1a₂·(μ-N₂)** dissolved in toluene-*d*₈ that were sealed under an atmosphere of dinitrogen, the initially deep green solutions (300K) turned to red-brown (reversibly) upon cooling below 250K; conversely, only deep green solutions were observed over this temperature range for samples that had been thoroughly degassed. Low-temperature NMR data for **1a₂·(μ-N₂)**: ¹H NMR (250.1 MHz, 223K, toluene-*d*₈, *under dinitrogen*): δ 7.19-6.96 (m, 4H, aryl-Hs), 3.60-3.15 (AB multiplet, 2H, C(H_a)(H_b)), 2.86 (m, 1H, P(CHMe_aMe_b)), 2.04 (m, 1H, P(CHMe_cMe_d)), 1.78-0.97 (m, 27H, C₅Me₅ and P(CHMe_aMe_b) and P(CHMe_cMe_d)); ³¹P{¹H} NMR (101.3 MHz, 223K, toluene-*d*₈, *under dinitrogen*): δ 52.1 (Δν_{1/2} = 9 Hz); ³¹P{¹H} NMR (101.3 MHz, 223K, toluene-*d*₈, *degassed sample*): δ 52.0 (Δν_{1/2} = 10 Hz), 39.1 (Δν_{1/2} = 65 Hz) (1:1 ratio). We are hesitant to provide a definitive interpretation of these temperature-dependent observations. However, it is feasible that in solution **1a₂·(μ-N₂)** exists in a dynamic equilibrium with **1a·(σ-N₂)**, whereby the position of this equilibrium is dependent both on temperature and on the availability of dissolved dinitrogen.^{S5} Furthermore, some aspects of the observed temperature-dependent lineshape changes may

be attributable to the exchange of free and bound N₂ in both **1a₂·(μ-N₂)** and **1a·(σ-N₂)**, as well as restricted rotation about the Ru-N-N-Ru axis in **1a₂·(μ-N₂)** at low temperatures.

Synthesis of 1a·CO. Within a glovebox, a J. Young NMR tube was charged with **1a₂·(μ-N₂)** (0.045 g, 0.045 mmol) and 0.8 mL of C₆D₆. The tube was sealed and the solution was mixed by inversion of the tube several times. The tube containing the resulting deep green solution was removed from the glovebox, connected to a Schlenk line, and degassed via three repeated freeze-pump-thaw cycles. An atmosphere of CO was introduced to the NMR tube, upon which the solution was observed to change gradually in color to brown over the course of several min. After 30 min, ³¹P and ¹H NMR data collected on this reaction mixture indicated quantitative conversion to **1a·CO**. Upon removal of solvent and other volatile materials *in vacuo*, followed by trituration with pentane (2 x 1.5 mL), **1a·CO** was isolated as an analytically pure, tan powder (0.043 g, 0.084 mmol, 93 %). Anal. Calcd. for C₂₆H₃₅PO₂Ru: C 61.02; H 6.90; N 0.00. Found: C 61.01; H 6.97; N < 0.3. ¹H NMR (C₆D₆): δ 7.22 (m, 1H, C5-H or C6-H), 7.01 (d, ³J_{HH} = 7.5 Hz, 1H, C4-H or C7-H), 6.93-6.87 (m, 2H, aryl-Hs), 3.28-3.17 (m, 2H, C(H_a)(H_b)), 2.84 (m, 1H, P(CHMe_aMe_b)), 2.01 (m, 1H, P(CHMe_cMe_d)), 1.59 (d, J = 1.0 Hz, 15H, C₅Me₅), 1.38 (d of d, ³J_{PH} = 16.0 Hz, ³J_{HH} = 7.0 Hz, 3H, P(CHMe_aMe_b)), 1.23 (d of d, ³J_{PH} = 11.5 Hz, ³J_{HH} = 7.0 Hz, 3H, P(CHMe_cMe_d)), 1.02-0.94 (m, 6H, P(CHMe_aMe_b) and P(CHMe_cMe_d)); ¹³C {¹H} (C₆D₆): δ 208.6 (d, ²J_{PC} = 19.1 Hz, CO), 200.8 (d, ²J_{PC} = 21.3 Hz, C2), 146.7 (C3a or C7a), 139.7 (d, J = 8.6 Hz, C7a or C3a), 127.2 (C5 or C6), 124.4 (aryl-CH), 120.0 (aryl-CH), 116.4 (C4 or C7), 99.9 (d, ¹J_{PC} = 48.8 Hz, C3), 94.1 (C₅Me₅), 38.6 (d, ³J_{PC} = 8.8 Hz, C1), 27.0 (d, ¹J_{PC} = 18.6 Hz, P(CHMe_cMe_d)), 24.2 (d, ¹J_{PC} = 35.6 Hz, P(CHMe_aMe_b)), 19.8 (d, ²J_{PC} = 6.3 Hz, P(CHMe_cMe_d)), 19.8 (d, ²J_{PC} = 6.3 Hz, P(CHMe_aMe_b) or P(CHMe_cMe_d)), 18.9-18.8 (m, P(CHMe_aMe_b) and either P(CHMe_cMe_d) or P(CHMe_aMe_b)), 10.3 (C₅Me₅); ³¹P {¹H} NMR (C₆D₆): δ 63.0. FTIR (CsI; cm⁻¹) ν(CO): 1903.

Synthesis of 1a·NCPh. To a glass vial containing a magnetically stirred solution of **1a₂·(μ-N₂)** (0.11 g, 0.11 mmol) in benzene was added PhCN (0.21 mL, 0.22 mmol) all at once via Eppendorf pipette. A

change in the color of the solution from dark green to orange-red was observed upon the addition of PhCN. The vial was sealed with a PTFE-lined cap, and the solution was stirred for 30 min. ^{31}P NMR data collected on an aliquot of this solution indicated quantitative conversion to **1a·NCPh**. The solvent and other volatile materials were removed *in vacuo*, yielding an oily dark red-brown solid. The residue was triturated with pentane (2 x 1.5 mL), and the pentane was removed *in vacuo* to yield **1a·NCPh** as an analytically pure, orange-brown powder, 91%. Anal. Calcd. for $\text{C}_{32}\text{H}_{40}\text{PONRu}$: C 65.49; H 6.88; N 2.39. Found: C 65.49; H 6.64; N 2.31. ^1H NMR (C_6D_6): δ 7.25 (t, $^3J_{\text{HH}} = 7.5$ Hz, 1H, C5-H or C6-H), 7.16 (m, 1H, C4-H or C7-H), 7.02-6.97 (m, 3H, 2 NC-aryl-Hs and either C7-H or C4-H), 6.85 (t, $^3J_{\text{HH}} = 7.0$ Hz, 1H, C6-H or C5-H), 6.81 (t, $^3J_{\text{HH}} = 7.0$ Hz, 1H, NC-aryl-H), 6.64 (apparent t, $^3J_{\text{HH}} = 7.5$ Hz, 2H, NC-aryl-Hs), 3.44-3.35 (broad s, 2H, $\text{C}(\text{H}_a)(\text{H}_b)$), 1.74 (s, 15H, C_5Me_5), 1.43-1.25 (m, 14H, $\text{P}(\text{CHMe}_a\text{Me}_b)$ and $\text{P}(\text{CHMe}_c\text{Me}_d)$ and $\text{P}(\text{CHMe}_a\text{Me}_b)$ and $\text{P}(\text{CHMe}_c\text{Me}_d)$); $^{13}\text{C}\{^1\text{H}\}$ (C_6D_6): δ 199.8 (d, $^2J_{\text{PC}} = 23.7$ Hz, C2), 149.0 (C3a or C7a), 139.0 (d, $J = 7.8$ Hz, C7a or C3a), 131.6-131.4 (m, NC-aryl-CHs), 129.0 (NC-aryl-CHs), 126.7 (C5 or C6), 123.9 (C4 or C7), 118.7 (C6 or C5), 115.9 (C7 or C4), 113.7 (NC-aryl-C), 98.5 (d, $^1J_{\text{PC}} = 41.6$ Hz, C3), 82.8 (C_5Me_5), 39.3 (d, $^3J_{\text{PC}} = 8.1$ Hz, C1), 20.9-19.2 (broad m, $\text{P}(\text{CHMe}_a\text{Me}_b)$ and $\text{P}(\text{CHMe}_c\text{Me}_d)$ and $\text{P}(\text{CHMe}_a\text{Me}_b)$ and $\text{P}(\text{CHMe}_c\text{Me}_d)$), 10.8 (C_5Me_5); $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6): δ 53.9.

Synthesis of 1a·($\sigma\text{-H}_2$). A protocol analogous to that described for the synthesis of **1a·CO** was employed, using H_2 in place of CO. Introduction of an atmosphere of H_2 to a degassed solution of **1a₂·($\mu\text{-N}_2$)** (0.020 g, 0.020 mmol) in toluene- d_8 (0.8 mL) caused the solution to lighten gradually in color from deep green to lime green over the course of several min. After 20 min, ^{31}P and ^1H NMR data collected on this reaction mixture indicated the quantitative conversion of **1a₂·($\mu\text{-N}_2$)** into **1a·($\sigma\text{-H}_2$)**. Whereas solutions of **1a·($\sigma\text{-H}_2$)** prepared in this manner were found to be stable for a minimum of 8 h, some decomposition (^{31}P NMR) was detected upon standing for 18 h. For freshly prepared solutions of **1a·($\sigma\text{-H}_2$)**, removal of volatiles *in vacuo* led to the quantitative conversion of **1a·($\sigma\text{-H}_2$)** back to **1a₂·($\mu\text{-N}_2$)**.

N₂) (as determined by ³¹P NMR analysis of a C₆D₆ solution of the dried solid that had been prepared under an atmosphere of dinitrogen). ¹H NMR (500.1 MHz, 300K, toluene-*d*₈): δ 7.20 (t, ³J_{HH} = 7.5 Hz, 1H, C5-H or C6-H), 7.01 (d, ³J_{HH} = 7.5 Hz, 1H, C4-H or C7-H), 6.93 (d, ³J_{HH} = 7.0 Hz, 1H, C7-H or C4-H), 6.86 (t, ³J_{HH} = 7.0 Hz, 1H, C6-H or C5-H), 3.25 (s, 2H, CH₂), 2.45 (m, 2H, P(CHMe_aMe_b)), 1.64 (s, 15H, C₅Me₅), 1.19 (d of d, ³J_{PH} = 13.5 Hz, ³J_{HH} = 7.0 Hz, 6H, P(CHMe_aMe_b)), 1.11 (d of d, ³J_{PH} = 16.0 Hz, ³J_{HH} = 6.5 Hz, 6H, P(CHMe_aMe_b)), -5.73 (broad s, Δν_{1/2} = 23 Hz, 2H, Ru(H₂)); ¹³C{¹H} (125.8 MHz, 300K, toluene-*d*₈): δ 199.9 (m, C2), 146.8 (m, C3a or C7a), 139.9 (m, C7a or C3a), 126.8 (C5 or C6), 124.2 (C4 or C7), 119.7 (C6 or C5), 116.3 (C7 or C4), 81.1 (C₅Me₅), 38.6 (d, ³J_{PC} = 8.4 Hz, C1), 24.5 (broad m, P(CHMe_aMe_b)), 19.6-19.3 (broad m, P(CHMe_aMe_b)), 11.1 (C₅Me₅); ³¹P{¹H} NMR (202.5 MHz, 300K, toluene-*d*₈): δ 65.2 (broad m, Δν_{1/2} = 180 Hz). The *T*_{1(min)} relaxation time value (218K, 17 ms, 250 MHz) associated with the σ-H₂ unit in **1a**·(σ-H₂) was obtained by using the inversion-recovery technique.^{S6} *Variable-temperature behavior of 1a*·(σ-H₂). The initially green toluene solution of **1a**·(σ-H₂) observed at 300K becomes brown in appearance (reversibly) upon cooling below 253K. ¹H NMR (250.1 MHz, 223K, toluene-*d*₈): δ 7.34-6.94 (m, 4H, aryl-Hs), 3.40-3.15 (AB multiplet, 2H, C(H_a)(H_b)), 2.53 (m, 1H, P(CHMe_aMe_b)), 1.98 (m, 1H, P(CHMe_cMe_d)), 1.63 (s, 15H, C₅Me₅), 1.42-0.83 (m, 12H, P(CHMe_aMe_b) and P(CHMe_cMe_d)), -6.40 (broad s, Δν_{1/2} = 51 Hz, 2H, Ru(H₂)); ³¹P{¹H} NMR (101.3 MHz, 223K, toluene-*d*₈): δ 72.2 (Δν_{1/2} = 20 Hz). While ¹H and ¹³C NMR data for **1a**·(σ-H₂) collected at 300K are consistent with a C_s-symmetric structure, the ¹H NMR spectrum of **1a**·(σ-H₂) collected at 223K is in keeping with the C₁-symmetry expected for this complex. We tentatively attribute these temperature-dependent NMR features to the exchange of free and bound H₂ in **1a**·(σ-H₂) – a process which is slowed (on the NMR timescale) at 223K.

Synthesis of 2a. To a glass vial containing a magnetically stirred deep green suspension of **1a**₂·(μ-N₂) (0.020 g, 0.020 mmol) in C₆D₆ (2 mL), was added PhSiH₃ (0.0051 mL, 0.041 mmol) via microsyringe. The vial was sealed with a PTFE-lined cap and magnetic stirring was initiated. Over the course of several seconds, the reaction mixture became an orange-yellow homogeneous mixture. After 3 h, ³¹P

NMR data collected on an aliquot of this crude reaction mixture indicated the quantitative formation of **2a**. The benzene solvent and other volatile materials were removed in vacuo, yielding an oily orange solid. The residue was triturated with pentane (2 x 1 mL), after which the pentane was removed in vacuo to yield **2a** as an orange powder (0.023 g, 0.038 mmol, 95 %). Anal. Calcd. for C₃₁H₄₃POSiRu: C 62.91; H 7.32; N 0.00. Found: C 62.95; H 7.04; N < 0.3. ¹H NMR (C₆D₆): δ 8.18-8.15 (m, 2H, Si-aryl-Hs), 7.42-7.36 (m, 3H, 2 Si-aryl-Hs and aryl-H), 7.26 (m, 1H, Si-aryl-H), 7.16 (m, 1H, aryl-H), 6.96-6.89 (m, 2H, aryl-Hs), 6.61 (m, 1H, Si-H), 3.26-2.98 (m, 2H, C(H_a)(H_b)), 2.74-2.61 (m, 2H, P(CHMe_aMe_b) and P(CHMe_cMe_d)), 1.73 (s, 15H, C₅Me₅), 1.09-1.00 (m, 9H, P(CHMe_aMe_b) and P(CHMe_cMe_d)), 0.94 (d of d, ³J_{PH} = 16.0 Hz, ³J_{HH} = 7.0 Hz, 3H, P(CHMe_cMe_d)), -11.14 (d, 1H, J = 34.0 Hz, Ru-H_a), -11.92 (apparent d of d, 1H, J = 32.5 Hz, J = 5.0 Hz, Ru-H_b); ¹³C {¹H} (C₆D₆): δ 177.0 (d, ²J_{PC} = 8.6 Hz, C2), 146.5 (C3a or C7a), 145.5 (Si-aryl-C), 135.2-135.1 (m, Si-aryl-CHs and either C7a or C3a), 128.9 (Si-aryl-CH), 128.2-128.1 (Si-aryl-CHs), 126.2 (aryl-CH), 123.5 (aryl-CH), 122.5 (aryl-CH), 120.2 (aryl-CH), 103.1 (d, ¹J_{PC} = 54.1 Hz, C3), 95.6 (C₅Me₅), 42.7 (d, ³J_{PC} = 7.7 Hz, C1), 29.1 (d, ¹J_{PC} = 25.9 Hz, P(CHMe_cMe_d)), 27.9 (d, ¹J_{PC} = 27.2 Hz, P(CHMe_aMe_b)), 20.7 (P(CHMe_cMe_d)), 20.4 (d, ²J_{PC} = 7.9 Hz, P(CHMe_aMe_b) or P(CHMe_aMe_b) or P(CHMe_cMe_d)), 20.3 (P(CHMe_aMe_b) or P(CHMe_cMe_d) or P(CHMe_aMe_b)), 19.0 (d, ²J_{PC} = 5.9 Hz, P(CHMe_cMe_d) or P(CHMe_aMe_b) or P(CHMe_aMe_b)), 11.6 (C₅Me₅); ³¹P {¹H} NMR (C₆D₆): δ 67.4; ²⁹Si {¹H} NMR (C₆D₆): δ 60.4 (¹H-²⁹Si HMBC/HMQC), ¹J_{SiH} = 199.7 Hz (¹H-coupled ¹H-²⁹Si HMQC), ²J_{SiH} = 9.4 Hz (J-HMBC).

Synthesis of 2b. To a glass vial containing a magnetically stirred deep green suspension of **1a**·(μ-N₂) (0.060 g, 0.060 mmol) in benzene (8 mL), was added Ph₂SiH₂ (0.025 mL, 0.13 mmol) via Eppendorf pipette. The vial was sealed with a PTFE-lined cap and magnetic stirring was initiated. Over the course of several seconds, the reaction mixture became an orange-yellow homogeneous mixture. After 15 min, ³¹P NMR data collected on an aliquot of this crude reaction mixture indicated the quantitative formation of **2b**. The benzene solvent and other volatile materials were removed in vacuo, yielding an

oily orange solid. The residue was triturated with pentane (2 x 1 mL), after which the pentane was removed in vacuo to yield **2b** as a peach powder (0.079 g, 0.12 mmol, 95 %). Anal. Calcd. for $C_{37}H_{47}POSiRu$: C 66.53; H 7.09; N 0.00. Found: C 66.13; H 6.89; N < 0.3. 1H NMR (C_6D_6): δ 8.03-8.01 (m, 4H, Si-aryl-Hs), 7.41 (d, $^3J_{HH} = 8.0$ Hz, 1H, C4-H or C7-H), 7.36 (apparent t, $^3J_{HH} = 7.0$ Hz, 4H, Si-aryl-Hs), 7.27-7.23 (m, 2H, Si-aryl-Hs), 7.13 (m, 1H, aryl-H), 6.96-6.92 (m, 2H, aryl-Hs), 3.17 (s, 2H, CH_2), 2.63 (m, 2H, $P(CHMe_aMe_b)$), 1.67 (s, 15H, C_5Me_5), 1.09 (d of d, $^3J_{PH} = 17.0$ Hz, $^3J_{HH} = 7.0$ Hz, 6H, $P(CHMe_aMe_b)$), 0.94 (d of d, $^3J_{PH} = 15.5$ Hz, $^3J_{HH} = 7.0$ Hz, 6H, $P(CHMe_aMe_b)$), -11.02 (d, 2H, $^2J_{PH} = 32.5$ Hz, Ru-Hs); $^{13}C\{^1H\}$ (C_6D_6): δ 177.1 (d, $^2J_{PC} = 9.1$ Hz, C2), 146.5 (C3a or C7a), 146.2 (Si-aryl-C), 135.9 (Si-aryl-CHs), 135.1 (d, $J = 6.9$ Hz, C7a or C3a), 128.4 (Si-aryl-CHs), 127.4 (Si-aryl-CHs), 126.4 (aryl-CH), 123.5 (aryl-CH), 122.4 (C5 or C6), 120.3 (C4 or C7), 103.1 (d, $^1J_{PC} = 52.3$ Hz, C3), 96.1 (C_5Me_5), 42.8 (d, $^3J_{PC} = 7.4$ Hz, C1), 28.6 (d, $^1J_{PC} = 26.9$ Hz, $P(CHMe_aMe_b)$), 20.3 ($P(CHMe_aMe_b)$), 19.5 (d, $^2J_{PC} = 5.8$ Hz, $P(CHMe_aMe_b)$), 11.6 (C_5Me_5); $^{31}P\{^1H\}$ NMR (C_6D_6): δ 65.1; $^{29}Si\{^1H\}$ NMR (C_6D_6): δ 57.4 (1H - ^{29}Si HMBC), $^2J_{SiH} = 9.8$ Hz (J-HMBC). A crystal of **2b** suitable for X-ray diffraction analysis was grown from a concentrated pentane solution at -35 °C.

Crystallographic Solution and Refinement Details

Crystallographic Characterization of (κ^2 -*P,O*-1-diisopropylphosphino-2-

indanone) $Cp^*RuCl \cdot 0.5C_6H_6$ and $1a_2 \cdot (\mu-N_2)$. Crystallographic data for these complexes were obtained at 173(±2) K on a Nonius KappaCCD 4-Circle Kappa FR540C diffractometer using a graphite-monochromated Mo $K\alpha$ ($\lambda = 0.71073$ Å) radiation, employing samples that were mounted in inert oil and transferred to a cold gas stream on the diffractometer. Cell parameters were initially retrieved by using the COLLECT software (Nonius), and refined with the HKL DENZO and SCALEPACK software.^{S7a} Data reduction and absorption correction (multi-scan) were also performed with the HKL DENZO and SCALEPACK software. The structures were solved by using the direct methods package

in SIR-97,^{S7b} and refined by use of the SHELXL97-2 program,^{S8} employing 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-H atoms. For (κ^2 -*P*,*O*-1-diisopropylphosphino-2-indanone)Cp*RuCl·0.5C₆H₆, the H-atom attached to C1 was located in the Fourier difference map and its coordinates and isotropic thermal parameter were allowed refine. Otherwise, all H-atoms were added at calculated positions and refined by using 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 CIFs: (κ^2 -*P*,*O*-1-diisopropylphosphino-2-indanone)Cp*RuCl·0.5C₆H₆ (CCDC 654073) and **1a**·(μ -N₂) (CCDC 654074). ORTEP diagrams featured in the manuscript were prepared by use of ORTEP-3 for Windows version 1.074.^{S9}

Crystallographic Characterization of 2b. Crystallographic data for **2b** were obtained at 193(±2) K on a Bruker PLATFORM/SMART 1000 CCD diffractometer using a graphite-monochromated Mo K α (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, data reduction, and absorption correction (including SAINT and SADABS) were supplied by Bruker. The structure was solved by use of direct methods, and 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-H atoms. The positions of the Ru-*H*s (H1 and H2) were located in the Fourier difference map and refined, with the Ru-H distances fixed at 1.55 Å. All other H-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. The final refined value of the absolute structure parameter (-0.024(19)) supported that the absolute structure had been chosen correctly.^{S10} Additional crystallographic information is provided in the deposited CIF

(CCDC 654072). The ORTEP diagram featured in the manuscript was prepared by use of ORTEP-3 for Windows version 1.074.^{S9}

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