

SUPPORTING INFORMATION for:

**Neutral, Cationic, and Zwitterionic Ru(II) Atom Transfer Radical Addition
Catalysts Supported by P,N-Substituted Indene or Indenide Ligands**

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Contents:

1. Experimental Section (general considerations, numbering scheme, synthetic details, and characterization data).

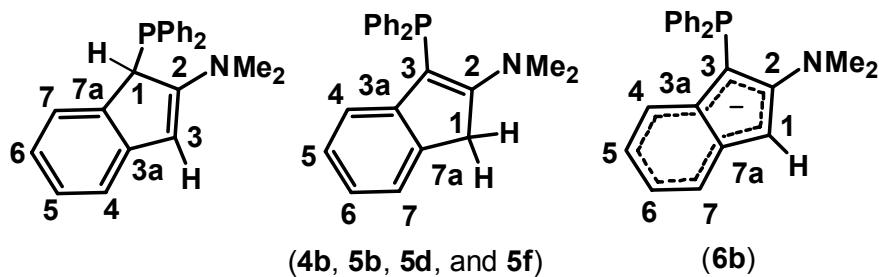
2. Crystallographic Solution and Refinement Details for 5f.

Experimental Section

General Considerations. Unless otherwise stated, 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, tetrahydrofuran, toluene, 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 and tetrahydrofuran were purified over two alumina-packed columns, while toluene and pentane were purified over one alumina-packed column and one column packed with copper-Q5 reactant. Carbon tetrachloride and chloroform (Aldrich) were degassed by sparging with dinitrogen gas, and were stored over activated 4 Å molecular sieves for 24 h prior to use. Purification of acetonitrile was achieved by refluxing over CaH₂ for 4 d under dinitrogen, followed by distillation. Purification of NEt₃ was achieved by stirring over KOH for 7 d, followed by distillation; the distilled NEt₃ was then refluxed over CaH₂ for 3 d under dinitrogen, followed by distillation. CD₃CN (Cambridge Isotopes) was degassed by using three repeated freeze-pump-thaw cycles, dried over CaH₂ for 7 days, distilled in vacuo, and stored over 4 Å molecular sieves for 24 h prior to use. CD₂Cl₂ (Cambridge Isotopes) was degassed by using three repeated freeze-pump-thaw cycles, and stored over 4 Å molecular sieves for 24 h prior to use. Styrene (Aldrich) was degassing by several freeze-pump-thaw cycles, 1-hexene (Alfa Aesar) was degassing by several freeze-pump-thaw cycles and stored over 4 Å molecular sieves, α -methylstyrene, *p*-chlorostyrene, and methyl methacrylate (Aldrich) were treated with 4 Å molecular sieves for several hours then distilled under an atmosphere of N₂ and stored at -35 °C. All silver (Aldrich), sodium (Aldrich), and lithium (Boulder Scientific) salts, as well as anhydrous K₂CO₃ (Aldrich), were dried in vacuo for a minimum of 12 h prior to use. AIBN (AIBN = azobis(isobutyronitrile)) (Aldrich) was used as received. The following

compounds were prepared by employing literature procedures and were dried in vacuo for 24 h prior to use: $[\text{Cp}^*\text{RuCl}]_4$,^{S1} 1-Ph₂P-2-Me₂N-indene (**1b**),^{S2} **2a-c**,^{S3} **3**,^{S3} **4a**,^{S4} **5a,c,e**,^{S4} **6a**,^{S4} and **7**.^{S4} All ¹H, ¹³C, and ³¹P NMR characterization data were collected at 300K on a Bruker AV-500 spectrometer operating at 500.1, 125.8, and 202.5 MHz (respectively) with chemical shifts reported in parts per million downfield of SiMe₄ (for ¹H and ¹³C) 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. In some cases, fewer than expected unique ¹H or ¹³C NMR resonances were observed, despite prolonged acquisition times. Elemental analyses were performed by Canadian Microanalytical Service Ltd., Delta, British Columbia, Canada.

Atomic Numbering Scheme:



Synthesis of $\text{Cp}^*\text{Ru}(\text{Cl})(\kappa^2\text{-1-Ph}_2\text{P-2-Me}_2\text{N-indene})$. To a glass vial containing a magnetically stirred solution of $(\text{Cp}^*\text{RuCl})_4$ (0.21 g, 0.19 mmol) in CH_2Cl_2 (7 mL), solid **1b** (0.26 g, 0.76 mmol) was added all at once. The addition caused an immediate color change from dark brown to dark red. The vial was then sealed with a PTFE-lined cap and the solution was stirred magnetically for 60 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 a dark red oily solid. The solid was then triturated with pentane (1.5 mL) and the pentane was removed *in vacuo* to afford the target complex as an orange powder (0.46 g, 0.74 mmol, 97 %). ^1H NMR (CD_2Cl_2): δ 7.90-7.84 (m, 2H, P-aryl-Hs), 7.48-7.44 (m,

3H, P-aryl-Hs), 7.32-7.26 (m, 2H, aryl-Hs), 7.17 (m, 1H, aryl-H), 7.09 (m, 1H, aryl-H), 7.00 (m, 2H, aryl-Hs), 6.89-6.82 (m, 2H, aryl-Hs), 6.66 (m, 1H, indene-aryl-H), 5.99 (d, $^4J_{\text{PH}} = 2.5$ Hz, 1H, C3-H), 5.67 (d, $^2J_{\text{PH}} = 11.0$ Hz, 1H, C1-H), 3.15 (broad s, 6H, NMe_a and NMe_b), 1.46 (d, $J = 2.0$ Hz, 15H, C₅Me₅); $^{13}\text{C}\{\text{H}\}$ NMR (CD₂Cl₂): δ 167.3 (m, C2), 142.6 (C3a or C7a), 139.6 (m, C7a or C3a), 136.1 (d, $J_{\text{PC}} = 13.1$ Hz, P-aryl-CHs), 132.1 (d, $J_{\text{PC}} = 8.1$ Hz, P-aryl-CHs), 131.9 (d, $^1J_{\text{PC}} = 45.9$ Hz, P-aryl-C), 129.4 (aryl-CH), 127.9 (d, $J_{\text{PC}} = 7.5$ Hz, P-aryl-CHs), 127.0 (aryl-CH), 126.5 (d, $J_{\text{PC}} = 9.8$ Hz, P-aryl-CHs), 124.5 (aryl-CHs), 123.7 (aryl-CH), 120.9 (indene-aryl-CH), 115.2 (d, $^3J_{\text{PC}} = 7.5$ Hz, C3), 80.4 (C₅Me₅), 54.6 (broad s, NMe_a and NMe_b), 54.0 (multiplicity obscured by CD₂Cl₂ signal, C1), 10.6 (C₅Me₅); $^{31}\text{P}\{\text{H}\}$ NMR (CD₂Cl₂): δ 61.0.

Synthesis of [Cp^{*}Ru(MeCN)(κ²-3-Ph₂P-2-Me₂N-indene)]⁺BF₄⁻ (5b). A protocol analogous to that described for **5f** was used with **4b** (0.098 g, 0.16 mmol) and AgBF₄ (0.032 g, 0.016 mmol) in MeCN (8 mL) to yield **5b** as a yellow powder (0.11 g, 0.015 mmol, 94 %). ^1H and ^{31}P NMR spectral data obtained for **5b** were identical to those of **5f**.

Synthesis of [Cp^{*}Ru(MeCN)(κ²-3-Ph₂P-2-Me₂N-indene)]⁺B(C₆F₅)₄⁻ (5d). A protocol analogous to that described for **5f** was used with **4b** (0.058 g, 0.094 mmol) and Li(Et₂O)_{2.5}B(C₆F₅)₄ (0.082 g, 0.094 mmol) in MeCN (7 mL) to yield **5d** as a yellow powder (0.11 g, 0.085 mmol, 91 %). ^1H and ^{31}P NMR spectral data obtained for **5d** were identical to those of **5f**.

Crystallographic Solution and Refinement Details for 5f. Crystallographic data for **5f** were obtained at 193(±2) K on a Bruker PLATFORM/SMART 1000 CCD diffractometer using a graphite-monochromated Mo K α ($\lambda = 0.71073$ 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, 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 $F_{\text{o}}^2 \geq 2\sigma(F_{\text{o}}^2)$ and wR_2 based on $F_{\text{o}}^2 \geq -3\sigma(F_{\text{o}}^2)$. During

the solution process, two crystallographically independent molecules of **5f** were located in the asymmetric unit and refined in a satisfactory manner. For simplicity, metrical data for only one of the two crystallographically independent molecules of **5f** are presented in the text. Anisotropic displacement parameters were employed throughout for the non-H atoms. All 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. Additional crystallographic information is provided in the deposited CIF. The ORTEP diagram featured in the text was prepared by use of ORTEP-3 for Windows version 1.074.^{S5}

References

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