SUPPORTING INFORMATION

for

Fluorous Phase-Transfer Activation of Catalysts:
Application of a New Rate-Enhancement Strategy to Alkene Metathesis

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**General.** All reactions were conducted under N\textsubscript{2} unless noted. Chemicals were treated as follows: Diethyl ether, toluene, hexanes, distilled from Na/benzophenone; CF\textsubscript{3}C\textsubscript{6}F\textsubscript{11} (Oakwood or ABCR), distilled from P\textsubscript{2}O\textsubscript{5}; CF\textsubscript{3}C\textsubscript{6}H\textsubscript{5} (ABCR), distilled from CaH\textsubscript{2}; diallyl diethyl malonate (ABCR), tridecane (Aldrich), perfluoro-2-butyl-tetrahydrofuran (Apollo), C\textsubscript{6}F\textsubscript{14} (Fluorochem), CDCl\textsubscript{3} (Cambridge Isotope or Aldrich) and other solvents, used as received.

NMR spectra were recorded on 400 MHz spectrometers at ambient probe temperatures and referenced to residual internal CHDCl\textsubscript{2} (\textsuperscript{1}H, \( \delta \) 5.32) or CD\textsubscript{2}Cl\textsubscript{2} (\textsuperscript{13}C, \( \delta \) 53.23). IR spectra were measured on an ASI React-IR spectrometer. GC data were acquired using a ThermoQuest Trace GC 2000 instrument fitted with a capillary column (OPTIMA-5-0.25 \( \mu \)m; 25 m x 0.32 mm). HPLC data were acquired using a Thermoquest instrument package (pump/autosampler/detector P4000/AS3000/UV6000LP). DSC and TGA data were recorded with a Mettler-Toledo DSC821 instrument and treated by standard methods.\textsuperscript{1} Elemental analyses were conducted with a Carlo Erba EA1110 instrument.

\((\text{H}_2\text{IMes})((\text{Rf6CH}_2\text{CH}_2)\text{3P})(\text{Cl})_2\text{Ru(=CHPh)}\) (2a). A Schlenk flask was charged with (H\textsubscript{2}IMes)(Py)(Cl\textsubscript{2})Ru(=CHPh) (1a;\textsuperscript{2} 0.0924 g, 0.127 mmol), P(CH\textsubscript{2}CH\textsubscript{2}R\textsubscript{f6})\textsubscript{3} (a;\textsuperscript{3} 0.1524 g, 0.142 mmol), and CF\textsubscript{3}C\textsubscript{6}H\textsubscript{5} (3.0 mL). The mixture was stirred (1 h). The solvent was removed by oil pump vacuum to give a brownish pink residue that was passed through a silica gel plug (4 x 2 cm) using hexanes and then hexanes/diethyl ether (10:1 v/v). The solvent was removed from the filtrate by rotary evaporation and oil pump vacuum to give 2a as a pink solid (0.1482 g, 0.090 mmol, 71%).

M.p. 113-118 °C (capillary). DSC: \( T_i/T_e/T_p/T_c/T_f \) 83.8/114.3/123.7/128.0/129.3 °C (endotherm), 129.4/134.6/146.8/154.0/159.5 °C (exotherm). TGA: onset of first and second mass loss regimes, 127.7 and 262.0 °C (\( T_e \)). Calcd (%) for C\textsubscript{58}H\textsubscript{44}Cl\textsubscript{2}F\textsubscript{51}N\textsubscript{2}PRu (1641.2): C 38.03, H 2.68, N 1.71; found C 37.85, H 2.83, N 1.67.

\textsuperscript{1}H NMR (400.1 MHz, CD\textsubscript{2}Cl\textsubscript{2}): \( \delta \) 18.91 (s, 1H, Ru=CH), 7.83 (d, J = 7.6 Hz, 2H, Ar), 7.51 (t, J = 7.7 Hz, 1H, Ar), 7.18 (t, J = 7.8 Hz, 2H, Ar), 6.99 (s, 2H, Mes), 6.37 (s, 2H, Mes), 4.20-3.90 (dm, J = 36.7 Hz, 4H, NCH\textsubscript{2}CH\textsubscript{2}N), 2.59 (s, 6H, Mes), 2.28 (s, 3H, Mes), 2.23 (s, 6H, Mes), 1.94 (s, 3H, Mes), 1.90-1.60 (br m, 12H P(CH\textsubscript{2})\textsubscript{2}; \textsuperscript{13}C\textsuperscript{1}H NMR (100.5 MHz, CD\textsubscript{2}Cl\textsubscript{2}, partial): \( \delta \) 217.8 (d, J = 90.2 Hz, Ru-C(N)\textsubscript{2}), 150.4, 139.0, 138.7, 137.9, 136.5, 136.5, 136.3, 133.7, 130.2,
130.1, 129.2, 128.9, 128.2, 121.3, 29.5, 24.8 (t, J = 22.7 Hz), 20.4, 20.3, 19.6, 17.8, 11.8 (d, J = 21.6 Hz, CH₂CF₂); ³¹P{¹H} NMR (161.9 MHz, CD₂Cl₂): δ 19.96 (s); ¹⁹F NMR (282.4 MHz, CD₂Cl₂, partial): δ −81.64 (t, J = 9.3, CF₃). MS (FAB, 3-NBA, m/z (%)): 1640 (5) [M]+, 1605 (2.5) [M – Cl]+, 1073 (2.5) [P(CH₂CH₂R₈)₃ + H]+.

(H₂IMes)((R₈CH₂CH₂)₃P)(Cl)₂Ru(=CHPh) (2b). Complex 1a (0.1201 g, 0.165 mmol), P(CH₂CH₂R₈)₃ (b; 0.1524 g, 0.142 mmol), and CF₃C₆H₅ (4.0 mL) were combined in a procedure analogous to that for 2a. An identical workup gave 2b as a pink solid (0.2050 g, 0.106 mmol, 64%).

M.p. 113-115 °C (capillary). DSC: Tᵣ/Tₚ/Tₚ/Tᵣ/Tᵣ 96.6/112.4/117.1/120.0/130.3 °C (endotherm), 159.5/175.7/178.8/180.0/186.8 °C (exotherm). TGA: onset of first and second mass loss regimes, 154.8 and 270.7 °C (Tₑ). Calcd (%) for C₅₈H₄₄Cl₂F₅₁N₂PRu (1940.8): C 35.88, H 2.27, N 1.44; found C 35.31, H 2.38, N 1.31.

¹H NMR (400.1 MHz, CD₂Cl₂): δ 18.90 (s, 1H, Ru=CH), 7.83 (d, J = 7.7 Hz, 2H, Ar), 7.50 (t, J = 7.3 Hz, 1H, Ar), 7.18 (t, J = 7.7 Hz, 2H, Ar), 6.99 (s, 2H, Mes), 6.40 (s, 2H, Mes), 4.20-4.90 (dm, J = 36.6 Hz, 4H, NCH₂CH₂N), 2.59 (s, 6H, Mes), 2.27 (s, 3H, Mes), 2.23 (s, 6H, Mes), 1.93 (s, 3H, Mes), 1.90-1.60 (br m, 12H P(CH₂CH₂CH₂)), 13C{¹H} NMR (100.5 MHz, CD₂Cl₂): δ 218.4 (d, J = 90.5 Hz, Ru-C(N)), 150.9, 139.6, 139.3, 138.4, 137.0, 136.9, 134.2, 130.7, 130.6, 129.7, 129.4, 128.5, 25.4 (t, J = 22.9 Hz), 20.9, 20.8, 20.2, 18.4, 12.2 (dt, 21.1 Hz, CH₂CF₂); ³¹P{¹H} NMR (161.9 MHz, CH₂Cl₂): δ 20.17 (s); ¹⁹F NMR (282.4 MHz, CD₂Cl₂, partial): δ −81.74 (t, J = 10.0 Hz, CF₃). MS (FAB, 2-nitrophenyl octyl ether, m/z (%)): 1982 (30) [M]+, 1905 (10) [M – Cl]+, 1415 (40) [P(CH₂CH₂CH₂R₈)₃ + H]+, 568 (60) [M⁺ – P(CH₂CH₂R₈)₃], 532 (50) [M⁺ – P(CH₂CH₂R₈)₃ – Cl].

(H₂IMes)((R₁₀CH₂CH₂)₃P)(Cl)₂Ru(=CHPh) (2c). Complex 1a (0.0800 g, 0.110 mmol), P(CH₂CH₂R₁₀)₃ (c; 0.1840 g, 0.110 mmol), and CF₃C₆H₅ (3.0 mL) were combined in a procedure analogous to that for 2a. An identical workup gave 2c as a pink solid (0.1806 g, 0.081 mmol, 73%).

M.p. 111-114 °C (capillary). DSC: Tᵣ/Tₚ/Tₚ/Tᵣ/Tᵣ 100.9/115.1/118.0/119.4/131.2 °C (endotherm), 129.4/134.6/146.8/154.0/159.5 °C (exotherm). TGA: onset of first and second mass loss regimes, 173.4 and 279.4 °C (Tₑ). Calcd (%) for C₆₄H₄₄Cl₂F₆₃N₂PRu (2240.2): C 34.28, H 1.96, N 1.25; found C 34.31, H 2.00, N 1.21.
$^1$H NMR (400 MHz, CD$_2$Cl$_2$): δ 18.90 (s, 1H), 7.83 (d, J = 7.7 Hz, 2H, Ar), 7.49 (t, J = 7.3 Hz, 1H, Ar), 7.17 (t, J = 7.7 Hz, 2H, Ar), 6.98 (s, 2H, Mes), 6.36 (s, 2H, Mes), 4.12-3.90 (dm, J = 36.5 Hz, 4H, NCH$_2$CH$_2$N), 2.62 (s, 6H), 2.30 (s, 3H), 2.26 (s, 6H), 1.96 (s, 3H), 1.82-1.70 (br m, 12H, P(CH$_2$)$_2$); $^{31}$P{$^1$H} NMR (161.8 MHz, CH$_2$Cl$_2$): δ 20.24 (s); $^{19}$F NMR (282.4 MHz, CD$_2$Cl$_2$, partial): δ –81.80 (t, J = 10.0 Hz, CF$_3$).

Ring Closing Metathesis. The following is representative for Scheme 4. A two-neck flask was charged with diethyl 2-allyl-2-methallylmalonate, 5 (0.0524 g, 0.206 mmol) and hexadecane (0.0530 g, 0.234 mmol; GC standard), and flushed with nitrogen. Freshly distilled CH$_2$Cl$_2$ (4.1 mL) was added to give a 0.05 M solution of the substrate. The solution was stirred and the catalyst (0.0100 g, 5.155 × 10$^{-3}$ mmol, 2.5 mol%) was added against a stream of nitrogen. The flask was sealed with a septum and flushed with nitrogen. The flask was sealed with a septum and flushed with nitrogen. Samples were periodically taken by syringe for GC analysis.

Partition Coefficients. The following is representative. A 10 mL vial was charged with the 2a (0.0104 g, 5.36 × 10$^{-3}$ mmol), CF$_3$C$_6$F$_{11}$ (2.000 mL) and toluene (2.000 mL), fitted with a mininert valve, and vigorously shaken (2 min). After 2 h (24 °C), aliquots were removed from the fluorous (0.700 mL) and non-fluorous (0.300 mL) phases. The solvents were evaporated and the residues dried by oil pump vacuum (1 h). Each residue was taken up in hexane (1.000 mL) and analyzed by HPLC (average of 5 injections, 200 × 4 mm Nucleosil 100-5 column, UV/visible detector). The relative peak intensities gave (after normalization to the aliquot volumes) the values in the text.

Figure 2s: Rate of Formation of 6 in Scheme 4 using catalyst 2b. Solvent systems: ○ CH₂Cl₂/CF₃-C₆F₁₁ (4 mL/2 mL); ■ CH₂Cl₂ only (4 mL)

Figure 3s: Rate of Formation of 6 in Scheme 4 using catalyst 2a. Solvent systems: ○ CH₂Cl₂/CF₃-C₆F₁₁ (4 mL/2 mL); ■ CH₂Cl₂ only (4 mL)
Figure 4s: Rate of Formation of $\mathbf{8}$ in Scheme 4. Solvent systems: ● CH$_2$Cl$_2$/Perfluoro(2-butyltetrahydrofuran) (2 mL/1 mL); ▣ CH$_2$Cl$_2$ only (2 mL). The second trace is reproducible.

Figure 5s: Rate of Formation of $\mathbf{8}$ in Scheme 4, but using Grubbs’ Second Generation Catalyst ($(\text{H}_2\text{IMes})(\text{Cy}_3\text{P})(\text{Cl})_2\text{Ru}(-\text{CHPh})$. Solvent systems: ● CH$_2$Cl$_2$/Perfluoro(2-butyltetrahydrofuran (2 mL/1 mL); ▣ CH$_2$Cl$_2$ only (2 mL)
Figure 6s: Rate of Formation of 4 in Scheme 4, but using Grubbs’ Second Generation Catalyst \((\text{H}_2\text{IMes})(\text{Cy}_3\text{P})(\text{Cl})_2\text{Ru}(=\text{CHPh})\). Solvent systems: ○ \(\text{CH}_2\text{Cl}_2/\text{CF}_3\text{C}_6\text{F}_{11}\) (4 mL/2 mL); ■ \(\text{CH}_2\text{Cl}_2\) only (4 mL)

Figure 7s: Rate of Formation of 4 in Scheme 4, but using Grubbs’ Second Generation Catalyst \((\text{H}_2\text{IMes})(\text{Cy}_3\text{P})(\text{Cl})_2\text{Ru}(=\text{CHPh})\). Solvent systems: ■ \(\text{CH}_2\text{Cl}_2/\text{Perfluoro}(2\text{-butyl-tetrahydrofuran})\) (4 mL/2 mL); ■ \(\text{CH}_2\text{Cl}_2\) only (4 mL)