

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 N₂ unless noted. Chemicals were treated as follows: Diethyl ether, toluene, hexanes, distilled from Na/benzophenone; CF₃C₆F₁₁ (Oakwood or ABCR), distilled from P₂O₅; CF₃C₆H₅ (ABCR), distilled from CaH₂; diallyl diethyl malonate (ABCR), tridecane (Aldrich), perfluoro-2-butyl-tetrahydrofuran (Apollo), C₆F₁₄ (Fluorochem), CDCl₃ (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 CHDCl₂ (¹H, δ 5.32) or CD₂Cl₂ (¹³C, δ 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 μm; 25 m × 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.¹ Elemental analyses were conducted with a Carlo Erba EA1110 instrument.

(H₂IMes)((R_{f6}CH₂CH₂)₃P)(Cl)₂Ru(=CHPh) (2a). A Schlenk flask was charged with (H₂-IMes)(Py)₂(Cl)₂Ru(=CHPh) (**1a**;² 0.0924 g, 0.127 mmol), P(CH₂CH₂R_{f6})₃ (**a**;³ 0.1524 g, 0.142 mmol), and CF₃C₆H₅ (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 × 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 C₅₈H₄₄Cl₂F₅₁N₂PRu (1641.2): C 38.03, H 2.68, N 1.71; found C 37.85, H 2.83, N 1.67.

¹H NMR (400.1 MHz, CD₂Cl₂): δ 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, NCH₂CH₂N), 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(CH₂)₂); ¹³C{¹H} NMR (100.5 MHz, CD₂Cl₂, partial): δ 217.8 (d, J = 90.2 Hz, Ru-C(N)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, $\underline{\text{C}}\text{H}_2\text{CF}_2$); $^{31}\text{P}\{^1\text{H}\}$ NMR (161.9 MHz, CD_2Cl_2): δ 19.96 (s); ^{19}F NMR (282.4 MHz, CD_2Cl_2 , partial): δ -81.64 (t, $J = 9.3$, CF_3). MS (FAB, 3-NBA, m/z (%)): 1640 (5) $[\text{M}]^+$, 1605 (2.5) $[\text{M} - \text{Cl}]^+$, 1073 (2.5) $[\text{P}(\text{CH}_2\text{CH}_2\text{R}_{f6})_3 + \text{H}]^+$.

(H₂IMes)((R_{f8}CH₂CH₂)₃P)(Cl)₂Ru(=CHPh) (2b). Complex **1a** (0.1201 g, 0.165 mmol), $\text{P}(\text{CH}_2\text{CH}_2\text{R}_{f8})_3$ (**b**; ³ 0.1524 g, 0.142 mmol), and $\text{CF}_3\text{C}_6\text{H}_5$ (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: $T_i/T_e/T_p/T_c/T_f$ 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 (T_e). Calcd (%) for $\text{C}_{58}\text{H}_{44}\text{Cl}_2\text{F}_{51}\text{N}_2\text{PRu}$ (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, CD_2Cl_2): 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, $\text{NCH}_2\text{CH}_2\text{N}$), 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 $\text{P}(\underline{\text{C}}\text{H}_2)_2$); $^{13}\text{C}\{^1\text{H}\}$ NMR (100.5 MHz, CD_2Cl_2): δ 218.4 (d, $J = 90.5$ Hz, Ru-C(N)₂), 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, $\underline{\text{C}}\text{H}_2\text{CF}_2$); $^{31}\text{P}\{^1\text{H}\}$ NMR (161.9 MHz, CH_2Cl_2): δ 20.17 (s); ^{19}F NMR (282.4 MHz, CD_2Cl_2 , partial): δ -81.74 (t, $J = 10.0$ Hz, CF_3). MS (FAB, 2-nitrophenyl octyl ether, m/z (%)): 1982 (30) $[\text{M}]^+$, 1905 (10) $[\text{M} - \text{Cl}]^+$, 1415 (40) $[\text{P}(\text{CH}_2\text{CH}_2\text{CH}_2\text{R}_{f8})_3 + \text{H}]^+$, 568 (60) $[\text{M}^+ - \text{P}(\text{CH}_2\text{CH}_2\text{R}_{f8})_3]$, 532 (50) $[\text{M}^+ - \text{P}(\text{CH}_2\text{CH}_2\text{R}_{f8})_3 - \text{Cl}]$.

(H₂IMes)((R_{f10}CH₂CH₂)₃P)(Cl)₂Ru(=CHPh) (2c). Complex **1a** (0.0800 g, 0.110 mmol), $\text{P}(\text{CH}_2\text{CH}_2\text{R}_{f10})_3$ (**c**; ³ 0.1840 g, 0.110 mmol), and $\text{CF}_3\text{C}_6\text{H}_5$ (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: $T_i/T_e/T_p/T_c/T_f$ 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 (T_e). Calcd (%) for $\text{C}_{64}\text{H}_{44}\text{Cl}_2\text{F}_{63}\text{N}_2\text{PRu}$ (2240.2): C 34.28, H 1.96, N 1.25; found C 34.31, H 2.00, N 1.21.

^1H NMR (400 MHz, CD_2Cl_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, $\text{NCH}_2\text{CH}_2\text{N}$), 2.62 (s, 6H), 2.30 (s, 3H), 2.26 (s, 6H), 1.96 (s, 3H), 1.82-1.70 (br m, 12H, $\text{P}(\text{CH}_2)_2$); $^{31}\text{P}\{^1\text{H}\}$ NMR (161.8 MHz, CH_2Cl_2): δ 20.24 (s); ^{19}F NMR (282.4 MHz, CD_2Cl_2 , partial): δ -81.80 (t, $J = 10.0$ Hz, CF_3). MS (FAB, 3-NBA, m/z (%)): 2240 (28) $[\text{M}]^+$, 2204 (12) $[\text{M} - \text{Cl}]^+$, 1673 (17) $[\text{P}(\text{CH}_2\text{CH}_2\text{R}_{\text{f}10})_3 + \text{H}]$, 568 (32) $[\text{M}^+ - \text{P}(\text{CH}_2\text{CH}_2\text{R}_{\text{f}10})_3]$, 532 (55) $[\text{M}^+ - \text{P}(\text{CH}_2\text{CH}_2\text{R}_{\text{f}10})_3 - \text{Cl}]$.

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_2Cl_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. 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), $\text{CF}_3\text{C}_6\text{F}_{11}$ (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 fluororous (0.700 mL) and non-fluororous (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.

(1) Cammenga, H. K.; Epple, M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1171; *Angew. Chem.* **1995**, *107*, 1284.

(2) Trnka, M. S.; Morgan, J. P.; Sanford, M. S.; Wilhelm, T. E.; Scholl, M.; Choi, T.-L.; Ding, S.; Day, M. W.; Grubbs, R. H. *J. Am. Chem. Soc.* **2003**, *125*, 2546.

(3) Alvey, L. J.; Rutherford, D.; Juliette, J. J. J.; Gladysz, J. A. *J. Org. Chem.* **1998**, *63*, 6302.

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)

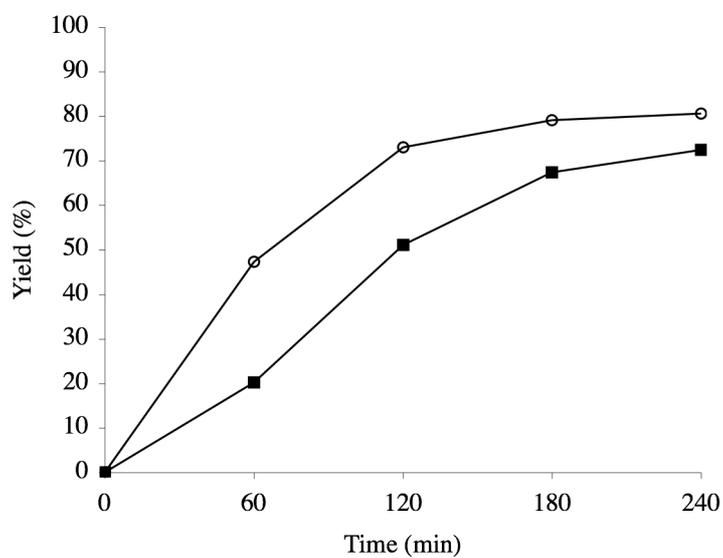


Figure 3s: Rate of Formation of **6** in Scheme 4 using catalyst **2a**. Solvent systems: ○ CH₂Cl₂/CF₃-C₆F₁₁ (4 mL/2 mL); ■ CH₂Cl₂ only (4 mL)

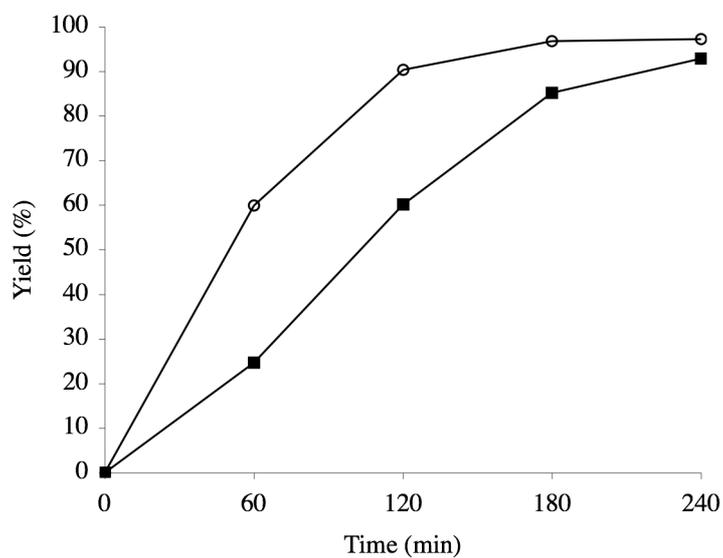


Figure 4s: Rate of Formation of **8** in Scheme 4. Solvent systems: ◆ CH₂Cl₂/Perfluoro(2-butyltetrahydrofuran) (2 mL/1 mL); ■ CH₂Cl₂ only (2 mL). The second trace is reproducible.

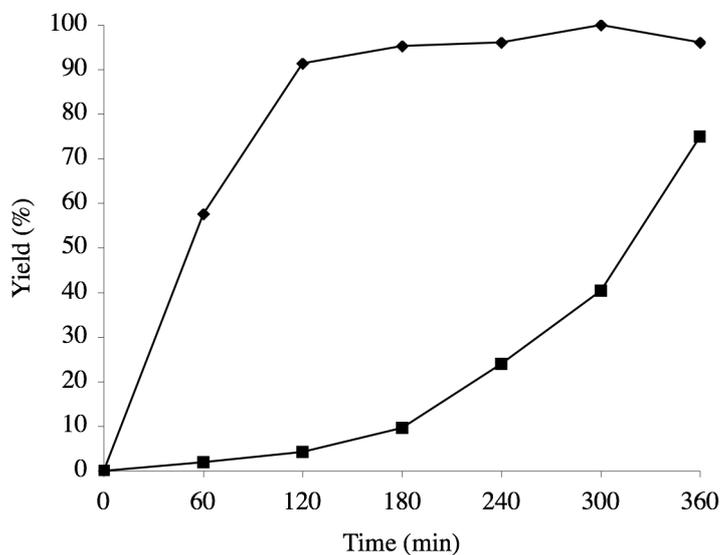


Figure 5s: Rate of Formation of **8** in Scheme 4, but using Grubbs' Second Generation Catalyst ((H₂IMes)(Cy₃P)(Cl)₂Ru(=CHPh)). Solvent systems: ◆ CH₂Cl₂/Perfluoro(2-butyltetrahydrofuran) (2 mL/1 mL); ■ CH₂Cl₂ only (2 mL)

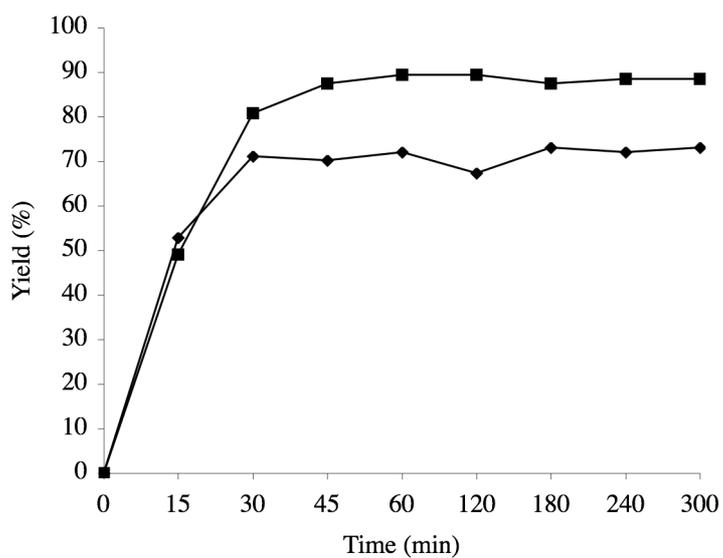


Figure 6s: Rate of Formation of **4** in Scheme 4, but using Grubbs' Second Generation Catalyst $(H_2IMes)(Cy_3P)(Cl)_2Ru(=CHPh)$. Solvent systems: \circ $CH_2Cl_2/CF_3C_6F_{11}$ (4 mL/2 mL); \blacksquare CH_2Cl_2 only (4 mL)

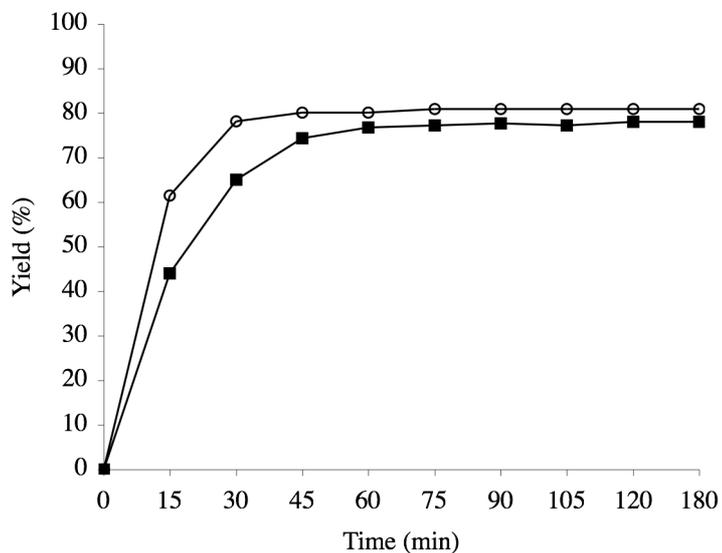


Figure 7s: Rate of Formation of **4** in Scheme 4, but using Grubbs' Second Generation Catalyst $(H_2IMes)(Cy_3P)(Cl)_2Ru(=CHPh)$. Solvent systems: \blacklozenge $CH_2Cl_2/Perfluoro(2-butyl-tetrahydrofuran)$ (4 mL/2 mL); \blacksquare CH_2Cl_2 only (4 mL)

