Supporting Information

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Mechanism-based Design of a ROMP Catalyst for Sequence-Selective Copolymerization

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1 Supporting information

1.1 General remarks

Unless otherwise stated, all manipulations were carried out under an argon atmosphere on a vacuum line using standard Schlenk techniques. The solvents were dried by distillation from the following drying agents prior to use and were transferred under N\textsubscript{2}: diethyl ether (Na/K), n-hexane (Na/K), THF (K), CH\textsubscript{2}Cl\textsubscript{2} (CaH\textsubscript{2}), ethanol (Mg), methanol (Mg). Flash chromatography: Fluka silica gel 60, type 60752 (230–400 mesh). TLC: Merck silica gel 60 254 plates; visualization by UV\textsubscript{254} light. ESI-MS measurements: Finnigan MAT LCQ MS. NMR: Varian Mercury XL 300 (\textsuperscript{1}H: 300 MHz, \textsuperscript{13}C: 75 MHz, \textsuperscript{31}P: 121 MHz) spectrometer, chemical shifts (\(\delta\) values) are reported in ppm with respect to Me\textsubscript{4}Si (\(\delta = 0\) ppm) used as an internal standard for \textsuperscript{13}C and \textsuperscript{1}H NMR and a to 85% aqueous H\textsubscript{3}PO\textsubscript{4} solution used as an external standard for \textsuperscript{31}P NMR, respectively; coupling constants (\(J\)) are given in Hz. \textsuperscript{13}C NMR and \textsuperscript{31}P NMR spectra were proton broad-band-decoupled. The multiplicities of peaks are denoted by the following abbreviations: s: singlet, d: doublet, t: triplet, m: multiplet, br: broad. Elemental analysis: performed by the Microanalytical Laboratory of the Laboratorium für Organische Chemie, ETH–Zürich.

1.2 Ligand synthesis

\textit{t-Butylphenylchlorophosphine:} A 0.95 M \textit{t-BuMgCl} solution in Et\textsubscript{2}O was prepared by addition of 60 g (652 mmol) \textit{t-BuCl} to a suspension of 23.8 g (978 mmol) magnesium turnings in 400 ml Et\textsubscript{2}O. The suspension was stirred for 2 h at room temperature, filtered and titrated. To a solution of 33 g (188 mmol) phenyl dichlorophosphine in 100 ml Et\textsubscript{2}O at -50°C 200 ml (188 mmol) of the 0.95 M \textit{t-BuMgCl} solution were added during 1 h under vigorous stirring. The formed
grey white suspension was allowed to reach room temperature during 2 additional hours of stirring. Filtration, evaporation of the solvent and distillation under reduced pressure at 44-52°C and 1*10^-2 mbar yielded 28.8 g (144 mmol, 77%) of t-butylphenylchlorophosphine as colourless liquid. 1H-NMR (300 MHz, CD2Cl2): δ = 7.70-7.64 (m, 2H, Ph(m-H)), 7.47-7.40 (m, 3H, Ph(o-p-H), 1.06 (d, 3JH,P = 13.8 Hz, CH3). 13C-NMR (75 MHz, CD2Cl2): δ = 135.9 (d, 1JC,P = 40.3 Hz, Ph(i-C)), 132.2 (d, 2JC,P = 25.1 Hz, Ph(o-C)), 130.6 (s, Ph(m-C)), 128.3 (d, 4JC,P = 8.6 Hz, Ph(p-C)), 34.4 (d, 1JC,P = 30.0 Hz, (C(CH3)3), 25.2 (d, 2JC,P = 17.7 Hz, (CH3). 31P-NMR (125 MHz, CD2Cl2): δ = 109.1.

t-Butyl-(o-methoxyphenyl)phenylphosphine: 3.11 ml (25 mmol) 2-bromoanisole were dissolved in 40 ml of Et2O and stirred at 0°C under argon. 16.45 ml of a 1.52 M n-BuLi solution in hexane were added dropwise during 30 min. After 2 h 5 g (25 mmol) of t-butylphenylchlorophosphine were added dropwise to the suspension at 0°C. The cooling bath was removed and the reaction mixture was allowed to reach room temperature. After 2 h stirring the suspension was filtered and the solvent was removed under vacuum. An oily yellowish residue was left which was distilled under high vacuum in a kugelrohr oven. At 160°C and 8*10^-2 mbar 6.15 g (22.6 mmol, 90%) of t-butyl-(o-methoxyphenyl)phenylphosphine as a colourless oil could be isolated. 1H-NMR (300 MHz, CD2Cl2): δ = 7.57-7.46 (m, 3H, PhH), 7.39-7.31 (m, 4H, PhH), 7.00-6.90 (m, 2H, PhH), 3.73 (s, 3H, OCH3), 1.25 (d, 3JH,P = 12.60 Hz, 9H, CCH3). 13C-NMR (75 MHz, CD2Cl2): δ = 162.3 (d, 2JC,P = 15.32 Hz, oMeOPh(C(2))), 138.4 (d, 2JC,P = 19.54 Hz, oMeOPh(C(6))), 135.1 (d, 1JC,P = 2.49 Hz, Ph(C(1))), 134.7 (d, 2JC,P = 20.15 Hz, Ph(C(2))), 130.3 (s, oMeOPh(C(4))), 128.3 (s, Ph(C(4))), 128.1 (d, 3JC,P = 6.72 Hz, Ph(C(3))), 126.0 (d, 1JC,P = 22.56 Hz, oMeOPh(C(1))), 120.7 (s, oMeOPh(C(5))), 111.2 (s, oMeOPh(C(3))), 55.7 (s, OCH3), 30.8 (d, 1JC,P = 15.92 Hz, PC(CH3)3), 29.1 (d, 2JC,P = 15.24 Hz, PC(CH3)3). 31P-NMR (125 MHz, CD2Cl2): δ = 4.13. elemental analysis calcd (%) for C17H23OP (272.33 g/mol): C 74.98, H 7.77, O 5.88, P 11.37, found: C 75.00, H 7.82, O 5.76, P 11.42.

2-[t-Butyl(phenyl)phosphoryl]phenol: To a solution of 2.18 g (8 mmol) t-butyl-(o-methoxyphenyl)phenylphosphine in 20 ml of dry CH2Cl2 at -78°C was added 18.4 ml (18.4 mmol, 2.3 eq) of a 1 M solution of BBr3 in CH2Cl2 during 10 min under argon. The brown mixture was stirred and allowed to warm to room temperature for 14 h. The resulting solution was evaporated to dryness and 40 ml of dry MeOH were added. The solution was stirred and heated to reflux for 3 h. The solution was again evaporated and 40 ml of dry Et2O and 4 ml of absolute NET3 were added and the resulting mixture was stirred for 2 h at room temperature. All volatiles were evaporated and the residue was distilled under vacuum (175°C, 2*10^-2 mbar) to yield 1.15 g (4.46 mmol, 56%) of a colourless oil which became a colourless solid at room temperature and was identified as 2-[t-Butyl(phenyl)phosphoryl]phenol. 1H-NMR (300 MHz, CDCl3): δ = 7.62-7.51 (m, 3H, PhH), 7.37-7.31 (m, 5H, PhH& OHH), 7.03-6.92 (m, 2H,
Sodium-2-[t-butyl(phenyl)phosphanylidene]phenolate: 7.4 mg (0.31 mmol) of NaH were suspended in 6 ml of dry THF and at -30 °C a solution of 80 mg (0.31 mmol) 2-[t-butyl(phenyl)phosphanylidene]phenol in 10 ml dry THF was added under argon. Immediately the formation of bubbles indicates that the reaction takes place. The suspension was allowed to warm to room temperature and was stirred for totally 2 h. The solids were allowed to deposit and the supernatant was transferred via cannula filtration into an argon filled flask. The solvent was evaporated and a colourless oily substance was obtained which was left on high vacuum for several hours to solidify. 77 mg (0.275 mmol, 89%) of sodium-2-[t-butyl(phenyl)phosphanylidene]phenolate were obtained as a colourless solid. 

![$^1$H-NMR (300 MHz, CDCl$_3$): $\delta = 7.50-7.47$ (m, 1H), 7.26 (t, $^3$J$_{H-H} = 5.4$ Hz, 1H, PhH), 7.16 (m, 1H), 7.15-7.01 (m, 4H), 6.50 (t, $^3$J$_{H-H} = 7.20$ Hz, 1H), 6.12 (t, $^3$J$_{H-H} = 7.05$ Hz, 1H), 1.07 (d, $^3$J$_{H-H} = 12.30$ Hz, 9H, t-BuH).

![$^{13}$C-NMR (75 MHz, CDCl$_3$): $\delta = 172.3$ (d, $^3$J$_{C,P} = 17.14$ Hz, 1H, PhP), 131.6 (s, C(6)), 121.1 (s, C(5)), 127.9 (s, PhC(4)), 127.8 (d, $^3$J$_{C,P} = 4.30$ Hz, PhC(3)), 136.6 (d, $^3$J$_{C,P} = 12.22$ Hz, C(3)), 134.2 (s, PhC(1)), 133.8 (d, $^3$J$_{C,P} = 16.45$ Hz, PhC(2)), 130.6 (s, C(5)), 112.4 (s, C(6)), 30.0 (d, $^3$J$_{C,P} = 8.53$ Hz, PC(CH$_3$)$_3$), 28.6 (d, $^3$J$_{C,P} = 12.83$ Hz, PC(CH$_3$)$_3$).

Di-t-butyl-o-methoxyphenylphosphine: 1.07 ml (8.60 mmol) 2-bromoanisole were dissolved in 20 ml of Et$_2$O and stirred at 0 °C under argon. 7.00 ml of a 1.23 M n-BuLi solution in hexane were added dropwise during 30 min. After 2 h 1.55 g (8.60 mmol) of di-t-butylchlorophosphine were added dropwise to the suspension at 0 °C. The cooling bath was removed and the reaction mixture was allowed to reach room temperature. After 2 h stirring the suspension was filtered and the solvent was removed under vacuum. An oily brown residue was left which was distilled under high vacuum in a kugelrohr oven. At 160 °C and 8*10$^{-2}$ mbar 1.83 g (7.3 mmol, 85%) of di-t-butyl-o-methoxyphenylphosphine as a colourless oil could be isolated. 

![$^1$H-NMR (300 MHz, CD$_2$Cl$_2$): $\delta = 7.66-7.57$ (m, 1H, PhH), 7.36 (m, 1H, PhH), 6.94-6.87 (m, 2H, PhH), 3.79 (s, 3H, OCH$_3$), 1.18 (d, $^3$J$_{H,P} = 11.40$ Hz, 18H, CCH$_3$).

![$^{13}$C-NMR (75 MHz, CD$_2$Cl$_2$): $\delta = 142.9, 142.2, 136.3, 131.3, 130.5, 120.2, 119.9, 111.4, 110.6, 55.9, 32.8, 32.5, 32.2, 30.8, 30.6. (Due to coexistence of two conformers at room temperature the peaks are not assigned. For interpretation see literature: H. David Empsall, Bernard L. Shaw and Brian L. Turtle in J.C.S. Dalton, 1976, 1500-1506.)

![$^{31}$P-NMR (125 MHz, CD$_2$Cl$_2$): $\delta = 55.7$ (s, 37%, conf 2), 10.5 (s, 63% conf 1).
2-[Di-t-butylphosphanyl]phenol: To a solution of 1.0 g (3.97 mmol) di-t-butyl-o-methoxyphenylphosphine in 10 ml of dry CH₂Cl₂ at -78°C was added 0.86 ml (9.10 mmol, 2.3 eq) of BBr₃ under argon during 10 min. The brown mixture was allowed to warm to room temperature and stirred for 14 h. The resulting solution was evaporated to dryness and 10 ml of dry MeOH were added. The solution was stirred and heated to reflux for 5 h. The solution was again evaporated and 20 ml of dry Et₂O with 1 ml of absolute NEt₃ were added and the resulting mixture was stirred for 1 h at room temperature. All volatiles were evaporated and the residue was distilled under vacuum (200°C, 4*10⁻¹ mbar) to yield 640 mg (2.69 mmol, 68%) of a colourless oil which crystallised at room temperature and was identified as 2-[di-t-butylphosphanyl]phenol. ¹H-NMR (300 MHz, CD₂Cl₂): δ = 7.59-7.53 (m, 1H, PhH), 7.31-7.25 (m, 1H, PhH), 6.97-6.91 (m, 1H, PhH), 6.91-6.84 (m, 1H, PhH), 1.22 (d, 3J_H,P = 12.90 Hz, 18H, CCH₃). ¹³C-NMR (75 MHz, CD₂Cl₂): δ = 162.4 (d, 2J_C,P = 20.70 Hz, C(1)), 134.4 (s, C(3)), 131.3 (s, C(5)), 119.4 (s, C(2)), 119.2 (s, C(4)), 114.8 (s, C(6)), 32.4 (d, 1J_C,P = 13.43 Hz, PCCH₃). ³¹P-NMR (125 MHz, CD₂Cl₂): δ = -5.7.

Sodium-2-[di-t-butylphosphanyl]phenolate: 500 mg (2.10 mmol) of 2-[di-t-butylphosphanyl]phenol were dissolved in 2.5 ml of dry ethanol and at 0°C a solution of 48 mg (2.10 mmol) sodium in 1.00 ml dry ethanol was added under argon. The solution was allowed to warm to room temperature and stirred for 2 h. The solvent was removed and a colourless foam was obtained which was left on high vacuum for several hours. 520 mg (2.00 mmol, 95%) of sodium-2-[di-t-butylphosphanyl]phenolate were obtained as a colourless solid. ¹H-NMR (300 MHz, CD₂Cl₂): δ = 7.47-7.45 (m, 1H, PhH), 7.08 (t, 1H, ³J_H,P = 7.65 Hz, PhH), 6.71 (t, ³J_H,H = 7.20 Hz, 1H, PhH), 6.53 (t, ³J_H,H = 7.20 Hz, 1H, PhH), 1.14 (d, ³J_H,P = 12.60 Hz, 18H, t-BuH). ¹³C-NMR (75 MHz, CD₂Cl₂): δ = 170.8 (d, ²J_C,P = x Hz, C(1)), 136.1 (s, C(3)), 131.4 (s, C(5)), 121.2 (s, C(2)), 118.6 (s, C(4)), 114.5 (s, C(6)), 32.5 (d, 1J_C,P = 12.83 Hz, PCCH₃), 30.7 (d, ²J_C,P = 13.43 Hz, PC(CH₃)). ³¹P-NMR (125 MHz, CD₂Cl₂): δ = 4.6.

1.3 Complex synthesis

Ruthenium complex 3 A solution of 64 mg (229 mmol) sodium-2-[t-butyl-(phenyl)phosphanyl]phenolate in 2 ml of CH₂Cl₂ was added at room temperature over 15 min to a solution of 180 mg (219 mmol) Grubbs’ 1ˢᵗ generation metathesis catalyst, 2 in 10 ml CH₂Cl₂. 1 g silicagel was added to the reaction mixture and the mixture was evaporated to dryness. The resulting red brown powder was transferred under careful exclusion of oxygen to a silicagel column and eluted with hexane/Et₂O 96:4 as a solvent. The red brown fraction was collected and dried under high vacuum. 73 mg (96 mmol, 44%) of complex 3 were isolated as a red brown foam. The complex is moderately air stable as a solid but decomposing within one day if left in solution. ¹H-NMR (300 MHz, CD₂Cl₂): δ = 19.52 (s, 1H, Ru=C), 8.25 (d, 1H), 7.96-7.91 (m, 2H), 7.60 (m, 1H), 7.51 (m, 1H), 7.40 (m, 3H), 7.25 (m, 2H), 7.19-7.10 (m, 2H), 6.90 (m, 1H), 6.89 (m, 1H), 6.83 (m, 1H), 6.70 (m, 1H), 6.58 (m, 1H).
5.75 (m, 1H), 2.39 (d, 3H), 1.80-1.41 (m, 12H), 1.27-0.84 (m, 18H) 1.04 (d, 9H).

$^{31}$P-NMR (125 MHz, CD$_2$Cl$_2$): $\delta = 65.33$ (d, 1P, $^2J_{P,P} = 194$ Hz, P-O ligand), 42.19 (d, $^2J_{P,P} = 196$ Hz, PCy$_3$). MS (ESI, CH$_2$Cl$_2$): $m/z$: 763 [M-H$^-$]+.

Ruthenium complex 4 A solution of 50 mg (0.192 mmol, 1.2 eq) sodium-2-[di-t-butylyphosphanyl]phenolate in 1 ml of CH$_2$Cl$_2$ was added at room temperature to a solution of 132 mg (0.160 mmol) Grubbs’ 1st generation metathesis catalyst, 2 in 1 ml CH$_2$Cl$_2$. 1 g silicagel was added to the reaction mixture and the mixture was evaporated to dryness. The resulting red brown powder was transferred under careful exclusion of oxygen to a silicagel column packed with 5 g of dry and oxygen free silicagel and eluted with hexane/Et$_2$O 96:4 as a solvent. The purple fraction was collected and dried under high vacuum. 96 mg (0.129 mmol, 81%) of complex 4 were isolated as a purple solid. The complex is air stable as a solid but decomposing within one day if left in solution. $^1$H-NMR (300 MHz, CD$_2$Cl$_2$): $\delta = 19.69$ (d, $^2J_{H,P} = 2.40$ Hz, 1H, Ru=C), 8.23 (d, $^3J_{H,H} = 7.50$ Hz, 2H), 7.52 (t, $^3J_{H,H} = 7.35$ Hz, 1H), 7.40 (t, $^3J_{H,H} = 6.75$ Hz, 1H), 7.25 (t, $^3J_{H,H} = 7.20$ Hz, 2H), 7.08 (t, $^3J_{H,H} = 7.35$ Hz, 1H), 6.84 (m, 1H), 6.48 (t, $^3J_{H,H} = 7.35$ Hz, 1H), 2.46-2.12 (m, 3H, PCy), 1.80-1.60 (m, 15H, PCy), 1.54 (d, $^3J_{H,P} = 13.50$ Hz, 9H, CH$_3$), 133-1.22 (m, 15H, PCy), 1.03 (d, $^3J_{H,P} = 13.20$ Hz, 9H, CH$_3$)$_3$. $^{31}$P-NMR (125 MHz, CD$_2$Cl$_2$): $\delta = 70.49$ (d, 1P, $^2J_{P,P} = 200$ Hz, P-O ligand), 37.12 (d, $^2J_{P,P} = 200$ Hz, PCy$_3$). MS (ESI, CH$_2$Cl$_2$): $m/z$: 743 [M-H$^-$]+.

1.4 Polymerisation experiments:

In a typical polymerisation experiment a solution of 1 g monomeric cycloalkenes in 15 ml of solvent, either CH$_2$Cl$_2$ or neat cyclooctene was treated with 4 mg (0.05%) of the catalyst dissolved in 1 ml of CH$_2$Cl$_2$. The mixture was stirred at room temperature for 1 to 17 h and the resulting polymer solution was poured into 100 ml of MeOH acidified with 1% of HCl. After 1 h the coagulated polymer was filtered, washed with MeOH and dried by high vacuum at 10$^{-2}$ mbar. 30 mg of the polymer were dissolved in 0.7 ml of CDCl$_3$ and the distribution of the bonds was determined by $^{13}$C-NMR. The transversal relaxation time $t_2$ was set to 5 seconds to allow integration of the characteristic olefinic $^{13}$C signals.