Mechanistically Designed Dual-Site Catalysts for the Alternating ROMP of Norbornene and Cyclooctene

Marc Bornand, Sebastian Torker, and Peter Chen*

Laboratorium für Organische Chemie, ETH Zürich, Switzerland

Received April 18, 2007

Mechanistic work on the olefin metathesis reaction by well-characterized ruthenium carbene complexes led to the rational design and synthesis of a modified, unsymmetrical "first-generation" catalyst, which, in contrast to either first- or second-generation systems with symmetrical ligands, converts a mixture of two cycloolefin monomers to a largely alternating copolymer. The mechanistic concept of a homogeneous catalyst that switches between more than one state at each turnover is general. The structures of the complexes, determined by mass spectrometry, NMR, and X-ray crystallography, reveal some unexpected features, which explain sequence errors in the copolymer.

Introduction

Beyond the gross formation of new chemical bonds, progress in the methodology of organic synthesis has moved up a hierarchy of selectivities: first chemoselectivity, then regioselectivity, and finally stereoselectivity. Progress in the methodology of coordination polymerization by transition metal catalysts currently focuses on finding new reactivity, with selectivity issues entering in a curiously chronologically inverted order. Stereoselectivity in homopolymerizations, or more specifically, the control of tacticity in polypropylene, has been the arena of great effort starting with catalysts by Natta[1] and continuing through the C_s- and C_2-symmetric metallocene catalysts.[2] The most basic selectivity, however, chemoselectivity in copolymerizations, is described by reactivity ratios,[3] which can be used to predict the composition of random or blocky copolymers produced from a mixture of monomers in the same pot, but there are very few instances where chemoselectivity in a copolymerization has been designed into a catalyst.[4,5] Given that biopolymers, inherently copolymers of a limited number of simple monomers, achieve many of their exemplary functional properties from structural control that derives from control of their primary sequence, it would be highly desirable to have the same kind of control in the production of synthetic copolymers produced by coordination polymerization. Seen from the context of organic synthesis, the challenge is to build chemoselective catalysts for the sequence-selective copolymerization of a mixture of monomers. In a preliminary communication,[6] we reported a sequence-selective ring-opening metathesis polymerization (ROMP) of norbornene and cyclooctene by a mechanistically designed ruthenium carbene complex. Further work on the catalyst for alternating copolymerization, related complexes, and the resulting polymer is described in the present report.

Experimental Section

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_2: diethyl ether (Na/K), *n*-hexane (Na/K), THF (K), CH_2Cl_2 (CaH_2), ethanol (Mg), methanol (Mg). Flash chromatography employed Fluka silica gel 60, type 60752 (230−400 mesh). TLC was done with Merck silica gel 60 F_{254} plates and visualized by UV_{254} light. Low-resolution ESI-MS measurements were done on a Finnigan MAT LCQ MS ion trap mass spectrometer, which were then used to set up high-resolution mass spectrometric measurements on a Finnigan MAT TSQ Quantum instrument with tetradodecylammonium bromide as an external standard for absolute mass calibration. NMR measurements are reported for a Varian Mercury XL 300 (^{1}H, 300 MHz; ^{13}C, 75 MHz; ^{31}P, 121 MHz) spectrometer. Chemical shifts (δ values) are reported in ppm with respect to Me_4Si ($\delta = 0$ ppm), used as an internal standard for ^{13}C and ^{1}H NMR, and an 85% aqueous H_3PO_4 solution, used as an external standard for ^{31}P NMR. Coupling constants (J) are given in Hz. ^{13}C NMR and ^{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 was performed by the Microanalytical Laboratory of the Laboratorium für Organische Chemie, ETH−Zürich. Gel permeation chromatography (GPC) was carried out with a Polymer Laboratories PL-GPC 220 fitted with a refractive index and viscometry detector using 1,3,5-trichlorobenzene at 140 °C and a polystyrene reference.

Ligand Syntheses. *tert*-Butylphenylchlorophosphine. A 0.95 M *t*-BuMgCl solution in Et_2O was prepared by addition of 60 g (652 mmol) of *t*-BuCl to a suspension of 23.8 g (978 mmol) of magnesium turnings in 400 mL of Et_2O. The suspension was stirred for 2 h at room temperature, filtered, and titrated. To a solution of 33 g (188 mmol) of phenyldichlorophosphine in 100 mL of Et_2O at −50 °C was added 200 mL (188 mmol) of the 0.95 M *t*-BuMgCl solution over 1 h with vigorous stirring. The formed gray-white suspension was allowed to reach room temperature over an additional 2 h of stirring. Filtration, evaporation of the solvent, and vacuum distillation at 44−52 °C and a pressure of 1×10^{-1} mbar yielded 28.8 g (144 mmol, 77%) of *tert*-butylphenylchlorophosphine as a colorless liquid.

* Corresponding author. Tel: +41-44-632-2898. Fax: +41-44-632-1280. E-mail: chen@org.chem.ethz.ch.

(1) Natta, G.; Pino, P.; Mantica, E.; Danusso, F.; Mazzanti, G.; Peraldo, M. *Chim. Ind. (Milan)* **1956**, *38*, 124.

(2) Brintzinger, H. H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. B. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143.

(3) Polic, A. L.; Duever, T. A.; Penlidis, A. *J. Polym. Sci. A* **1998**, *36*, 813−822.

(4) Drent, E.; van Broekhoven, J. A. M.; Doyle, M. J. *J. Organomet. Chem.* **1991**, *417*, 235.

(5) Darensbourg, D. J.; Holtcamp, M. W. *Coord. Chem. Rev.* **1996**, *153*, 155.

(6) Bornand, M.; Chen, P. *Angew. Chem., Int. Ed.* **2005**, *44*, 7909.

10.1021/om700321a CCC: $37.00
Publication on Web 06/09/2007

^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.70−7.64 (m, 2H, Ph(*m*-H), 7.47−7.40 (m, 3H, Ph(*o*-*p*-H), 1.06 (d, $^3J_{H,P}$ = 13.8 Hz, CH_3). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 135.9 (d, $^1J_{C,P}$ = 40.3 Hz, Ph(*i*-C)), 132.2 (d, $^2J_{C,P}$ = 25.1 Hz, Ph(*o*-C)), 130.6 (s, Ph(*m*-C)), 128.3 (d, $^4J_{C,P}$ = 8.6 Hz, Ph(*p*-C)), 34.4 (d, $^1J_{C,P}$ = 30.0 Hz, ($C(CH_3)_3$), 25.2 (d, $^2J_{C,P}$ = 17.7 Hz, CH_3). ^{31}P NMR (121 MHz, CD_2Cl_2): δ 109.1.

***tert*-Butyl-(*o*-methoxyphenyl)phenylphosphine.** A 3.11 mL (25 mmol) amount of 2-bromoanisole was dissolved in 40 mL of Et_2O and stirred at 0 °C under argon. Then 16.45 mL of a 1.52 M *n*-BuLi solution in hexane was added dropwise over 30 min. After 2 h, 5 g (25 mmol) of *tert*-butylphenylchlorophosphine was 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 a pressure of 8×10^{-2} mbar, the Kugelrohr distillation produced 6.15 g (22.6 mmol, 90%) of *tert*-butyl-(*o*-methoxyphenyl)phenylphosphine as a colorless oil.

^{1}H NMR (300 MHz, CD_2Cl_2): 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, OCH_3), 1.25 (d, $^3J_{H,P}$ = 12.60 Hz, 9H, CCH_3). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 162.3 (d, $^2J_{C,P}$ = 15.32 Hz, *o*-MeOPh(C(2))), 138.4 (d, $^2J_{C,P}$ = 19.54 Hz, *o*-MeOPh(C(6))), 135.1 (d, $^1J_{C,P}$ = 2.49 Hz, Ph(C(1))), 134.7 (d, $^2J_{C,P}$ = 20.15 Hz, Ph(C(2))), 130.3 (s, *o*-MeOPh(C(4))), 128.3 (s, Ph(C(4))), 128.1 (d, $^3J_{C,P}$ = 6.72 Hz, Ph(C(3))), 126.0 (d, $^1J_{C,P}$ = 22.56 Hz, *o*-MeOPh(C(1))), 120.7 (s, *o*-MeOPh(C(5))), 111.2 (s, *o*-MeOPh(C(3))), 55.7 (s, OCH_3), 30.8 (d, $^1J_{C,P}$ = 15.92 Hz, $PC(CH_3)_3$), 29.1 (d, $^2J_{C,P}$ = 15.24 Hz, $PC(CH_3)_3$). ^{31}P NMR (121 MHz, CD_2Cl_2): δ 4.13. Anal. Calcd (%) for $C_{17}H_{21}OP$ (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-[*tert*-Butyl(phenyl)phosphanyl]phenol. To a solution of 2.18 g (8 mmol) of *tert*-butyl-(*o*-methoxyphenyl)phenylphosphine in 20 mL of dry CH_2Cl_2 at −78 °C was added, under argon, 18.4 mL (18.4 mmol, 2.3 equiv) of a 1 M solution of BBr_3 in CH_2Cl_2 over 10 min. 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 was added. The solution was stirred and heated to reflux for 3 h. The solution was again evaporated, 40 mL of dry Et_2O and 4 mL of absolute NEt_3 were then 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 colorless oil, which solidified to a colorless solid at room temperature and could be identified as 2-[*tert*-butyl-(phenyl)phosphanyl]phenol.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.62−7.51 (m, 3H, PhH), 7.37−7.31 (m, 5H, PhH and OH), 7.03−6.92 (m, 2H, Ph(H), 1.24 (d, $^3J_{H,P}$ = 13.81 Hz, 9H, CCH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 160.7 (d, $^2J_{C,P}$ = 21.36 Hz, C(1)), 134.7 (s, C(3)), 134.3 (d, $^1J_{C,P}$ = 10.57 Hz, PhC(1)), 133.4 (d, $^2J_{C,P}$ = 17.14 Hz, PhC(2)), 131.6 (s, C(5)), 128.3 (s, PhC(4)), 128.1 (d, $^3J_{C,P}$ = 6.72 Hz, PhC(3)), 119.9 (s, C(4)), 119.0 (d, $^1J_{C,P}$ = 3.77 Hz, C(2)), 115.2 (s, C(6)), 31.4 (d, $^1J_{C,P}$ = 8.00 Hz, $PC(CH_3)_3$), 28.6 (d, $^2J_{C,P}$ = 13.44 Hz, $PC(CH_3)_3$). ^{31}P NMR (121 MHz, $CDCl_3$): δ −19.44. Anal. Calcd (%) for $C_{16}H_{19}OP$ (258.30 g/mol): C 74.40, H 7.41. Found: C 73.74, H 7.53.

Sodium 2-[*tert*-butyl(phenyl)phosphanyl]phenolate. A 7.4 mg (0.31 mmol) sample of NaH was suspended in 6 mL of dry THF, to which was added at −30 °C under argon a solution of 80 mg (0.31 mmol) of 2-[*tert*-butyl(phenyl)phosphanyl]phenol in 10 mL of dry THF. The immediate formation of bubbles indicates that the reaction takes place. The suspension was allowed to warm to room temperature and was stirred for 2 h. The solids were allowed to deposit, and the supernatant was transferred via canula filtration into an argon-filled flask. The solvent was evaporated, leaving a colorless, oily substance, which was left under high vacuum for several hours to solidify. A total of 77 mg (0.275 mmol, 89%) of sodium 2-[*tert*-butyl(phenyl)phosphanyl]phenolate was obtained as a colorless solid.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.50−7.47 (m, 1H), 7.26 (*t*, $^3J_{H,H}$ = 5.4 Hz, 1H, PhH), 7.16 (m, 1H), 7.15−7.01 (m, 4H), 6.50 (t, $^3J_{H,H}$ = 7.20 Hz, 1H), 6.12 (t, $^3J_{H,H}$ = 7.05 Hz, 1H), 1.07 (d, $^3J_{H,P}$ = 12.30 Hz, 9H, *t*-BuH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.3 (d, $^1J_{C,P}$ = 18.34 Hz, C(1)), 137.6 (d, $^1J_{C,P}$ = 12.22 Hz, C(3)), 134.2 (s, PhC(1)), 133.8 (d, $^1J_{C,P}$ = 16.45 Hz, PhC(2)), 130.6 (s, C(5)), 127.9 (s, PhC(4)), 127.8 (d, $^1J_{C,P}$ = 4.30 Hz, PhC(3)), 121.1 (s, C(4)), 119.2 (s, C(2)), 112.4 (s, C(6)), 30.0 (d, $^1J_{C,P}$ = 8.53 Hz, $PC(CH_3)_3$), 28.6 (d, $^1J_{C,P}$ = 12.83 Hz, $PC(CH_3)_3$). ^{31}P NMR (121 MHz, $CDCl_3$): δ −3.85.

Di-*tert*-butyl-*o*-methoxyphenylphosphine. A 1.07 mL (8.60 mmol) amount of 2-bromoanisole was dissolved in 20 mL of Et_2O and stirred at 0 °C under argon. Then 7.00 mL of a 1.23 M *n*-BuLi solution in hexane was added dropwise over 30 min. After 2 h, 1.55 g (8.60 mmol) of di-*tert*-butylchlorophosphine was 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-*tert*-butyl-*o*-methoxyphenylphosphine could be isolated as a colorless oil.

^{1}H NMR (300 MHz, CD_2Cl_2): δ 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, $^3J_{H,P}$ = 11.40 Hz, 18H, CCH_3). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 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. An interpretation has been given by Empsall et al.[7]) ^{31}P NMR (121 MHz, CD_2Cl_2): δ 55.7 (s, 37%, conf 2), 10.5 (s, 63% conf 1).

2-[Di-*tert*-butylphosphanyl]phenol. To a solution of 1.0 g (3.97 mmol) of di-*tert*-butyl-*o*-methoxyphenylphosphine in 10 mL of dry CH_2Cl_2 at −78 °C was added 0.86 mL (9.10 mmol, 2.3 equiv) of BBr_3 under argon over 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 was added. The solution was stirred and heated to reflux for 5 h. The solution was again evaporated, 20 mL of dry Et_2O with 1 mL of absolute NEt_3 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 colorless oil, which crystallized at room temperature and was identified as 2-[di-*tert*-butylphosphanyl]phenol.

^{1}H NMR (300 MHz, CD_2Cl_2): 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, Ph(H), 1.22 (d, $^3J_{H,P}$ = 12.90 Hz, 18H, CCH_3). ^{13}C NMR (75 MHz, CD_2Cl_2): 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, $PC(CH_3)_3$), 30.2 (d, $^2J_{C,P}$ = 13.36 Hz, $PC(CH_3)$). ^{31}P NMR (121 MHz, CD_2Cl_2): δ −5.7.

Sodium 2-[di-*tert*-butylphosphanyl]phenolate. A 500 mg (2.10 mmol) portion of 2-[di-*tert*-butylphosphanyl]phenol was dissolved in 2.5 mL of dry ethanol. A solution of 48 mg (2.10 mmol) of sodium in 1.00 mL of dry ethanol was then added at 0 °C under argon. The solution was allowed to warm to room temperature and stirred for 2 h. The solvent was removed, leaving a colorless foam, which was left under high vacuum for several hours. A total of 520 mg (2.00 mmol, 95%) of sodium 2-[di-*tert*-butylphosphanyl]-phenolate was obtained as a colorless solid.

(7) Empsall, H. D.; Shaw, B. L.; Turtle, B. L. *J. Chem. Soc., Dalton Trans.* **1976**, 1500.

^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.47−7.45 (m, 1H, PhH), 7.08 (t, 1H, $^3J_{H,H}$ = 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). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 170.8 (d, $^2J_{C,P}$ = 36.67 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, $PC(CH_3)_3$), 30.7 (d, $^2J_{C,P}$ = 13.43 Hz, $PC(CH_3)$). ^{31}P NMR (121 MHz, CD_2Cl_2): δ 4.6.

Cyclohexylphenylchlorophosphine. A 95 mL (75 mmol) amount of a 0.79 M cyclohexyl magnesium chloride solution in Et_2O was added over 45 min to a solution of 13.4 g (75 mmol) of phenyldichlorophosphine in 50 mL of dry Et_2O at −40 °C. The mixture was allowed to warm to room temperature and heated to reflux for 1.5 h. The formed gray-white precipitate was allowed settle. Filtration, evaporation of the solvent, and distillation in the Kugelrohr oven under reduced pressure at 130−160 °C and 1 × 10^{-2} mbar yielded 12.71 g (56 mmol, 75%) of cyclohexylphenylchlorophosphine as a colorless liquid, which solidified at 0 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.76−7.70 (m, 2H, Ph(*o*-H), 7.44−7.40 (m, 3H, Ph(*m*/*p*-H), 2.08−2.02 (m, 1H, Cy(*i*-H), 1.79−1.77 (m, 5H, Cy(*eq*-H), 1.29−1.09 (m, 5H, Cy(*ax*-H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 135.9 (d, $^2J_{C,P}$ = 38.4 Hz, Ph(*i*-C)), 132.5 (d, $^2J_{C,P}$ = 25.0 Hz, Ph(*o*-C)), 130.5 (s, Ph(*p*-C)), 128.4 (d, $^3J_{C,P}$ = 7.9 Hz, Ph(*m*-C)), 42.8 (d, $^1J_{C,P}$ = 29.9 Hz, Cy(*i*-C)), 28.2 (d, $^2J_{C,P}$ = 15.9 Hz, Cy(*o*-C)), 26.4 (d, $^3J_{C,P}$ = 11.0 Hz, Ph(*m*-C)), 26.0 (s, Cy(*p*-C)). ^{31}P NMR (121 MHz, $CDCl_3$): δ 92.05.

Cyclohexyl-(*o*-methoxyphenyl)phenylphosphine. A 1.87 mL (15 mmol) sample of 2-bromoanisole was dissolved in 40 mL of Et_2O and stirred at 0 °C under argon. Then 38.5 mL of a 0.38 M *n*-BuLi solution in hexane was added dropwise over 30 min. After 2 h, 3.39 g (15 mmol) of cyclohexylphenylchlorophosphine was 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 recrystallized from 40 mL of ethanol at −20 °C, yielding 2.52 g (8.45 mmol, 56%) of cyclohexyl(*o*-methoxyphenyl)phenylphosphine, which could be isolated as a colorless solid with a melting point of 70−71 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.51−7.45 (m, 2H, Ph(*o*-H), 7.37−7.27 (m, 5H, Ph(*m*/*p*-H + 2Cy(H)), 6.96 (d, t, $J_{H,H}$ = 0.90 Hz, $J_{H,H}$ = 7.81 Hz, 1H, Ph(H)), 6.84 (d,d,d, $J_{H,H}$ = 7.81 Hz, $J_{H,H}$ = 4.20 Hz, $J_{H,H}$ = 0.90 Hz, 1H, Ph(H)), 3.74 (s, 3H, OMe), 2.27 (br, s, 1H, Cy(*i*-H), 1.79−1.63 (m, 5H, Cy(*eq*-H), 1.36−1.26 (m, 5H, Cy(*ax*-H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 161.9 (d, $^2J_{C,P}$ = 12.8 Hz, COMe), 137.1 (d, $^1J_{C,P}$ = 19.8 Hz, Ph(*i*-C)), 133.7 (d, $^2J_{C,P}$ = 19.5 Hz, Ph(*o*-C)), 133.0 (d, $^2J_{C,P}$ = 5.5 Hz, An(*o*-C)), 130.0, (s, An(*p*-C)), 128.3 (s, Ph(*p*-C)), 128.0 (d, $^3J_{C,P}$ = 7.3 Hz, Ph(*m*-C)), 125.3 (d, $^1J_{C,P}$ = 15.9 Hz, An(*i*-C)), 55.5 (s, MeO), 34.6 (d, $^1J_{C,P}$ = 9.1 Hz, Cy(*i*-C)), 29.9 (d, $^2J_{C,P}$ = 16.5 Hz, Cy(*o*-C)), 29.6 (d, $^2J_{C,P}$ = 15.8 Hz, Cy(*o*-C)), 26.9 (d, $^3J_{C,P}$ = 11.6 Hz, Cy(*m*-C)), 26.4 (s, Cy(*p*-C)). ^{31}P NMR (121 MHz, $CDCl_3$): δ −16.31. Anal. Calcd (%) for $C_{19}H_{23}OP$ (298.36 g/mol): C 76.49, H 7.77, O 5.36, P 10.38. Found: C 76.53, H 7.91, O 5.25, P 10.39.

2-[Cyclohexyl(phenyl)phosphanyl]phenol. To a solution of 1.53 g (5.13 mmol) of cyclohexyl(*o*-methoxyphenyl)phosphine in 20 mL of dry CH_2Cl_2 was added, at −78 °C under argon, 12.0 mL (12.0 mmol, 2.3 equiv) of a 1 M BBr_3 solution in CH_2Cl_2 over 10 min. The brown mixture was allowed to warm to room temperature and stirred for 13 h. The resulting solution was evaporated to dryness, and 30 mL of dry MeOH was added. The solution was stirred and heated to reflux for 3 h. The solution was again evaporated, 40 mL of dry Et_2O with 4 mL of absolute NEt_3 was added, and the resulting mixture was stirred for 2 h at room temperature. All volatiles were evaporated, and the residue was dissolved in 30 mL of hexane. At −20 °C a colorless oil precipitated from the solution, which solidified after some hours to 1.12 g (3.95 mmol, 77%) of a colorless solid, which could be identified as 2-[cyclohexylphenylphosphanyl]phenol with a melting point of 85−86 °C.

^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.56−7.50 (m, 2H, Ph(*o*-H)), 7.38−7.31 (m, 4H, Ph(*m*/*p*-H)), 7.27 (d, t, $J_{H,H}$ = 1.80 Hz, $J_{H,H}$ = 7.80 Hz, 1H, Ph(H)), 6.95−6.87 (m, 1H, Ph(H)), 6.81 (br, s, 1H, OH), 2.41−2.30 (m, 1H, Cy(*i*-H)), 1.85−1.66 (m, 4H, Cy(*eq*-H)), 1.66−1.54 (m, 1H, Cy(*eq*-H)), 1.39−1.12 (m, 5H, Cy(*ax*-H)). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 160.5 (d, $^2J_{C,P}$ = 20.15 Hz, C(1)), 135.5 (d, $^1J_{C,P}$ = 6.72 Hz, PhC(1)), 133.6 (s, C(3)), 133.3 (d, $^2J_{C,P}$ = 5.51 Hz, PhC(2)), 131.5 (s, C(5)), 129.2 (s, PhC(4)), 128.9 (d, $^3J_{C,P}$ = 7.32 Hz, PhC(3)), 121.0 (s, C(4)), 120.8 (d, $^1J_{C,P}$ = 6.11 Hz, C(2)), 115.4 (s, C(6)), 35.2 (d, $^1J_{C,P}$ = 3.62 Hz, Cy(*i*-C)), 30.3 (d, $^2J_{C,P}$ = 17.05 Hz, Cy(*o*-C)), 29.3 (d, $^2J_{C,P}$ = 12.83 Hz, Cy(*o*-C)), 27.1 (s, Cy(*p*-C)), 26.8 (d, $^3J_{C,P}$ = 18.94 Hz, Cy(*m*-C)). ^{31}P NMR (121 MHz, CD_2Cl_2): δ −35.85. Anal. Calcd (%) for $C_{18}H_{21}OP$ (284.34 g/mol): C 76.04, H 7.44, O 5.63, 10.89. Found: C 75.89, H 7.42, O 5.71, P 10.78.

Sodium 2-[Cyclohexyl(phenyl)phosphanyl]phenolate. A 300 mg (1.06 mmol) portion of 2-[cyclohexyl(phenyl)phosphanyl]phenol was dissolved in 2.0 mL of dry methanol, to which was added under argon at 0 °C a solution of 25.5 mg (1.11 mmol, 1.05 equiv) of sodium in 2.00 mL of dry methanol. The solution was allowed to warm to room temperature and stirred for 2 h. The solvent was removed, and a colorless foam was obtained, which was left under high vacuum for several hours. A total of 321 mg (1.05 mmol, 99%) of sodium 2-[cyclohexyl(phenyl)phosphanyl]phenolate was obtained as a colorless solid.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.27−7.18 (m, 3H, Ph(*o*-H), 7.11 (t, $^3J_{H,H}$ = 7.30 Hz, 1H, NaOPhH), 6.98 (t, $^3J_{H,H}$ = 7.30 Hz, 3H, PhH + NaOPhH), 6.57 (t, $^3J_{H,H}$ = 7.30 Hz, 1H, NaOPhH), 6.16 (t, $^3J_{H,H}$ = 7.30 Hz, 1H, NaOPhH), 2.10−2.02 (m, 1H, Cy(*i*-H)), 1.92−1.78 (m, 1H, Cy(*eq*-H)), 1.73−1.56 (m, 3H, Cy(*eq*-H)), 1.46−1.31 (m, 1H, Cy(*eq*-H)), 1.31−1.10 (m, 5H, Cy(*ax*-H)). ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.1 (d, $^2J_{C,P}$ = 18.19 Hz, C(1)), 137.1 (d, $^1J_{C,P}$ = 7.93 Hz, PhC(1)), 133.5 (d, $^2J_{C,P}$ = 18.27 Hz, PhC(2)), 132.1 (s, C(3)), 130.6 (s, C(5)), 128.1 (s, PhC(4)), 128.0 (d, $^3J_{C,P}$ = 7.32 Hz, PhC(3)), 121.4 (d, $^3J_{C,P}$ = 4.30 Hz, C(4)), 118.5 (s, C(2)), 114.0 (s, C(6)), 34.6 (s, Cy(*i*-C)), 30.2 (d, $^2J_{C,P}$ = 15.85 Hz, Cy(*o*-C)), 29.7 (d, $^2J_{C,P}$ = 14.04 Hz, Cy(*o*-C)), 26.9 (d, $^3J_{C,P}$ = 11.63 Hz, Cy(*m*-C)), 26.5 (s, Cy(*p*-C)). ^{31}P NMR (121 MHz, $CDCl_3$): δ −24.51.

Dicyclohexyl(*o*-methoxyphenyl)phosphine. A 1.07 mL (8.60 mmol) amount of 2-bromoanisole was dissolved in 20 mL of Et_2O and stirred at 0 °C under argon. Then 7.00 mL of a 1.23 M *n*-BuLi solution in hexane was added dropwise over 30 min. After 2 h, 2.00 g (8.60 mmol) of dicyclohexylchlorophosphine was 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. A total of 2.90 g of an oily, orange residue was left, which was then dissolved in 15 mL of dry ethanol, to which addition of 3 mL of degassed water led to precipitation of a colorless solid. After drying under high vacuum, 2.25 g (7.40 mmol, 86%) of dicyclohexyl(*o*-methoxyphenyl)phosphine was isolated as a colorless solid with a melting point of 65−66 °C.

^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.39−7.31 (m, 2H, Ph−H), 6.93 (t, $^3J_{H,H}$ = 7.95 Hz, 1H, Ph-H), 6.86 (d,d, $^3J_{H,H}$ = 7.95 Hz, $^3J_{H,H}$ = 3.30 Hz, 1H, Ph-(H)), 3.79 (s, 3H, OCH_3), 2.01 (t, J = 11.85 Hz, 2H, CyH), 1.86 (d, 2H, CyH), 1.76 (d, J = 12.30 Hz, 2H, CyH), 1.64 (d, J = 9.60 Hz, 4H, CyH), 1.53 (d, J = 13.20 Hz, 2H, CyH), 1.39−1.07 (m, 8H, CyH), 1.02−0.89 (m, 2H, CyH). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 163.2 (d, $^2J_{C,P}$ = 9.13 Hz, PhC(2)), 135.8 (d, $^1J_{C,P}$ = 14.03 Hz, PhC(6)), 130.3 (s, PhC(4)), 123.7 (d, $^1J_{C,P}$ = 23.24 Hz, PhC(1)), 120.4 (d, $^2J_{C,P}$ = 5.66 Hz, PhC(5)), 110.8 (s, PhC(3)), 55.5 (s, OCH_3), 33.3 (d, $^1J_{C,P}$ = 12.83 Hz, Cy(*i*-C)), 30.1 (d, $^2J_{C,P}$ = 17.66 Hz, Cy(*o*-C)), 29.8 (d, $^2J_{C,P}$ = 8.60 Hz, Cy(*o*-C)), 27.6 (d, $^3J_{C,P}$ = 20.15 Hz, Cy(*m*-C)), 27.6 (s, Cy(*m*-C)),

26.9 (s, Cy(*p*-C)). ^{31}P NMR (121 MHz, CD_2Cl_2): δ −6.58. ^{31}P NMR (121 MHz, $CDCl_3$): δ −9.29.

2-[Dicyclohexylphosphanyl]phenol. To a solution of 1.0 g (3.29 mmol) of dicyclohexyl(*o*-methoxyphenyl)phosphine in 10 mL of dry CH_2Cl_2 was added 0.73 mL (7.70 mmol, 2.3 equiv) of BBr_3 at −78 °C under argon over 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 was added. The solution was stirred and heated to reflux for 5 h. The solution was again evaporated, and 20 mL of dry Et_2O with 1 mL of absolute NEt_3 was added. The resulting mixture was stirred for 1 h at room temperature. After filtration via canula all volatiles were evaporated and 832 mg (2.87 mmol, 87%) of 2-[dicyclohexylphosphanyl]phenol was obtained as a colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.29−7.23 (m, 2H, Ph(H), 7.04 (br, s, 1H, OH), 6.94−6.87 (m, 2H, Ph(H)), 1.99−1.54 (m, 12H, cyclohexyl-H), 1.33−1.03 (m, 10H, cyclohexyl-H). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 161.1 (d, $^2J_{C,P}$ = 18.94 Hz, PhC(2)), 132.9 (s, PhC(6)), 130.9 (s, PhC(4)), 119.8 (s, PhC(1)), 117.8 (s, PhC(5)), 114.8 (s, PhC(3)), 32.3 (d, $^1J_{C,P}$ = 6.11 Hz, Cy(*i*-C)), 30.2 (d, $^2J_{C,P}$ = 15.85 Hz, Cy(*o*-C)), 28.5 (d, $^2J_{C,P}$ = 5.43 Hz, Cy(*o*-C)), 26.9 (d, $^3J_{C,P}$ = 26.79 Hz, Cy(*m*-C)), 26.9 (d, $^3J_{C,P}$ = 5.51 Hz, Cy(*p*-C)). ^{31}P NMR (121 MHz, CD_2Cl_2): δ −33.03.

Sodium 2-dicyclohexylphosphanyl]phenolate. A 390 mg (1.34 mmol) sample of 2-[dicyclohexylphosphanyl]phenol was dissolved in 2.0 mL of dry ethanol, to which was then added, at 0 °C under argon, a solution of 40 mg (1.74 mmol, 1.3 equiv) of sodium in 1.00 mL of dry ethanol. The solution was allowed to warm to room temperature and stirred for 2 h. The solvent was removed, producing a colorless foam, which was left under high vacuum for several hours. A total of 405 mg (1.30 mmol, 97%) of sodium 2-[dicyclohexylphosphanyl]phenolate was obtained as a colorless solid.

^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.07 (d, $^3J_{H,H}$ = 6.91 Hz, 1H, Ph(H)), 6.97 (t, $^3J_{H,H}$ = 6.91 Hz, 1H, Ph(H)), 6.49 (br, s, 1H, Ph(H)), 6.35 (t, $^3J_{H,H}$ = 7.21 Hz, 1H, Ph(H)), 1.90−1.72 (m, 4H, CyH), 1.62−1.57 (m, 8H, CyH), 1.25−0.96 (m, 10H, CyH). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 174.6 (C(1)), 134.2 (s, C(3)), 130.7 (s, C(5)), 119.0 (d, C(2)), 112.2 (s, C(6)), 32.9 (s, Cy(*i*-C)), 30.9 (d, $^2J_{C,P}$ = 13.13 Hz, Cy(*o*-C)), 29.0 (s, Cy(*o*-C)), 27.8 (d, $^3J_{C,P}$ = 11.70 Hz, Cy(*m*-C)), 27.6 (s, Cy(*m*-C)), 26.8 (s, Cy(*p*-C)). ^{31}P NMR (121 MHz, CD_2Cl_2): δ −22.48.

Syntheses of Complexes 1−5. [*t*-BuPhP(*o*-OPh)](PCy$_3$)Ru=CHPh, 1. A solution of 64 mg (229 μmol) of sodium 2-[*tert*-butyl(phenyl)phosphanyl]phenolate in 2 mL of CH_2Cl_2 was added at room temperature over 15 min to a solution of 180 mg (219 μmol) of $(Cy_3P)_2RuCl_2$(=CHPh), **6**, in 10 mL of CH_2Cl_2. Then 1 g of silica gel was added to the reaction mixture, which was then evaporated to dryness. The resulting red-brown powder was transferred under careful exclusion of oxygen to a degassed silica gel column and eluted with hexane/Et_2O (96:4) as a solvent. The red-brown fraction was collected and dried under high vacuum. A total of 73 mg (96 μmol, 44%) of [*t*-BuPhP(*o*-OPh)](PCy$_3$)Ru=CHPh, **1**, was isolated as a red-brown foam. The complex is moderately air stable as a solid but decomposes within 1 day if left in solution. Crystals suitable for X-ray analysis were obtained by slow diffusion of heptane into a concentrated solution of **1** in benzene.

^{1}H NMR (300 MHz, CD_2Cl_2): δ 19.52 (s, 1H, Ru=CH), 8.25 (d, J = 7.20 Hz, 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), 5.75 (m, 1H), 2.39 (d, J = 9.90 Hz, 3H), 1.80−1.41 (m, 12H), 1.27−0.84 (m, 18H) 1.04 (d, 9H). ^{31}P NMR (121 MHz, CD_2Cl_2): δ 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_2Cl_2): *m*/*z* 764.26166 (calc, M^+), 764.26170 (found).

[*t*-Bu$_2$P(*o*-OPh)](PCy$_3$)Ru=CHPh, 2. A solution of 50 mg (0.192 mmol, 1.2 equiv) of sodium 2-[di-*tert*-butylphosphanyl]-phenolate in 1 mL of CH_2Cl_2 was added at room temperature to a solution of 132 mg (0.160 mmol) of $(Cy_3P)_2RuCl_2$(=CHPh), **6**, in 1 mL of CH_2Cl_2. Then 1 g of silica gel was added to the reaction mixture, which was then evaporated to dryness. The resulting red-brown powder was transferred under careful exclusion of oxygen to a degassed silica gel column packed with 5 g of dry and oxygen-free silica gel and eluted with hexane/Et_2O (96:4) as a solvent. The purple fraction was collected and dried under high vacuum. A total of 96 mg (0.129 mmol, 81%) of [*t*-Bu$_2$P(*o*-OPh)](PCy$_3$)Ru=CHPh, **2**, was isolated as a purple solid. The complex is air stable as a solid but decomposes within 1 day if left in solution. Crystals suitable for X-ray analysis were obtained by slow diffusion of heptane into a concentrated solution of **2** in benzene.

^{1}H NMR (300 MHz, CD_2Cl_2): δ 19.69 (d, $^2J_{H,P}$ = 2.40 Hz, 1H, Ru=CH), 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, CCH_3) 1.33−1.22 (m, 15H, PCy), 1.03 (d, $^3J_{H,P}$ = 13.20 Hz, 9H, CCH_3). ^{31}P NMR (121 MHz, CD_2Cl_2): δ 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_2Cl_2): *m*/*z* 744.29296 (calc, M^+), 744.29290 (found).

[CyPhP(*o*-OPh)](PCy$_3$)Ru=CHPh, 3. A solution of 100 mg (0.352 mmol, 1.05 equiv) of sodium 2-[cyclohexylphenylphosphanyl]phenolate in 5 mL of CH_2Cl_2 was added at room temperature to a solution of 300 mg (0.365 mmol) of $(Cy_3P)_2RuCl_2$(=CHPh), **6**, in 10 mL of CH_2Cl_2. After 1 h at room temperature, 1 g of silica gel was added to the reaction mixture, which was then evaporated to dryness. The resulting red-brown powder was transferred under careful exclusion of oxygen to a degassed silica gel column packed with 5 g of dry and oxygen-free silica gel and eluted with hexane/Et_2O (96:4) as a solvent. The red-brown fraction was collected and dried under high vacuum. A total of 128 mg (0.162 mmol, 46%) of [CyPhP(*o*-OPh)](PCy$_3$)Ru=CHPh, **3**, was isolated as a purple foam. The complex is air stable as a solid but decomposes within 1 day if left in solution.

^{1}H NMR (300 MHz, C_6D_6): δ 19.42 (d, $^2J_{H,P}$ = 10.81 Hz, 1H, Ru=CH), 8.20 (t, $^3J_{H,H}$ = 8.56 Hz, 1H), 7.53−6.61 (m, 13H), 2.80 (m, 1H), 2.55 (m, 3H), 2.12 (m, 4H), 1.81−1.61 (m, 17H), 1.52−1.21 (m, 15H), 1.05−0.86 (m, 4H). ^{31}P NMR (121 MHz, C_6D_6): δ 43.82 (d, 1P, $^2J_{P,P}$ = 269 Hz, P−O ligand), 29.20 (d, $^2J_{P,P}$ = 269 Hz, PCy_3). MS (ESI, CH_2Cl_2): *m*/*z* 790.27739 (calc, M^+), 790.27731 (found).

[Cy$_2$P(*o*-OPh)](PCy$_3$)Ru=CHPh, 4. A solution of 25 mg (0.086 mmol, 1.08 equiv) of sodium 2-[dicyclohexylphosphanyl]phenolate in 5 mL of CH_2Cl_2 was added at room temperature to a solution of 66 mg (0.080 mmol) of $(Cy_3P)_2RuCl_2$(=CHPh), **6**, in 5 mL of CH_2Cl_2. After 1 h at room temperature, 1 g of silica gel was added to the reaction mixture, which was then evaporated to dryness. The resulting red-brown powder was transferred under careful exclusion of oxygen to a degassed silica gel column packed with 5 g of dry and oxygen-free silica gel and eluted with hexane/Et_2O (96:4) as a solvent. The red-brown fraction was collected and dried under high vacuum. A total of 14 mg (0.018 mmol, 20%) of [*t*-Bu$_2$P(*o*-OPh)](PCy$_3$)Ru=CHPh was isolated as a red-brown solid. The complex is air stable as a solid but decomposes within 1 day if left in solution.

^{1}H NMR (300 MHz, CD_2Cl_2): δ 19.21 (s, 1H, Ru=CH), 8.12 (d, $^3J_{H,H}$ = 7.20 Hz, 2H), 7.26−7.15 (m, 4H), 7.00 (t, $^3J_{H,H}$ = 7.80 Hz, 2H), 6.67 (m, 1H), 2.51 (t, J = 12.00 Hz, 4H), 2.19−0.74 (m, 51H). ^{31}P NMR (121 MHz, CD_2Cl_2): δ 47.69 (d, 1P, $^2J_{P,P}$ = 213 Hz, P−O ligand), 34.64 (d, $^2J_{P,P}$ = 213 Hz, PCy_3). MS (ESI, CH_2Cl_2): *m*/*z* 796.32425 (calc, M^+), 796.32415 (found).

Dicyclohexylmethyltosylate.[8] To a solution of 2.00 g (10.1 mmol) of dicyclohexylmethanol and 2.34 g (20.9 mmol, 2.0 equiv)

(8) Hartung, J.; Hünig, S.; Kneuer, R.; Schwarz, M.; Wenner, H. *Synth. Pap.* **1997**, 1433.

of DABCO in 20 mL of dry dichloromethane under argon at 0 °C was added 3.10 g (16.3 mmol, 1.6 equiv) of TsCl in small portions over 15 min. After removal of the ice bath the reaction was stirred for 22 h at rt while monitoring with TLC (hexane/ethyl acetate, 4:1, detection with $KMnO_4$). Then 40 mL of ether was added, the solution was filtered, and the filtrate was washed twice with 30 mL of 2 M HCl and twice with 30 mL of saturated $NaHCO_3$. After drying over $MgSO_4$ the solvent was removed under vacuum to yield 3.54 g (99%) of pure dicyclohexylmethyltosylate as a colorless oil, which forms a solid on drying at high vacuum ($\sim 10^{-2}$ mbar).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.77 (d, 2H, ArH, J_{HH} = 8.4 Hz), 7.30 (d, 2H, ArH, J_{HH} = 8.4 Hz), 4.36 (t, 1H, HC(OArCy$_2$), J_{HH} = 5.3 Hz), 1.74−1.50 (m, 12 H, CyH), 1.24−0.92 (m, 10H, CyH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 144.1 (1C, C_{Ar}(Me)), 135.6 (1C, C_{Ar}(SO_3R)), 129.6 (2C, C_{Ar}(H)), 127.7 (2C, C_{Ar}(H)), 94.0 (1C, C(OArCy$_2$)), 39.5 (2C, C_{Cy}), 30.5 (2C, C_{Cy}), 28.0 (2C, C_{Cy}), 26.4 (2C, C_{Cy}), 26.3 (2C, C_{Cy}), 26.2 (2C, C_{Cy}), 21.8 (1C, Me(Ar)). Anal. Calcd (%) for $C_{20}H_{30}O_3S$ (350.51 g/mol): C 68.53, H 8.63. Found: C 68.64, H 8.59.

2-(Dicyclohexylmethoxy)benzaldehyde. A Schlenk tube was charged with 3.54 g (10.1mmol) of dicyclohexylmethyltosylate, 1.89 g (13.1 mmol, 1.3 equiv) of sodium 2-formylphenolate, and 20 mL of dry DMSO and then heated for 19 h at 60 °C under argon. Conversion was monitored with TLC (hexane/ethyl acetate, 4:1, $KMnO_4$). Then 100 mL of ether was added and the organic phase washed twice with 100 mL of 0.5 M NaOH and once with 50 mL of saturated $NaHCO_3$. After drying over $MgSO_4$ and evaporation of the solvent, the raw product was subjected to column chromatography (silica gel) with hexane/ethyl acetate (98:2) as the eluent. The product fraction (0.75 g) contained dicyclohexyl ketone as a side product, which could easily be distilled off via Kugelrohr distillation at 60 °C at high vacuum (10^{-3} mbar), giving 2-(dicyclohexylmethoxy)benzaldehyde in 20% yield (0.61 g).

^{1}H NMR (300 MHz, $CDCl_3$): δ 10.58 (s, 1H, RCHO), 7.81 (dd, 1H, ArH, J_{HH} = 1.8, 7.8 Hz), 7.46 (m, 1H, ArH, J_{HH} = 1.8, 7.5, 8.4 Hz), 7.00 (d, 1H, ArH, J_{HH} = 8.4 Hz), 6.92 (t, 1H, ArH, J_{HH} = 7.5 Hz), 4.12 (t, 1H, HC(OArCy$_2$), J_{HH} = 5.4 Hz), 1.85−1.55 (m, 12H, CyH), 1.30−1.00 (m, 10H, CyH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 190.5 (1C, RCHO), 163.7 (1C, C_{Ar}(OAr)), 135.9 (1C, C_{Ar}(H)), 128.5 (1C, C_{Ar}(H)), 125.0 (1C, C_{Ar}(CHO)), 119.9 (1C, C_{Ar}(H)), 113.6 (1C, C_{Ar}(H)), 87.1 (1C, C(OArCy$_2$)), 40.1 (2C, C_{Cy}), 30.6 (2C, C_{Cy}), 28.3 (2C, C_{Cy}), 26.6 (2C, C_{Cy}), 26.5 (2C, C_{Cy}), 26.3 (2C, C_{Cy}). Anal. Calcd (%) for $C_{20}H_{28}O_2$ (300.44 g/mol): C 79.96, H 9.39. Found: C 79.72, H 9.57.

2-(Dicyclohexylmethoxy)styrene.[9] A 1.06 mL (1.69 mmol, 1.05 equiv) portion of BuLi (1.6 M in hexane) was added over a few minutes under stirring to 603 mg (1.69 mmol, 1.05 equiv) of methyltriphenylphosphonium bromide in 15 mL of dry ether. The reaction was stirred under argon for 1 h, during which the solid completely dissolved. Then 483 mg (1.61 mmol) of 2-(dicyclohexylmethoxy)benzaldehyde in 6 mL of dry ether was added slowly with a syringe, upon which a precipitate was formed. The suspension was refluxed under argon for 20 h, and the conversion was monitored with TLC (hexane, $KMnO_4$ detection). The solution was filtered and washed with ether and hexane, and the solvent was evaporated under vacuum. The residue was subjected to column chromatography (silica gel) with hexane as the eluent, which gave 2-(dicyclohexylmethoxy)styrene in 86% yield (414 mg).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.47 (dd, 1H, ArH, J_{HH} = 1.5, 7.8 Hz), 7.14 (m, 2H, ArH + CH(=CH_2)), 6.89 (d, 1H, ArH, J_{HH} = 8.4 Hz), 6.85 (t, 1H, ArH, J_{HH} = 8.0 Hz), 5.72 (dd, 1H, CH_2(=CHAr), J_{HH} = 1.8, 18.0 Hz), 5.24 (dd, 1H, CH_2(=CHAr), J_{HH} = 1.8, 11.1 Hz), 4.01 (t, 1H, HC(OArCy$_2$), J_{HH} = 5.7 Hz), 1.86−1.56 (m, 12H, CyH), 1.30−1.02 (m, 10H, CyH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.2 (1C, C_{Ar}(OR)), 132.4 (1C, CH(=CH_2)), 128.7 (1C, C_{Ar}(H)), 126.9 (1C, C_{Ar}(CH=CH_2)), 126.6 (1C, C_{Ar}(H)), 119.8 (1C, C_{Ar}(H)), 113.7 (1C, CH_2(=CHAr)), 113.0 (1C, C_{Ar}(H)), 86.6 (1C, C(OArCy$_2$)), 40.2 (2C, C_{Cy}), 30.5 (2C, C_{Cy}), 28.3 (2C, C_{Cy}), 26.7 (2C, C_{Cy}), 26.6 (2C, C_{Cy}), 26.5 (2C, C_{Cy}). Anal. Calcd (%) for $C_{21}H_{30}O$ (298.47 g/mol): C 84.51, H 10.13. Found: C 84.41, H 10.34.

(PCy$_3$)Ru=CH[(*o*-OCHCy$_2$)Ph]·DCM.[10] A 94 mg (0.95 mmol, 2.1 equiv) sample of CuCl[11] was added in small portions at rt over 30 min to a solution of 363 mg (0.44 mmol) of Grubbs's first-generation catalyst and 197 mg (0.66 mmol, 1.5 equiv) of 2-(dicyclohexylmethoxy)styrene in 6 mL of dry dichloromethane (DCM). A color change from purple to red-brown was observed. The reaction was stirred for a further 15 min, after which it was filtered and the solvent removed under vacuum. The residue was again dissolved in 1.5 mL of dichloromethane, to which 22.5 mL of hexane was added to precipitate PCy_3CuCl. After a second filtration and evaporation of the solvent the residue was subjected to a short column (4.5 g silica gel) with hexane (450 mL) as the eluent to remove excess styrene ether (95 mg, 48% recovered) as well as the corresponding stilbene as metathesis side product. The complex was then isolated with hexane/ether (85:15), redissolved in dichloromethane, and obtained in 77% yield (280 mg, red-brown solid) as the dichloromethane adduct after removal of solvent. Crystals were grown at rt from a concentrated dichloromethane solution after evaporation of solvent almost to complete dryness.

^{1}H NMR (300 MHz, CD_2Cl_2): δ 17.54 (d, 1H, CH(=Ru), J_{HH} = 3.9 Hz), 7.62 (m, 2H, ArH), 7.23 (d, 1H, ArH, J_{HH} = 8.1 Hz), 7.04 (t, 1H, ArH, J_{HH} = 7.2 Hz), 4.82 (m, 1H, HC(OArCy$_2$)), 2.46−2.26, 2.12−2.02, 1.92−1.50, 1.40−1.14 (4m, 55H, CyH). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 282.3 (1C, CH(=Ru)), 156.7 (1C, C_{Ar}(OR)), 144.4 (1C, C_{Ar}(CH=Ru)), 130.0 (1C, C_{Ar}(H)), 123.2 (1C, C_{Ar}(H)), 122.5 (1C, C_{Ar}(H)), 114.3 (1C, C_{Ar}(H)), 93.5 (1C, C(OArCy$_2$)), 40.5 (2C, C_{CHCy2}), 35.8 (d, 3C, C_{PCy3}, J_{CP} = 25.4 Hz), 30.8 (2C, C_{CHCy2}), 30.6 (6C, C_{PCy3}), 30.2 (2C, C_{CHCy2}), 28.4 (d, 6C, C_{PCy3}, J_{CP} = 10.4 Hz), 27.0 (3C, C_{PCy3}), 26.9 (4C, C_{CHCy2}), 26.5 (2C, C_{CHCy2}). ^{31}P NMR (121 MHz, CD_2Cl_2): δ 60.2 (s, 1P). Anal. Calc (%) for $C_{39}H_{63}Cl_4OPRu$ (821.78 g/mol): C 57.00, H 7.73. Found: C 57.11, H 7.60.

[*t*-BuPhP(*o*-OPh)]Ru=CH[(*o*-OCHCy$_2$)Ph], 5. A solution of 32 mg (114 μmol, 0.9 equiv) of sodium 2-[*tert*-butyl(phenyl)-phosphanyl]phenolate in 2 mL of dry dichloromethane was added dropwise at rt to 105 mg (128 μmol) of (PCy$_3$)Ru=CH[(*o*-OCHCy$_2$)Ph]·DCM in 2 mL of dichloromethane and stirred for 15 min. Then 29 mg (293 μmol, 2.1 equiv) of CuCl was added and the suspension stirred for 30 min. After evaporation of the solvent the residue was taken up in hexane and put on a column prepared with the same solvent. The complex was eluted with hexane/ether (9:1) and obtained in 58% yield (50 mg) as a red-brown solid. Crystals were grown at rt via diffusion of dichloromethane from a hexane/dichloromethane solution (5:1) into hexane.

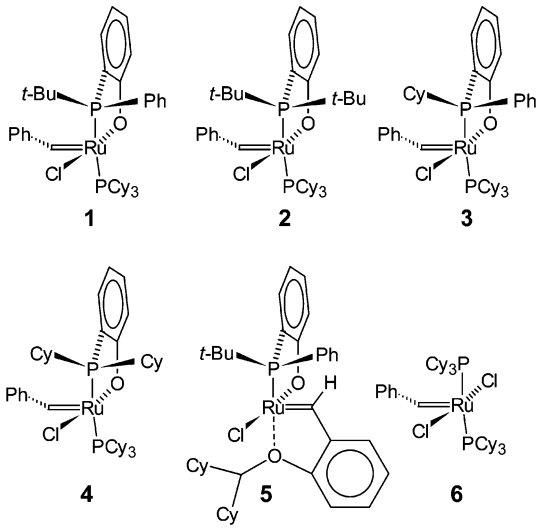
^{1}H NMR (300 MHz, CD_2Cl_2): δ 15.14 (d, 1H, CH(=Ru), J_{HH} = 7.8 Hz), 8.07 (m, 2H, Ar(P)H), 7.75 (t, 1H, Ar(PO)H, J_{HH} = 7.6 Hz), 7.62−7.46 (m, 4H, Ar(P)H + Ar(O)H), 7.27 (d, 1H, Ar(O)H, J_{HH} = 8.7 Hz), 7.16 (t, 1H, Ar(PO)H, J_{HH} = 7.6 Hz), 7.07 (dd, 1H, Ar(O)H, J_{HH} = 1.5, 8.1 Hz), 6.90 (t, 1H, Ar(O)H, J_{HH} = 7.4 Hz), 6.74 (m, 2H, Ar(PO)H), 4.95 (m, 1H, HC(OArCy$_2$)), 2.44 (m, 2H, CyH), 1.92−1.52, 1.45−1.16 (2m, 20H, CyH), 1.33 (d, 9H, *t*-BuH, J_{HP} = 14.7 Hz). ^{13}C NMR (125 MHz, CD_2Cl_2): δ 275.57 (1C, CH(=Ru)), 178.47 (d, 1C, $C_{Ar(PO)}$(ORu), J_{CP} = 13.9 Hz), 157.99 (1C, $C_{Ar(O)}$(OR)), 142.20 (1C, $C_{Ar(O)}$(CH=Ru)), 133.39 (d, 2C, $C_{Ar(P)}$(H), J_{CP} = 8.4 Hz), 132.25 (1C, $C_{Ar(PO)}$(H)), 131.41 (1C, $C_{Ar(PO)}$(H)), 129.74 (1C, $C_{Ar(P)}$(H)), 127.64 (1C, $C_{Ar(O)}$(H)), 127.39 (d, 2C, $C_{Ar(P)}$(H), J_{CP} = 10.1 Hz), 126.36 (d, 1C, $C_{Ar(P)}$(PRu),

(9) Hollywood, F.; Suschitzky, H. *Synth. Commun.* **1982**, 662.

(10) Kingsbury, J. S.; Harrity, J. P. A.; Bonitatebus, P. J., Jr.; Hoveyda, A. H. *J. Am. Chem. Soc.* **1999**, *121*, 791. Hoveyda, A. H.; Gillingham, D. G.; Van Veldhuizen, J. J.; Kataoka, O.; Garber, S. B.; Kingsbury, J. S.; Harrity, J. P. A. *Org. Biomol. Chem.* **2004**, *2*, 8.

(11) Lipshutz, B. H.; Frieman, B.; Birkedal, H. *Org. Lett.* **2004**, *6*, 2305.

Scheme 1



J_{CP} = 46.2 Hz), 121.73 (1C, $C_{Ar(O)}$(H)), 121.14 (1C, $C_{Ar(O)}$(H)), 117.52 (d, 1C, $C_{Ar(PO)}$(H), J_{CP} = 10.4 Hz), 116.03 (d, 1C, $C_{Ar(PO)}$(H), J_{CP} = 6.5 Hz), 115.49 (d, 1C, $C_{Ar(PO)}$(PRu), J_{CP} = 45.6 Hz), 112.83 (1C, $C_{Ar(O)}$(H)), 92.38 (1C, C($OArCy_2$)), 39.03 (1C, C_{Cy}), 38.61 (1C, C_{Cy}), 34.80 (d, 1C, C(Me_3), J_{CP} = 29.8 Hz), 29.08 (1C, C_{Cy}), 28.88 (1C, C_{Cy}), 28.86 (1C, C_{Cy}), 28.65 (1C, C_{Cy}), 25.88 (d, 3C, Me_3(CP), J_{CP} = 3.7 Hz), 25.73 (2C, C_{Cy}), 25.64 (1C, C_{Cy}), 25.51 (1C, C_{Cy}), 25.18 (1C, C_{Cy}), 25.15 (1C, C_{Cy}). ^{31}P NMR (121 MHz, CD_2Cl_2): δ 84.0 (s, 1P). Anal. Calcd (%) for $C_{36}H_{46}ClO_2PRu$ (678.25 g/mol): C 63.75, H 6.84. Found: C 63.53, H 6.95.

Polymerization Experiments. In a typical polymerization experiment, a solution of 1 g of monomeric cycloalkenes in 15 mL of solvent, either CH_2Cl_2 or neat cyclooctene, was treated with 4 mg (0.05%) of the catalyst dissolved in 1 mL of CH_2Cl_2. The mixture was stirred at room temperature for 1 to 17 h. 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 under high vacuum ($<10^{-2}$ mbar) for 1 day. ^{13}C NMR analysis was performed on 30 mg of the polymer, which was dissolved in 0.7 mL of $CDCl_3$. The relative relaxation times of the different sp^2-carbon atoms are similar, and the integrals could be compared quantitatively. Longer relaxation times did not change those values.

Quantum Chemical Calculations. Density functional theory (DFT) calculations were performed using ADF 2005 at the PW91/ZORA-TZP level of theory.[12] All structures were fully optimized without constraints and checked with frequency calculations to ensure that they were minima. While there were some negative frequencies, these could be identified as rotations of the *tert*-butyl group or the phenyl ring of the benzylidene moiety. The geometries and relative energies were virtually identical to those produced with BP86 and any comparably sized basis set.

Results

To test the mechanistic concept derived from the proposed potential surface for olefin metathesis presented in earlier work, complexes **1**−**5**, shown in Scheme 1, were prepared by ligand exchange with the "first-generation" ruthenium carbene complex[13] $(Cy_3P)_2RuCl_2$(=CHPh), **6**.

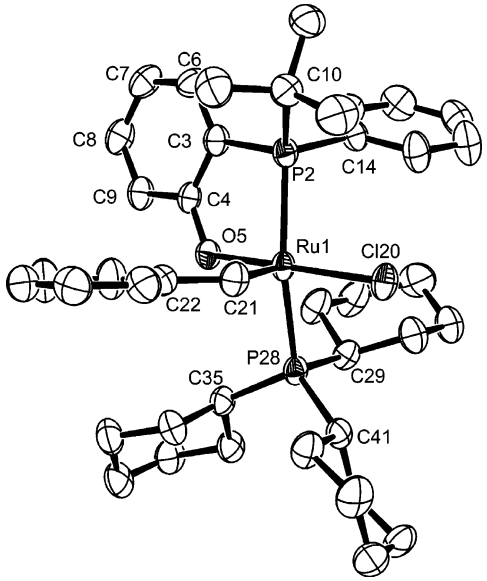


Figure 1. X-ray structure of complex **1**. Note the orientation of the benzylidene moiety on the same side as the *tert*-butyl group of the bidentate P,O ligand. Ellipsoids are drawn at the 50% probablility level. Hydrogen atoms are omitted for clarity. Selected bond length [Å] and angles [deg]: Ru1−P2 2.3372(8), Ru1−P28 2.3879(8), Ru1−Cl 2.4056(7), Ru1−O5 2.0685(18), Ru1−C21 1.831(3), C21−C22 1.461(4), P28−C29 1.851(3), P28−C35 1.852(3), P28−C41 1.846(3), P2−C3 1.807(3), P2−C10 1.879(3), P2−C14 1.830(3); P2−Ru1−P28 152.78(2), O5−Ru1−Cl20 172.31(6), P2−Ru1−O5 82.22(6), P2−Ru1−C21 101.23(10), Ru1−P2−C3 100.56(10), Ru1−P2−C10 125.16(10), Ru1−P2−C14 105.44(10), Ru1−P28−C29 104.10(10), Ru1−P28− C35 113.93(10), Ru1−P28−C41 116.41(10).

The complexes were purified by column chromatography to free them of traces of the precursor complexes and then further purified by fractional crystallization. All of the new complexes were characterized by NMR, mass spectrometry, and, where possible, elemental analysis. For **1**, **2**, and **5**, crystals of quality sufficient for X-ray crystallography were produced for structural studies. The obtained structures are depicted in Figures 1−3. Of particular interest is the orientation of the carbene moiety in the crystal structures. Close examination of **1** reveals that the carbene moiety lies unexpectedly on the same side as the *tert*-butyl group of the phosphine with the phenyl group on the benzylidene oriented away from the chloride on ruthenium. Given that the *tert*-butyl group is sterically more demanding than the phenyl group on the phosphine, the structure was examined for other factors, leading to the surprising orientation of the carbene. One immediately notices that the P−Ru−P axis deviates strongly from linearity—the P−Ru−P angle is 152.78°—placing one of the C−H bonds (on the 2-position of the cyclohexyl group) of the bound PCy_3 close to the formally empty sixth coordination site on ruthenium. With a Ru−C distance of 3.54 Å, one can postulate that the axial hydrogen on that carbon is close enough to the Ru so that there could be an agostic interaction between the C−H bond and the metal center. Bound in this fashion, the remaining part of the cyclohexane chair protrudes up into the proximity of the substituents on the bidentate phosphine ligand. The placement of the carbene proximal or distal to the *tert*-butyl group in **1** would depend accordingly on which group, the carbene or the cyclohexyl group, experiences a more unfavorable steric interaction with the bulky *tert*-butyl moiety. It should be noted that the same structural features are visible in the crystal structure of **2**, as well as the previously reported structure for $(Cy_3P)_2$-

(12) te Velde, G.; Bickelhaupt., F. M.; van Gisbergen, S. J. A.; Fonseca Guerra, C.; Baerends, E. J.; Snijders, J. G.; Ziegler, T. *J. Comput. Chem.* **2001**, *22*, 931−967.

(13) Schwab, P.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1996**, *118*, 100.

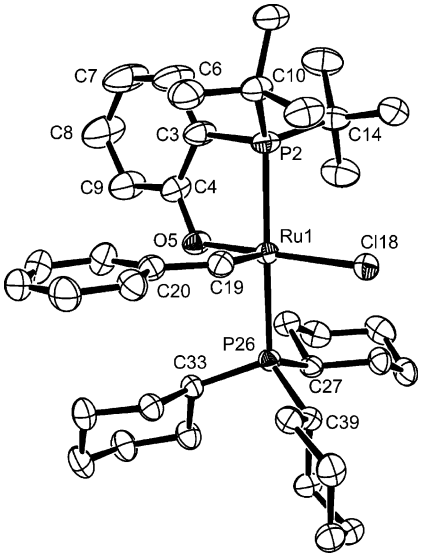


Figure 2. X-ray structure of complex **2**. Ellipsoids are drawn at the 50% probablility level. Hydrogen atoms are omitted for clarity. Selected bond length [Å] and angles [deg]: Ru1−P2 2.3747(5), Ru1−P26 2.4192(5), Ru1−Cl18 2.4161(5), Ru1−O5 2.0674(14), Ru1−C19 1.835(2), C19−C20 1.471(3), P26−C27 1.8567(18), P26−C33 1.8617(19), P26−C39 1.8556(19), P2−C3 1.813(2), P2−C10 1.880(2), P2−C14 1.885(2); P2−Ru1−P26 162.005(18), O5−Ru1−Cl18 168.98(4), P2−Ru1−O5 82.22(4), P2−Ru1−C19 98.15(6), Ru1−P2−C3 99.24(7), Ru1−P2−C10 121.92(7), Ru1−P2−C14 107.91(7), Ru1−P26−C27 111.69(6), Ru1−P26−C33 111.21(6), Ru1−P26−C39 116.89(6).

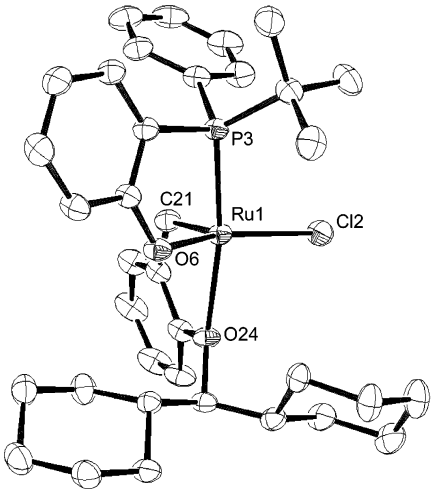


Figure 3. X-ray structure of complex **5**. Ellipsoids are drawn at 30% probability, and the hydrogen atoms are omitted for clarity. Selected bond length [Å] and angles [deg]: Ru1−C21 1.825(4), Ru1−O6 1.997(2), Ru1−P3 2.2201(9), Ru1−O24 2.310(2), Ru1−Cl2 2.3397(10), C21−Ru1−O6 104.49(14), C21−Ru1−P3 92.72(12), O6−Ru1−P3 84.51(7), C21−Ru1−O24 79.67(13), O6−Ru1−O24 92.10(9), P3−Ru1−O24 170.66(7), C21−Ru1−Cl2 102.07(12), O6−Ru1−Cl2 153.13(8), P3−Ru1−Cl2 98.31(3), O24−Ru1−Cl2 88.65(7).

$RuCl_2(=CHPh)$.[13] In each of the cases, an apparent C−H agostic interaction between ruthenium and the same position on a cyclohexyl group is accompanied by a deviation of the P−Ru−P axis from linearity. An overlay of the X-ray structures on top of the optimized geometries of **1** and **2**, computed with DFT at the PW91/ZORA-TZP level of theory, is shown in Figure 4, from which one can see that the geometry is not due to solid-state effects. In an alternative, experimental test to determine whether packing effects in the solid state may have biased the

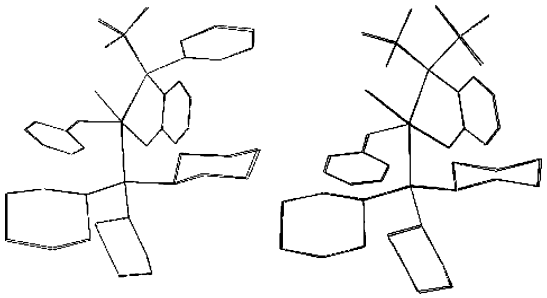


Figure 4. Overlay of the X-ray structures with the optimized structures of **1** and **2** computed using DFT at the PW91/ZORA-TZP level of theory.

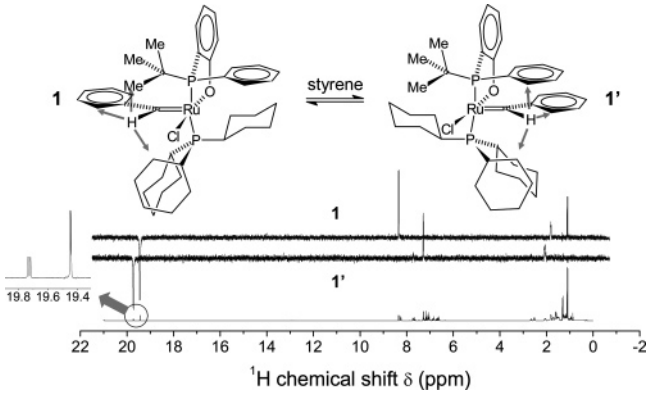


Figure 5. ^{1}H NMR spectrum of the solution of **1**, after equilibration with styrene (bottom trace), and nuclear Overhauser effect (NOE) spectra produced by irradiation of first one carbene signal and then the other.

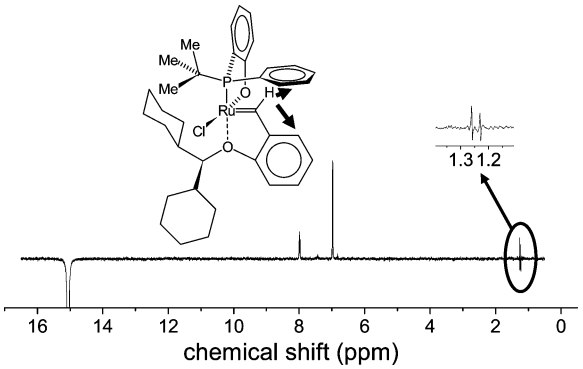


Figure 6. Nuclear Overhauser effect (NOE) spectrum of **5**, showing that the carbene moiety is proximal to the phenyl substituent on the ligand in solution. Examination of the small signals at δ 1.25 show that they are artifacts from an incomplete subtraction.

structure, solution-phase structures were investigated by NMR. Solutions of crystals of **1**, dissolved in C_6D_6, showed a single carbene resonance in the ^{1}H NMR at 19.45 ppm. Addition of styrene and equilibration at 25 °C for 210 min produced additional signals which strongly overlapped those present before. Looking downfield, it is evident that a single new carbene species, with a peak at 19.74 ppm, has been produced in solution. Irradiation of the two carbene resonances, one after the other, produced two different nuclear Overhauser effect (NOE) spectra, shown in Figure 5, which identify the original complex as the species with the carbene proximal to *tert*-butyl; the NOE experiment also indicates that the new carbene produced in solution by equilibration with styrene has the carbene distal to *tert*-butyl. From the integrations of the downfield ^{1}H NMR signals, the equilibrium ratio of the two carbenes is approximately 57:43, with the isomer in the crystal

Table 1. Conditions and Yields of Test Copolymerizations of Norbornene, N, and Cyclooctene, C, with Catalysts 1−5, as Well as Control Copolymerizations with 6 (the *r* value indicates the degree of sequence selectivity in the copolymerization)

entry	catalyst	mole ratio N/C	mole ratio N/catalyst	*T* (°C)	time (h)	yield (%)	N−N (%)	N−C (%)	C−C (%)	*r*
1	**6**	1:1	2000	25	1	191	55	0	45	∞
2	**6**	1:10	2000	25	1	>95[a]	4	0	96	∞
3	**6**	1:100	2000	25	1	>95[a]	0	0	100	∞
4	**1**	100:0	2000	25	1	93	100	0	0	∞
5	**1**	1:1	2000	25	1	101	100	0	0	∞
6	**1**	1:10	2000	25	1	72	100	0	0	∞
7	**1**	1:100	2000	25	1	13	21	66	14	0.28
8	**1**	1:100	2000	25	17	211	19	62	19	0.38
9	**1**	1:200	2000	60	7	234	8	67	25	0.24
10	**1**	1:100	2000	0	4	66	36	42	22	1.80
11	**1**	1:200	2000	0	4	53	30	51	19	0.88
12	**1**	0:100	200 000[a]	0	4	0[a]	0	0	0	
13	**1**	0:100	2000[a]	25	17	<0.3[a]	0	0	100	∞
14	**2**	100:0	2000	25	1	85	100	0	0	∞
15	**2**	1:1	2000	25	1	174	59	0	41	∞
16	**2**	1:10	2000	25	1	239	52	0	48	∞
17	**2**	1:100	2000	25	1	437	25	0	75	∞
18	**2**	0:100	2000[a]	25	1	11[a]	0	0	100	∞
19	**3**	100:0	2000	25	1	99	100	0	0	∞
20	**3**	1:1	2000	25	1	98	100	0	0	∞
21	**3**	1:10	2000	25	1	129	77	11	13	73
22	**3**	1:100	2000	25	1	155	44	43	13	1.8
23	**3**	1:100	2000	0	4	126	33	60	7	0.47
24	**3**	1:100	2000	60	1	47	62	29	9	6.0
25	**3**	1:100	10 000	25	1.5	51	47	53	0	0.77
26	**3**	1:750	2000	25	4	175	21	56	23	0.60
27	**3**	0:100	2000[a]	25	1	0	0	0	0	
28	**3**	0:100	2000[a]	60	1	0	0	0	0	
29	**4**	100:0	2000	25	1	95	100	0	0	∞
30	**4**	1:1	2000	25	1	101	91	0	9	∞
31	**4**	1:10	2000	25	1	140	66	0	34	∞
32	**4**	1:100	2000	25	1	280	14	0	86	∞
33	**4**	0:100	2000[a]	25	1	0	0	0	0	
34	**5**	100:0	2000	25	1 s	97	100	0	0	∞
35	**5**	1:100	2000	25	1.5	181	19	72	9	0.13
36	**5**	1:200	2000	25	1.5	194	13	76	11	0.10
37	**5**	1:100	200 000[a]	25	1.5	0.02[a]	0	0	100	∞
38[b]	**5**	1:100	2000	0	1.5	88	32	67	1	0.03
39[b]	5	1:200	2000	0	1.5	89	21	76	3	0.04
40[b]	5	0:100	200 000[a]	0	1.5	0	0	0	0	

[a] Mole ratios and (apparent) yields are computed on the basis of moles of norbornene except where indicated by an asterisk, in which case they are based on moles of cyclooctene. [b] The selectivity does not change between 1.5 and 4 h reaction time.

being also the more abundant species in solution at room temperature. Looking at Figures 3 and 6, one sees that **5**, which has no PCy_3 ligand, has its carbene moiety distal to the *tert*-butyl group, both in the solid state and in solution, as one would expect on steric grounds. For **5**, it might be expected that the steric interactions of the carbene are larger because the Hoveyda-type complex has the plane of the carbene moiety rotated by approximately 90°, pointing the carbenic hydrogen directly up into the space occupied by the P,O ligand. A last piece of evidence implicating the tricyclohexylphosphine in **1** as the cause for the unexpected orientation of the carbene comes from computed geometries of the 14-electron complex derived from **1**. DFT calculations at the same PW91/ZORA-TZP level of theory as before find the expected stability order for the two 14-electron complexes, with an energy difference of 3 kcal/mol in favor of the complex with the benzylidene moiety distal from the *tert*-butyl group. The structures are shown in Figure 7. Further structural work on the less hindered complexes **3** and **4**, both clean according to NMR, was stymied because they were insufficiently stable to purify by crystallization.[14] Of importance to the interpretation of polymerization results later, the decomposition of **3** during equilibration experiments with styrene produces a new carbene signal in the ^{1}H NMR that

Figure 7. Optimized PW91/ZORA-TZP structures of the 14-electron complexes derived from **1** after dissociation of tricyclohexylphosphine. With removal of the tricyclohexylphosphine, the benzylidene moiety prefers to be distal to the *tert*-butyl substituent.

exactly matches that of $(Cy_3P)_2RuCl_2(=CHPh)$, **6**. The same decomposition presumably occurs during attempts at recrystallization. One should also note that the lower than expected yield in polymerizations by **3** and **4**, as in, for example, entry 24 in Table 1, may also stem from catalyst decomposition, although the mode and products of a putative decomposition have not been characterized.

Polymerizations of norbornene and cyclooctene, either singly or in mixtures, were performed with the neat olefins as solvent, or with CH_2Cl_2 as diluent. Typically, a substrate-to-catalyst ratio (S/C) of 2000 was employed. The gross behavior of **1**−**5** in

(14) Ulman, M.; Grubbs, R. H. *J. Org. Chem.* **1999**, *64*, 7202.

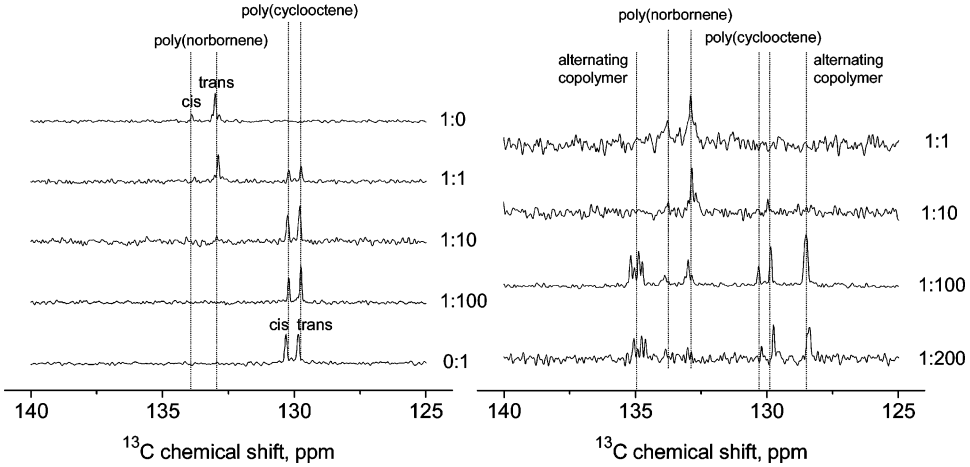


Figure 8. Olefinic regions of the ^{13}C NMR spectra of the polymer samples prepared from norbornene/cyclooctene mixture at different mole ratios. The left-hand side shows results for the standard first-generation catalyst, $(Cy_3P)_2RuCl_2(=CHPh)$, **6**; spectra for catalyst **1** are on the right. The olefinic carbon resonances for the ring-opening metathesis homopolymers of norbornene and cyclooctene are marked, as well as those for the alternating copolymer. There are at least two partially resolved peaks in the high-field resonance for the alternating copolymer, assigned to the end of the double bond derived from cyclooctene, *cis* and *trans*, whereas there are four peaks in the low-field resonance, assigned to the end derived from norbornene. One presumes that not only the *cis* and *trans* configuration of the double bond but also the *cis* and *trans* configuration of the next double bond cause the splitting.

the homopolymerization of norbornene was very similar to that of $(Cy_3P)_2RuCl_2(=CHPh)$, **6**. Homopolymerization of cyclooctene, however, showed interesting differences. Whereas $(Cy_3P)_2RuCl_2(=CHPh)$ and **2** polymerized cyclooctene, albeit more slowly than norbornene, **1**, **3**, and **5** showed little or no reactivity in the ROMP of cyclooctene, even when dissolved in neat cyclooctene for up to 7 h at 60 °C for the most extreme cases. In the copolymerization, however, complexes with unsymmetrical ligands, **1**, **3**, and **5**, could produce increasing amounts of alternating copolymers of norbornene and cyclooctene as the mole ratio of cyclooctene to norbornene is increased. For a given mixture of monomers, the copolymerization by the complexes with symmetrical ligands, **2** and **4**, proceeded by homopolymerization of the strained cyclic olefin followed by homopolymerization of the unstrained one once the strained monomer was exhausted. Results for the different catalysts are summarized in Table 1.

Given the central role of the copolymerization as an assay for the performance of a designed catalyst, the polymer analysis requires some comment. From gravimetric analysis of the cleaned and dried copolymer from **1**, it is clear that up to approximately 1 equiv of cyclooctene must have been incorporated into the polymer along with the norbornene. From the GPC trace, one surmises that the material produced by polymerization of a mixture of norbornene and cyclooctene is not poly(norbornene). The refractive index of poly(norbornene) is coincidentally identical to that of the 1,3,5-trichlorobenzene solvent,[15] which means that the pure homopolymer would not appear in the refractive index trace. Given that the same peak appears in the GPC trace using either refractive index or viscosity detectors, that peak must be something other than poly(norbornene). Static and dynamic light scattering measurements find for the copolymer $M_w \approx 10^6$ and M_w/M_n between 1.5 and 2.0. Last, the sequence information was obtained from ^{13}C NMR spectra, in which the signals in the olefinic region, assigned previously,[16] clearly distinguish between the *N*−N, *N*−C, *C*−C, and *C*−N dyads (N = norbornene, C = cyclooctene), depicted in Figure 8. With sufficiently long T_2 relaxation times, the integration of the olefinic resonances in the ^{13}C NMR spectrum gives the relative abundances of the four possible olefinic carbons in the copolymer listed in Table 1. From the dyad intensities, one can construct a quantitative measure of the selectivity in the copolymerization. Each copolymer can be characterized by an *r* value,[3] where the monomers M_1 and M_2 that form homo versus hetero dyads, e.g., M_1M_1 and M_2M_2 versus M_1M_2 and M_2M_1, give the following relationship:

$$r = \frac{(M_1M_1)(M_2M_2)}{(M_1M_2)(M_2M_1)}$$

An *r* value of 1.0 means that the monomer units are distributed statistically in the copolymer. When $r \gg 1$, the copolymer will be composed of long homopolymeric blocks. The much more unusual situation of $r = 0$ corresponds to perfect alternation. The integrated ^{13}C peak intensities give between 0.2 and 0.3 for the best cases with catalyst **1**, indicating predominant alternation. *r* values much less than unity occur in certain free radical polymerizations,[17] but only very rarely in coordination polymerization catalyzed by transition metal complexes.[4] Sections of the ^{13}C NMR spectra of the copolymers produced by catalysts **2** and **5** are shown in Figures 9 and 10 for comparison.

Discussion

In earlier mechanistic work, we had found that the near-thermoneutral cross-metathesis in the gas phase by the mass-selected 14-electron reactive intermediate derived from a first-generation ruthenium benzylidene complex displayed an inverse secondary deuterium kinetic isotope effect for deuteration of the carbenic center. Interestingly, the microscopic reverse reaction also showed an inverse deuterium kinetic isotope effect, which led us to postulate that the metallacyclobutane structure was necessarily a transition state.[18] In contrast, DFT calculations,

(15) n^{20} (1,2,4-Trichlorobenzene) = 1.5717. *CRC Handbook of Chemistry and Physics*, 49th ed.; The Chemical Rubber Company, 1969.

(16) Amir-Ebrahimi, V.; Rooney, J. J. *J. Mol. Catal. A* **2004**, *208*, 115−121.

(17) Rzaev, Z. M. O. *Prog. Polym. Sci.* **2000**, *25*, 163−217.

(18) Adlhart, C.; Hinderling, C.; Baumann, H.; Chen, P. *J. Am. Chem. Soc.* **2000**, *122*, 8204.

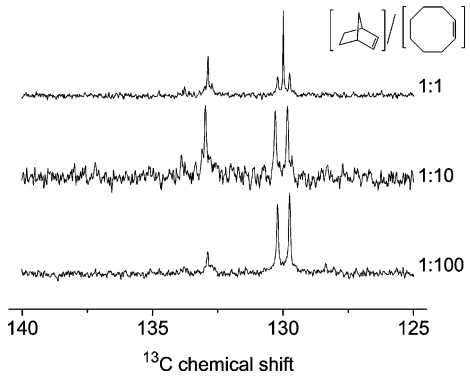


Figure 9. Olefinic regions of the ^{13}C NMR spectra of the polymer samples prepared with catalyst **2** from a norbornene/cyclooctene mixture at different mole ratios, showing no evidence of alternating copolymerization. The sharp singlet at δ 130 in the top trace comes from traces of unreacted cyclooctene.

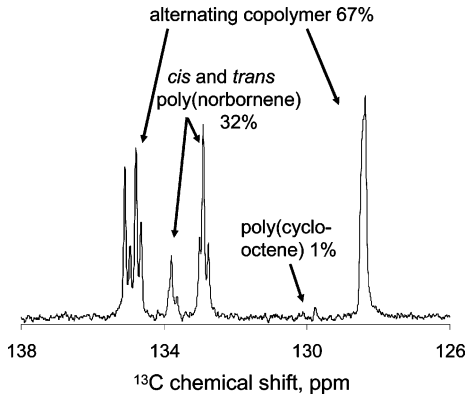


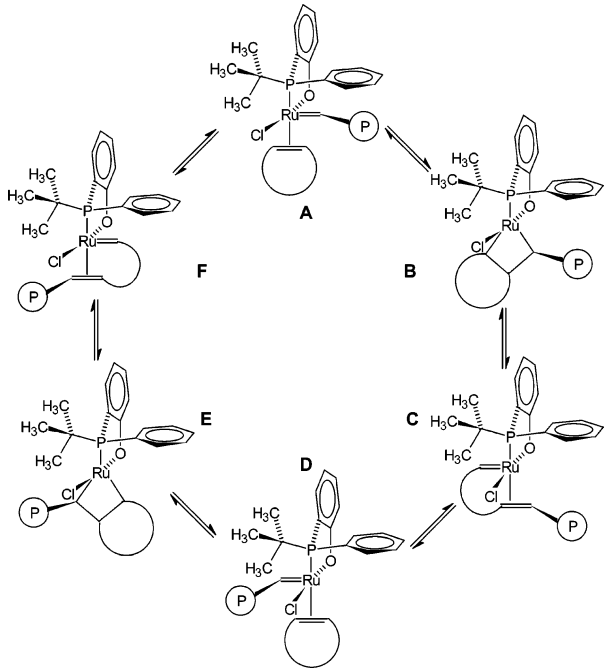
Figure 10. Olefinic regions of the ^{13}C NMR spectra of the polymer samples prepared with catalyst **5** from a norbornene/cyclooctene mixture at a mole ratio of 1:100, showing alternating copolymerization with $r = 0.03$. Some poly(norbornene) homopolymer stretches are also visible, but there is almost no poly(cyclooctene).

in our own group[19,20] and by others,[21,22] at increasingly higher levels, persistently identified the metallacyclobutane structure as an intermediate, with the lowest energy structure showing the metallacyclobutane ring *trans* to the supporting ligand on the ruthenium. For second-generation catalysts, the metallacyclobutane with the *trans* orientation has been recently observed *in situ* by low-temperature NMR.[23] The resolution of the contradiction came from the computational work in which it was shown that first-generation complexes required rotation of the tricyclohexylphosphine ligand along the lowest energy pathway for a near-thermoneutral metathesis reaction.[19] A rate-limiting rotation at the metallacyclobutane structure, energetically plausible in the calculations, would result in a rate-determining step whose transition state connects two intermediates, both of which are metallacyclobutanes. Accordingly, one would expect an inverse isotope effect for the investigated reaction in both the forward and the reverse direction. The preceding mechanistic explanation demonstrated a feature of the metathesis reaction that, while obvious in hindsight, had until then escaped consideration. A series of productive metathesis reactions would swing the carbene unit from one side of the complex to the other. In the original $(Cy_3P)_2RuCl_2(=CHPh)$ complex, rotation of the phosphine ligand during the reaction renders the alternation moot, allowing degenerate metatheses. In the usual second-generation complexes, the 2-fold symmetry of the N-heterocyclic carbene ligand makes the two sides identical, so that there is in fact no preference for one side over the other. If, however, the two sides were to be made different, one might expect that the complex might behave as a dual-site catalyst with alternating selectivity in a polymerization reaction if there were to be no rotation of the ligand.[24] The simplest embodiment of the concept is complex **1**, where a bidentate P,O-ligand cannot rotate, and the remaining two substituents on phosphorus are the sterically distinguishable phenyl and *tert*-butyl groups. One should note at this point that our previous mechanistic work in the gas phase,[25] as well as comparable solution-phase studies by Grubbs,[26] suggests that the first-generation catalysts, with fast ligand olefin-for-phosphine ligand exchange and slower metathesis, should be better candidates for the design of alternation in ROMP than the second-generation catalysts, where ligand exchange is slow and metathesis fast. Second-generation catalysts with unsymmetrical N-heterocyclic carbene ligands have been reported by Mol,[27] Hoveyda,[28] and Blechert,[29] but none have been tested in ROMP. It should be noted that there are isolated reports of alternating copolymerization in ROMP based on a different mechanistic concept.[30,31] In our original concept, it was presumed that steric interactions would lead a metallacyclobutane intermediate to cleave preferentially to place the carbene distal to the sterically most demanding substituent on the phosphine unless another factor would override the intrinsic preference. The overriding factor is strain release in the present copolymerization of cyclooctene and norbornene.

As depicted in Scheme 2, the carbene moiety in the propagating species can lie either on the right, as in species **A**, or on the left, as in species **D**. We expect **A** to be sterically more favorable than **D**, which breaks what would have been a degeneracy in the more usual case of a rotatable phosphine or a phosphine with at least two identical substituents. If we consider the productive direction around the catalytic cycle for ROMP, **A** → **B** → **C** → **D** → **E** → **F** → **A**, with each step reversible, we would expect that the forward reaction **A** → **B** → **C** would occur only if there is a large strain release in the **B** → **C** step so that the intermediate metallacyclobutane **B** would preferentially partition forward to **C** rather than return to **A**. On the other hand, the reaction **D** → **E** → **F** should proceed in the forward direction for any cycloalkene, strained or not, because the metallacyclobutane **E** should partition forward to the sterically less hindered carbene **F**. Consequently, the intermediate **A** can incorporate only norbornene into the growing chain, but intermediate **D** can take either norbornene or cyclooctene, the probability being largely determined by relative

(19) Adlhart, C.; Chen, P. *Angew. Chem., Int. Ed.* **2002**, *41*, 4484.
(20) Adlhart, C.; Chen, P. *J. Am. Chem. Soc.* **2004**, *126*, 3496.
(21) Cavallo, L. *J. Am. Chem. Soc.* **2002**, *124*, 8965.
(22) Vyboishchikov, S. F.; Bühl, M.; Thiel, W. *Chem.−Eur. J.* **2002**, *8*, 3962.
(23) Romero, P. E.; Piers, W. E. *J. Am. Chem. Soc.* **2005**, *127*, 5032.
(24) It has been brought to our attention by a reviewer that unsymmetrical monodentate NHC ligands may rotate. Sanford, M. S. Ph.D. Thesis, California Institute of Technology, Pasadena, CA, 2001. This would make a bidentate ligand as in the present complexes a prerequisite for the mechanistically designed alternation.
(25) Adlhart, C.; Chen, P. *Helv. Chim. Acta* **2003**, *86*, 941.
(26) Sanford, M. S.; Love, J. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **2001**, *123*, 6543.
(27) Dinger, M. B.; Nieczypor, P.; Mol, J. C. *Organometallics* **2003**, *22*, 5291.
(28) Van Veldhuizen, J. J.; Gillingham, D. G.; Garber, S. B.; Katakoa, O.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2003**, *125*, 12502.
(29) Vehlow, K.; Maechling, S.; Blechert, S. *Organometallics* **2006**, *25*, 25.
(30) Choi, T. L.; Rutenberg, I. M.; Grubbs, R. H. *Angew. Chem., Int. Ed.* **2002**, *41*, 3839.
(31) Ilker, M. F.; Coughlin, E. B. *Macromolecules* **2002**, *35*.

Scheme 2



concentrations. Accordingly, dilute norbornene in cyclooctene solution should yield a largely 1:1 alternating copolymer as long as there is no overriding difference in the stabilities of the intramolecular olefin π-complexes **C** and **F** derived from norbornene or cyclooctene.[32]

Analysis of the copolymer produced by the unsymmetrical complexes **1**, **3**, and **5** clearly shows alternation increasing as the ratio of cyclooctene to norbornene gets larger. Integration of the *N*−N, *N*−C, *C*−C, and *C*−N dyads gives predominantly alternating linkages in the best cases, with *r* values coming in as low as 0.03 for catalyst **5**. Alternative explanations based on electronic effects from the peculiar P,O-bidentate phosphine are definitively excluded by the control polymerizations with **2** and **4**. Not only does the symmetrically substituted system **2** homopolymerize cyclooctene, but **2** and **4** also make no alternating copolymer when used with norbornene/cyclooctene mixtures. The results clearly support the designed mechanistic concept.

The experimental structure for **1**, both in solid state and solution, belies the expected energetic difference between the sites proximal and distal to the *tert*-butyl group. Resolution of the issue comes from the realization that the structural work for **1** pertains to the 16-electron complex **1** with the P,O-bidentate ligand and a bound tricyclohexylphosphine, which is not the resting state in the catalytic cycle. Kinetic work by Grubbs had indicated that the tricyclohexylphosphine does not rebind after each turnover,[26] in agreement with our electrospray ionization mass spectrometric study of an active polymerizing ROMP system in which the only observable intermediate at steady state has the stoichiometry of the backbiting complex with an olefinic unit on the growing polymer chain bound to the ruthenium.[33] With the π-complex, the fortuitously placed C−H bond on the cyclohexyl group is absent, which should reinstate the expected sterically determined energetic preference for the carbene distal to the *tert*-butyl group. The π-complex is also more likely to have the plane of the carbene moiety oriented with the carbenic hydrogen pointing up toward the substituents on the phosphine, which would increase the steric preference. Evidence supporting this hypothesis can be seen in the structure of **5**, where the absence of tricyclohexylphosphine in the Hoveyda-type complex, as well as the carbene moiety rotated to form the chelate, gives a complex with a clear preference for the carbene moiety distal to *tert*-butyl. It should be noted that the rotation of the carbene moiety is supported by the ^{1}H spectrum. Shielding of the carbene proton in **5** (15.14 ppm) results in an upfield shift of ∼4.4 ppm relative to complex **1**. Chelation is also seen by coupling of the phosphorus nucleus and the carbene proton (J_{HP} = 7.8 Hz). Such a coupling is absent in **1** due to rotation of the benzylidene by about 90°. One notes further that the X-ray analysis of **5** shows that the length of the Ru(1)−O(24) bond is 2.310(2) Å, which is typical for that of previously reported structures of similar compounds.[34]

Whereas the alternating sequences, evidenced by the *N*−C and *C*−N dyads, are clear support for the mechanistic concept, from where do the homopolymer stretches come? The *N*−N dyads are easily understood as arising because the cyclooctene/norbornene ratio is still small enough for some homopolymerization of the much more reactive norbornene to compete. The *C*−C dyads in Figure 8, on the other hand, are more difficult to understand, especially given that **1** and **3** homopolymerize cyclooctene only inefficiently, if at all, even when cyclooctene is the neat solvent. One notes, though, that the more labile complex **3** decomposes to produce the standard first-generation catalyst $(Cy_3P)_2RuCl_2(=CHPh)$, **6**, which does homopolymerize cyclooctene quite efficiently. Supporting the conjecture that a small extent of decomposition of either **1** or **3** to $(Cy_3P)_2RuCl_2(=CHPh)$ occurs is the observation that the copolymer of cyclooctene and norbornene produced by **5**, which wholly lacks tricyclohexylphosphine, contains a very much reduced amount of *C*−C dyads according to the ^{13}C NMR spectrum.

A last comment on alternating ROMP copolymers concerns the fact that such copolymers have been reported before,[16] albeit without any systematic explanation for their occurrence and often with no structural characterization of the catalyst formed *in situ*. If the intermediate carbene complexes are configurationally stable in the absence of reactive olefins, then there can always be alternation if the two potential sites for the carbene moiety are sufficiently different. Furthermore, the concept can be generalized further for selection according to other properties beyond strain release. Work in this direction is underway.

Conclusion

We report a comprehensive structural and selectivity study of a class of ruthenium carbene complexes for which the mechanistic concept predicts an alternating copolymerization of cyclooctene and norbornene in appropriate mixtures of the monomers. The predicted stereoselectivity does indeed appear, and the initially curious anomalies in the structures and reactivity turn out to be only apparent anomalies when the catalytic cycle is considered and decomposition routes are identified. Moreover, preparation of a complex wholly lacking tricyclohexylphosphine eliminates the anomalies, as predicted.

Acknowledgment. Support for this project from the Research Commission of the ETH and the Swiss National Science Foundation is acknowledged. We thank Mr. Paul Seiler (ETH

(32) Patton, P. A.; McCarthy, T. J. *Macromolecules* **1987**, *20*, 778.
(33) Adlhart, C.; Chen, P. *Helv. Chim. Acta* **2000**, *83*, 2192.
(34) Hoveyda, A. H.; Gillingham, D. G.; Van Veldhuizen, J. J.; Kataoka, O.; Garber, S. B.; Kingsbury, J. S.; Harrity, J. P. A. *Org. Biomol. Chem.* **2004**, *2*, 8.

Zürich) for performing the X-ray crystallograpy, Ms. Brigitte Brandenberg for the NOE measurements, and Prof. Dr. Manfred Schmitt (Institut für Physikalische Chemie, Johannes-Gutenberg-Universität Mainz) for the light scattering measurements on the copolymers. Helpful discussions with Prof. Dr. Dieter Schlüter (ETH Zürich) are also acknowledged.

Supporting Information Available: Crystallographic data for compounds **1**, **2**, **5**, and **7**, details of the DFT calculations, and data on the polymer characterization are available free of charge via the Internet at http://pubs.acs.org.

OM700321A