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Tuning the Steric Properties of a Metathesis Catalyst for Copolymerization of Norbornene and Cyclooctene toward Complete Alternation

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We have recently published a mechanistic concept for the olefin metathesis reaction with ruthenium catalysts that explains the independent control of chemo- and stereoselectivity by substitution in two orthogonal planes. The basic structure from which we started the structural modifications for improved stereoselectivity had been optimized substantially for chemoselectivity, as compared to the prototype that had been published. We designed the catalyst according to a concept in which the factor that governs alternation is directly related to the size difference of the substituents on the bidentate phosphine/phenolate ligand **2a**−**e** and in which the origin of chemoselectivity arises from diastereomeric site control. The most selective catalyst (**11d**) outperforms our prototype (**3**) in selectivity as well as reactivity. Synthetic problems, i.e., the undesired formation of 2:1-complexes (bidentate ligand-to-ruthenium ratio) (**8**) by reaction of the bidentate phosphine/phenolate ligands **2a** and **2b** with the first-generation Hoveyda−Grubbs catalyst **4**, were solved by introduction of a larger carbene unit, which not only favors the formation of 1:1-complexes but also results in increased initiation rates. The work is supported by NMR data and X-ray crystallography, which give insights into the steric properties of the investigated system.

Introduction

In 2005 we reported a mechanistic concept for chemoselectivity in the olefin metathesis reaction based on our preceding computational and gas phase studies.[1−3] We confirmed our mechanistic hypotheses by the design of a solution phase system (catalyst **3**, Schemes 1 and 3), which, in contrast to the first-generation Grubbs catalyst **1**, is able to produce a largely alternating copolymer from norbornene and cyclooctene.[4,5] A first improved catalyst was already published in 2007 containing a Hoveyda-type carbene unit, rather than PCy_3 as dissociating ligand, without mentioning the problems we encountered during synthesis.[5] In a more recent communication we have shown an essentially completely chemoselective catalyst (**11d**) on which we extended our concept to stereoselectivity issues (see Chart 1).[6] We were able to demonstrate that replacement of the chloride anion by sulfonates with increasing steric bulk can increase the content of *cis* double bonds in the produced polymer. Here we summarize now our efforts in improving the first type of selectivity, i.e., the factor that governs alternation that went into the design and optimization of the lead structure and demonstrates that it is directly related to the size difference between the two substituents on the phosphine ligand by a series containing four catalysts (**11a**−**d**). Our simple ligand exchange approach[5] (in analogy to preparation of **3** from **1**, Scheme 1) with the first-generation Hoveyda−Grubbs catalyst **4** was disappointing in the beginning, since the desired 1:1-complexes with the bidentate phosphine/phenolate ligand **2a** could not be synthesized (Scheme 2). However, through the solution of the synthetic problem we gained insight into the steric requirements for catalyst formation, which finally resulted in the introduction of a larger, faster initiating carbene unit (**10**), which we employed as the lead structure for our subsequent further developments.

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), methanol (Mg). Flash chromatography employed Fluka silica gel 60, type 60752 (230−400 mesh). NMR measurements were either done on 300 (^{1}H: 300 MHz, ^{13}C: 75 MHz, ^{31}P: 121 MHz) or 600 MHz instruments (^{1}H: 600 MHz, ^{13}C: 150 Hz). Chemical shifts

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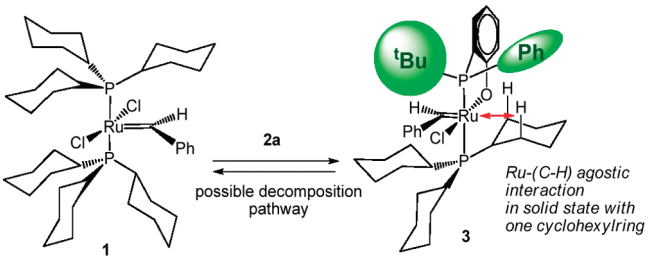
Scheme 1. Synthesis of the Prototype of a Chemoselective Catalyst (3)



(δ-values) are reported in ppm and calibrated with respect to the residual solvent signal for ^{1}H and ^{13}C NMR (CD_2Cl_2: 5.32 and 53.80 ppm; $CDCl_3$: 7.26 and 77.00 ppm). An 85% aqueous H_3PO_4 solution is 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, dd: doublet of doublets, t: triplet, tm: triplet with an additional unresolved m, m: multiplet, br: broad. Elemental analysis was performed by the Microanalytical Laboratory of the Laboratorium für Organische Chemie, ETH−Zürich. Syntheses of ligands **2a** and **2e** as well as of complexes **10** and **11a** have been reported previously.[5]

Polymerizations. A 150−200 mg amount of norbornene (NBE) was polymerized in the presence of 20, 100, or 200 equiv of cyclooctene (COE) under argon. Prior to polymerization, the reaction volume was filled up to 20 mL with CH_2Cl_2 or hexane if indicated. The catalyst (1:2000 with respect to NBE) was then added and the reaction temperature kept at either room temperature or 0 °C (investigating the temperature dependence with catalysts **11a** and **11b**). The yields were usually around 90%, and the reaction was stopped by precipitation with 100 mL of MeOH when it was reasonably viscous. The coagulated polymer was dried at HV for 2 h and analyzed by NMR in $CDCl_3$. The NMR measurements were conducted with 30 mg of polymer that was left overnight in the NMR solvent.

Syntheses of Ligands 2b, 2c, and 2d. Adamantylphenylphosphorus Chloride, 17b. A 5.37 g (25.0 mmol) sample of 1-adamantylbromide (**15b**) and 9.03 g of Mg turnings (375 mmol, 15 equiv, the turnings were preactivated with I_2 and a heat gun) were gently refluxed in 100 mL of absolute ether without stirring (!) for 17 h.[7] The solution was filtered and titrated with 2-propanol in toluene and phenanthroline as an indicator (45% yield, 11.25 mmol). Then 10.6 mmol of this Grignard solution was added slowly to 1.90 g (10.6 mmol, 1.0 equiv) of phenylphosphorus dichloride in 20 mL of dry ether at −78 °C, and the solution was allowed to warm to rt overnight. The precipitate was filtered and washed with ether, and the filtrate concentrated *in vacuo*. The residual oil was taken up in CH_2Cl_2 (filtered and concentrated) and once more in ether and filtered again to yield 4.04 g (100% estimated) of crude **17b** (mixture of chloride and bromide). ^{31}P NMR (121 MHz, $CDCl_3$): δ 104.22 (s) and 100.94 (s).

Adamantyl-(*o*-methoxyphenyl)phenylphosphine·BH_3, 20. This compound was prepared by a different route than in a reported literature procedure.[8] A 5.74 mL portion of 1.6 M BuLi in hexane (9.19 mmol, 1.0 equiv) was added dropwise to 2-bromoanisole in 25 mL of dry ether at 0 °C, and the solution was stirred for 2.5 h at the same temperature. Then 3.50 g of **17b** (9.19 mmol, as a mixture of chloride and bromide) in 20 mL of ether was added at 0 °C, and the suspension was stirred overnight, filtered, and washed with ether to yield crude **19b**. ^{31}P NMR (121 MHz, $CDCl_3$): δ 0.54 (s). To the filtrate was added 13.8 mL of BH_3 in THF (1.0 M, 13.8 mmol, 1.5 equiv), and the solution quenched by slow addition of MeOH until formation of H_2 has ceased. The crude product was subjected to a column (300 mL silica) and eluted with hexane/ethyl acetate (9:1) to give 2.38 g (71%) of **20**. The compound can be recrystallized by vapor diffusion of CH_2Cl_2 out of a 1:1 CH_2Cl_2/hexane solution into hexane, mp = 143−144 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.00 (dd, 1H, $J_{H,H}$ = 7.8 and 12.6 Hz), 7.68 (m, 2H), 7.50 (m, 1H), 7.36 (m, 3H), 7.06 (m, 1H), 6.92 (dd, 1H, $J_{H,H}$ = 3.6 and 8.4 Hz), 3.60 (s, 3H), 2.03 (m, 9H), 1.71 (br s, 6H), 0.95 (v br m, 3H, BH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 160.83 (s, 1C), 137.88 (d, 1C, $J_{C,P}$ = 12.8 Hz), 133.13 (s, 1C), 132.58 (d, 2C, $J_{C,P}$ = 7.9 Hz), 129.68 (s, 1C), 129.57 (d, 1C, $J_{C,P}$ = 53.9 Hz), 127.71 (d, 2C, $J_{C,P}$ = 9.2 Hz), 120.89 (d, 1C, $J_{C,P}$ = 11.6 Hz), 115.38 (d, 1C, $J_{C,P}$ = 48.5 Hz), 111.19 (d, 1C, $J_{C,P}$ = 4.3 Hz), 54.75 (s, 1C), 38.25 (s, 3C), 36.58 (s, 3C), 34.99 (d, 1C, $J_{C,P}$ = 30.4 Hz), 28.58 (d, 3C, $J_{C,P}$ = 9.2 Hz). ^{31}P NMR (121 MHz, $CDCl_3$): δ 33.73 (br peak). Anal. Calcd (%) for $C_{23}H_{30}OBP$ (364.27 g/mol): C 75.84, H 8.30. Found: C 75.65, H 8.37.

2-(Adamantylphenylphosphanyl)phenol, 21b. To 325 mg (0.89 mmol) of adamantyl-(*o*-methoxyphenyl)phenylphosphine·BH_3 (**20**) in 5 mL of dry CH_2Cl_2 was added at −78 °C 2.3 equiv of BBr_3 (0.51 g, 0.194 mL, 2.05 mmol). The reaction mixture was allowed to warm to rt overnight, and the solvent was then evaporated. To the residue was carefully added 8 mL of degassed water, and the white suspension was heated to 90 °C for 4 h. Afterward $NaHCO_3$ was added to neutralize the acid and the product extracted under argon three times with 20 mL of ether. After drying the solution with $MgSO_4$ and evaporation of the solvent a white foam was obtained. The residue was taken up in 2 mL of MeOH, upon which a white solid (**21b**) precipitated, which was washed with 2 mL of MeOH (221 mg, 74%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.61 (m, 3H), 7.34 (m, 5H incl. OH), 6.98 (m, 2H), 2.00−1.65 (several m, 15H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 161.42 (d, 1C, $J_{C,P}$ = 21.9 Hz), 135.56 (s, 1C), 134.25 (d, 2C, $J_{C,P}$ = 17.6 Hz), 133.34 (d, 1C, $J_{C,P}$ = 9.2 Hz), 131.87 (s, 1C), 128.71 (s, 1C), 128.36 (d, 2C, $J_{C,P}$ = 7.3 Hz), 120.08 (s, 1C), 117.82 (d, 1C, $J_{C,P}$ = 5.3 Hz), 115.55 (s, 1C), 39.93 (d, 3C, $J_{C,P}$ = 10.4 Hz), 36.86 (s, 3C), 35.12 (d, 1C, $J_{C,P}$ = 7.3 Hz), 28.76 (d, 3C, $J_{C,P}$ = 9.8 Hz). ^{31}P NMR (121 MHz, $CDCl_3$): δ −21.95 (s). Anal. Calcd (%) for $C_{22}H_{25}OP$ (336.41 g/mol): C 78.55, H 7.49. Found: C 78.07, H 7.76.

Sodium 2-(Adamantylphenylphosphanyl)phenolate, 2b. A 34.1 mg amount of NaOH (0.85 mmol, 1.0 equiv) in 1.9 mL of MeOH was added to 287 mg (0.85 mmol) of **21b** in 4 mL of CH_2Cl_2. The solvent was removed to yield a white foam in quantitative yield, which was used without further purification.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.55 (m, 1H), 7.34 (m, 2H), 7.14 (m, 3H), 6.90 (t, 1H, $J_{H,H}$ = 7.4 Hz), 6.45 (t, 1H, $J_{H,H}$ = 7.2 Hz), 6.19 (m, 1H), 1.85−1.50 (several m, 15H). ^{31}P NMR (121 MHz, $CDCl_3$): δ −6.71 (s).

Neopentylphenylphosphorus Chloride, 17c. A 5.00 g (33.1 mmol) portion of neopentyl bromide (**15c**) in 20 mL of dry THF was added dropwise to 1.22 g (50.0 mmol, 1.5 equiv) of Mg in 10 mL of refluxing THF.[9] The dry, solid Mg was preactivated with I_2 and application of heat (heat gun). After refluxing for 2 h the solution was filtered and titrated with 2-propanol in toluene and phenanthroline as indicator (70% yield, 23.1 mmol). A 21.8 mmol sample of this Grignard solution was added to 3.90 g (2.96 mL, 21.8 mmol, 1.0 equiv) of phenylphosphorus dichloride in 10 mL of ether at −78 °C. The mixture was allowed to warm to rt overnight; afterward the solvent was evaporated, yielding **17c** as a mixture of chloride and bromide, which was used without workup. ^{31}P NMR (121 MHz, $CDCl_3$): δ 91.16 (s) and 80.55 (s).

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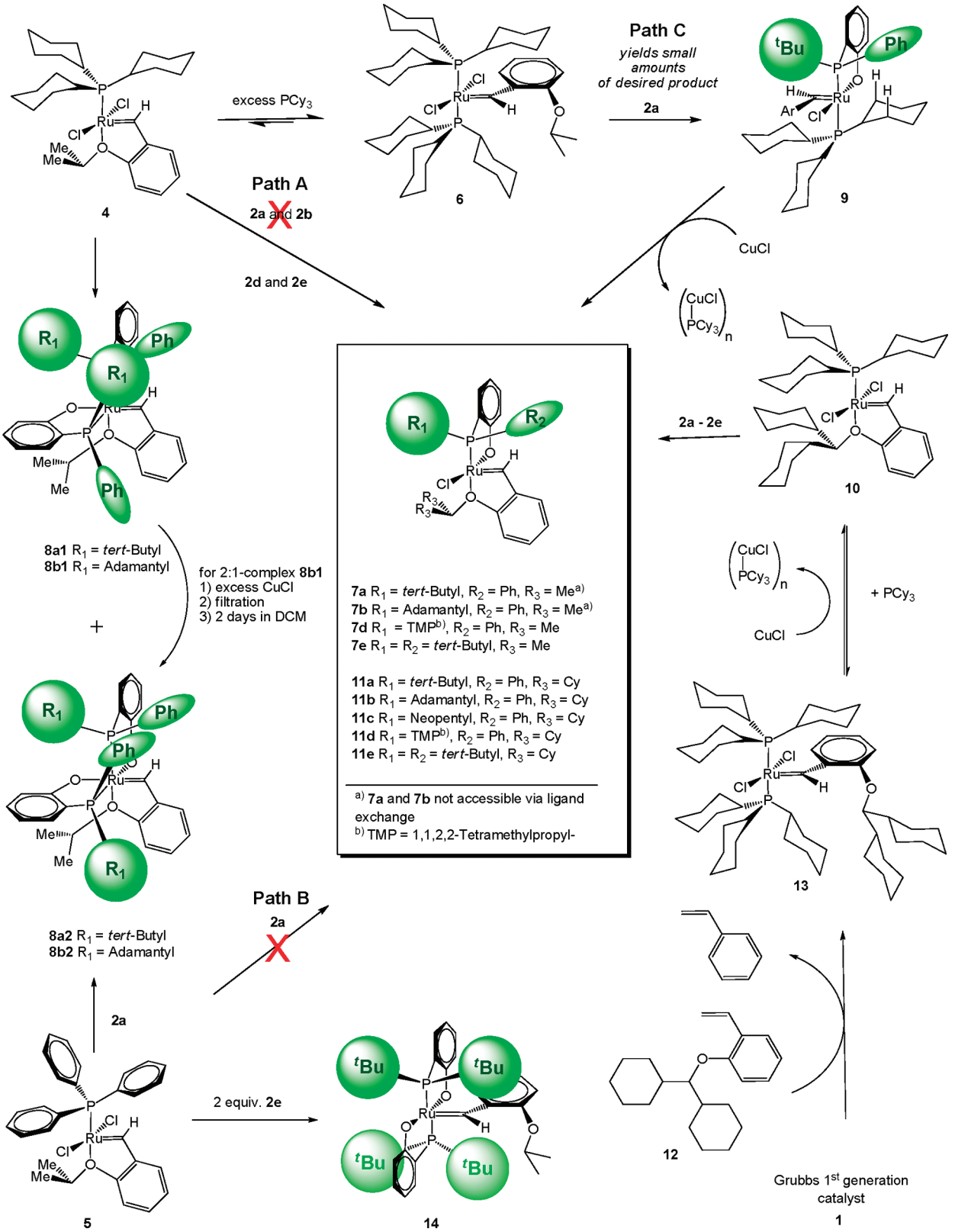
Scheme 2. Syntheses of 1:1- and 2:1-Complexes



(*o*-Methoxyphenyl)neopentylphenylphosphine, 19c. A solution of 21.8 mmol of 2-methoxyphenyllithium (**18**) was prepared by addition of 13.9 mL of 1.6 M BuLi in hexane (22.2 mmol, 1.02 equiv) to 4.08 g (21.8 mmol, 2.72 mL) of *o*-bromoanisole in 30 mL of dry ether at 0 °C (stirring for 2 h). This solution was then added to the crude precursor **17c** in 20 mL of ether, and the mixture was stirred overnight. The precipitate was filtered off and washed with ether, and the filtrate was concentrated *in vacuo*. The residue was subjected to Kugelrohr distillation at 180 °C under reduced pressure (0.1 mbar), giving the pure product **19c** in 72% yield (4.50 g).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.58 (t, 2H, $J_{H,H}$ = 7.8 Hz), 7.36 (m, 3H), 7.29 (t, 1H, $J_{H,H}$ = 7.8 Hz), 7.09 (t, 1H, $J_{H,H}$ = 6.5 Hz), 6.90 (t, 1H, $J_{H,H}$ = 7.5 Hz), 6.84 (dd, 1H, $J_{H,H}$ = 3.9

Scheme 3. Syntheses of Bidentate Phosphine/Phenolate Ligands 2a−2e

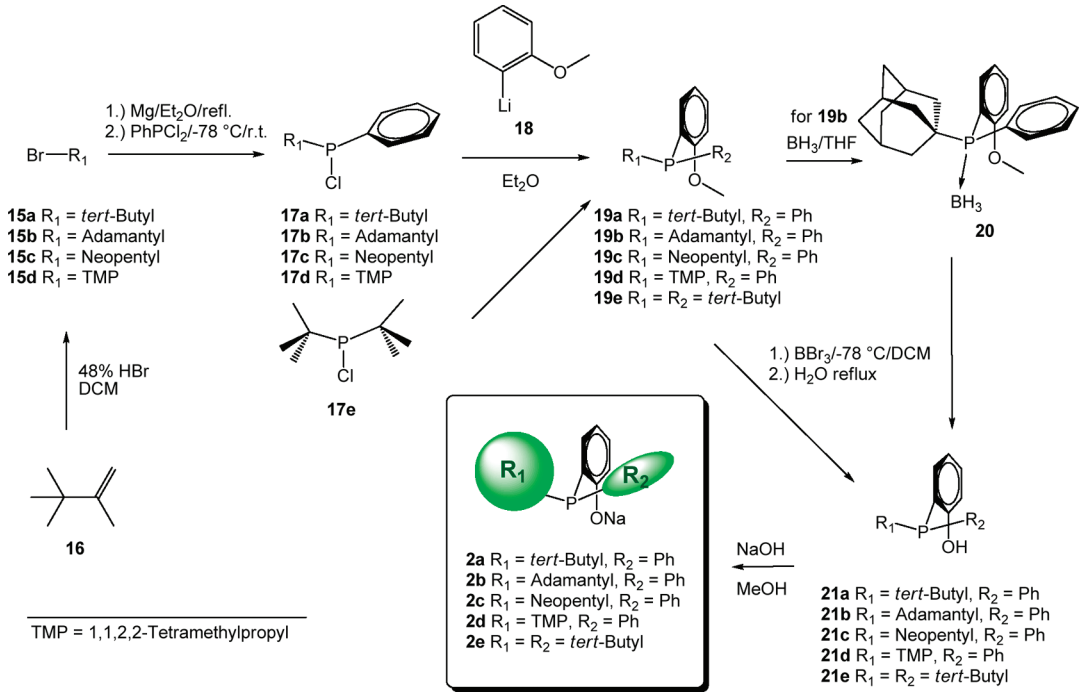


Chart 1. Exchange of Chloride by Various Sulfonates Shows an Impact on the Stereoselectivity of Double Bonds

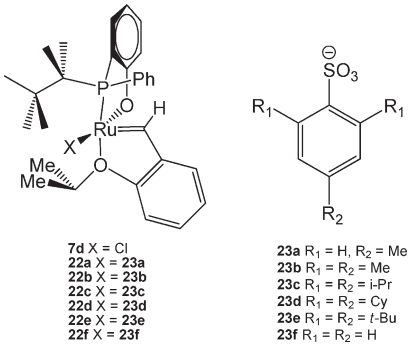
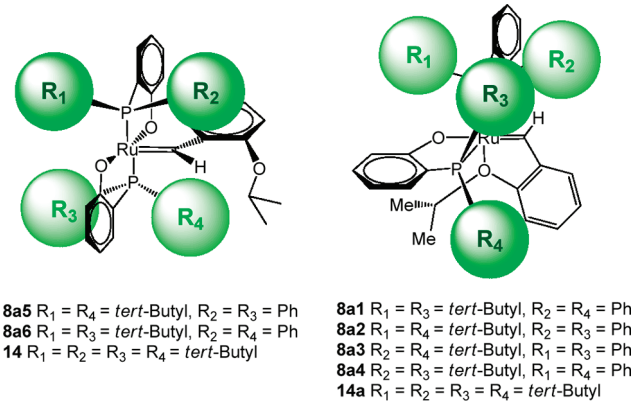


Chart 2. Several Isomers of *trans* (8a5, 8a6, 14) and *cis* (8a1, 8a2, 8a3, 8a4, 14a) 2:1-Complexes[a]



[a] In the *trans* complexes the carbene unit is not chelating.

and 8.1 Hz), 3.81 (s, 3H), 2.17 (d, 2H, $J_{H,P}$ = 4.2 Hz), 1.06 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 160.53 (d, 1C, $J_{C,P}$ = 13.4 Hz), 138.85 (d, 1C, $J_{C,P}$ = 11.6 Hz), 133.39 (d, 2C, $J_{C,P}$ = 20.7 Hz), 132.39 (d, 1C, $J_{C,P}$ = 5.5 Hz), 129.50 (s, 1C), 128.22 (s, 1C), 128.2−128.0 (hidden signal, 1C), 128.05 (d, 2C, $J_{C,P}$ = 7.3 Hz), 120.56 (d, 1C, $J_{C,P}$ = 2.3 Hz), 110.14 (s, 1C), 55.37 (s, 1C), 41.78 (d, 1C, $J_{C,P}$ = 15.2 Hz), 31.55 (d, 1C, $J_{C,P}$ = 15.8 Hz), 31.03 (d, 3C, $J_{C,P}$ = 9.1 Hz). ^{31}P NMR (121 MHz, $CDCl_3$): δ −33.01 (s). Anal. Calcd (%) for $C_{18}H_{23}OP$ (286.35 g/mol): C 75.50, H 8.10. Found: C 75.29, H 8.22.

2-(Neopentylphenylphosphanyl)phenol, 21c. A 2.3 equiv sample of BBr_3 (2.01 g, 0.76 mL, 8.03 mmol) was added to 1.00 g (3.49 mmol) of **19c** in 10 mL of dry CH_2Cl_2 at −78 °C. The reaction mixture was allowed to warm to rt overnight. The CH_2Cl_2 was then evaporated under reduced pressure followed by slow addition of 10 mL of degassed H_2O. The mixture was refluxed for 45 min, followed by neutralization with $NaHCO_3$. The phenol was extracted with 20 and 15 mL of ether under argon and the solvent evaporated. The residue was subjected to Kugelrohr distillation under reduced pressure (180 °C, 0.05 mbar), which gave 0.82 g of product (86%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.44 (tm, 2H, $J_{H,H}$ = 7.8 Hz), 7.32 (m, 5H), 6.94 (t, 2H, $J_{H,H}$ = 7.4 Hz), 6.81 (br d, OH, $J_{H,P}$ = 8.7 Hz), 2.26 (dd, 1H, $J_{H,H}$ = 6.9 and 14.4 Hz), 2.19 (dd, 1H, $J_{H,H}$ = 3.3 and 14.1 Hz), 1.04 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.11 (d, 1C, $J_{C,P}$ = 20.0 Hz), 137.97 (d, 1C, $J_{C,P}$ = 4.5 Hz), 133.25 (s, 1C), 131.79 (d, 2C, $J_{C,P}$ = 17.6 Hz), 131.19 (s, 1C), 128.38 (d, 2C, $J_{C,P}$ = 6.6 Hz), 128.11 (s, 1C), 122.91 (d, 1C, $J_{C,P}$ = 4.5 Hz), 120.87 (s, 1C), 115.14 (s, 1C), 43.17 (d, 1C, $J_{C,P}$ = 10.4 Hz), 31.50 (d, 1C, $J_{C,P}$ = 13.4 Hz), 31.04 (d, 3C, $J_{C,P}$ = 9.1 Hz). Anal. Calcd (%) for $C_{17}H_{21}OP$ (272.33 g/mol): C 74.98, H 7.77. Found: C 74.37, H 8.03 (purity after distillation).

Sodium 2-(Neopentylphenylphosphanyl)phenolate, 2c. A 118 mg (2.94 mmol) amount of NaOH in 7.5 mL of MeOH was added to 0.80 g (2.94 mmol) of phenol **21c**. The solvent was evaporated, yielding a white foam in quantitative yield, which was used without further purification.

2-Bromo-2,3,3-trimethylbutane, 15d. This was produced according to a reported procedure.[10] A 12 mL (8.4 g, 86 mmol) amount of 2,3,3-trimethylbutene (**16**) in 20 mL of CH_2Cl_2 was stirred vigorously with 25 mL of 48% HBr for 2 h. Phase

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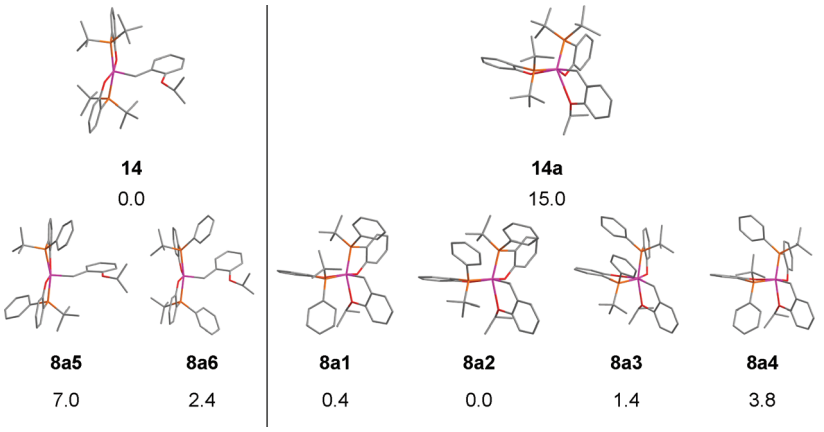
Chart 3. Computed Structures and Relative Energies in kcal/mol (BP86/TZP) of Open (*trans*-Phosphines) (8a5, 8a6, 14) and Closed (*cis*, Chelating) 2:1-Complexes (8a1, 8a2, 8a3, 8a4, 14a)



separation, extraction with CH_2Cl_2, and drying over $MgSO_4$ yielded 10.1 g (66%) of **15d**, which was used without further purification.

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.81 (s, 6H), 1.12 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 79.78 (1C), 40.03 (1C), 30.72 (3C), 26.91 (2C).

Phenyl-(1,1,2,2,tetramethylpropyl)phosphorus Chloride, 17d. A 3.9 g (21.8 mmol) portion of **15d** in 100 mL of dry ether was added with a syringe pump to 10.6 g of Mg powder (436 mmol) in 20 mL of ether at reflux over 45 min. Reflux was continued for 15 min, and then the cooled Grignard solution (0 °C) was slowly filtered via a cannula into a solution of 1.56 g (8.72 mmol) of phenylphosphorus dichloride ($PhPCl_2$) in 10 mL of ether at −78 °C. The reaction was allowed to warm to rt overnight and the ether evaporated to give crude **17d** as a mixture of chloride and bromide, which was used without purification. ^{31}P NMR (121 MHz, $CDCl_3$): δ 106.05 (s) and 104.40 (s).

(*o*-Methoxyphenyl)phenyl-(1,1,2,2-tetramethylpropyl)phosphine, 19d. An aryllithium solution of **18** prepared from 3.26 g (17.4 mmol) of *o*-bromoanisole and 10.9 mL of 1.6 M BuLi (hexane solution, 17.4 mmol) in THF at 0 °C (2 h stirring) was then added to **17d**, and the reaction was refluxed for 2 h. Quenching with 2 mL of MeOH and filtration yielded crude **19d**, which was purified by Kugelrohr distillation (190−210 °C, 8×10^{-2} mbar), 2.05 g (75% based on $PhPCl_2$).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.75 (m, 2H), 7.61 (m, 1H), 7.27 (m, 4H), 6.91 (m, 1H), 6.85 (m, 1H), 3.80 (s, 3H), 1.26 (d, 3H, $J_{H,P}$ = 7.5 Hz), 1.05 (s, 9H), 1.03 (d, 3H, $J_{H,P}$ = 9.9 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 161.95 (d, 1C, $J_{C,P}$ = 15.8 Hz), 139.22 (d, 1C, $J_{C,P}$ = 20.6 Hz), 136.72 (d, 1C, $J_{C,P}$ = 7.4 Hz), 135.37 (d, 2C, $J_{C,P}$ = 23.0 Hz), 129.99 (s, 1C), 127.88 (s, 1C), 127.53 (d, 2C, $J_{C,P}$ = 7.9 Hz), 126.37 (d, 1C, $J_{C,P}$ = 21.2 Hz), 120.21 (d, 1C, $J_{C,P}$ = 2.4 Hz), 110.55 (d, 1C, $J_{C,P}$ = 1.8 Hz), 55.41 (s, 1C), 42.63 (d, 1C, $J_{C,P}$ = 24.9 Hz), 37.66 (d, 1C, $J_{C,P}$ = 20.0 Hz), 27.31 (d, 3C, $J_{C,P}$ = 10.9 Hz), 22.61 (d, 1C, $J_{C,P}$ = 3.6 Hz), 22.24 (d, 1C, $J_{C,P}$ = 7.9 Hz). ^{31}P NMR (121 MHz, $CDCl_3$): δ −7.00 (s). Anal. Calcd (%) for $C_{20}H_{27}OP$ (314.41 g/mol): C 76.40, H 8.66. Found: C 75.34, H 8.56 (purity after distillation).

2-[Phenyl-(1,1,2,2-tetramethylpropyl)phosphanyl]phenol, 21d. To a solution of 2.0 g (6.36 mmol) of **19d** in 15 mL of CH_2Cl_2 was added at −78 °C 3.66 g of BBr_3 (14.6 mmol). The reaction was allowed to warm to rt overnight, the solvent evaporated, and the residue first quenched carefully with 10 mL of H_2O and then refluxed for 1 h. Solid $NaHCO_3$ was added in small portions to neutralize the reaction, and the product was extracted with CH_2Cl_2 under argon via a cannula. After evaporation of the solvent 1.5 mL of CH_2Cl_2 was added, and a precipitate was formed upon addition of 20 mL of ether. The filtrate was concentrated and purified by Kugelrohr distillation (175−190 °C, 10^{-2} mbar), 1.45 g (76%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.77 (m, 4H, incl. −OH), 7.32 (m, 3H), 7.26 (m, 1H), 6.91 (m, 2H), 1.21 (d, 3H, $J_{H,P}$ = 10.5 Hz), 1.14 (d, 3H, $J_{H,P}$ = 10.2 Hz), 0.99 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 160.19 (d, 1C, $J_{C,P}$ = 22.5 Hz), 135.79 (d, 2C, $J_{C,P}$ = 21.3 Hz), 135.46 (d, 1C, $J_{C,P}$ = 7.3 Hz), 134.92 (d, 1C, $J_{C,P}$ = 1.7 Hz), 133.32 (s, 1C), 129.07 (d, 1C, $J_{C,P}$ = 1.2 Hz), 128.12 (d, 2C, $J_{C,P}$ = 8.9 Hz), 121.35 (d, 1C, $J_{C,P}$ = 5.0 Hz), 119.89 (s, 1C), 115.29 (d, 1C, $J_{C,P}$ = 1.4 Hz), 42.46 (d, 1C, $J_{C,P}$ = 14.0 Hz), 37.53 (d, 1C, $J_{C,P}$ = 16.8 Hz), 27.04 (d, 3C, $J_{C,P}$ = 10.4 Hz), 22.71 (d, 1C, $J_{C,P}$ = 6.6 Hz), 22.05 (d, 1C, $J_{C,P}$ = 4.9 Hz). ^{31}P NMR (121 MHz, $CDCl_3$): δ −35.44 (s). Anal. Calcd (%) for $C_{19}H_{25}OP$ (300.38 g/mol): C 75.97, H 8.39. Found: C 74.98, H 8.14 (purity after distillation).

Sodium 2-[Phenyl-(1,1,2,2-tetramethylpropyl)phosphanyl]phenolate, 2d. The sodium salt was produced by reacting **21d** with 1.0 equiv of NaOH in MeOH and used without further purification after evaporation of the solvent.

Syntheses of Complexes. Crystallization of Grubbs First-Generation Catalyst 1. Crystals suitable for X-ray analysis were grown by slowly concentrating a hexane/ether solution of the complex via solvent diffusion through a rubber septum.

Attempted Synthesis of 7a (Path B) and Isolation of 8a1. a. Slow Addition of a Substoichiometric Amount of Ligand 2a. To 16.4 mg (28 μmol) of complex **5** in 2 mL of CH_2Cl_2 was added dropwise 2.8 mg (10 μmol, 0.35 equiv) of ligand **2a** in 2 mL of CH_2Cl_2. After evaporation of the solvent the mixture was analyzed by NMR. ^{1}H NMR (300 MHz, CD_2Cl_2, only carbene region): δ 16.69 (d, $J_{H,P}$ = 6.6 Hz, **5**), 14.96 (t or dd, 1H, $J_{H,P}$ = 6.2 Hz, **8a1**), 14.53 (dd, 1H, $J_{H,P}$ = 6.0 and 7.8 Hz, **8a2**); relative intensities of carbene protons: **5**:**8a1**:**8a2** = 87:8:5. ^{31}P NMR (121 MHz, CD_2Cl_2): δ 80.66 (d, $J_{P,P}$ = 30 Hz, **8a2**), 77.82 (d, $J_{P,P}$ = 30 Hz, **8a1**), 67.61 (d, $J_{P,P}$ = 30 Hz, **8a1**), 60.77 (s, **5**), 57.42 (d, $J_{P,P}$ = 30 Hz, **8a2**), −5.34 (s, PPh_3).

b. After Addition of More Than 2 equiv of Ligand 2a. To the same sample another 16.8 mg (2.1 equiv) of ligand **2a** was added and the conversion monitored by NMR. ^{1}H NMR (300 MHz, CD_2Cl_2, only carbene region): δ 14.97 (t or dd, 1H, $J_{H,P}$ = 6.2 Hz, **8a1**), 14.55 (dd, 1H, $J_{H,P}$ = 6.0 and 7.8 Hz, **8a2**); relative intensity of carbene protons: **8a1**:**8a2** = 65:35. The sample was subjected to column chromatography (10 g of silica gel) under argon using hexane/Et_2O as the eluent. Two yellow fractions were collected with 50% and 70−100% ether, respectively. The first one was pure and assigned to **8a1**.

^{1}H NMR (300 MHz, CD_2Cl_2): δ 14.95 (t or dd, 1H, $J_{H,P}$ = 6.2 Hz), 7.98 (m, 2H), 7.56 (m, 3H), 7.40 (m, 2H), 7.30 (m, 2H), 7.03 (m, 5H), 6.84 (m, 2H), 6.52 (m, 3H), 6.36 (m, 2H), 5.85 (m, 1H), 5.07 (m, 1H), 1.47 (d, 3H, $J_{H,H}$ = 6.6 Hz), 1.16 (d, 9H, $J_{H,P}$ = 14.7 Hz), 0.94 (d, 3H, $J_{H,H}$ = 6.9 Hz), 0.69 (d, 9H, $J_{H,P}$ = 14.7 Hz). ^{31}P NMR (121 MHz, CD_2Cl_2): δ 77.80 (d, 1P, $J_{P,P}$ = 30 Hz), 67.62 (d, 1P, $J_{P,P}$ = 30 Hz).

Attempted Synthesis of 7a (Path C) and *in Situ* Observation of 6, 9, and 7a. a. NMR Observation of Intermediate 6. A 12 mg (20 μmol) amount of first-generation Hoveyda−Grubbs catalyst **4** and 45 mg (160 μmol, 8.0 equiv) of PCy_3 were mixed in an NMR tube in CD_2Cl_2. ^{1}H NMR (300 MHz, CD_2Cl_2, only selected peaks): δ 20.55 (s, carbene proton of **6**), 17.36 (d, $J_{H,P}$ = 4.5 Hz, carbene proton of **4**), 5.27 (m, (C)-H of isopropyl of **4**), 4.67 (m, (C)-H of isopropyl of **6**); relative intensities of carbene protons: **6**:**4** = 70:30. ^{31}P NMR (121 MHz, CD_2Cl_2): δ 59.64 (s, complex **4**), 36.05 (s, intermediate **6**), 11.16 (s, PCy_3).

b. NMR Observation of Intermediate 9. To the same NMR sample 4.4 mg of ligand **2a** (16 μmol, 0.8 equiv) was added. ^{1}H NMR (300 MHz, CD_2Cl_2, only selected peaks): δ 20.54 (s, carbene proton of **6**), 19.94 (s, carben proton of intermediate **9**), 17.35 (d, $J_{H,P}$ = 5.1 Hz, carbene proton of **4**), very weak signals for **8a1** and **8a2**; relative intensities of carbene protons: **6**:**9**:**4** = 54:11:35. ^{31}P NMR (121 MHz, CD_2Cl_2): δ 63.36 (d, $J_{P,P}$ = 200 Hz, P−O ligand in **9**), 59.64 (s, **4**), 40.61 (d, $J_{P,P}$ = 200 Hz, PCy_3 in **9**), 36.05 (s, **6**), 11.15 (s, PCy_3).

c. NMR Observation of 7a. The same NMR solution was stirred with 39 mg (0.39 mmol, 20 equiv) of CuCl for 30 min and then filtered. ^{1}H NMR (300 MHz, CD_2Cl_2, only selected peaks): δ 17.36 (d, $J_{H,P}$ = 4.2 Hz, carbene proton of **4**), 15.16 (d, $J_{H,P}$ = 8.7 Hz, carbene proton of **7a**), 14.95 (m, carbene proton of **8a1**), 14.52 (m, carbene proton of **8a2**); relative intensities of carbene protons: **4**:**7a**:**8a1**:**8a2** = 77:12:4:7. ^{31}P NMR (121 MHz, CD_2Cl_2): δ 83.31 (s, **7a**), 59.62 (s, **4**), 28.62 (br s, PCy_3CuCl-adduct), doublets of **8a1** and **8a2** very weak.

2:1-Complexes 8b1 and 8b2. A 100 mg amount of first-generation Hoveyda−Grubbs catalyst **4** (166 μmol) and 131 mg (366 μmol, 2.2 equiv) of ligand **2b** were stirred in 5 mL of CH_2Cl_2 for 30 min and filtered afterward to remove NaCl. The proton NMR shows two new carbene products in a ratio of 61:39 (**8b1** and **8b2**). ^{1}H NMR (300 MHz, CD_2Cl_2, only carbene region): δ 14.92 (t, $J_{H,P}$ = 6.6 Hz, **8b1**), 14.40 (dd, $J_{H,P}$ = 5.8 and 8.5 Hz, **8b2**). ^{31}P NMR (CD_2Cl_2): δ 76.70 (d, $J_{P,P}$ = 30 Hz, **8b2**), 73.08 (d, $J_{P,P}$ = 30 Hz, **8b1**), 61.75 (d, $J_{P,P}$ = 30 Hz, **8b1**), 55.08 (d, $J_{P,P}$ = 30 Hz, **8b2**). Leaving the two isomers in solution for 2 days did not result in a change of the isomer ratio. Crystals suitable for X-ray analysis were grown by diffusion of CH_2Cl_2 into ether out of a 1:1 solution of CH_2Cl_2 and ether of the isomer mixture. Both isomers crystallized, predominantly **8b1**, of which the structure could be resolved. Stirring the sample with excess of CuCl in CH_2Cl_2 and filtration of the excess CuCl still shows both isomers. However, after leaving the solution for 2 days only **8b2** was detected, which was purified by column chromatography under argon (substance adsorbed on Celite, column: silica, eluent: ether/hexane, 1:4). Crystals suitable for X-ray analysis were grown by diffusion of CH_2Cl_2 into ether out of a 1:1 solution of CH_2Cl_2 and ether of the complex, giving the structure of **8b2**.

^{1}H NMR (600 MHz, CD_2Cl_2): δ 14.42 (dd, 1H, CH(=Ru), $J_{H,P}$ = 5.9 and 8.4 Hz), 7.95 (v br s almost in the baseline, 2H, $Ar(P)_1H_{ortho}$), 7.63 (t, 1H, $Ar(PO)_1H$, $J_{H,H}$ = 7.1 Hz), 7.57 (t, 1H, Ar(O)H, $J_{H,H}$ = 7.8 Hz), 7.41 (dd, 1H, Ar(O)H, $J_{H,H}$ = 1.4 and 7.6 Hz), 7.37 (t, 1H, $Ar(P)_1H_{para}$, $J_{H,H}$ = 6.0 Hz), 7.36 (t, 1H, $Ar(P)_2H_{para}$, $J_{H,H}$ = 6.0 Hz), 7.32 (tm, 1H, $Ar(PO)_1H$, $J_{H,H}$ = 7.2 Hz), 7.30 (d, 1H, Ar(O)H, $J_{H,H}$ = 7.8 Hz), 7.17 (ddd, 1H, $Ar(PO)_1H$, $J_{H,H}$ = 1.1, 5.0, and 8.4 Hz), 7.09 (peak max., several very broad peaks from 7.6 to 6.1 ppm, 6H, $Ar(P)_{1+2}H_{ortho+meta}$), 7.04 (t, 1H, Ar(O)H, $J_{H,H}$ = 7.4 Hz), 6.98 (tm, 1H, $Ar(PO)_2H$, $J_{H,H}$ = 7.8 Hz), 6.59 (m, 2H, $Ar(PO)_2H$ and $Ar(PO)_1H$), 6.55 (dd, 1H, $Ar(PO)_2H$, $J_{H,H}$ = 4.2 and 8.3 Hz), 6.29 (tm, 1H, $Ar(PO)_2H$, $J_{H,H}$ = 7.2 Hz), 5.84 (m, 1H, CH(isopropoxy)), 1.91 (d, 3H, CH_3(isopropoxy), $J_{H,H}$ = 6.7 Hz), 1.81 (br d, 3H, H(adamantyl), $J_{H,P}$ = 11.0 Hz), 1.74 (d, 3H, CH_3(isopropoxy), $J_{H,H}$ = 6.7 Hz), 1.62 (br s, 3H, H(adamantyl)), 1.42 (br m, 12H, H(adamantyl)), 1.30 (br t, 6H, H(adamantyl), $J_{H,H}$ = 10.6 Hz), 1.06 (br d, 3H, H(adamantyl), $J_{H,H}$ = 11.0 Hz), 0.65 (br m, 3H, H(adamantyl)). ^{13}C NMR (150 MHz, CD_2Cl_2): δ 282.93 (m, 1C, C(=Ru)), 177.89 (d, 1C, $C_{Ar(PO),1}$(ORu), $J_{C,P}$ = 18.2 Hz), 177.17 (d, 1C, $C_{Ar(PO),2}$(ORu), $J_{C,P}$ = 12.5 Hz), 157.07 (s, 1C, $C_{Ar(O)}$(OR)), 146.45 (s, 1C, $C_{Ar(O)}$(CH=Ru)), ∼134.7 (v br s, 2C, $C_{Ar(P),1+2}$(*ortho* or *meta*)), 133.11 (s, 1C, $C_{Ar(PO),1}$(H)), ∼132.8 (v br s, 1C, $C_{Ar(P),1+2}$(*ortho* or *meta*)), 132.50 (s, 1C, $C_{Ar(PO),1}$-(H)), 132.42 (d, 1C, $C_{Ar(P),1}$(*ipso*), $J_{C,P}$ = 40.7 Hz), 132.21 (s, 1C, $C_{Ar(PO),2}$(H)), 131.72 (s, 1C, $C_{Ar(PO),2}$(H)), ∼131.0 (v br s, 1C, $C_{Ar(P),1+2}$(*ortho* or *meta*)), 129.95 (s, 1C, $C_{Ar(O)}$(H)), 129.24 (d, 1C, $C_{Ar(P),1}$(*para*), $J_{C,P}$ = 1.9 Hz), 129.00 (d, 1C, $C_{Ar(P),2}$(*para*), $J_{C,P}$ = 2.0 Hz), 128.26 (d, 1C, $C_{Ar(P),2}$(*ipso*), $J_{C,P}$ = 42.7 Hz), ∼128.0 (v br s, 4C, $C_{Ar(P),1+2}$(*ortho* or *meta*)), 127.42 (s, 1C, $C_{Ar(O)}$(H)), 123.30 (s, 1C, $C_{Ar(O)}$(H)), 121.48 (d, 1C, $C_{Ar(PO),1}$-(H), $J_{C,P}$ = 7.3 Hz), 121.29 (dd, 1C, $C_{Ar(PO),2}$(PRu), $J_{C,P}$ = 2.5 and 52.2 Hz), 118.10 (s, 1C, $C_{Ar(O)}$(H)), 115.95 (dd, 1C, $C_{Ar(PO),2}$(H), $J_{C,P}$ = 2.6 and 9.4 Hz), 114.29 (d, 1C, $C_{Ar(PO),1}$-(PRu), $J_{C,P}$ = 46.5 Hz), 113.98 (d, 1C, $C_{Ar(PO),2}$(H), $J_{C,P}$ = 7.0 Hz), 112.31 (d, 1C, $C_{Ar(PO),1}$(H), $J_{C,P}$ = 5.9 Hz), 79.51 (s, 1C, $C_{isopropoxy}$), 41.55 (d, 1C, $C_{adamantyl}$, $J_{C,P}$ = 23.1 Hz), 40.46 (d, 1C, $C_{adamantyl}$, $J_{C,P}$ = 23.5 Hz), 37.66 (s, 3C, $C_{adamantyl}$), 36.75 (s, 3C, $C_{adamantyl}$), 36.71 (s, 3C, $C_{adamantyl}$), 36.44 (s, 3C, $C_{adamantyl}$), 28.86 (d, 3C, $C_{adamantyl}$, $J_{C,P}$ = 9.4 Hz), 28.67 (d, 3C, $C_{adamantyl}$, $J_{C,P}$ = 9.1 Hz), 22.72 (s, 1C, $C_{isopropoxy}$), 22.04 (s, 1C, $C_{isopropoxy}$). ^{31}P NMR (121 MHz, CD_2Cl_2): δ 76.71 (d, $J_{P,P}$ = 30 Hz), 55.08 (d, $J_{P,P}$ = 30 Hz).

1:1-Complex 7d. A 250 mg sample of first-generation Hoveyda−Grubbs catalyst **4** (0.42 mmol) and 148 mg of ligand **2d** (0.46 mmol, 1.1 equiv) were stirred in 4.5 mL of CH_2Cl_2 for 1.5 h. An excess of CuCl (91 mg, 0.92 mmol, 2.2 equiv) was added and the reaction stirred for a further 20 min. A 22 mL amount of hexane was added, and after 30 min the precipitate was filtered off. After evaporation of the solvent the residue was adsorbed on Celite and transferred onto a column (silica, hexane/ether, 85:15) under argon. The complex was eluted by increasing the polarity to 40% ether. The yield was 125 mg (52%).

^{1}H NMR (300 MHz, CD_2Cl_2): δ 15.65 (d, 1H, $J_{H,P}$ = 7.5 Hz), 8.17 (br s, 2H), 7.92 (td, 1H, $J_{H,H}$ = 1.5 and 7.7 Hz), 7.54 (m, 4H), 7.18 (d, 1H, $J_{H,H}$ = 8.7 Hz), 7.13 (m, 2H), 6.96 (t, 1H, $J_{H,H}$ = 7.2 Hz), 6.75 (tm, 1H, $J_{H,H}$ = 7.4 Hz), 6.63 (dd, 1H, $J_{H,H}$ = 7.5 and 4.5 Hz), 5.34 (m, 1H), 1.87 (d, 3H, $J_{H,H}$ = 5.7 Hz), 1.79 (d, 3H, $J_{H,H}$ = 6.6 Hz), 1.37 (d, 3H, $J_{H,P}$ = 17.1 Hz), 1.28 (d, 3H, $J_{H,P}$ = 11.7 Hz), 1.12 (s, 9H). ^{13}C NMR (150 MHz, CD_2Cl_2): δ 284.58 (dd, 1C, C(=Ru), $J_{C,P}$ = 37.5 and 12.0 Hz), 178.91 (d, 1C, $C_{Ar(PO)}$(ORu), $J_{C,P}$ = 14.4 Hz), 154.61 (d, 1C, $C_{Ar(O)}$(OR), $J_{C,P}$ = 1.4 Hz), 143.93 (s, 1C, $C_{Ar(O)}$(CH=Ru)), ∼139.0 and 133.0 (2 v br s almost in the baseline, 2C, $C_{Ar(P)}$-(*ortho*)), 133.18 (d, 1C, $C_{Ar(PO)}$(H), $J_{C,P}$ = 1.6 Hz), 132.52 (d, 1C, $C_{Ar(PO)}$(H), $J_{C,P}$ = 2.1 Hz), 130.66 (d, 1C, $C_{Ar(P)}$(*para*), $J_{C,P}$ = 2.6 Hz), 129.50 (s, 1C, $C_{Ar(O)}$(H)), 128.15 (d, 2C, $C_{Ar(P)}$(*meta*), $J_{C,P}$ = 10.2 Hz), 127.98 (d, 1C, $C_{Ar(P)}$(*ipso*), $J_{C,P}$ = 47.7 Hz), 123.31 (s, 1C, $C_{Ar(O)}$(H)), 122.19 (s, 1C, $C_{Ar(O)}$(H)), 120.83 (d, 1C, $C_{Ar(PO)}$(PRu), $J_{C,P}$ = 41.6 Hz), 119.30 (d, 1C, $C_{Ar(PO)}$(H), $J_{C,P}$ = 10.1 Hz), 117.62 (d, 1C, $C_{Ar(PO)}$(H), $J_{C,P}$ = 6.3 Hz), 113.81 (s, 1C, $C_{Ar(O)}$(H)), 75.29 (s, 1C, $C_{isopropoxy}$), 47.93 (d, 1C, C_{TMP}, $J_{C,P}$ = 24.1 Hz), 37.22 (d, 1C, C_{TMP}, $J_{C,P}$ = 5.3 Hz), 29.21 (d, 3C, C_{TMP}, $J_{C,P}$ = 5.7 Hz), 22.33 (s, 1C, $C_{isopropoxy}$), 22.10 (s, 1C, $C_{isopropoxy}$), 21.57 (d, 1C, C_{TMP}, $J_{C,P}$ = 5.9 Hz), 20.50 (d, 1C, C_{TMP}, $J_{C,P}$ = 4.5 Hz). ^{31}P NMR (121 MHz, CD_2Cl_2): δ 81.62 (s).

1:1-Complex 7e. To 49 mg (81 μmol) of first-generation Hoveyda−Grubbs catalyst **4** was added 24 mg (91 μmol, 1.1 equiv) of ligand **2e** dropwise, and the solution was stirred for 15 min. An excess of CuCl (>2 equiv) was added and the suspension stirred for additional 25 min. After filtration and evaporation of the solvent the sample was transferred in hexane onto a column (10 g of silica) prepared under argon and eluted with gradually increasing polarity by adding up to 40% ether. A brown-orange band was collected in 56% yield (24 mg).

^{1}H NMR (300 MHz, CD_2Cl_2): δ 16.73 (d, 1H, $J_{H,P}$ = 5.4 Hz), 7.65 (t, 1H, $J_{H,H}$ = 8.7 Hz), 7.58 (d, 1H, $J_{H,H}$ = 8.1 Hz), 7.41 (t, 1H, $J_{H,H}$ = 8.1 Hz), 7.18 (d, 1H, $J_{H,H}$ = 8.4 Hz), 7.09 (m, 2H), 6.66 (m, 2H), 5.33 (m, 1H), 1.80 (d, 3H, $J_{H,H}$ = 6.0 Hz), 1.71

(d, 3H, $J_{H,H}$ = 6.0 Hz), 1.70 (d, 9H, $J_{H,P}$ = 14.1 Hz), 1.56 (d, 9H, $J_{H,P}$ = 14.1 Hz). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 271.94 (m, 1C, C(=Ru)), 178.13 (d, 1C, $C_{Ar(PO)}$(ORu), $J_{C,P}$ = 12.2 Hz), 152.85 (s, 1C, $C_{Ar(O)}$(OR)), 144.23 (s, 1C, $C_{Ar(O)}$(CH=Ru)), 132.43 (s, 1C, $C_{Ar(PO)}$(H)), 132.06 (s, 1C, $C_{Ar(PO)}$(H)), 128.83 (s, 1C, $C_{Ar(O)}$(H)), 123.39 (s, 1C, $C_{Ar(O)}$(H)), 122.24 (s, 1C, $C_{Ar(O)}$(H)), 119.68 (d, 1C, $C_{Ar(PO)}$(PRu), $J_{C,P}$ = 38.7 Hz), 118.37 (d, 1C, $C_{Ar(PO)}$(H), $J_{C,P}$ = 9.5 Hz), 117.22 (d, 1C, $C_{Ar(PO)}$(H), $J_{C,P}$ = 6.4 Hz), 113.55 (s, 1C, $C_{Ar(O)}$(H)), 75.73 (s, 1C, $C_{isopropoxy}$), 40.36 (d, 1C, $C_{tert\text{-}butyl}$, $J_{C,P}$ = 21.4 Hz), 34.63 (d, 1C, $C_{tert\text{-}butyl}$, $J_{C,P}$ = 21.4 Hz), 31.53 (s, 3C, $C_{tert\text{-}butyl}$), 28.60 (d, 3C, $C_{tert\text{-}butyl}$, $J_{C,P}$ = 2.8 Hz), 22.12 (s, 1C, $C_{isopropoxy}$), 21.57 (s, 1C, $C_{isopropoxy}$). ^{31}P NMR (121 MHz, CD_2Cl_2): δ 92.62 (s).

1:1-Complex 11b. A 56 mg (156 μmol, 1.2 equiv) amount of ligand **2b** in 2 mL of CH_2Cl_2 was added dropwise to a solution of 105 mg (128 μmol) of modified first-generation Hoveyda−Grubbs catalyst **10**, and the mixture was stirred for 30 min. After stirring with CuCl for another 25 min the solid was filtered off. ^{31}P NMR showed full conversion of **10** to **11b**. After evaporation of the solvent the substance was transferred with hexane onto a column (12 g silica) under argon. An orange-brown spot was isolated with 5−7% ether/hexane as the eluent, in 40% yield (39 mg).

^{1}H NMR (300 MHz, CD_2Cl_2): δ 15.23 (d, 1H, $J_{H,P}$ = 7.8 Hz), 8.06 (t, 2H, $J_{H,H}$ = 9.0 Hz), 7.75 (t, 1H, $J_{H,H}$ = 7.1 Hz), 7.53 (m, 4H), 7.26 (d, 1H, $J_{H,H}$ = 8.7 Hz), 7.16 (t, 1H, $J_{H,H}$ = 7.7 Hz), 7.07 (d, 1H, $J_{H,H}$ = 7.2 Hz), 6.90 (t, 1H, $J_{H,H}$ = 7.4 Hz), 6.74 (m, 2H), 4.94 (m, 1H), 2.43 (m, 2H), 2.20−1.16 (several m, 35H). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 276.98 (m, 1C, C(=Ru)), 179.61 (d, 1C, $C_{Ar(PO)}$(ORu), $J_{C,P}$ = 14.1 Hz), 157.85 (s, 1C, $C_{Ar(O)}$(OR)), 143.34 (s, 1C, $C_{Ar(O)}$(CH=Ru)), 134.62 (d, 2C, $C_{Ar(P)}$(*ortho*), $J_{C,P}$ = 8.3 Hz), 133.72 (s, 1C, $C_{Ar(PO)}$(H)), 132.27 (s, 1C, $C_{Ar(PO)}$(H)), 130.64 (d, 1C, $C_{Ar(P)}$(para), $J_{C,P}$ = 2.4 Hz), 128.56 (s, 1C, $C_{Ar(O)}$(H)), 128.26 (d, 2C, $C_{Ar(P)}$(meta), $J_{C,P}$ = 10.2 Hz), 126.02 (d, 1C, $C_{Ar(P)}$(*ipso*), $J_{C,P}$ = 46.1 Hz), 122.72 (s, 1C, $C_{Ar(O)}$(H)), 122.06 (s, 1C, $C_{Ar(O)}$(H)), 118.45 (d, 1C, $C_{Ar(PO)}$(H), $J_{C,P}$ = 10.2 Hz), 116.80 (d, 1C, $C_{Ar(PO)}$(H), $J_{C,P}$ = 6.3 Hz), 115.44 (d, 1C, $C_{Ar(PO)}$(PRu), $J_{C,P}$ = 45.6 Hz), 113.86 (s, 1C, $C_{Ar(O)}$(H)), 93.31 (s, 1C, $C_{(O)CHCy2}$), 40.19 (s, 1C, C_{Cy}), 39.72 (s, 1C, C_{Cy}), 39.30 (d, 1C, C_{Ad}, $J_{C,P}$ = 26.9 Hz), 37.70 (s, 3C, C_{Ad}), 36.79 (s, 3C, C_{Ad}), 30.45 (s, 1C, C_{Cy}), 30.18 (s, 1C, C_{Cy}), 29.91 (2s overlapping, 2C, C_{Cy}), 28.89 (d, 3C, C_{Ad}, $J_{C,P}$ = 9.7 Hz), 26.87 (3s overlapping, 3C, C_{Cy}), 26.77 (s, 1C, C_{Cy}), 26.36 (s, 1C, C_{Cy}), 26.25 (s, 1C, C_{Cy}). ^{31}P NMR (121 MHz, CD_2Cl_2): δ 80.82 (s).

1:1-Complex 11c. A 56 mg (68 μmol) portion of modified first-generation Hoveyda−Grubbs catalyst **10** (CH_2Cl_2 adduct) and 19 mg (64 μmol, 0.95 equiv) of ligand **2c** were stirred for 20 min in 4 mL of CH_2Cl_2. After treatment with a few equivalents of CuCl for 25 min the solid was filtered off. ^{31}P NMR showed full conversion of **10** to **11c**. The solvent was evaporated and the residue taken up in hexane and transferred onto a column (silica) prepared under argon. The desired complex was eluted with 5−6% ether/hexane in 55% yield (26 mg). Crystals suitable for X-ray analysis were grown by diffusion of CH_2Cl_2 into hexane out of a 1:1 solution of CH_2Cl_2 and hexane of the complex.

^{1}H NMR (300 MHz, CD_2Cl_2): δ 14.98 (d, 1H, $J_{H,P}$ = 8.4 Hz), 7.80 (m, 2H), 7.52 (m, 4H), 7.41 (m, 1H), 7.27 (d, 1H, $J_{H,H}$ = 8.4 Hz), 7.19 (m, 1H), 7.02 (dd, 1H, $J_{H,H}$ = 1.5 and 7.5 Hz), 6.90 (t, 1H, $J_{H,H}$ = 7.2 Hz), 6.78 (m, 2H), 4.94 (m, 1H), 2.88 (dd, 1H, $J_{H,H(P)}$ = 10.2 and 14.4 Hz), 2.39 (m, 1H), 2.27 (m, 1H), 2.12 (dd, 1H, $J_{H,H(P)}$ = 14.1 and 17.1 Hz), 1.89−1.16 (several m, 20H), 1.11 (d, 9H, $J_{H,P}$ = 0.9 Hz). ^{13}C NMR (150 MHz, CD_2Cl_2): δ 279.49 (m, 1C, C(=Ru)), 179.72 (d, 1C, $C_{Ar(PO)}$(ORu), $J_{C,P}$ = 14.6 Hz), 158.25 (s, 1C, $C_{Ar(O)}$(OR)), 142.90 (s, 1C, $C_{Ar(O)}$(CH=Ru)), 133.12 (d, 1C, $C_{Ar(PO)}$(H), $J_{C,P}$ = 1.8 Hz), 132.22 (s, 1C, $C_{Ar(PO)}$(H)), 131.98 (d, 2C, $C_{Ar(P)}$(*ortho*), $J_{C,P}$ = 8.4 Hz), 131.67 (d, 1C, $C_{Ar(P)}$(*ipso*), $J_{C,P}$ = 55.5 Hz), 130.67 (d, 1C, $C_{Ar(P)}$(*para*), $J_{C,P}$ = 2.6 Hz), 129.04 (d, 2C, $C_{Ar(P)}$(*meta*), $J_{C,P}$ = 10.6 Hz), 129.00 (s, 1C, $C_{Ar(O)}$(H)), 122.82 (s, 1C, $C_{Ar(O)}$(H)), 122.18 (s, 1C, $C_{Ar(O)}$(H)), 119.00 (d, 1C, $C_{Ar(PO)}$(H), $J_{C,P}$ = 10.8 Hz), 117.90 (d, 1C, $C_{Ar(PO)}$(H), $J_{C,P}$ = 7.5 Hz), 116.27 (d, 1C, $C_{Ar(PO)}$(PRu), $J_{C,P}$ = 49.1 Hz), 114.07 (s, 1C, $C_{Ar(O)}$(H)), 93.47 (s, 1C, $C_{(O)CHCy2}$), 42.66 (d, 1C, C_{Np}, $J_{C,P}$ = 28.9 Hz), 39.98 (s, 1C, C_{Cy}), 39.44 (s, 1C, C_{Cy}), 32.60 (d, 3C, C_{Np}, $J_{C,P}$ = 7.1 Hz), 31.81 (d, 1C, C_{Np}, $J_{C,P}$ = 1.4 Hz), 30.06 (s, 1C, C_{Cy}), 29.87 (s, 1C, C_{Cy}), 29.69 (s, 1C, C_{Cy}), 29.09 (s, 1C, C_{Cy}), 26.95 (s, 1C, C_{Cy}), 26.80 (s, 1C, C_{Cy}), 26.58 (s, 1C, C_{Cy}), 26.53 (s, 1C, C_{Cy}), 26.46 (s, 1C, C_{Cy}), 26.24 (s, 1C, C_{Cy}). ^{31}P NMR (121 MHz, CD_2Cl_2): δ 62.42 (s).

1:1-Complex 11d. A 150 mg (0.20 mmol) sample of modified first-generation Hoveyda−Grubbs catalyst **10** and 72 mg (0.22 mmol, 1.1 equiv) of ligand **2d** were stirred in 5 mL of CH_2Cl_2 for 30 min. After treatment with a few equivalents of CuCl for 30 min, the solid was filtered off, and the residue was transferred with hexane onto a column (10 g of silica) prepared under argon. The complex was eluted with 5% ether/hexane in 35% yield (52 mg). Crystals suitable for X-ray analysis were grown by diffusion of CH_2Cl_2 into hexane out of a 1:1 solution of CH_2Cl_2 and hexane of the complex.

^{1}H NMR (300 MHz, CD_2Cl_2): δ 15.51 (d, 1H, $J_{H,P}$ = 7.2 Hz), 8.13 (br s, 2H), 7.93 (td, 1H, $J_{H,H}$ = 1.5 and 7.5 Hz), 7.51 (m, 4H), 7.24 (d, 1H, $J_{H,H}$ = 9.0 Hz), 7.14 (tm, 1H, $J_{H,H}$ = 7.8 Hz), 6.98 (dd, 1H, $J_{H,H}$ = 1.8 and 7.5 Hz), 6.88 (td, 1H, $J_{H,H}$ = 0.9 and 7.2 Hz), 6.74 (m, 2H), 4.84 (m, 1H), 2.40−1.20 (several m, 22H), 1.35 (d, 3H, $J_{H,P}$ = 16.8 Hz), 1.26 (d, 3H, $J_{H,P}$ = 12.3 Hz), 1.12 (s, 9H). ^{13}C NMR (150 MHz, CD_2Cl_2): δ 284.62 (m, 1C, C(=Ru)), 179.39 (d, 1C, $C_{Ar(PO)}$(ORu), $J_{C,P}$ = 14.0 Hz), 158.51 (s, 1C, $C_{Ar(O)}$(OR)), 143.66 (s, 1C, $C_{Ar(O)}$(CH=Ru)), ~137.5 and 132.5 (2 v br s almost in the baseline, 2C, $C_{Ar(P)}$(*ortho*)), 133.21 (d, 1C, $C_{Ar(PO)}$(H), $J_{C,P}$ = 1.3 Hz), 132.50 (d, 1C, $C_{Ar(PO)}$(H), $J_{C,P}$ = 1.9 Hz), 130.57 (d, 1C, $C_{Ar(P)}$(*para*), $J_{C,P}$ = 2.5 Hz), 129.46 (s, 1C, $C_{Ar(O)}$(H)), 128.65 (d, 1C, $C_{Ar(P)}$(*ipso*), $J_{C,P}$ = 48.2 Hz), 128.06 (d, 2C, $C_{Ar(P)}$(*meta*), $J_{C,P}$ = 10.1 Hz), 122.73 (s, 1C, $C_{Ar(O)}$(H)), 122.35 (s, 1C, $C_{Ar(O)}$(H)), 120.24 (d, 1C, $C_{Ar(PO)}$(PRu), $J_{C,P}$ = 42.0 Hz), 119.46 (d, 1C, $C_{Ar(PO)}$(H), $J_{C,P}$ = 10.2 Hz), 117.36 (d, 1C, $C_{Ar(PO)}$(H), $J_{C,P}$ = 6.4 Hz), 114.53 (s, 1C, $C_{Ar(O)}$(H)), 94.06 (s, 1C, $C_{(O)CHCy2}$), 48.31 (d, 1C, C_{TMP}, $J_{C,P}$ = 24.3 Hz), 40.21 (s, 1C, C_{Cy}), 39.38 (s, 1C, C_{Cy}), 37.33 (d, 1C, C_{TMP}, $J_{C,P}$ = 4.9 Hz), 30.49 (s, 1C, C_{Cy}), 30.01 (s, 1C, C_{Cy}), 29.83 (s, 1C, C_{Cy}), 29.30 (d, 3C, C_{TMP}, $J_{C,P}$ = 5.6 Hz), 28.52 (s, 1C, C_{Cy}), 27.16 (s, 1C, C_{Cy}), 26.93 (s, 1C, C_{Cy}), 26.64 (s, 1C, C_{Cy}), 26.53 (s, 1C, C_{Cy}), 26.44 (s, 1C, C_{Cy}), 26.35 (s, 1C, C_{Cy}), 21.63 (d, 1C, C_{TMP}, $J_{C,P}$ = 5.5 Hz), 20.95 (d, 1C, C_{TMP}, $J_{C,P}$ = 4.3 Hz). ^{31}P NMR (121 MHz, CD_2Cl_2): δ 81.62 (s). Anal. Calcd (%) for $C_{39}H_{52}ClO_2PRu$ (720.34 g/mol): C 65.03, H 7.28. Found: C 64.79, H 7.42.

1:1-Complex 11e. An 11.4 mg (43.8 μmol, 1.0 equiv) amount of ligand **2e** in 2 mL of CH_2Cl_2 was added dropwise to 31.9 mg (43.3 μmol) of modified first-generation Hoveyda−Grubbs catalyst **10**. A few equivalents of CuCl were added, and the suspension was stirred for 30 min. After filtration and evaporation of the solvent, the residue was transferred in hexane onto a column (silica) prepared under argon. An orange fraction was collected in 70% yield (20 mg). Crystals were grown at rt via diffusion of dichloromethane from a hexane/CH_2Cl_2 solution (1:1) into hexane.

^{1}H NMR (300 MHz, CD_2Cl_2): δ 16.78 (d, 1H, $J_{H,P}$ = 5.1 Hz), 7.57 (t, 1H, $J_{H,H}$ = 8.1 Hz), 7.52 (d, 1H, $J_{H,H}$ = 7.5 Hz), 7.41 (t, 1H, $J_{H,H}$ = 7.7 Hz), 7.26 (d, 1H, $J_{H,H}$ = 8.7 Hz), 7.08 (t, 1H, $J_{H,H}$ = 6.9 Hz), 7.05 (t, 1H, $J_{H,H}$ = 5.1 Hz), 6.70 (dd, 1H, $J_{H,H}$ = 3.6 and 8.1 Hz), 6.63 (t, 1H, $J_{H,H}$ = 7.4 Hz), 4.86 (m, 1H), 2.29 (m, 2H), 1.84−1.16 (several m, 20H), 1.69 (d, 9H, $J_{H,P}$ = 14.1 Hz), 1.55 (d, 9H, $J_{H,P}$ = 14.1 Hz). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 272.80 (1C, C(=Ru), very weak signal), 178.42 (d, 1C, $C_{Ar(PO)}$(ORu), $J_{C,P}$ = 11.9 Hz), 156.74 (s, 1C, $C_{Ar(O)}$(OR)), 143.91 (s, 1C, $C_{Ar(O)}$(CH=Ru)), 132.41 (s, 1C, $C_{Ar(PO)}$(H)), 132.04 (s, 1C, $C_{Ar(PO)}$(H)), 128.83 (s, 1C, $C_{Ar(O)}$(H)), 122.85 (s, 1C, $C_{Ar(O)}$(H)), 122.60 (s, 1C, $C_{Ar(O)}$(H)), 118.99 (d, 1C, $C_{Ar(PO)}$(PRu), $J_{C,P}$ = 39.6 Hz), 118.43 (d, 1C, $C_{Ar(PO)}$(H), $J_{C,P}$ = 9.6 Hz), 116.87 (d, 1C, $C_{Ar(PO)}$(H), $J_{C,P}$ = 6.3 Hz), 114.03 (s, 1C, $C_{Ar(O)}$(H)), 93.42 (s, 1C, $C_{(O)CHCy2}$), 39.83 (s, 1C, C_{Cy}), 39.41 (s, 1C, C_{Cy}), 39.04 (d, 1C, $C_{tert\text{-}butyl}$, $J_{C,P}$ = 21.8 Hz),

35.02 (d, 1C, $C_{tert\text{-butyl}}$, $J_{C,P}$ = 21.5 Hz), 31.65 (s, 3C, $C_{tert\text{-butyl}}$), 29.85 (s, 1C, C_{Cy}), 29.71 (s, 1C, C_{Cy}), 29.62 (s, 1C, C_{Cy}), 29.47 (s, 1C, C_{Cy}), 28.80 (s, 3C, $C_{tert\text{-butyl}}$), 26.82 (2s overlapping, 2C, C_{Cy}), 26.64 (s, 1C, C_{Cy}), 26.34 (2s overlapping, 2C, C_{Cy}), 26.28 (s, 1C, C_{Cy}). ^{31}P NMR (121 MHz, CD_2Cl_2): δ 94.59 (s). Anal. Calcd (%) for $C_{34}H_{50}ClO_2PRu$ (658.26 g/mol): C 62.04, H 7.66. Found: C 61.98, H 7.72.

2:1-Complex 14. A 30 mg amount of PPh_3-Hoveyda−Grubbs catalyst **5** (52 μmol) and 32.5 mg (125 μmol, 2.4 equiv) of ligand **2e** were stirred in CH_2Cl_2 for 30 min. A color change to deep purple was observed. A few equivalents of CuCl were added, and the sample was filtered after 5 min. The substance was adsorbed on Celite and purified by a column under argon (silica, hexane/5% ether as the eluent) to give the complex in 80% yield (30 mg). Crystals suitable for X-ray analysis were grown out of an ether/MeOH solution of the complex by diffusion of ether into MeOH. ^{1}H NMR (600 MHz, CD_2Cl_2): δ 20.04 (d, 1H, $J_{H,P}$ = 5.7 Hz), 8.27 (dd, 1H, $J_{H,H}$ = 7.9 and 1.8 Hz), 7.52 (m, 2H), 7.41 (t, 1H, $J_{H,H}$ = 6.7 Hz), 7.09 (m, 2H), 6.84 (dd, 1H, $J_{H,H}$ = 8.2 and 3.6 Hz), 6.80 (dd, 1H, $J_{H,H}$ = 8.4 and 3.4 Hz), 6.72 (d, 1H, $J_{H,H}$ = 8.3 Hz), 6.55 (t, 1H, $J_{H,H}$ = 7.6 Hz), 6.51 (t, 1H, $J_{H,H}$ = 7.4 Hz), 6.46 (t, 1H, $J_{H,H}$ = 7.3 Hz), 4.58 (m, 1H), 1.44 (dd, 9H, $J_{H,P}$ = 11.3 and 2.0 Hz), 1.40 (dd, 9H, $J_{H,P}$ = 11.3 and 2.0 Hz), 1.29 (d, 3H, $J_{H,H}$ = 6.0 Hz), 1.23 (d, 3H, $J_{H,H}$ = 6.0 Hz), 1.03 (dd, 9H, $J_{H,P}$ = 11.5 and 2.1 Hz), 0.99 (dd, 9H, $J_{H,P}$ = 11.8 and 2.1 Hz). ^{13}C NMR (150 MHz, CD_2Cl_2): δ 291.65 (m, 1C), 182.61 (dd, 1C, $J_{C,P}$ = 5.3 and 10.3 Hz), 182.49 (dd, 1C, $J_{C,P}$ = 5.3 and 10.3 Hz), 148.53 (s, 1C), 145.42 (s, 1C), 133.60 (s, 1C), 133.38 (s, 1C), 133.03 (s, 1C), 131.94 (s, 1C), 131.46 (s, 1C), 131.22 (s, 1C), 121.97 (s, 1C), 121.57 (d, 1C, $J_{C,P}$ = 6.9 Hz), 121.51 (d, 1C, $J_{C,P}$ = 6.9 Hz), 114.81 (dd, 1C, $J_{C,P}$ = 29.7 and 3.8 Hz), 114.49 (d, 1C, $J_{C,P}$ = 4.8 Hz), 114.17 (s, 1C), 113.79 (dd, 1C, $J_{C,P}$ = 28.8 and 4.1 Hz), 112.89 (d, 1C, $J_{C,P}$ = 5.0 Hz), 70.50 (s, 1C), 38.41 (dd, 1C, $J_{C,P}$ = 14.3 and 3.8 Hz), 37.11 (dd, 1C, $J_{C,P}$ = 12.6 and 3.1 Hz), 36.97 (dd, 1C, $J_{C,P}$ = 13.2 and 3.9 Hz), 34.95 (dd, 1C, $J_{C,P}$ = 12.6 and 3.5 Hz), 30.51 (d, 3C, $J_{C,P}$ = 2.6 Hz), 30.08 (d, 3C, $J_{C,P}$ = 3.0 Hz), 29.63 (d, 3C, $J_{C,P}$ = 3.1 Hz), 29.11 (d, 3C, $J_{C,P}$ = 2.5 Hz), 22.15 (s, 1C), 22.05 (s, 1C). ^{31}P NMR (121 MHz, CD_2Cl_2): δ 67.03 (d, 1P, $J_{P,P}$ = 214 Hz), 65.07 (d, 1P, $J_{P,P}$ = 213 Hz). The two signals show a very strong roof effect.

Computational Details

Density functional theory (DFT) calculations were performed using ADF 2006 at the BP86/ZORA-TZP level of theory. All structures were fully optimized without constraints and checked with frequency calculations to ensure that they were minima.

Results

The results shown here reflect the different stages (1−4) of catalyst development that guided us on our way toward improved chemoselectivity. It should be mentioned that the systematic optimization of the catalyst was severely hampered in the beginning by 2:1-complexes (bidentate ligand-to-ruthenium ratio), whose undesired, and initially unexpected, formation needed to be suppressed. An overview of all experiments is given in Scheme 2. Ligand syntheses are described in Scheme 3. From unsuccessful direct ligand exchange with catalyst **4** (1), via discovery of the similar, but unexpected, behavior of the adamantyl substituent versus a *tert*-butyl group (2)—*the adamantyl group was assumed to disfavor 2:1-complexes due to its size*—we were led to the introduction of a larger carbene unit, which favors 1:1-complexes (3). This stage then allowed us to establish a series in which the size of substituent R_1 was systematically increased (4). Point 5 is not directly related to catalyst improvement but demonstrates, from a coordination chemistry point of view, that the larger ligand **2e**, upon ligand exchange, does not form a 2:1-complex with an intact chelate ring involving the carbene unit. We have already shown in our previous paper that a 1:1-complex with this ligand behaves similarly to the nonselective first-generation Grubbs catalyst **1**.[5]

1. Attempted Syntheses of 7a. When the bidentate phosphine/phenolate ligand **2a** is added dropwise to the first-generation Hoveyda−Grubbs catalyst **4** (path A, Scheme 2), one would expect a new singlet to appear in the ^{31}P NMR spectrum in case a 1:1-complex were to be formed. However, we saw four doublets indicating the formation of two isomers of a 2:1-complex (**8a1**: 77.82 and 67.61 ppm; **8a2**: 80.66 and 57.42 ppm) with a *cis* coordination of the two phosphines, suggested by the low coupling constants of $J_{P,P}$ = 30 Hz. In contrast, the bis-phosphine complex **3**, where the two different phosphines are *trans*, shows a coupling constant of $J_{P,P}$ = 194 Hz.[5] The corresponding peaks in the ^{1}H NMR spectrum are two doublet of doublets at 14.97 and 14.55 ppm that show coupling of the carbene proton to both phosphorus atoms. Disappointed by these results, we thought that the PCy_3 ligand in **4** could be too strongly bound, which would favor attack of a second ligand molecule **2a** on **7a** over replacement of the tricyclohexylphosphine in **4**. Therefore we subjected catalyst **5**,[11] which contains the more loosely bound PPh_3 ligand, to the exchange reaction with ligand **2a** (path B, Scheme 2). Also this approach was unsuccessful, since we observed exactly the same two isomers of the 2:1-complex (**8a1** and **8a2** in Scheme 2), even with only small amounts of ligand added (0.35 equiv; see Figures S4 and S5). Looking again at the ^{1}H NMR spectrum suggested a possible explanation: The chemical shifts of the carbene protons of the two isomers are shifted upfield relative to catalyst **4** (17.36 ppm) and are much lower than for the first-generation Grubbs catalyst **1** (20.02 ppm),[12] which we interpreted in such a way that the carbene unit must be chelating and that electron density is donated from the oxygen to the metal. Before we completely gave up this approach, we added our bidentate phosphine/phenolate ligand **2a** to a mixture of catalyst **4** with an 8-fold excess of PCy_3 (path C, Scheme 2). The excess of phosphine is able to break the oxygen/ruthenium chelate ring, to form an intermediate (**6**) (^{1}H NMR: singlet at 20.55 ppm; ^{31}P NMR: singlet at 36.05 ppm; see Figure S6), which resembles the first-generation Grubbs catalyst **1** (^{1}H NMR: singlet at 20.02 ppm; ^{31}P NMR: singlet at 36.61 ppm).[12] The ratio between **6** and **4** is 70:30. Ligand **2a** is now not able to fully displace PCy_3, which results in formation of an intermediate (**9**) in analogy with catalyst **3**,[5] which shows a singlet at 19.94 ppm in the ^{1}H NMR and two doublets at 63.36 and 40.61 ppm in the ^{31}P NMR (see Figure S7). The coupling constant $J_{P,P}$ = 200 Hz is indicative of a *trans* orientation. Intermediate **9** releases tricyclohexylphosphine upon treatment with CuCl[13] to form complex **7a** (see Figure S8). This route, however, did not seem to be practical as a preparative procedure, since a large excess of phosphine needs to be applied even though formation of 2:1-complexes **8a1** and **8a2** could be reduced (see Experimental Section). However, CuCl[13] also scavenges ligand **2a** and leaves large amounts of unreacted catalyst **4**. Another strategy was needed.

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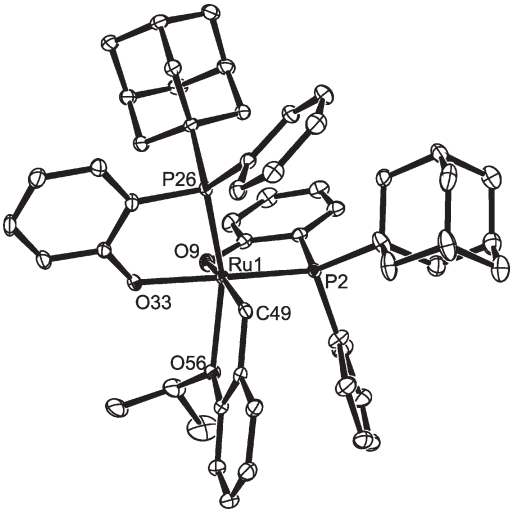

Figure 1. Crystal structure of 2:1-complex **8b1** (ORTEP plot, 20% probability ellipsoids). Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (deg): Ru1—C49 1.878(5), Ru1—O33 2.047(3), Ru1—O9 2.172(3), Ru1—O56 2.273(3), Ru1—P26 2.2742(11), Ru1—P2 2.3528(11), C49—Ru1—O33 101.85(16), C49—Ru1—O9 164.29(17), O33—Ru1—O9 83.53(13), C49—Ru1—O56 78.80(15), O33—Ru1—O56 81.31(11), O9—Ru1—O56 87.56(12), C49—Ru1—P26 91.13(14), O33—Ru1—P26 82.16(9), O9—Ru1—P26 104.29(10), O56—Ru1—P26 158.40(9), C49—Ru1—P2 95.82(13), O33—Ru1—P2 160.92(10), O9—Ru1—P2 77.56(9), O56—Ru1—P2 95.27(9), P26—Ru1—P2 104.80(4).

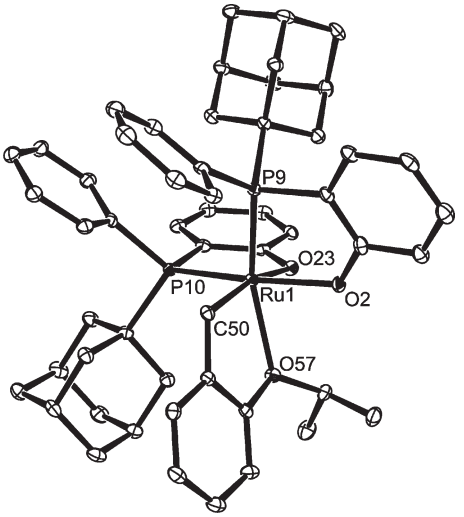

Figure 2. Crystal structure of 2:1-complex **8b2** (ORTEP plot, 20% probability ellipsoids). Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (deg): Ru1—C50 1.877(4), Ru1—O2 2.052(2), Ru1—O23 2.139(3), Ru1—O57 2.270(2), Ru1—P9 2.2742(9), Ru1—P10 2.3742(10), C50—Ru1—O2 104.36(13), C50—Ru1—O23 162.18(12), O2—Ru1—O23 82.13(10), C50—Ru1—O57 79.47(12), O2—Ru1—O57 77.54(9), O23—Ru1—O57 85.92(9), C50—Ru1—P9 91.73(11), O2—Ru1—P9 83.54(7), O23—Ru1—P9 105.61(7), O57—Ru1—P9 156.33(7), C50—Ru1—P10 93.52(11), O2—Ru1—P10 161.54(8), O23—Ru1—P10 79.42(7), O57—Ru1—P10 101.71(7), P9—Ru1—P10 100.73(3).

2. Changing *tert*-Butyl (2a) for Adamantyl (2b). If formation of hexacoordinated 2:1-complexes is favored due to steric effects, larger phosphine ligands could be expected to work against 2:1-complex formation. In this sense we replaced the *tert*-butyl group in **2a** with the larger adamantyl. The synthesis of the new ligand **2b** is similar to **2a**, except that formation of the adamantyl Grignard reagent required a particular published experimental procedure.[7] Subjecting ligand **2b** to the exchange reaction pushed us back to a stage where we were already. We see again four doublets in the ^{31}P NMR (73.08 and 61.75 ppm for **8b1**; 76.70 and 55.08 ppm for **8b2**) with coupling constants of 30 Hz. The ^{1}H NMR (14.92 ppm for **8b1** and 14.40 ppm for **8b2**) also shows an almost identical pattern to that obtained in experiments with ligand **2a**, with the ratio between the two isomers (**8b1** and **8b2**) being equal to 61:39. Crystallization of the mixture did not provide a pure sample of the dominant isomer **8b1** (both crystallize under the applied conditions; for the NMR spectrum see Figure S14), but at least gave single crystals of sufficient quality to obtain an X-ray structure of **8b1** (Figure 1). It indeed shows a hexacoordinated ruthenium with the two bidentate phosphine/phenolate ligands **2b** *cis* to each other. Purification attempts after reaction with CuCl[13] to remove excess phosphine ligand gave another interesting result. After filtration of the excess CuCl the isomer ratio remained unchanged. However, after two days in solution isomer **8b1** has completely disappeared, leaving only isomer **8b2**. We think that ligand exchange, catalyzed by CuCl, may transform a product formed under kinetic control (isomer **8b1**) to the thermodynamically more stable isomer **8b2**. Purification by column chromatography and crystallization allowed us now to get an X-ray structure of isomer **8b2**, for which the substituents on the equatorial phosphine are switched (Figure 2). In any case, as a preparative procedure for 1:1 complexes, the adamantyl approach failed and we needed again a new strategy.

3. Increasing the Size of the Carbene (4 ≫ 10). Since in the above-described 2:1-complexes **8a** and **8b** the carbene unit is chelating, a larger substituent there could potentially prevent this otherwise favorable interaction and destabilize the 2:1-complexes in favor of the 1:1-complex. To obtain a catalyst closely related to **3**, we synthesized the modified first-generation Hoveyda−Grubbs catalyst **10** by replacing the isopropoxy substituent by dicyclohexylmethoxy (Scheme 2), which had been reported previously.[5] Indeed, we were successful now, since the ligand exchange reaction with both **2a** and **2b** gave the desired 1:1-complexes **11a** and **11b** as the main products. Crystal structures for **10** and **11a** are given in Figures 5 and 6, but have been reported previously.[5] We tested **11a** and **11b** in copolymerization of NBE and COE and obtained high yields of largely alternating copolymers. The polymer microstructure was for both catalysts dependent on (a) the temperature and (b) the norbornene-to-cyclooctene ratio. Figures 3 and 4 show the olefinic region of the ^{13}C NMR spectra. Peak assignments have been done in accordance with the literature.[14−18] Lower temperatures and

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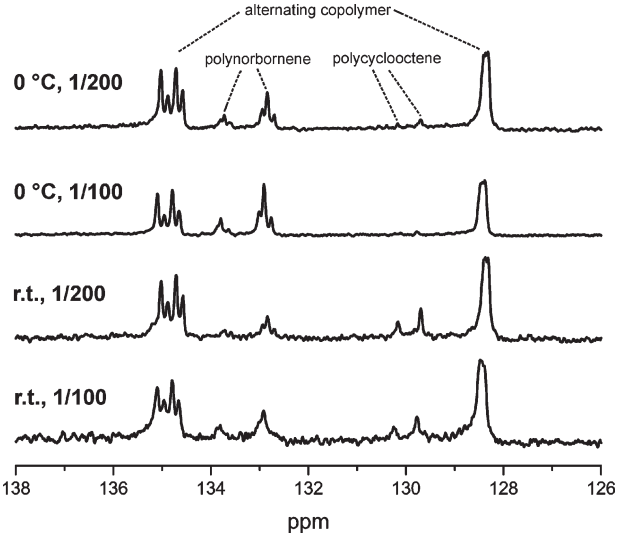


Figure 3. Temperature and NBE/COE ratio dependence with catalyst **11a**.

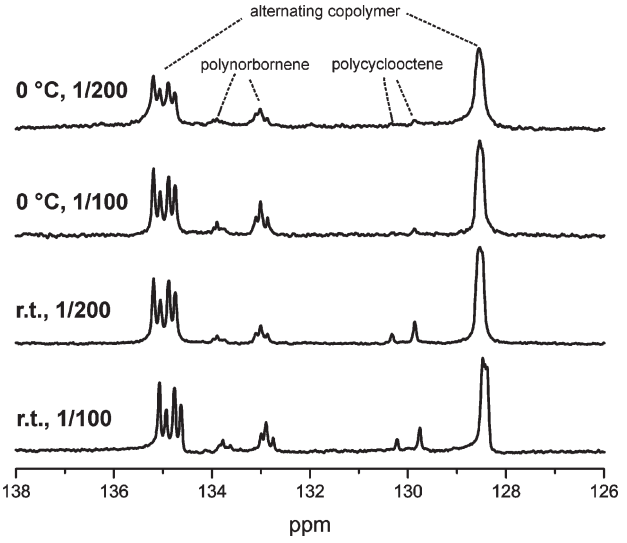


Figure 4. Temperature and NBE/COE ratio dependence with catalyst **11b**.

higher amounts of norbornene favor the norbornene homopolymer. Cooling from room temperature to 0 °C almost entirely suppresses the cyclooctene homopolymerization. Furthermore the substituents on the phosphine ligands have an influence, although not very pronounced. Analysis of the polymers (Table 1) shows that the degree of alternation goes up to 76% with catalyst **11a**. The overall performance of catalyst **11b** is slightly better, which gives up to 85% heterojunctions. The larger dicyclohexylmethoxy carbene has another advantage besides providing enough steric bulk for a successful formation of 1:1-complexes. We compared the performance of **10** with commercially available catalysts by performing NMR kinetics with cyclooctene, which demonstrate the higher activity of **10** versus **4** (Figure 7).

4. Improving the Selectivity toward Alternation to 100% with Catalyst 11d. As a next step, we tried to improve the selectivity of the catalyst even further and synthesized ligands **2c** and **2d** (Scheme 3). Synthesis of ligand **2c** was straightforward, whereas **2d** was more difficult to obtain. A Grignard solution of 2-bromo-2,3,3-trimethylbutane was

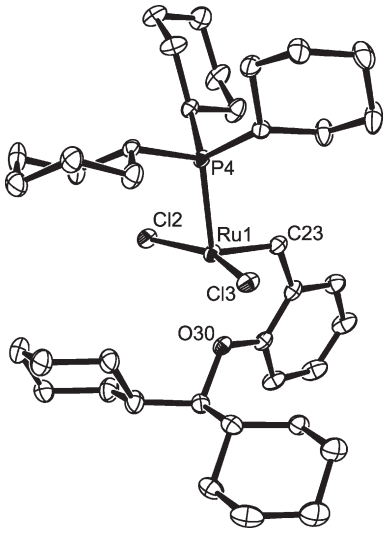


Figure 5. Crystal structure of complex **10** (ORTEP plot, 20% probability ellipsoids). Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (deg): Ru(1)−C(23) 1.825(4), Ru(1)−P(4) 2.2683(9), Ru(1)−Cl(2) 2.3385(9), Ru(1)−Cl(3) 2.3396(9), Ru(1)−O(30) 2.341(2), C(23)−Ru(1)−P(4) 98.86(12), C(23)−Ru(1)−Cl(2) 98.66(12), P(4)−Ru(1)−Cl(2) 91.29(3), C(23)−Ru(1)−Cl(3) 102.70(12), P(4)−Ru(1)−Cl(3) 90.61(3), Cl(2)−Ru(1)−Cl(3) 158.00(4), C(23)−Ru(1)−O(30) 79.53(13), P(4)−Ru(1)−O(30) 176.98(6), Cl(2)−Ru(1)−O(30) 86.45(6), Cl(3)−Ru(1)−O(30) 92.23(6).

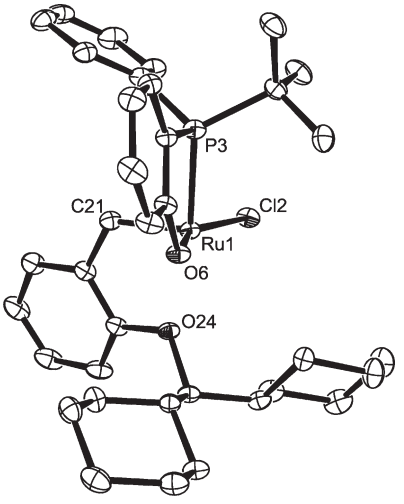


Figure 6. Crystal structure of 1:1-complex **11a** (ORTEP plot, 20% probability ellipsoids). Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (deg): Ru(1)−C(21) 1.825(4), Ru(1)−O(6) 1.997(2), Ru(1)−P(3) 2.2201(9), Ru(1)−O(24) 2.310(2), Ru(1)−Cl(2) 2.3397(10), C(21)−Ru(1)−O(6) 104.49(14), C(21)−Ru(1)−P(3) 92.72(12), O(6)−Ru(1)−P(3) 84.51(7), C(21)−Ru(1)−O(24) 79.67(13), O(6)−Ru(1)−O(24) 92.10(9), P(3)−Ru(1)−O(24) 170.66(7), C(21)−Ru(1)−Cl(2) 102.07(12), O(6)−Ru(1)−Cl(2) 153.13(8), P(3)−Ru(1)−Cl(2) 98.31(3), O(24)−Ru(1)−Cl(2) 88.65(7).

finally prepared in about 40−50% yield by slow addition of the alkyl bromide to a 15-fold excess of Mg powder in refluxing ether. Both complexes **11c** and **11d** could be prepared and also characterized by X-ray (Figures 8 and 9), and the steric bulk of the TMP substituent can readily be seen in the ^{1}H and ^{13}C NMR spectra (Figures S20 and S21). At room

Table 1. Polymerization Experiments Carried Out with 150−200 mg of Norbornene (NBE) and the Indicated Amount of COE (Cyclooctene) with the Reaction Volume Filled up to 20 mL with CH_2Cl_2 and a NBE/Catalyst Ratio of 2000:1

catalyst	T	NBE/COE	t [h][b]	yield [%][c]	alternating linkages [%][d]	*cis* content [%][e]
11a	rt	1:100	1.5	84	72	30
11a	rt	1:200	1.5	90	76	37
11a	0 °C	1:100	1.5	40	67	29
11a	0 °C	1:200	1.5	41	76	34
11b	rt	1:100	1	82	78	38
11b	rt	1:200	1	72	85	39
11b	0 °C	1:100	1	53	80	36
11b	0 °C	1:200	1	11	83	37
11c	rt	1:100	1.5	89	89	20
11d[a]	rt	1:20	0.25[a]	88	97	13

[a] Catalyst **11d** produces a highly viscous polymer solution within seconds after catalyst addition. [b] The polymerizations were quenched by addition of 100 mL of MeOH after the times indicated. [c] Yields were determined after drying the coagulated copolymer under high vacuum for 2 h. [d] The percentage of alternating linkages has been determined by integration of the olefinic region of the ^{13}C NMR spectrum. [e] The *cis* content was estimated by integration of the CH(CH=CHR) protons on the norbornene terminus of the double bond (see Supporting Information).

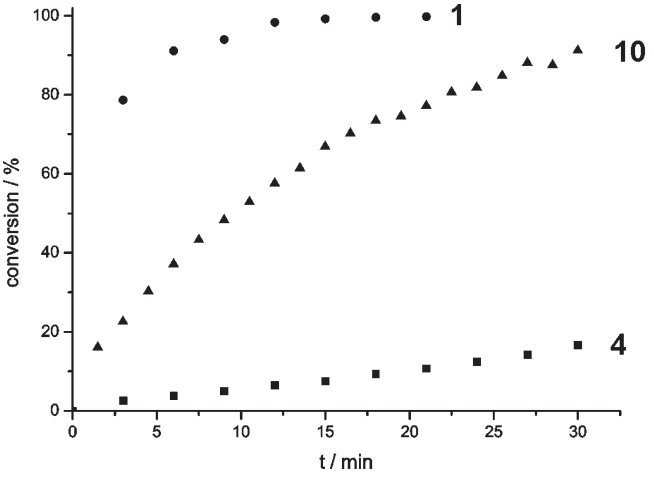


Figure 7. NMR kinetics showing the performance of our modified first-generation Hoveyda−Grubbs catalyst **10** versus Grubbs 1 (**1**) and Hoveyda−Grubbs 1 (**4**) in polymerization of cyclooctene (COE) in $CDCl_3$ at room temperature. $[C_0]_{COE}$ = 0.13 M, $[C_0]_{cat.}/[C_0]_{COE}$ = 1/200.

temperature the phenyl ring cannot freely rotate in **11d**, as documented by strong broadening of the signals of the *ortho* carbons, which almost disappear into the baseline. Similarly, although less pronounced, the peaks of the *ortho* and *meta* protons are broadened. Furthermore, the *ortho* protons do not show correlation to any aromatic carbon in an HSQC experiment. A similar effect is observed for complexes **7d** (Figures S9 and S10) and **22a−f** (see the 2D spectrum for complex **22a** (Chart 1) in the Supporting Information, Figure S25). Comparison of all four catalysts in copolymerization shows a systematic trend (Figure 10). Catalyst **11c** shows higher selectivity than **11a** and **11b**, and almost no polycyclooctene is obtained even at room temperature and a norbornene-to-cyclooctene ratio of 1:100. Catalyst **11d** outperforms all and displays complete selectivity for the formation of the alternating copolymer to within our detection limits, even at a norbornene-to-cyclooctene ratio of 1:20.

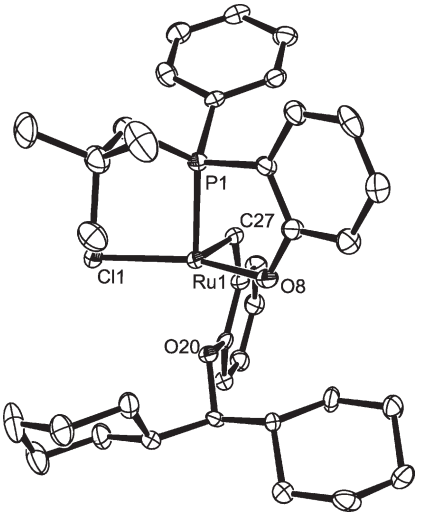


Figure 8. Crystal structure of 1:1-complex **11c** (ORTEP plot, 20% probability ellipsoids). Hydrogen atoms are omitted for clarity. The structure contains a heavily disordered hexane molecule, which is refined with restrained geometry. Selected distances (Å) and angles (deg): Ru1—C27 1.837(9), Ru1—O8 2.009(6), Ru1—P1 2.217(2), Ru1—O20 2.316(5), Ru1—Cl1 2.350(2), C27—Ru1—O8 105.6(3), C27—Ru1—P1 93.5(3), O8—Ru1—P1 84.69(17), C27—Ru1—O20 79.9(3), O8—Ru1—O20 91.8(2), P1—Ru1—O20 171.41(15), C27—Ru1—Cl1 97.6(3), O8—Ru1—Cl1 156.54(19), P1—Ru1—Cl1 97.58(8), O20—Ru1—Cl1 88.78(15).

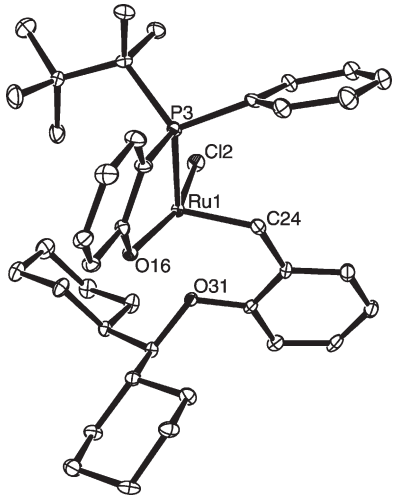


Figure 9. Crystal structure of 1:1-complex **11d** (ORTEP plot, 20% probability ellipsoids). Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (deg): Ru1—C24 1.851(5), Ru1—O16 1.996(3), Ru1—P3 2.2320(13), Ru1—O31 2.355(3), Ru1—Cl2 2.3617(14), C24—Ru1—O16 104.52(19), C24—Ru1—P3 93.53(17), O16—Ru1—P3 84.20(10), C24—Ru1—O31 78.34(18), O16—Ru1—O31 89.80(13), P3—Ru1—O31 168.40(9), C24—Ru1—Cl2 95.79(17), O16—Ru1—Cl2 158.68(10), P3—Ru1—Cl2 101.18(5), O31—Ru1—Cl2 87.98(9).

Furthermore it is much faster than the other three in this series and is able to produce a copolymer in high yields within seconds after catalyst addition, as seen by immediate gel formation. Since the TMP group is sterically very demanding, we also tried the synthesis of 1:1-complex **7d** (Scheme 2), which indeed could be obtained in good yield. Whereas **11d**

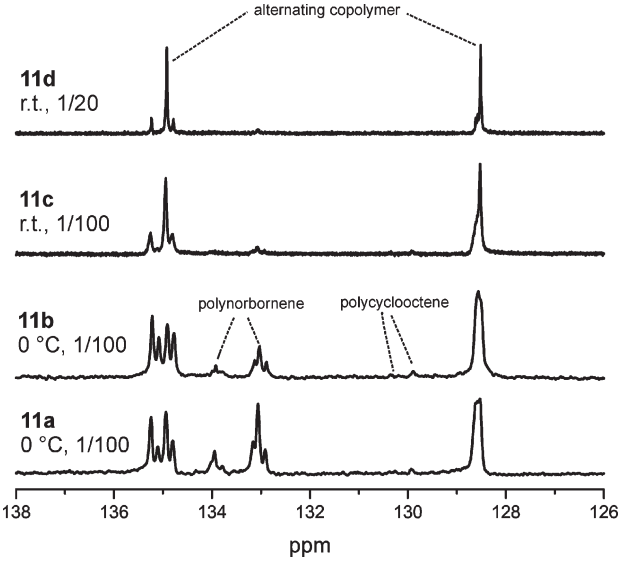


Figure 10. Dependence of the degree of alternation on the substituents in copolymerization of NBE and COE with catalysts **11a** (*tert*-butyl), **11b** (adamantyl), **11c** (neopentyl), and **11d** (TMP). For polymer characterization see Table 1.

gives a highly viscous polymer solution within a few seconds, **7d**, with the smaller and slower initiating carbene unit, needs about a minute to reach that stage. Additionally, the *cis* content of the polymers produced by **7d** and **11d** decreased to 13% (Table 1), which may be attributed to a more crowded metallacyclobutane structure, which avoids additional steric interaction by adopting a more favorable *trans* orientation of the substituents.

5. Synthesis of the *trans* 2:1-Complex 14 with the Bulky Ligand 2e. As a negative control for our mechanistic concept, we synthesized complex **11e**, and we could show that the symmetric ligand **2e** induces no chemoselectivity. The polymer microstructure contains blocks of the two homopolymers but no alternating units. We had already demonstrated this previously with the analogous complex based on the structure of **3**.[5] As a matter of interest we also synthesized symmetric complex **7e**, which could be obtained as a stable 1:1-complex. This demonstrates that the two *tert*-butyl groups in **2e** are too big for a stable 2:1-complex with a *cis* coordination of the phosphines and a chelating carbene unit (structure **14a** in Chart 2). A crystal structure for **11e** is given in Figure 12. A 2:1-complex (**14**), however, could be prepared and also characterized by X-ray crystallography (Figure 11). The coordination is different from that of the other 2:1-complexes (**8a** and **8b**), with the phosphines being *trans* to each other and no chelation of the carbene unit. The structure of **14** therefore resembles that of the first-generation Grubbs catalyst **1**.[12] Also the color of the complex is almost identical to that of **1**, deep purple in CH_2Cl_2, in contrast to all the other 1:1- and 2:1-complexes in the present paper, which give orange-brown solutions. Furthermore, the chemical shift of the carbene proton in CD_2Cl_2 (20.02 ppm) is identical to that reported for the Grubbs first-generation catalyst **1** (20.02 ppm),[12] although it shows a doublet ($J_{H,P}$ = 5.7 Hz), indicating that coupling to one of the phosphorus atoms is apparently stronger than to the second one. The ^{31}P NMR spectrum indicates that the two phosphines are chemically different, although not by much, since it shows two doublets with a very strong roof effect at 67.03 and 65.07 ppm (Figure S24). The distinction

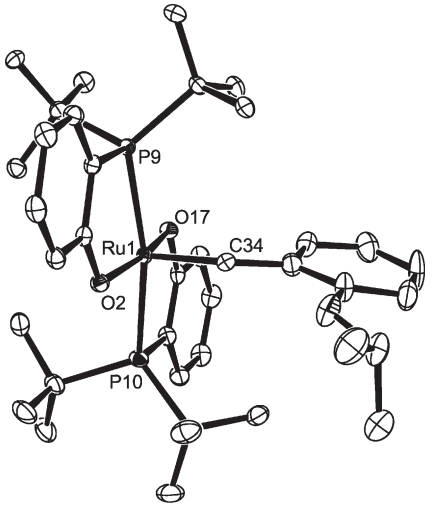


Figure 11. Crystal structure of 2:1-complex **14** (ORTEP plot, 20% probability ellipsoids). Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (deg): Ru1—C34 1.844(5), Ru1—O2 2.068(3), Ru1—O17 2.084(3), Ru1—P9 2.3774(10), Ru1—P10 2.3994(11), C34—Ru1—O2 89.5(2), C34—Ru1—O17 101.3(2), O2—Ru1—O17 169.24(11), C34—Ru1—P9 92.69(16), O2—Ru1—P9 82.79(8), O17—Ru1—P9 97.52(8), C34—Ru1—P10 98.78(16), O2—Ru1—P10 95.06(8), O17—Ru1—P10 82.45(8), P9—Ru1—P10 168.32(4).

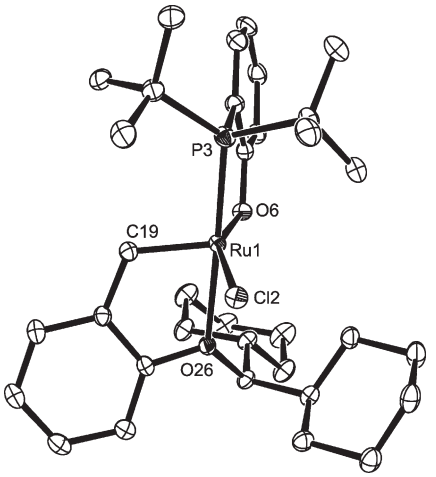


Figure 12. Crystal structure of 1:1-complex **11e** (ORTEP plot, 20% probability ellipsoids). Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (deg): Ru(1)−C(19) 1.834(4), Ru(1)−O(6) 1.992(2), Ru(1)−P(3) 2.2468(10), Ru(1)−O(26) 2.306(2), Ru(1)−Cl(2) 2.3481(10), C(19)−Ru(1)−O(6) 104.69(14), C(19)−Ru(1)−P(3) 99.55(12), O(6)−Ru(1)−P(3) 84.53(8), C(19)−Ru(1)−O(26) 79.06(13), O(6)−Ru(1)−O(26) 90.64(10), P(3)−Ru(1)−O(26) 174.47(7), C(19)−Ru(1)−Cl(2) 99.29(12), O(6)−Ru(1)−Cl(2) 154.63(8), P(3)−Ru(1)−Cl(2) 99.68(4), O(26)−Ru(1)−Cl(2) 85.83(7).

arises from a hindered rotation of the carbene unit. The coupling constant ($J_{P,P}$ = 213 Hz) is indicative of a *trans* orientation. The Ru−P distances of **14** in the crystal are relatively large, 2.3774(10) and 2.3994(11) Å. They are, however, still shorter than in the Grubbs first-generation catalyst **1** (2.4188(10) and 2.4265(10) Å), of which we also present a crystal structure (Figure 13) without *para* substitution on the benzylidene carbene, as has been reported earlier.[12] The carbene in **14** is not

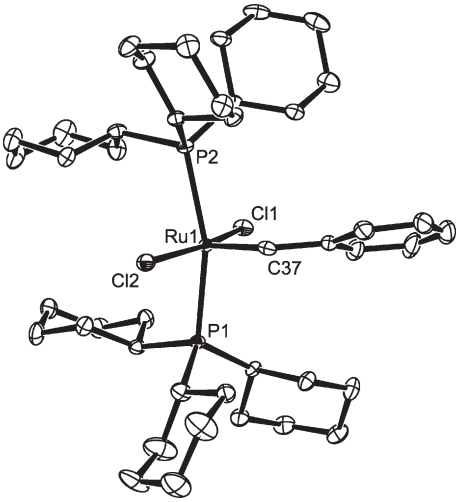


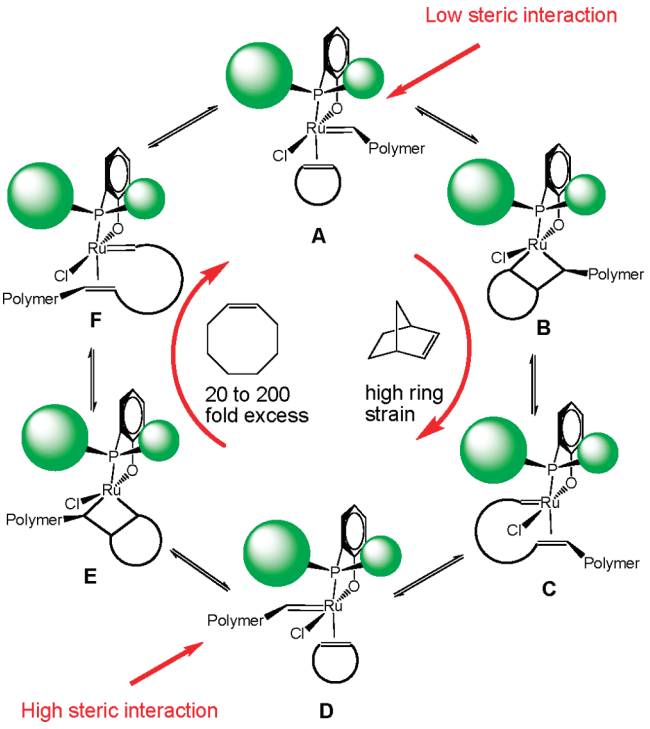
Figure 13. Crystal structure of the first-generation Grubbs catalyst **1** (ORTEP plot, 30% probability ellipsoids). Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (deg): Ru1—C37 1.834(4), Ru1—Cl1 2.3953(10), Ru1—Cl2 2.4012(10), Ru1—P1 2.4188(10), Ru1—P2 2.4265(10), C37—Ru1—Cl1 105.04(13), C37—Ru1—Cl2 86.94(13), Cl1—Ru1—Cl2 167.96(4), C37—Ru1—P1 100.23(12), Cl1—Ru1—P1 89.90(4), Cl2—Ru1—P1 89.03(4), C37—Ru1—P2 97.66(12), Cl1—Ru1—P2 89.07(4), Cl2—Ru1—P2 88.19(4), P1—Ru1—P2 161.72(4).

part of a chelate ring, and we found only a few other crystal structures in the literature, where the alkoxy substituent on the benzylidene does not coordinate to the metal.[19−21]

Discussion

In 1971 Chauvin was the first to postulate a metathesis mechanism involving (i) [2+2] cycloaddition of an olefin to a metal carbene to form (ii) a metallacyclobutane, which then undergoes (iii) cycloreversion to form a new olefin and a new metal carbene species.[22] The breakthrough of this reaction into synthetic organic chemistry, however, started with the report of a well-defined, stable, functional-group-tolerant ruthenium catalyst (**1**) by Grubbs in 1995,[12,23−25] which we took as a starting point to perform, among other things, kinetic isotope effect studies in the gas phase to elucidate the nature of the metallacyclobutane in ruthenium metathesis. We concluded at that time that it must be a transition state.[1] This was in contradiction with our own computational results, which predicted a minimum for it.[2,26,27] After a more careful investigation we realized that the rate-determining

Scheme 4. Catalytic Cycle for the Alternating Copolymerization of Norbornene and Cyclooctene with Catalyst 3[a]



[a] The catalyst switches between two different carbene states (**A** and **D**).

step is actually not formation of the metallacyclobutane itself, but rather a rotation of the tricyclohexylphosphine in **1** at a metallacyclobutane structure, which then led to an interpretation of the isotope effects for which the gas phase and computational results were in agreement.[2,3] A consequence of the new interpretation was the realization that during one productive turnover, i.e., carbene to *trans*-metallacyclobutane to carbene, the carbene switches from one "side" of the catalyst to the other. This was not obvious at the time in the case of catalyst **1** due to ligand rotation of the 3-fold symmetric PCy_3 ligand, which permits the generation of a carbene configuration of the same energy. In 2005 the group of Piers detected a metallacyclobutane intermediate with a modified second-generation Grubbs catalyst at low temperature, which was *trans* to the N-heterocyclic carbene (NHC) ligand,[28] which confirmed our previous computational results.[2]

As a further consequence, we reported later in the same year the design of a catalyst (**3**)[4] that is able to produce a largely alternating copolymer from norbornene and cyclooctene, based on a simple, general mechanistic picture, taking advantage of an asymmetric, bidentate phosphine ligand, which cannot rotate (Scheme 4). *The asymmetry is given by the two substituents on the phosphorus which differ in size:* Two cyclic olefins are distinguished by their ring strain, which was explained by two diastereomeric carbene states (**A** and **D**) of the catalyst that ideally interchange after each productive metathesis step.[4] This means that the step from one diastereomeric carbene (**A** ≫ **D**) proceeds only if one can pay the energetic price by release of ring strain, whereas the next transformation (**D** ≫ **A**) proceeds for either strained or

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Table 2. Comparison of Various Bond Lengths of Complexes[a]

complex	Ru−$O_{carbene}$ [Å]	Ru−$C_{carbene}$ [Å]	Ru−P [Å]
1	no chelating oxygen	1.834(4)	2.4265(10) and 2.4188(10)
8b1	2.273(3)	1.878(5)	2.2742(11) and 2.3528(11)
8b2	2.270(2)	1.877(4)	2.2742(9) and 2.3742(10)
10	2.341(2)	1.825(4)	2.2683(9)
11a	2.310(2)	1.825(4)	2.2201(9)
11c	2.316(5)	1.837(9)	2.217(2)
11d	2.355(3)	1.851(5)	2.2320(13)
11e	2.306(2)	1.834(4)	2.2468(10)
14	no chelate ring	1.844(5)	2.3774(10) and 2.3994(11)
22a	2.242(6)	1.831(7)	2.231(2)
22d	2.250(2)	1.833(3)	2.2311(7)
22e	2.232(4)	1.840(7)	2.2493(17)
22f	2.258(3)	1.837(4)	2.2373(11)

[a] Complexes **10** and **11a** have been published elsewhere,[5] as well as crystal structures of **22a**, **22d**, **22e**, and **22f**.[6]

unstrained cycloolefins. Our prototype of such a chemoselective catalyst **3** was synthesized by simple ligand exchange of the asymmetric bidentate phosphine/phenolate ligand **2a** with the first-generation Grubbs catalyst **1** (Schemes 1 and 3). In contrast to the latter one, which polymerizes first the more strained and more reactive norbornene, followed by blocks of polycyclooctene, the new complex exhibited the ability of inducing alternation. The new catalyst, however, showed low stability in solution and tended to form small amounts of first-generation Grubbs catalyst upon decomposition, which is also reflected in the produced copolymer that contains considerable amounts of polycyclooctene blocks (ca. 20%).[5] To test whether the lower selectivity comes from a decomposition product of the catalyst or an insufficient energetic difference between the two carbene states (**A** and **D**), we synthesized a PCy_3-free catalyst with a Hoveyda-type, chelating carbene unit (**11a**). We have already shown previously that this complex is able to suppress homopolycyclooctene at 0 °C, which is better than with **3**, which even at this low temperature gives a significant amount of polycyclooctene. We interpret the result as confirmation that **3** forms indeed nonselective catalyst **1** upon decomposition.[5] However, first attempts to synthesize 1:1-complex **7a** by direct ligand substitution from complex **4** failed because of formation of stable 2:1 complexes. We were successful, however, with the introduction of a larger carbene unit in **10**, which not only allowed for a clean formation of 1:1-complexes **11a**,**b** but also exhibits faster initiation kinetics. The origin of these two effects can readily be seen by structural analysis of 2:1-complexes **8b1** and **8b2** and 1:1-complexes **10**, **11a**, **11c**, and **11d**. Various bond lengths are compared in Table 2.

Stability of 2:1-Complexes. The unsuccessful attempts of the direct substitution reaction between ligands **2a**,**b** and the first-generation Hoveyda−Grubbs catalyst **4** are attributed to the formation of stable 2:1-complexes. The Ru−$O_{carbene}$ bond distances are 2.273(3) and 2.270(2) Å for **8b1** and **8b2**, a bit longer than in pentacoordinated sulfonate complexes **22a**−**f**[6] (between 2.232(4) and 2.258(3) Å), indicating a reasonably strong chelate ring (Table 2). A similar hexacoordinated 2:1-complex with two bidentate NHC/phenolate ligands has been reported by Jensen. There, the Ru−$O_{carbene}$ distance is 2.38 Å, probably due to the more electron-rich NHC ligands.[19] A hexacoordinated Ru dimer with a Ru−$O_{carbene}$ chelate ring has been published by Hoveyda,[11] and Grubbs reported a catalyst structure with a fluorine−ruthenium interaction.[29] Further hexacoordinated structures are reported by Grela for a dormant ruthenium catalyst bearing a chelating carboxylate ligand[30,31] and a complex containing a chelating trifluoroacetate ligand replacing the chloride anion by Buchmeiser.[32] The longer Ru−$O_{carbene}$ bond distances in **8b1** and **8b2** compared to our sulfonate complexes **22a**−**f**[6] are not surprising due to a more crowded and more electron-rich hexacoordinated ruthenium center. It is also seen by the rather long Ru−$C_{carbene}$ bond lengths of 1.878(5) and 1.877(4) Å, respectively. This is in agreement with the ^{1}H NMR signals that appear at rather high field (see Results). The Ru−P bond lengths are quite a bit longer than for monophosphine complexes **10**,[5] **11a**,[5] **11b**−**e**, and **22a**−**f**,[6] however, on average distinctly shorter than for the bisphosphine complexes **1** and **14**. The initial observation that **8a2** is the thermodynamic product (this has been demonstrated for **8b2**; see Results) is reproduced by calculations with BP86/TZP for the truncated *tert*-butyl model. They suggest isomer **8a2** to be in fact more stable than isomer **8a1** (by 0.4 kcal/mol). Charts 2 and 3 show structures of various chelating, hexacoordinated (**8a1**−**4**) and nonchelating, pentacoordinated (**8a5**,**6**) complexes. All are predicted to be higher in energy than **8a2**. If one has a closer look at the crystal structure, there might be a favored stabilization in **8b2** by a $\pi-\pi$ stacking interaction, since the two phenyl rings are aligned in a parallel fashion, although they are not on top of each other. ^{1}H and ^{13}C NMR spectra further show that both phenyl rings are not freely rotating at room temperature, since we observe broad peaks for the *ortho* and *meta* positions for the protons as well as for the corresponding carbons (Figures S15 and S16). In contrast, an NMR spectrum of complex **8a1** does not show this effect, where $\pi-\pi$ stacking is not possible (Figures S12 and S13). The calculations in Charts 2 and 3 also predict, in the case of the more bulky ligand **2e**, that nonchelating complex **14** should be more stable than structure **14a**, in which the phosphines are *cis* to each other and the carbene unit forms a chelate ring. This is again in perfect agreement with our experimental findings.

Larger Carbene Unit ≫ Faster Initiation. The oxygen/ruthenium chelation for complexes containing the larger dicyclohexylmethoxy-substituted benzylidene is weakened due to steric repulsion. If one takes a look at the Ru−$O_{carbene}$ bond distance of 2.341(2) Å in **10**, it is quite a bit longer than in sulfonate complexes **22a**−**f**,[6] and even longer than in the very crowded 2:1-complexes **8a** and **8b** (Table 2). Also for all other complexes with this larger carbene unit (**11a**−**e**) this distance is larger than 2.30 Å. Furthermore the Ru−$O_{carbene}$ bond distance of 2.355(3) Å for **11d** is the longest of all the complexes in the present paper, which also reflects the great steric bulk of the TMP substituent. We are aware of only two longer Ru−$O_{carbene}$ distances in the literature.[19,33] We checked the CCDC database and found actually only seven *ortho* alkoxy-substitued benzylidene complexes with Ru−$O_{carbene}$ distances ≥ 2.30 Å: catalyst **5** by Hoveyda (2.309(2) Å),[11] a complex with a four-membered NHC ligand by

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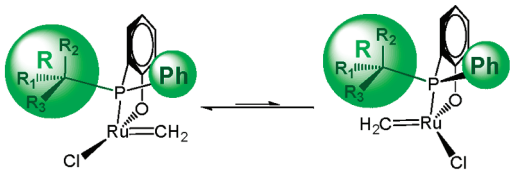
Chart 4. All Rotamers for the the Two Diastereomeric Carbene States[a]



S1 R = *tert*-Butyl
T1 R = Adamantyl
U1-1 R_1 = *tert*-Butyl, R_2 = R_3 = H
U1-2 R_2 = *tert*-Butyl, R_1 = R_3 = H
U1-3 R_3 = *tert*-Butyl, R_1 = R_2 = H
V1-1 R_1 = *tert*-Butyl, R_2 = R_3 = Me
V1-2 R_2 = *tert*-Butyl, R_1 = R_3 = Me
V1-3 R_3 = *tert*-Butyl, R_1 = R_2 = Me

S2 R = *tert*-Butyl
T2 R = Adamantyl
U2-1 R_1 = *tert*-Butyl, R_2 = R_3 = H
U2-2 R_2 = *tert*-Butyl, R_1 = R_3 = H
U2-3 R_3 = *tert*-Butyl, R_1 = R_2 = H
V2-1 R_1 = *tert*-Butyl, R_2 = R_3 = Me
V2-2 R_2 = *tert*-Butyl, R_1 = R_3 = Me
V2-3 R_3 = *tert*-Butyl, R_1 = R_2 = Me

[a] Truncated model using a methylidene carbene. Letter **S** for ligand **2a**, **T** for **2b**, **U** for **2c**, and **V** for **2d**.

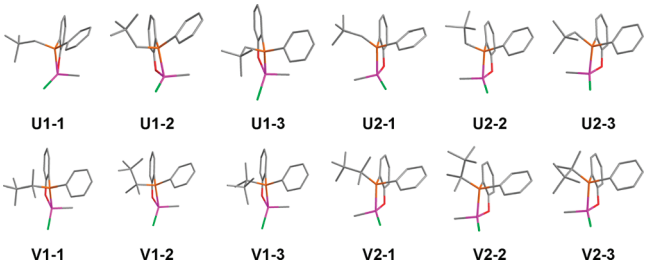
Grubbs (2.360 (3) Å),[33] the above-mentioned hexacoordinated 2:1 complex by Jensen (2.38 Å),[19] a complex with a chloride-substituted NHC ligand by Grubbs (2.300(4) Å),[29] one with a Ru=CRR′ ligand by Lehmann (2.301(3) Å),[20] a complex with a nitro substituent on the carbene by Buchmeiser (2.3103(16) Å),[34] and a catalyst with a backbone-substituted NHC ligand by Grubbs (2.3068(14) Å).[35] The shortest distances of such chelate rings are reported by Grela for a dormant ruthenium catalyst bearing a chelating carboxylate ligand (2.207(2) Å)[30,31] and for one pentacoordinated structure, where the oxygen of the benzylidene carbene coordinates *cis* to the NHC ligand (2.205(6) Å).[36] All other

Table 3. Comparison of the Energies of the Two Diastereomeric Carbene States in Chart 4 (BP86/TZP)

R	energy of carbene state 1 [kcal/mol][b]			energy of carbene state 2 [kcal/mol][b]		
tert-butyl	**S1**			**S2**		
	0.0			3.4		
adamantyl	**T1**			**T2**		
	0.0			3.4		
neopentyl	**U1-1**	**U1-2**	**U1-3**	**U2-1**	**U2-2**	**U2-3**
	0.0	1.4	4.5	6.4	3.8	1.7
TMP[a]	**V1-1**	**V1-2**	**V1-3**	**V2-1**	**V2-2**	**V2-3**
	0.0	1.7	5.5	7.7	5.3	4.0

[a] TMP = 1,1,2,2-tetramethylpropyl. [b] In the case of R = neopentyl or TMP, there are three rotamers for each carbene state.

Chart 5. Calculated Structures for Methylidene Carbenes U (R = Neopentyl as in Chart 4) and V (R = TMP)



structures show bond distances between those extremes.[11,20,29,32−56] Additionally the chelate ring in **10** is easily opened by tricyclohexylphosphine, since during formation of this catalyst by cross-metathesis with styrene **12** in the absence of CuCl intermediate **13** is almost exclusively observed (Scheme 2; see NMR spectrum in Figure S17), in contrast to catalyst **4**, which can be opened to a greater extent only by an excess of PCy_3 (Figure S6). As our NMR kinetics with cyclooctene confirm, initiation with **10** is faster than with **4** (see Figure 7). Initiation via phosphine loss in **1** is, however, still more favorable. Other, also faster initiating chelating carbene units with further substituents on the aromatic carbene ring in **4** have been reported by Hoveyda,[38] Blechert,[57,58] and Grela.[59,60] Further direct evidence for this effect is seen by comparison of catalyst **7d** versus **11d** in copolymerization experiments. The latter one is about 30 times faster in yielding the copolymer quantitatively.

Effect of the Size of Substituent R_1. The polymerization results with catalysts **11a**−**d** clearly indicate that the degree of alternation, i.e., the chemoselectivity, is directly related to the size difference of the two substituents on the phosphine (phenyl vs R_1). Some interesting aspects deserve being mentioned: It seems that the adamantyl substituent is not so different from the *tert*-butyl group, at least close to the metal center. This is also proven, by consideration in hindsight, by

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the similar behavior of the two ligands **2a** and **2b** in catalyst formation. Both give stable 2:1-complexes with catalyst **4**. The larger adamantyl group, which is pointing "up" (away from the carbene), has an additional effect only if the polymer chain gets larger, where it can impose steric repulsion better than the *tert*-butyl group. Calculations using BP86/TZP therefore show similar energetics for the two ligands, but they were run with a small carbene unit (Chart 4, Table 3). The neopentyl substituent was at first thought to be less selective since it can be oriented in such a way to avoid steric interaction with the carbene, but obviously other factors play a similar important role and increase selectivity. Calculations of all three possible rotamers for both carbene states predict an energy difference of only 1.7 kcal/mol between the most stable conformers (Chart 4, Chart 5, Table 3). Two rotamers for one state seem to be too high in energy (**U2-1** and **U2-2**), whereas for the other state this is the case only for **U1-3**. Hence, entropic contributions may play a role but would only add about 0.4 kcal/mol to the overall ΔG ($\Delta G = \Delta H - T\Delta S$; $\Delta S = R \ln(W)$; $W = 2/1$; $T = 298$ K). For the 1,1,2,2-tetramethylpropyl substituent (TMP) calculations predict an energy difference of 4.0 kcal/mol between the most stable conformers of the two diastereomeric 14-electron carbene states (**V1-1** and **V2-3**). Accordingly the TMP substituent should give higher selectivity than the *tert*-butyl and adamantyl substituent, for which only a difference of 3.4 kcal/mol between the two states is predicted. Additionally entropy may contribute to the overall steric energy. The temperature and concentration dependence with catalysts **11a**−**d** shows that the steric price for the energetically disfavored step (**A** ≫ **D**) can still be paid to some extent by cyclooctene, at least when polymerizations are carried out at room temperature (Figures 3 and 4). Wiberg has given a value for the ring strain in cyclooctene being equal to 4.2 kcal/mol,[61] which is in reasonable relationship to our computed number for the energy difference between the two carbene states (3.4 kcal/mol). For the very bulky TMP substituent it seems that the less strained cyclooctene cleanly reacts efficiently fast with only one diastereomeric form of the carbene, whereas norbornene shows the same high activity toward both. The computed number of 4.0 kcal/mol between the two carbene states seems to present a lower bound, and all possible rotamers and the actual transition states need to be considered. A polymer produced from a 1:5 mixture of norbornene and cyclooctene contains about 10% polynorbornene units, as expected for this high selectivity that seems to be controlled only by strain[61] release of monomers (purely diastereomeric site control; see below). The TMP substituent obviously provides enough steric energy that cyclooctene can compete equally with norbornene in the energetically favored step of the catalytic cycle (**D** ≫ **A** in Scheme 4).

Diastereomeric Site Control versus Chain-End Control. If one compares our system to literature precedents, one finds an analogous situation in stereoselective Ziegler−Natta polymerization of propylene.[62] Two possible mechanisms for stereoselective polypropylene formation were identified: enantiomorphic site control and growing chain-end control. The former mechanism relies on the alternate switching of the catalyst between two enantiomorphic states with each productive turnover, very much in analogy with the mechanism for alternating copolymerization in our ROMP systems. The experimental embodiment of enantiomorphic site control can be seen in chiral ethylene-bridged *ansa*-metallocene catalysts at room temperature and also in an unbridged metallocene catalyst with unsubstituted Cp rings (Cp_2TiPh_2/MAO) below −40 °C, both of which form highly isotactic polypropylene. The catalyst itself controls the stereochemistry. The alternative mechanism, growing chain-end control, relies on the preference for one or the other prochiral face of an inserting propylene unit being governed by the stereochemical result of the immediately preceding insertion. Blechert's proposed mechanism for alternating copolymerization would resemble this kind of control (see below, example b). Our catalysts operate unambiguously by the mechanism analogous to enantiomorphic site control, which we should properly designate as diastereomeric site control, because the chelating bidentate ligand prevents any rotation of the phosphine bearing the substituents that control selectivity. Logically, the two stereogenic centers, at P and at Ru, necessitate four stereoisomers, which appear as two enantiomeric pairs of diastereomers. The diastereomers have neither the same energy nor the same reactivity, which is the underlying basis for the chemoselectivity in the present work. For the growing chain-end control, several proposals can be found in the literature:

(a) Hoveyda et al. published stereogenic-at-metal ruthenium complexes bearing enantiomerically pure bidentate NHC/binaphthol ligands that effectively catalyze ROCM of norbornene derivatives with two equivalents of styrene.[38,63] He also claimed that chiral Mo catalysts would readily give polymers under these conditions.[43] One might therefore hypothesize other effects than pure ring strain that could account for this high chemoselectivity. Since this catalyst is stereogenic at Ru, one could expect, on the basis of our mechanistic picture, two different diastereomeric carbenes taking part in the catalytic cycle. This could lead to the following conclusion: If the highly strained norbornene would react faster than styrene with both sides, a ROMP polymer would be the expected result. The presence of only two equivalents of styrene, however, could be a strong indication that the release of ring strain is needed only to effect a change of the carbene's position to the energetically disfavored side. Once there, the norbornene unit on the carbene would provide too much steric crowding so that only the smaller styrene can react (diastereomeric site control with a strong contribution of "chain-end" or substrate control).

(b) Blechert and Buchmeiser use unsymmetrical, monodentate, chiral, and achiral NHC ligands for the alternating copolymerization of norbornene and cyclooctene.[14,15] The high tendency for alternation was explained by an enhanced cyclooctene insertion rate into a norbornene-initiator-derived terminus and, *vice versa*, an enhanced norbornene insertion rate into a cyclooctene-initiator-derived terminus. In other words they speculated that the norbornene-initiator-derived terminus makes the catalyst more crowded, providing steric energy for a faster cyclooctene insertion, but too bulky, with the effect that it slows down consecutive norbornene incorporation. The chain-end control would arise from a relatively

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fast rotation of the NHC ligand, which would not allow for distinction of the two otherwise diastereomeric sites.

(c) A similar effect may be seen in the alternating copolymerization of cyclopentene and norbornene using $RuCl_3$ in the presence of phenol as a cocatalyst, for which it has been proposed that the catalyst is made more crowded by formation of hydrogen-bonded solvent cages.[16,17] Due to the great steric bulk around the complex, the more reactive but bulkier norbornene cannot perform two consecutive metathesis steps. The alternation would arise purely from the appropriate combination of the two monomers (chain-end or substrate control).

To return to the precedent for a mechanistic duality, a clean, experimentally accessible distinction between these two cases can be made by assignment of pentad signals in the ^{13}C NMR spectrum. A single defect in the polymer chain would give the following microstructures: LLLLLRRRRR for chain-end control and LLLLLRLLLL for enantiomorphic site control (L and R stand for propylene units where the methyl group is left or right in a Fischer projection). In the latter one the catalyst center of fixed chirality overrules the error (R) and forces subsequent olefin insertions to return to the previous preference (L). Taken over to the ruthenium ROMP systems a single defect would result in the following structure: NCNCNNCNCN for chain-end control and NCNCNNNCNCN for diastereomeric site control (N and C stand for norbornene and cyclooctene). We have examined the ^{13}C spectra carefully to evaluate the possibility that the consequences of sequence errors could provide a tool to distinguish between the two mechanisms, but the spectra are unfortunately less informative than in the corresponding case of stereoregular polypropylene (see Figures S26−S29). Nevertheless, we are designing further mechanistic tests that should help determine which mechanism is operative in chemoselective, alternating ROMP for catalysts where rotation is, in principle, possible. These experiments are ongoing.

Conclusion

We have shown that careful, systematic tuning of the sterics of ligands of a ruthenium metathesis catalyst bearing a bidentate phosphine/phenolate ligand resulted, step by step, in more selective variants. We were able to demonstrate by a four-point series that chemoselectivity is directly related to the size difference between the substituents on the phosphine ligand. A strong indication is provided by the fact that the ring strain in cyclooctene lies in the same range as the computed energy differences between the two diastereomeric carbene states. Calculations predict some activity toward cyclooctene homopolymerization for catalysts **11a**,**b** and complete shut-down of this channel for catalyst **11d**, which is in perfect agreement with our experiments. Further investigations are underway that focus on the different control mechanism between our system and the one reported by Blechert and Buchmeiser, who use second-generation catalysts with a rotating NHC ligand.

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Supporting Information Available: ^1H NMR spectra of polymers (Figures S1−S3), NMR spectra showing the ligand exchange reaction of **2a** with **5** (Figures S4, S5), NMR spectra for observation of intermediates **6** and **9** and complex **7a** (Figures S6−S8), NMR spectra of several 1:1- and 2:1-complexes (Figures S9−S16 and S18−S24), NMR observation of intermediate **13** (Figure S17), HSQC experiment for complex **22a** (Figure S25), peak assignment in ^{13}C NMR spectra of homo- and copolymers (Figures S26−S29), and coordinates of calculated structures. This material is available free of charge via the Internet at http://pubs.acs.org.