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FULL PAPER

Rhodium catalysts with a chiral cyclopentadienyl ligand derived from natural R-myrtenal

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Dedicated to academician Aziz M. Muzafarov in recognition of his strategic work for development of science in Russia and on the occasion his 70th anniversary.

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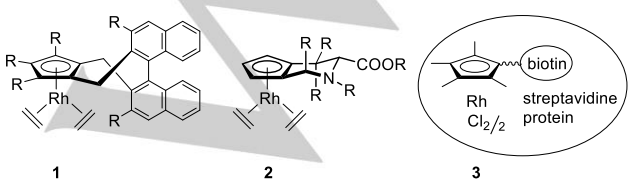
Abstract: A new chiral cyclopentadiene $Cp^{myr}H$ was synthesized from the natural terpene *R*-myrtenal in 5 steps and about 40% total yield. The key step was the reaction of vinyl-dibromocyclopropane derivative with MeLi which provided the diene $Cp^{myr}H$ via Skattebøl rearrangement. The reaction of $Cp^{myr}H$ with $[(cod)Rh(OAc)]_2$ gave the rhodium(I) complex $(Cp^{myr})Rh(cod)$ and subsequent oxidation with halogens X_2 gave the rhodium(III) complexes $[(Cp^{myr})RhX_2]_2$ (X = Br, I). Complex $(Cp^{myr})Rh(cod)$ in combination with benzoyl peroxide catalyzed the C-H activation of O-pivaloyl-phenylhydroxamic acid and its subsequent annulation with alkenes giving dihydroisoquinolinones with high yield (70−90%) but moderate enantioselectivity (16−36% ee).

Introduction

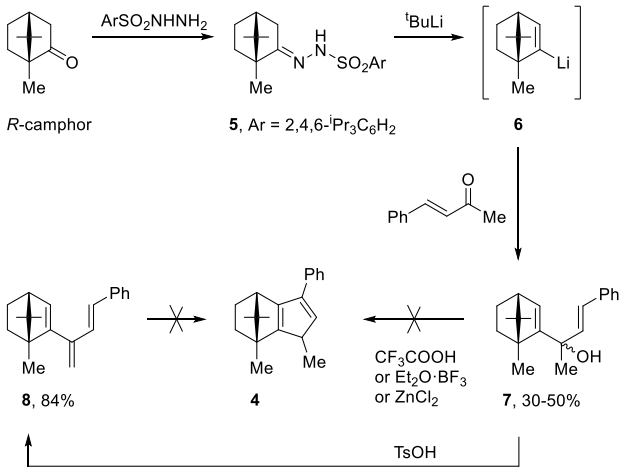
Rhodium catalysts with chiral cyclopentadienyl ligands have recently attracted a lot of attention thanks to their successful application in C-H activation reactions.[1–6] The most explored catalysts of this type are the binaphthyl derivatives **1** developed by Cramer et al. and You et al.,[7–11] the amino acid derivatives **2** developed by Antonchik and Waldmann et al.,[12] the streptavidine-docked derivatives **3** developed by Ward and Rovis et al.,[13,14] as well as some others[15–20] (Scheme 1). A wide application of these catalysts is still somewhat limited by their multi-step synthesis involving rather expensive starting materials and reagents. In attempt to solve this problem and to expand the library of ligands we focused our attention on complexes with cyclopentadienes derived from cheap natural chiral terpenes. Some complexes of this type have been synthesized previously,[21–23] but they have been rarely applied in catalysis.[24,25]



Scheme 1. Examples of rhodium catalysts with chiral cyclopentadienyl ligands.

Results and Discussion

We started our investigation with the synthesis of the camphor-based ligand **4** using the procedures similar to those developed by Halterman and Tretyakov (Scheme 2).[26] The camphor hydrazone derivative **5** reacted with 2 equivalents of ^{t}BuLi to generate the vinyl lithium species[27] **6** and following addition of benzylideneacetone produced the bis-allyl-alcohol **7** in 30-50% yields. Note that the use of different ketones on this stage would allow for straightforward variation of substituents in the final cyclopentadiene product. The yield of the alcohol **7** was sometimes diminished by a side process of deprotonation of the methyl group of the starting benzylideneacetone by the strongly basic lithium reagent **6**, which was indicated by the formation of 2-bornene as a byproduct. Complete purification of the compound **7** was also problematic.

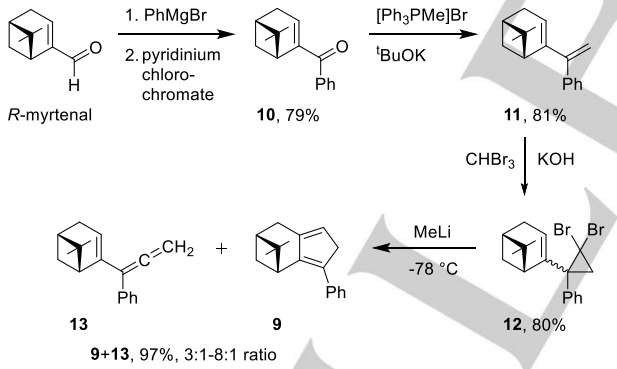


Scheme 2. Attempted synthesis of the chiral cyclopentadiene **4** from *R*-camphor.

The next crucial step was planned to be the Nazarov cyclization of **7** into the cyclopentadiene **4**. However, it was not successful: most of the acidic reagents (CF_3COOH, $Et_2O{\cdot}BF_3$, $ZnCl_2$)

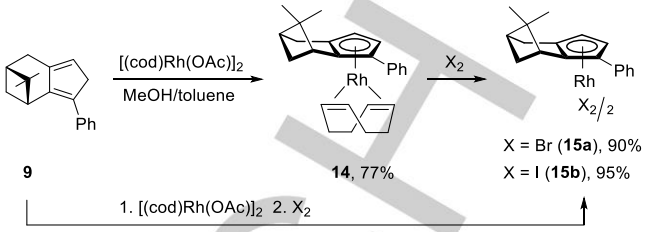
converted **7** into a mixture of products, while the only clean reaction in the presence of $TsOH \cdot H_2O$ produced the triene **8** in 84% yield. Attempts to convert the triene **8** into the target cyclopentadiene **4** by strong acids were also unsuccessful. It is worth noting that Halterman and Tretyakov have also observed problems with Nazarov cyclization of similar camphor-derived alcohols.[26]

We then turned to the synthesis of the alternative chiral cyclopentadiene $Cp^{myr}H$ (**9**) using the Skattebøl rearrangement[28,29] as a key step (Scheme 3). Cheap natural *R*-myrtenal (<100$ for 100 g) was used as a starting material. Addition of phenylmagnesium bromide to *R*-myrtenal followed by oxidation gave the ketone **10** in a good total yield 79%. Further Wittig olefination of **10** and cyclopropanation by $CHBr_3$/KOH produced the di-bromo-cyclopropane **12** as a mixture of two diastereomers with ca. 4:1 ratio. They can be separated by crystallization from petroleum ether, but this separation was not necessary for further synthesis. Methyl lithium converted the dibromide **12** into the carbene intermediate, which underwent the Skattebøl rearrangement to give the desired cyclopentadiene **9**. The minor byproduct of this reaction was presumably the allene **13**, similar to that noted by Paquette et al.[30] The amount of **13** can be reduced to ca. 10% by conducting reaction in diluted solution with efficient cooling. We could not fully separate this byproduct from **9** but fortunately it caused no problems in further applications and was separated during purification of the rhodium complex (vide infra). Although the synthesis of **9** requires 5 steps, it can be conveniently carried out on a multi-gram scale with a reasonable total yield of 35−40%. Neat diene **9** slowly polymerizes at room temperature but can be stored for months in hexane solution at −18 °C. Similar instability has been previously observed for the related diene without a phenyl substituent.[28]



Scheme 3. Synthesis of the chiral cyclopentadiene **9** from *R*-myrtenal.

The reaction of the diene **9** with $RhCl_3$ in refluxing ethanol failed to give the expected complex $[(Cp^{myr})RhCl_2]_2$, possibly because of the low thermal stability of the diene in the presence of acid. Fortunately, rhodium coordination was achieved by the reaction of **9** with $[(cod)Rh(OAc)]_2$ according to the method recently developed by Cramer et al (Scheme 4).[31] This way the cyclopentadienyl complex $(Cp^{myr})Rh(cod)$ (**14**) was obtained in 77% yield. Remarkably, the coordination selectively occurred to the less hindered face of the ligand Cp^{myr} and only one diastereoisomeric complex was observed in the ^1H NMR spectrum of the crude product. Complex **14** was also prepared by the reaction of **9** with thallium ethoxide followed by the addition of $[(cod)RhCl]_2$ albeit in a lower yield 32%.



Scheme 4. Synthesis of rhodium complexes with the chiral ligand Cp^{myr}.

The yellow complex **14** was stable in the solid state but notably decomposed in solution in air within a day (brownish color appeared). It was very soluble in non-polar solvents, so it can be separated from the excess of the starting diene **9** and **13** only by the column chromatography in petroleum ether. To avoid these complications **14** can be converted into the air-stable and less soluble rhodium(III) complexes $[(Cp^{myr})RhX_2]_2$ (**15a**,**b**; X = Br, I; 90-95%) by the oxidation with molecular bromine or iodine. Noteworthy, the complexes **15a**,**b** can be also obtained directly from **9** without isolation of the intermediate **14**. The structures of the compounds **14** (Figure 1; CCDC 2017672) and **15a** (supporting information; CCDC 2017673) were established by the X-ray diffraction, which confirmed the coordination of the metal from the less hindered side of the ligand, i.e. opposite CMe_2 group.

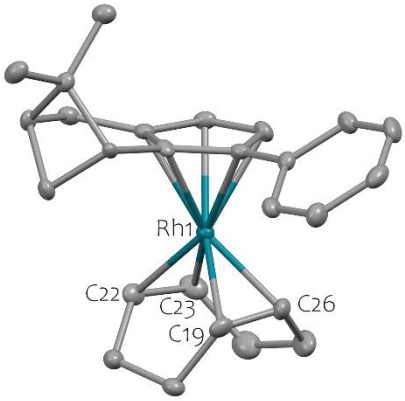
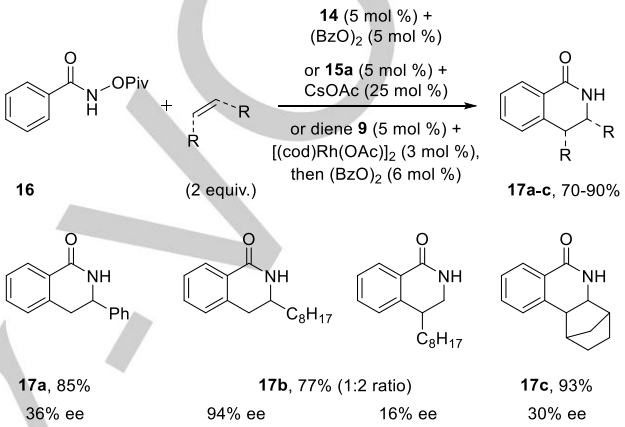


Figure 1. Crystal structure of the complex **14** represented in 50% thermal ellipsoids. All hydrogen atoms are omitted for clarity. Selected distances (Å): Rh1−C19 2.119(4), Rh1−C22 2.110(4), Rh1−C23 2.126(4), Rh1−C26 2.105(5), Rh1−C_{5plane} 1.911.

The catalytic performance of the complex **14** was tested in the benchmark C-H activation reaction[4] of O-pivaloyl phenylhydroxamic acid **16** with alkenes (Scheme 5). We generated the active rhodium(III) species $(Cp^{myr})Rh(OBz)_2$ by *in situ* oxidation of the rhodium(I) complex **14** with benzoyl peroxide as suggested by Cramer et al.[17] Interestingly, the complex **14** itself can be also generated *in situ* from the ligand **9** and $[(cod)Rh(OAc)]_2$ prior to the addition of $(BzO)_2$.[31] This approach allows fast screening of the enantioselectivity of the reactions. In the presence of the precatalyst **14** (5 mol-%) the tested reactions of **16** with styrene, 1-decene, and norbornene gave the expected

dihydroisoquinolinone products **17a–c** in high yields 80−90%. The yields were somewhat lower (40−70%) if **14** was generated *in situ*. Reaction of **16** with norbornene was also tested in the presence of the bromide **15a** as a catalyst and gave the target product **17c** in 83% yield. Noteworthy, the reaction of **16** with 1-decene gave a mixture of 3- and 4-octyl-substituted products **17b** with 1:2 ratio. This observation indirectly confirmed rather low steric hindrance of the new Cp^{myr} ligand, since the catalysts with bulkier cyclopentadienyl ligands typically gave 4-octyl-dihydroisoquinolinone as the only product.[32–34] Unfortunately, the enantioselectivities of the tested reactions with the catalyst **14** were moderate (16-36% ee). Only the minor 3-octyl-substituted isomer of **17b** was obtained with high 94% ee. Enantioselectivites were almost the same (±1% ee) when *in situ* generated **14** or **15a** were used as catalysts. Similar results were also obtained when O-Boc-phenylhydroxamic acid was used as a starting material instead of **16**.

In attempt to explain the observed enantioselectivity we generated the steric maps of the three catalysts **14, 18** and **19** with different chiral cyclopentadienyl ligands using the SambVca 2.1 tool (Figure 2).[35] The maps show the amount of space occupied by the ligands around the central rhodium atom. It can be seen, that in the case of the catalysts **18** and **19** the main steric influence is provided by the methyl groups of the cyclopentadienyl ligands shown in red. In the case of **14** the steric influence is provided mainly by CH_2 group of the myrtenal framework. Interestingly, the previously reported catalysts **18** and **19** gave the product **17a** with almost the same enantiomeric excess (92 and 90% ee) but with opposite configuration.[12,17] This correlates with very similar steric maps of opposite symmetry. Our new catalyst **14** seems to be less asymmetric, because it has substituents both on the right and on the left side from the key CH_2 group. This is reflected by steric map with 48% and 41% of volume occupied by the ligand in top left and bottom right quadrants, respectively (compare to 47% and 34% in the catalyst **18**). Probably this leads to the less efficient enantiomeric induction (36% ee). However, the numerical differences between the volumes occupied by ligands ($V_{burried}$) in the complexes **14** and **18** are small. Therefore, it seems that the steric maps can correctly predict the type of enantiomeric product (*R* or *S*) but have limited efficiency for prediction of enantiomeric excess in such reactions.



Scheme 5. Catalytic performance of the new rhodium complex **14**.

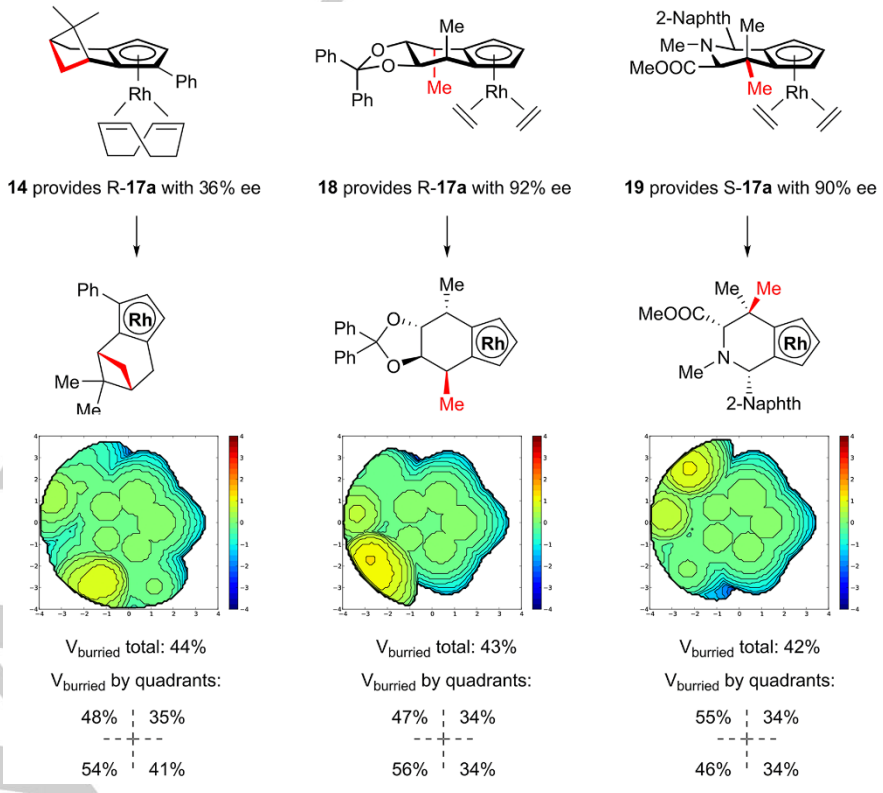


Figure 2. Steric maps of three chiral cyclopentadienyl ligands generated by SambVca 2.1 tool. $V_{burried}$ values show the amount of space occupied by ligand in the coordination sphere with 4 Å radius around the central metal atom. The Rh−Cp distance was set identical for all ligands to 1.77 Å (typical distance for Rh(III) complexes).

Conclusion

New chiral cyclopentadiene $Cp^{myr}H$ was synthesized from the natural *R*-myrtenal in 5 steps and ca. 35-40% yield. The advantage of using terpenes as a chirality source is their high availability, which allows for easy multi-gram synthesis. However, the possibilities of structural variation of their chiral elements are limited, and the strained framework can lead to side reactions such as acid-catalyzed rearrangements. The face-selective coordination of rhodium to Cp^{myr} ligand was conveniently achieved by reaction of the diene with $[(cod)Rh(OAc)]_2$ precursor. The chiral rhodium complex $(Cp^{myr})Rh(cod)$ in the presence of $(BzO)_2$ catalyzed C-H activation of O-pivaloyl-phenylhydroxamic acid and its subsequent annulation with alkenes to give dihydroisoquinolinones with high yield (70−90%) but moderate enantioselectivity (16−36% ee). Steric maps of the chiral cyclopentadienyl ligands can predict the efficiency of such rhodium catalysts to a limited extent.

Experimental Section

General information: Unless otherwise noted all reactions were carried out under argon atmosphere in anhydrous solvents, which were purified and dried using standard procedures. The isolation of products was carried out in air. Complexes $[Rh(cod)Cl]_2$[36] and $[Rh(cod)OAc]_2$,[37] as well as hydrazone **5**,[27] O-pivaloyl phenylhydroxamic acid (**16**),[38] and O-Boc phenylhydroxamic acid[17] were synthesized according to the published procedures. All other reagents were obtained from commercial sources (Acros, Aldrich, J&K Scientific, or Vekton) and used as received. High resolution mass spectra were recorded on a Bruker microTOF spectrometer with electrospray ionization (ESI). ^{1}H and ^{13}C NMR spectra were measured with a Bruker Avance 400 or AV-600 spectrometer at 20 °C. The chemical shifts are reported relative to residual signals of the solvent (for $CHCl_3$: 7.26 ^{1}H, 77.16 ^{13}C; for DMSO: 2.50 ^{1}H, 39.52 ^{13}C). The copies of NMR spectra of the new compounds are given in the supporting information file.

4-phenyl-2-(1,7,7-trimethylbicyclo[2.2.1]hept-2-en-2-yl)-but-3-en-2-ol (7): The stirred solution of hydrazone **5** (600 mg, 1.39 mmol) in anhydrous THF (6 mL) was cooled to –78 °C and *t*-BuLi (2 ml, 1.42 M in pentane, 2.92 mmol, 2.1 equiv) was added dropwise (the temperature should not exceed –50 °C). Then the cold bath was removed and the stirred orange solution was allowed to warm to 0 °C. Nitrogen began to evolve at –20 °C, the color of the mixture changed to dark red. The flask was kept immersed into an ice bath (0 °C) until nitrogen evolution ceases (ca. 40 min). Then the reaction mixture was again cooled to –78 °C and the solution of benzylideneacetone (304 mg, 2.08 mmol) in anhydrous THF (3 ml) was added. After 20 minutes the solution was warmed to room temperature and then stirred overnight. Saturated aqueous solution of NH_4Cl (9 ml) was added to reaction mixture and it was opened to air. The mixture was transferred to a separation funnel, the organic layer was collected, the aqueous layer was extracted with Et_2O (2×10 ml). The combined organic layers were washed with brine and dried over Na_2SO_4. The solvent was removed in vacuum and the residue was purified by column chromatography (eluted first with hexane, then hexane/AcOEt (2:1). The product **7** was obtained as a yellow oil (204 mg, 52%). It should be noted that the yield of **7** varies significantly apparently because the side process of deprotonation of benzylideneacetone by vinyl lithium reagent **6** becomes dominant if the temperature increases during the reaction. R_f = 0.41 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40 (d, J = 7.7 Hz, 2H), 7.33 (t, J = 7.5 Hz, 2H), 7.24 (t, J = 7.1 Hz, 1H), 6.67 (m from two overlapping doublets of diastereomers, 1H), 6.33 (m, from two overlapping doublets of diastereomers, 1H), 5.96–5.86 (m, 1H), 2.34–2.27 (m, 1H), 1.98–1.82 (m, 3H), 1.58–1.54 (m, 3H), 1.22–1.18 (m, 3H), 1.08–0.98 (m, 2H), 0.88–0.84 (m, 3H), 0.77 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 152.2, 137.3, 135.7, 135.4, 128.7, 128.6, 128.5, 127.3, 127.1, 127.0, 126.4, 73.9, 51.0, 33.1, 32.8, 27.9, 27.8, 25.4, 25.4, 19.8, 19.8, 19.7, 13.4. The ^{13}C NMR spectrum was complex due to the presence of two diastereomers. Only the major signals are given here. MS(EI) m/z: 282.2 $[M]^+$, 265.2 $[M-OH]^+$.

1,7,7-trimethyl-2-(4-phenylbuta-1,3-dien-2-yl)bicyclo[2.2.1]hept-2-ene (8): p-Toluenesulfonic acid (3 mg, 0.018 mmol, 10 mol%) was added to solution of alcohol **7** (50 mg, 0.18 mmol) in diethyl ether (3 ml). The mixture was stirred at room temperature overnight. The solvent was evaporated and the residue was purified by column chromatography (eluted with hexane) to give triene **8** as yellowish oil (40 mg, 84%). R_f = 0.42 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39 (d, J = 7.8 Hz, 2H), 7.30 (t, J = 7.6 Hz, 2H), 7.20 (t, J = 7.3 Hz, 1H), 6.82 (d, J = 16.0 Hz, 1H), 6.67 (d, J = 16.0 Hz, 1H), 5.94 (d, J = 2.8 Hz, 1H), 5.20 (s, 1H), 4.93 (s, 1H), 2.39 (t, J = 3.0 Hz, 1H), 1.91 (tt, J = 7.3, 4.2 Hz, 1H), 1.59 (m, 1H), 1.13–1.04 (m, 2H), 1.01 (s, 3H), 0.95 (s, 3H), 0.81 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 147.1, 143.6, 137.6, 133.3, 131.3, 130.8, 128.7, 127.6, 126.6, 114.8, 56.9, 55.5, 52.0, 32.0, 31.4, 25.8, 20.0, 12.5. MS(EI) m/z: 265.2 $[M+H]^+$.

Phenyl-(1,7,7-trimethylbicyclo[2.2.1]hept-2-en-2-yl)-methanone (10): The first step was carried out similar to the literature procedure.[39] Bromobenzene (15.7 g, 0.10 mol) was added dropwise to magnesium (2.67 g, 0.11 mol) in anhydrous THF (80 mL), extensive heating of the mixture was observed. After complete addition, the mixture was stirred at room temperature for 30 min and *R*-myrtenal (15.0 g, 0.10 mol) in anhydrous THF (20 ml) was added dropwise. The mixture was refluxed for 3 h, then cooled to 0 °C and quenched with 50 mL of a saturated aqueous solution of NH_4Cl. THF was removed by evaporation under reduced pressure and the remaining emulsion was extracted with ethyl ether. The organic layer was washed with a saturated solution of ammonium chloride, dried over anhydrous Na_2SO_4. The solvent was evaporated to give the α-(2-borenyl)-benzyl alcohol as a yellow oil (20.7 g, 92%), which was used without further purification in the next step.

A mixture of α-(2-borenyl)-benzyl alcohol (7.22 g, 31.6 mmol) from the previous step and pyridinium chlorochromate on alumina (63.2 g, 63.2 mmol, activity ~ 1 mmol/g) in dichloromethane (50 ml) was stirred for 3 hours at room temperature. The reaction mixture was filtered and the solids were washed with diethyl ether. The solvent was evaporated, the residue was dissolved in diethyl ether (10 ml), filtered through a silica gel plug and evaporated again in vacuum. The product **10** was obtained as yellow oil (6.18 g, 86%) and directly used without additional purification in the next step. Analytically pure sample can be obtained by vacuum distillation (150−160 °C at 2 mbar). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.69 (d, J = 7.4 Hz, 2H), 7.51 (t, J = 6.9 Hz, 1H), 7.42 (t, J = 7.3 Hz, 2H), 6.42 (s, 1H), 2.99 (t, J = 5.6 Hz, 1H), 2.59–2.46 (m, 3H), 2.18 (s, 1H), 1.38 (s, 3H), 1.21 (d, J = 9.2 Hz, 1H), 0.87 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 195.7, 148.7, 140.4, 138.4, 131.6, 129.3, 128.2, 41.5, 40.4, 37.8, 32.8, 31.4, 26.0, 21.1. HRMS (ESI) calculated for $C_{16}H_{18}O^+$ $[M+H]^+$: 227.1435, found: 227.1430. Elemental analysis calculated for $C_{16}H_{18}O$: C, 84.91; H, 8.02; found: C, 84.60; H, 8.19.

6,6-dimethyl-2-(1-phenylvinyl)bicyclo[3.1.1]hept-2-ene (11): THF (60 ml) was added to the solid methyltriphenylphosphonium bromide (12.2 g, 34.1 mmol) and potassium *tert*-butoxide (3.83 g, 34.1 mmol) and the mixture was stirred for 30 minutes to give a bright yellow suspension. Then the ketone **10** (7.02 g, 31.0 mmol) was added dropwise; strong heating of the mixture was observed. The reaction mixture was stirred for 24 hours and opened to air. The solvent was then evaporated in vacuum and the residue was triturated with petroleum ether (15 ml). The precipitate was removed by filtering the petroleum ether solution through silica gel plug and the solvent was evaporated in vacuum. The diene **11** was obtained as yellow oil (6.2 g, 89%). This crude product can be purified further by vacuum distillation (bp 135-140 °C at 2 mbar) to give **11** as colourless oil (4.0 g, 58%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.47–7.15 (m, 5H, Ph), 5.46 (s, 1H), 5.15 (s, 1H), 5.01 (s, 1H), 2.52–2.43 (m, 2H), 2.33 (qt, J = 18.6, 3.2 Hz, 2H), 2.16–2.10 (m, 1H), 1.32 (s, 3H), 1.27 (d, J = 8.2 Hz, 1H), 0.91

(s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 150.3, 147.9, 128.6, 127.9, 127.1, 123.6, 110.7, 43.8, 40.6, 37.9, 31.9, 31.6, 26.4, 20.9. MS(EI) m/z: 225.2 $[M+H]^+$. HRMS-ESI analysis was not successful because of reluctance of ionization of the diene **11**. Elemental analysis calculated for $C_{17}H_{20}$: C, 91.01; H, 8.99; found: C, 90.81; H, 8.85.

2-(2,2-dibromo-1-phenylcyclopropyl)-6,6-dimethylbicyclo-[3.1.1]-hept-2-ene (12): A mixture of the diene **11** (4.00 g, 17.9 mmol), powdered KOH (4.50 g, 80.4 mmol, 4.5 equiv.), phase-transfer catalyst Adogen 464 (2.40 g, 1.80 mmol, 10 mol%) and ethanol (520 µl, 9 mmol, 0.5 equiv.) was dissolved in dichloroethane (80 ml). To the stirred mixture a bromoform (13.6 g, 53.6 mmol, 3 equiv.) was added dropwise over 30 minutes at room temperature. Immediately afterwards, the addition of KOH (4.50 g, 80.4 mol, 4.5 equiv.) and $CHBr_3$ (13.6 g, 53.6 mol, 3 equiv.) was repeated, again over 30 min. The reaction mixture was then stirred for 30 minutes, filtered and the solid residue was rinsed with CH_2Cl_2 (ca. 30 ml) until its color was pale-brown (no further color change). The combined organic fractions were then extracted with H_2O (3×80 ml). The combined aqueous layers were extracted with CH_2Cl_2 (2×30 ml) and the combined organic fractions were then dried over $MgSO_4$. The solution was filtered through silica gel plug and the solvent was evaporated in vacuum. The vinyldibromo-cyclopropane product **12** was obtained as a light brown semi-solid (7.1 g, 80 %). The diastereoisomers of **12** can be separated by crystallization. A minimal amount of petroleum ether was added to dissolve the mixture of diastereomers. The resulting solution was kept at −30 °C until the major diastereomer precipitated as colorless needle crystals. The spectral data below is given for a pure diastereomer. The spectra of the initial mixture are given in the supporting information. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48–7.15 (m, 5H, Ph), 5.60 (s, 1H), 2.65 (t, J = 5.3 Hz, 1H), 2.51 (dt, J = 8.8, 5.8 Hz, 1H), 2.40–2.23 (m, 2H), 2.21–2.08 (m, 2H), 2.02 (s, 1H), 1.39 (d, J = 8.8 Hz, 1H), 1.21 (s, 3H), 0.09 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 148.86, 139.67, 129.81, 128.02, 127.32, 121.41, 47.09, 45.22, 40.30, 37.69, 34.34, 34.29, 32.20, 31.62, 25.97, 19.95. HRMS (ESI) calculated for $C_{20}H_{27}Br^+$ $[M-Br]^+$: 315.0743, found: 315.0741. Elemental analysis calculated for $C_{18}H_{20}Br_2$: C, 54.57; H, 5.09; found: C, 54.37; H, 5.02.

5,5-dimethyl-3-phenyl-4,5,6,7-tetrahydro-2H-4,6-methanoindene (9): The vinyldibromocyclopropane **12** (3.0 g, 7.57 mmol, 1.0 equiv.) was dissolved in Et_2O (60 ml). The mixture was stirred, cooled to –78 °C and MeLi (10 ml, 3.1 M in $(EtO)_2CH_2$, 30.3 mmol, 4 equiv.) was added dropwise. After stirring for 1.5 hours, saturated aqueous solution of NH_4Cl (20 ml) was added at –78 °C. The mixture was then opened to air, allowed to warm to room temperature, transferred to a separation funnel and the organic layer was separated. The aqueous layer was diluted with H_2O (30 ml) and extracted with Et_2O (3×20 ml). The combined organic layers were washed with brine and dried over Na_2SO_4. The solvent was removed under reduced pressure to give the mixture of the target cyclopentadiene **9** and the presumed isomeric vinylallene **13** (1.64 g, 91% total yield). We could not purify this mixture further by column chromatography because of the very low polarity of the compounds, similar R_f values and instability of the substances towards polymerization at room temperature. The ratio of **9**:**13** isomers vary from 3:1 to 8:1 according to ^{1}H NMR and GC-MS. The position of double bonds in the cyclopentadiene **9** was assigned to match best with the predicted spectra. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45–7.30 (m, 5H, Ph), 6.05 (s, 1H, CH^{Cp}), 3.43 (q, J = 20 Hz, 2H, CH_2^{Cp}) 3.22 (t, J = 5.3 Hz, 1H), 2.79 (q, J = 16 Hz, 2H, $CH_2^{myrtenal}$) 2.63 (m, 1H), 2.31 (m, 1H), 2.16 (m, 1H), 1.41 (s, 3H), 0.85 (s, 3H). The signals assigned to **13**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.45 (s, 1H), 5.12 (s, 2H), 1.36 (s, 3H), 0.96 (s, 3H). ^{13}C NMR spectrum of the mixture was too complicated for proper analysis. HRMS (ESI) calculated for $C_{20}H_{27}^+$ $[M+H]^+$: 237.1638, found: 237.1644.

(Cp^{myr})Rh(cyclooctadiene) (14): Complex $[Rh(cod)OAc]_2$ (83.0 mg, 0.155 mmol) and crude $Cp^{myr}H$ (**8**, 148.0 mg, 0.62 mmol, 2 equiv. per each rhodium atom, calculated according to 3:1 ratio of **8** and **13**) were dissolved in a mixture of MeOH (2.5 ml) and toluene (2.5 ml). The resulting orange solution was stirred for 48 hours, opened to air. A small amount of silica gel was added and the solvent was removed in vacuum. The residue was placed on a top of a silica gel column (20×1 cm) and eluted with petroleum ether under argon pressure (R_f = 0.9 in hexane). Yellow band was collected and evaporated to give 114 mg (77%) of complex **14** as a yellow solid. Similar reaction with 1 equiv. of $Cp^{myr}H$ gave complex **14** in 40% yield apparently because of the side polymerization of the starting diene. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.28 (d, 4H, J = 4.3 Hz, CH^{Ph}), 7.16 (m, 1H, CH^{Ph}), 5.17 (d, 1H, J = 2.6 Hz, CH^{Cp}), 4.84 (d, 1H, J = 2.7 Hz, CH^{Cp}), 3.61–3.54 (m, 2H, CH^{cod}), 3.45 (q, 2H, J = 6.1, 4.8 Hz, CH^{cod}), 2.85 (t, 1H, J = 5.5 Hz), 2.75 (dt, 1H, J = 9.1, 6.1 Hz), 2.71–2.53 (m, 2H), 2.19 (m, 5H, CH_2^{cod} + CH^{myr}), 1.89 (m, 5H, CH_2^{cod} + CH^{myr}), 1.34 (s, 3H, CH_3), 0.63 (s, 3H, CH_3). ^{13}C NMR (151 MHz, $CDCl_3$): δ = 128.84 (CH^{Ph}), 128.25 (CH^{Ph}), 127.88 (CH^{Ph}), 125.84 (CH^{Ph}), 116.39 (d, J_{Rh-C} = 3.4 Hz CH^{cod}), 102.61 (d, J_{Rh-C} = 3.4 Hz CH^{cod}), 102.11 (d, J_{Rh-C} = 3.7 Hz CH^{cod}), 81.84 (d, J_{Rh-C} = 4.0 Hz CH^{Cp}), 80.22 (d, J_{Rh-C} = 4.8 Hz CH^{Cp}), 68.25, 68.15, 66.67, 66.58, 42.19, 41.84, 40.35, 35.58, 32.69, 32.40, 27.06, 26.90 (CH_3), 21.70 (CH_3). HRMS (ESI) calculated for $C_{26}H_{31}Rh$ $[M]^+$: 446.1481, found: 446.1475.

Alternative synthesis of (Cp^{myr})Rh(cyclooctadiene) (14): A pale yellow solution of $Cp^{myr}H$ (**8**, 53.0 mg, 0.224 mmol, calculated according to 3:1 ratio of **8** and **13**) in hexane (2.5 ml) was added to a solution of TlOEt (56 mg, 0.224 mmol) in hexane (2.5 ml) in a Shlenk flask protected from light by aluminum foil. The brown precipitate was formed immediately. The mixture was stirred for 1 h and then $[Rh(cod)OAc]_2$ (60.0 mg, 0.112 mmol) and benzene (0.5 ml) were added. After stirring for 24 hours, the mixture was filtered through a short pad of celite topped with a layer of neutral aluminum oxide under argon atmosphere. The solvent was evaporated and the residue was eluted by petroleum ether on a silica gel column as described above to give **14** (32 mg, 32% yield) as yellow oily solid.

[(Cp^{myr})$RhBr_2$]$_2$ (15a): In air a solution of Br_2 (50 mg, 0.315 mmol) in hexane (4 ml) was added dropwise to a stirred solution of the complex **14** (50 mg, 0.105 mmol) in hexane (4 ml). The orange precipitate was formed immediately. After 5 minutes of stirring the precipitate was collected by centrifugation, washed with hexane (4×5 ml) and Et_2O (2×5 ml), and dried in vacuum to give product **15a** (50 mg, 90%) as an orange powder. ^{1}H NMR (400 MHz, DMSO-d6): δ = 7.78–7.72 (m, 2H, CH^{Ph}), 7.47–7.39 (m, 3H, CH^{Ph}), 6.33 (d, 1H, J = 2.5 Hz, CH^{Cp}), 5.66 (d, 1H, J = 2.5 Hz, CH^{Cp}), 2.91 (dd, 1H, J = 18.2, 2.9 Hz), 2.85 (t, 1H, J = 5.4 Hz), 2.69 (dd, 1H, J = 10.7, 5.7 Hz), 2.38 (d, 1H, J = 18.3 Hz), 2.15 (d, 2H, J = 7.9 Hz), 1.40 (s, 3H, CH_3), 0.76 (s, 3H, CH_3). ^{13}C NMR (101 MHz, DMSO-d6): δ = 129.42 (CH^{Ph}), 129.24 (CH^{Ph}), 129.12 (CH^{Ph}), 128.75 (CH^{Ph}), 117.75 (d, J_{Rh-C} = 5.8 Hz), 109.93, 91.28 (d, J_{Rh-C} = 7.8 Hz CH^{Cp}), 73.08 (d, J_{Rh-C} = 8.5 Hz CH^{Cp}), 38.83, 34.08, 25.88, 25.07 (CH_3), 21.35 (CH_3). HRMS (ESI) calculated for $C_{18}H_{19}BrRh$ [(Cp^{myr})RhBr]$^+$: 416.9725, found: 416.9725; calculated for $C_{20}H_{22}BrNRh$ [(Cp^{myr})RhBr+MeCN]$^+$: 457.9991, found: 457.9906.

[(Cp^{myr})RhI_2]$_2$ (15b): In air a solution of I_2 (27 mg, 0.105 mmol) in hexane (4 ml) was added dropwise to a stirred solution of the complex **14** (50 mg, 0.105 mmol) in hexane (4 ml). The dark precipitate was formed immediately. After 5 minutes of stirring the precipitate was collected by centrifugation, washed with hexane (4×5 ml) and dried in vacuum to give product **15b** (59 mg, 95%) as a dark violet powder. ^{1}H NMR (400 MHz, DMSO-d6): δ = 7.78–7.70 (m, 2H, CH^{Ph}), 7.42 (q, 3H, J = 4.6, 3.8 Hz, CH^{Ph}), 6.36 (d, 1H, J = 2.6 Hz, CH^{Cp}), 5.77 (d, 1H, J = 2.5 Hz, CH^{Cp}), 3.24 (dd, 1H, J = 18.2, 3.1 Hz), 2.92 (t, 1H, J = 5.4 Hz), 2.67–2.61 (m, 1H), 2.60–2.53 (m, 1H), 2.16–2.11 (m, 1H), 2.02 (d, 1H, J = 10.3 Hz), 1.42 (s, 3H, CH_3), 0.77 (s, 3H, CH_3). ^{13}C NMR (101 MHz, DMSO-d6): δ = 129.47 (CH^{Ph}), 129.40 (CH^{Ph}), 129.16 (CH^{Ph}), 128.67(CH^{Ph}), 118.01 (d, J_{Rh-C} = 5.0 Hz), 109.87 (d, J_{Rh-C} = 5.8 Hz), 97.71 (d, J_{Rh-C} = 5.9 Hz), 90.99 (d, J_{Rh-C} = 7.1 Hz CH^{Cp}), 75.93 (d, J_{Rh-C} = 7.4 Hz CH^{Cp}), 40.02, 35.79, 25.88, 25.77 (CH_3), 21.31 (CH_3). Elemental analysis calculated for $C_{18}H_{19}I_2Rh$: C, 36.52; H, 3.23; I, 42.87; Rh, 17.38; found: C, 36.33; H, 3.30; I, 42.40; Rh, 17.18.

General procedure for catalytic transformations of O-pivaloyl-phenylhydroxamic acid (16): Without protection from oxygen or moisture the complex **14** (2.4 mg, 5.0 µmol) and benzoyl peroxide (1.2 mg, 5.0 µmol)

were dissolved in mixture of MeOH (0.45 ml) and CH_2Cl_2 (0.050 ml, improves solubility of alkenes) and stirred for 10 min. Then, O-pivaloyl phenylhydroxamic acid (**16**, 44.2 mg, 0.2 mmol) was added to the mixture and stirred for 15 minutes, followed by addition of alkene (0.40 mmol, 2 equiv.). The mixture was then stirred for 24 hours at 25 °C, the solvent was evaporated in vacuum and the residue was purified on a silica gel column by using CH_2Cl_2:EtOAc (5:1) as eluent.

3-phenyl-3,4-dihydroisoquinolin-1-one (17a) prepared from 16 and styrene: Yield 38 mg (85%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.11 (d, J = 7.7 Hz, 1H, CH^{Ar}), 7.46 (t, J = 7.5 Hz, 1H, CH^{Ar}), 7.42–7.32 (m, 6H), 7.18 (d, J = 7.5 Hz, 1H), 6.31 (s, 1H, NH), 4.85 (dd, J = 10.6, 5.1 Hz, 1H, CH), 3.25−3.07 (m, 2H, CH_2). ^{1}H NMR data are in agreement with those reported previously.[38] Chiral HPLC: Chiralpak IA-3 column (4.6 × 150 mm), heptane/i-PrOH 90:10, 1.0 mL/min; tr (major) = 9.3 min, tr (minor) = 10.3 min, er 68/32. $[\alpha]_D^{20}$ = +62.9 (*c* 1.0, $CHCl_3$), which indicated predominance of R-enantiomer. Literature data for pure R-isomer $[\alpha]_D^{20}$ = +196.3,[17] +195.3,[40] for S-isomer $[\alpha]_D^{20}$ = −159.4,[12] −161.0.[41] There is a notable discrepancy between the reported rotation angles, however the sign of the rotation angle for our sample clearly indicate the predominance of R-enantiomer.

3-octyl-3,4-dihydroisoquinolin-1-one and 3-octyl-3,4-dihydroisoquinolin-1-one (17b) prepared from 16 and 1-decene: Total yield of both isomers 38 mg (74%), ratio 1:2 according to ^{1}H NMR. The isomers were separated by column chromatography and the analytical data were obtained for pure samples. For 3-octyl-isomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.03 (d, 1H, J = 7.7 Hz), 7.49–7.41 (m, 1H), 7.34 (t, 1H, J = 7.6 Hz), 7.19 (d, 1H, J = 7.5 Hz), 3.68 (dd, 1H, J = 10.3, 4.0 Hz, CHN), 2.97 (dd, 1H, J = 15.5, 4.4 Hz), 2.80 (dd, 1H, J=15.5, 10.2 Hz), 1.31–1.19 (m, 13H), 0.88 (t, 3H, J = 6.9 Hz). Chiral HPLC: Chiralpak IA-3 column (4.6 × 150 mm), heptane/i-PrOH 99:1, 1.0 mL/min; tr(minor) = 3.4 min, tr (major) = 3.8 min, er 97/3. For 4-octyl-isomer: 1H NMR (400 MHz, $CDCl_3$): δ = 8.05 (d, 1H, J = 7.6 Hz), 7.45 (t, 1H, J = 7.5 Hz), 7.34 (t, 1H, J = 7.5 Hz), 7.20 (d, 1H, J = 7.5 Hz), 6.72 (s, 1H, NH), 3.70 (dd, 1H, J = 12.4, 4.4 Hz, CH_2NH), 3.39 (dt, 1H, J = 12.5, 4.0 Hz, CH_2NH), 2.82 (tt, 1H, J = 7.6, 3.9 Hz, CH), 1.66 (q, 2H, J = 6.7 Hz), 1.25 (d, 12H, J = 9.0 Hz), 0.86 (t, 3H, J = 6.7 Hz). Chiral HPLC: Chiralpak IA-3 column (4.6 × 150 mm), heptane/i-PrOH 99:1, 1.0 mL/min; tr(major) = 4.2 min, tr (minor) = 4.6 min, er 58/42. ^{1}H NMR data are in agreement with those reported previously.[33]

1,3,4,4a,5,10b-hexahydro-1,4-methanophenanthridin-6-one (17c) prepared from 16 and norbornene: Yield 40 mg (93%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.10 (d, 1H, *J* = 7.8 Hz), 7.46 (t, 1H, *J* = 7.5 Hz), 7.29 (t, 1H, *J* = 7.6 Hz), 7.23 (d, 1H, *J* = 7.7 Hz), 6.48–6.32 (m, 1H, NH), 3.82 (d, 1H, *J* = 8.9 Hz), 3.13 (d, 1H, *J* = 8.9 Hz), 2.38–2.23 (m, 2H), 1.66 (dt, 3H, *J* = 9.8, 4.0 Hz), 1.53 (t, 1H, *J* = 8.6 Hz), 1.41–1.30 (m, 1H), 1.19 (d, 1H, *J* = 10.6 Hz). Chiral HPLC: Chiralpak IA-3 column (4.6 × 150 mm), heptane/i-PrOH 90:10, 1.0 mL/min; tr(major) = 7.0 min, tr (minor) = 16.1 min, er 65/35. ^{1}H NMR and chiral HPLC data are in agreement with those reported previously.[15]

General procedure for catalytic transformations of O-pivaloyl-phenylhydroxamic acid (16) with in situ generation of the catalyst 14: Without protection from oxygen or moisture, the complex $[Rh(cod)OAc]_2$ (3.2 mg, 6.0 μmol) and ligand $Cp^{myr}H$ (**8**, 2.4 mg, 10.0 μmol) were stirred for 1 hour in a mixture of MeOH (0.45 ml) and CH_2Cl_2 (0.050 ml). Then benzoyl peroxide (2.9 mg, 12.0 μmol) was added and the solution was stirred for 15 minutes. Then O-pivaloyl phenylhydroxamic acid (**16**, 44.2 mg, 0.20 mmol) was added, the mixture was stirred for 30 minutes, followed by addition of alkene (0.40 mmol, 2.0 equiv.) and stirring for 24 hours at 25 °C. The volatiles were removed in vacuum and the residue was purified on a silica gel column by using CH_2Cl_2:EtOAc (5:1) as eluent. The yields of the products were as following: **17a** (42%), **17b** (69%), **17c** (61%). The enantioselectivity remained essentially the same as reported above.

Reaction phenylhydroxamic acid (16) with norbornene catalyzed by the bromide complex 15a: Without protection from oxygen or moisture the complex **15a** (5.3 mg, 5.0 μmol) and CsOAc (9.6 mg, 50.0 μmol) were dissolved in mixture of MeOH (0.45 ml) and CH_2Cl_2 (0.050 ml) and stirred for 15 min. Then, O-pivaloyl phenylhydroxamic acid (**16**, 44 mg, 0.2 mmol) and norbornene (38 mg, 0.40 mmol, 2 equiv.) were added to the mixture and it was stirred for 2.5 hours at 25 °C. Then the solvent was evaporated in vacuum and the residue was purified on a silica gel column as described above. The product **17c** was obtained as pale yellow solid (35 mg, 83%).

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Keywords: rhodium • asymmetric catalysis • cyclopentadienyl • C-H activation

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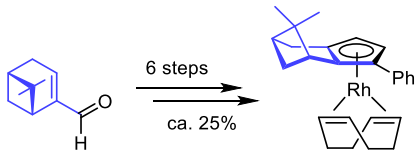

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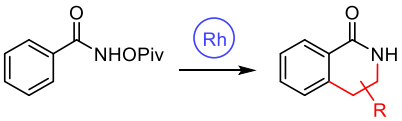

80-90%, 16-36% ee

Rhodium complex with a new chiral cyclopentadiene was synthesized from the natural *R*-myrtenal and tested as a catalyst in C-H activation reaction providing dihydroisoquinolinones with high yields and moderate enantioselectivity.