An $\eta^2$-Aryl-Metal Interaction Turns a Chiral Monodentate Phosphoramidite into a Chelating Ligand in $(S_{\text{ar}},S_{\text{Rar}},R_{C},R_{C})$-[RuCl($\eta^6$-p-cymene)(O,O'-(1,1'-dinaphthyl-2,2'-diyl)-N-(1-(1,2-\eta-1-naphthyl)ethyl)-N-(1-(1-naphthyl)ethyl)phosphoramidite-$\kappa P$)]PF$_6$

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Supporting Information
General. Reactions with air- or moisture-sensitive materials were carried out under an argon atmosphere using Schlenk techniques, or in a glove box under purified nitrogen. Bis[(R)-(−)-(1-naphthyl)ethyl]amine hydrochloride, bis[(S)-(−)-(1-naphthyl)ethyl]amine hydrochloride, ethyl diazoacetate, α-methylstyrene and n-decane were obtained from Aldrich. (S)-(−)-1,1′-Bi(2-naphthol), (R)-(−)-1,1′-bi(2-naphthol), styrene, n-dodecane, tritylloxonium hexafluorophosphate, (R)-(−)-α-phellandrene and phosphorus trichloride were purchased from Fluka, thallium hexafluorophosphate from Strem or Alfa Aesar, and ruthenium (III) chloride trihydrate from Pressure Chemicals. Ethyl diazoacetate was distilled and stored over 4 Å molecular sieves. All other commercially available reagents were used without further purification. Solvents were purified by standard procedures: CH$_2$Cl$_2$ was distilled from CaH$_2$. [RuCl$_2$(η$^6$-p-cymene)]$_2$ and ($S_a$,$R_c$,$R_c$)-O$O'$(1,1′-dinaphthyl-2,2′-diyl)-$N,N$-bis(1-(1-naphthyl)ethyl)phosphoramidite), ($S_a$,$R_c$,$R_c$)-I, were prepared according to literature procedures.$^{1,2}$ Infrared spectra were recorded on a Perkin Elmer Paragon 1000 FT-IR spectrometer. The samples were prepared as thin films (in CHCl$_3$). The data is being reported as absorption maxima (ν, cm$^{-1}$) with corresponding characteristic intensity (w = weak, m = medium, s = strong, br = broad). Optical rotations were measured using a Perkin Elmer 341 polarimeter with a 1 dm cell in CHCl$_3$. Mass spectra were measured by the MS-service (Laboratorium für Organische Chemie, ETH Zürich). The ESI-MS were recorded on a Micromass AutoSpecUltima mass spectrometer operating at 70 eV, the HR MALDI spectra on a IonSpec Ultima HR MALDI-FT-ICR mass spectrometer at 4.7 Tesla using a DCTB (trans-2-(3-(4-tert-butylphenyl)-2-methyl-2-propylidene)-malononitrile) matrix. The m/z peaks, the interpretation and the relative relative intensities are reported. Elemental analyses were carried out by the Laboratory of Microelemental Analysis (Laboratorium für Organische Chemie, ETH Zürich). $^1$H, $^{31}$P, and $^{13}$C spectra were recorded on Bruker Avance 400 and 500
MHz spectrometers. Chemical shifts are quoted in parts per million (ppm) downfield of tetramethylsilane. $^{31}$P NMR chemical shifts were referenced externally to 85% H$_3$PO$_4$ ($\delta$ 0.0).

[RuCl$_2$(η$^6$-p-cymene)(1-κP)] (2). [RuCl$_2$(η$^6$-p-cymene)]$_2$ (73 mg, 0.119 mmol) and 1 (160 mg, 0.250 mmol, 1.05 equiv) were dissolved in dry CH$_2$Cl$_2$ (10 mL) under an Ar atmosphere. The resulting solution was stirred at 23°C for 1 h. 2-Propanol (15 mL) was added and CH$_2$Cl$_2$ was evaporated. The precipitate was filtered off and dried in vacuum to give 2 as an orange solid. Yield: 64 mg (28%). [$\alpha$]$_{20}^D$: +155 (c=0.125, CHCl$_3$). $^1$H NMR (300 MHz, CD$_2$Cl$_2$): $\delta$ 1.07 (d, $J$ = 7.0 Hz, 3H, cymene-CH(C$_3$H$_3$)); 1.13 (d, $J$ = 7.0 Hz, 3H, cymene-CH(C$_3$H$_3$)); 1.92 (s, 9H, cymene-CH$_3$ and CH(Ph)(CH$_3$)$_2$); 2.74 (m, 1H, cymene-CH(CH$_3$)$_2$); 4.76 (d, 1H, $J$ = 6.0 Hz, cymene-H$_{arom}$); 4.83 (d, 1H, $J$ = 6.0 Hz, cymene-H$_{arom}$); 4.87 (d, $J$ = 6.5 Hz, 1H, cymene-H$_{arom}$); 5.06 (d, $J$ = 11.5 Hz, 1H, NCH); 5.26 (d, 1H, $J$ = 5.5 Hz, cymene-H$_{arom}$); 6.69–8.06 (m, 26H, H$_{arom}$). 31P NMR (121.5 MHz, CD$_2$Cl$_2$): $\delta$ 146.6 (s, 96%, complex 2); 148.3 (s, 4%, free ligand 1). MS (HiRes MALDI): 776 ([2–p-cymene–Cl]$^+$, 100); 640 ([1+H]$^+$, 64); 486 ([1–naphthyl+2H]$^+$, 79). Anal. Calcd for C$_{54}$H$_{48}$Cl$_2$NO$_2$PRu: C, 68.57; H, 5.11; N, 1.48. Found: C, 68.62; H, 5.27; N, 1.51.

[RuCl(η$^6$-p-cymene)(1,2-η-1-κP)]PF$_6$ (3). [RuCl$_2$(η$^6$-p-cymene)]$_2$ (65 mg, 0.107 mmol) and 1 (150 mg, 0.234 mmol, 1.1 equiv) were dissolved in dry CH$_2$Cl$_2$ (12 mL) under an Ar atmosphere. After stirring at 23°C for 1 h, TIPF$_6$ (78 mg, 0.224 mmol, 1.05 equiv) was added and the resulting solution was stirred at 23°C for 21 h. Then, TlCl was filtered off, 2-propanol (18 mL) was added and CH$_2$Cl$_2$ was evaporated. The precipitate was filtered off and dried in vacuum to give 3 as an red solid. Yield: 201 mg (89%). [$\alpha$]$_{20}^D$: +381 (c=0.125, CHCl$_3$). $^1$H NMR (500 MHz, CD$_2$Cl$_2$): $\delta$ 0.08 (s, 3H, cymene-CH$_3$); 1.18 (d, $J$ = 7.0 Hz, 3H, cymene-CH(CH$_3$)$_2$); 1.47 (d, $J$ = 7.0 Hz, 3H, cymene-CH(CH$_3$)$_2$); 1.54 (d, $J$ = 7.0 Hz, 3H, CH(Np)$_{coord}$(CH$_3$)); 1.73 (d, $J$ = 6.5 Hz, 3H, CH(Np)$_{free}$(CH$_3$)); 2.62 (d, $J$ = 5.5 Hz, 1H,
cymene-$H_{\text{arom}}$; 2.90 (m, 1H, cymene-$CH(CH_3)_2$); 3.55 (m, 1H, NCH$_{\text{coord}}$); 3.81 (d, $J = 5.0$ Hz, 1H, cymene-$H_{\text{arom}}$); 4.62 (d, $J = 5.5$ Hz, 1H, cymene-$H_{\text{arom}}$); 5.05 (m, 1H, NCH$_{\text{free}}$); 5.71 (d, $J = 5.5$ Hz, 1H, cymene-$H_{\text{arom}}$); 6.75–8.20 (m, 25H, $H_{\text{arom}}$); 9.24 (d, $J = 8.5$ Hz, 1H, $H_{\text{arom}}$). 

$^{31}$P NMR (202.5 MHz, CD$_2$Cl$_2$): δ 168.0 (s). MS (ESI): 910.1 ([3]$^+$, 100). Anal. Calcd for C$_{54}$H$_{48}$ClF$_6$NO$_2$P$_2$Ru: C, 61.45; H, 4.58; N, 1.33. Found: C, 61.31; H, 4.66; N, 1.35.

**X-Ray Structure Determination of 3.** Red crystals of 3 were grown by layering hexane over a CH$_2$Cl$_2$ solution of (rac)-3 (obtained by mixing (S$_a$R$_c$,R$_c$)-1 and (R$_a$S$_c$,S$_c$)-1 in 1:1 ratio). Crystal data: triclinic, $P$–1, 0.76 x 0.49 x 0.28 mm, $a = 13.3040(8)$, $b = 13.7074(8)$, $c = 15.1350(9)$ Å, $\alpha = 98.822(1)$, $\beta = 96.636(1)$, $\gamma = 11.659(1)^\circ$, $V = 2489.9(3)$ Å$^3$, $Z = 2$, $F(000) = 1200$, $D_{\text{calc}} = 1.574$ g cm$^{-3}$, $\mu = 0.661$ mm$^{-1}$. Data were collected at room temperature on a Bruker AXS SMART APEX platform in the $\theta$ range 1.64 – 28.28°. The structure was solved with SHELXTL using direct methods. Of the 25 914 measured (–17$\leq$h$\leq$17, –18$\leq$k$\leq$18, –20$\leq$l$\leq$20), 12 262 unique reflections were used in the refinement (full-matrix least squares on $F^2$ with anisotropic displacement parameters). $R_1 = 0.0405$ (11 071 data with $F_o$$>$$4\sigma(F_o)$), $wR_2 = 0.1112$ (all data). Max. and min. difference peaks were +1.501 and –0.865 eÅ$^{-3}$. See also CIF file below.

**Catalyst Preparation and Standard Catalytic Run.** Complex [RuCl$_2$(η$_6$-$p$-cymene)$_2$] (7.3 mg, 12 µmol), 1 (30.7 mg, 48 µmol), and (Et$_3$O)PF$_6$ (6.6 mg, 26 µmol, 1.1 equiv) were dissolved in CH$_2$Cl$_2$ (1 mL) and stirred at 23°C for 17 h. The internal standard and the olefin (0.48 mmol) were added to the solution of the catalyst (24 µmol, 5 mol%). Ethyl diazoacetate (50.5 µL, 0.48 mmol, 1 equiv vs. olefin) in CH$_2$Cl$_2$ (1 mL) was added over 6 h by syringe pump. The solution, which was protected from light, was stirred for additional 14 h at 23°C and then analyzed by GC. The total reaction time was 20 h at 23°C. Each
experiment was at least reproduced once. A control reaction without the catalyst indicated that there is no formation of the cyclopropane derivatives under the conditions used.

**Styrene.** Olefin conversion and yields of cis and trans product were determined by GC analyses with n-decane as internal standard. Samples for GC analyses were prepared by filtration over a plug of alumina to remove the catalyst. Achiral GC analysis: Optima, 25 m, He carrier (100 kPa). Temperature program: 50°C isotherm for 5 min, then to 200°C at 5°C min⁻¹. Rₜ (min): styrene, 8.5; decane (internal standard), 12.8; ethyl cis-2-phenyl-cyclopropane carboxylate, 26.5; ethyl trans-2-phenyl-cyclopropane carboxylate, 27.9. The enantiomeric excesses of the cis and trans products were determined by chiral GC analysis: Supelco Beta Dex 120, 1.4 mL He min⁻¹; temperature program: 120°C isotherm. Rₜ (min): cis-(1S,2R), 52.8; cis-(1R,2S), 55.5; trans-(1R,2R), 62.7; trans-(1S,2S), 64.6. The absolute configuration was determined for cis- and trans-ethyl 2-phenylcyclopropane-1-carboxylate by comparison of the sign of the optical rotation with literature values.³

**α-Methylstyrene.** As for styrene with n-dodecane as internal standard. Achiral GC analysis: as for styrene. Rₜ (min): α-methylstyrene, 12.0; dodecane 19.6; ethyl (cis)-2-methyl-phenylcyclopropane-1-carboxylate, 26.3; ethyl (trans)-2-methyl-phenylcyclopropane-1-carboxylate, 27.6. Chiral GC analysis: as for styrene. Rₜ (min): cis-(1R,2S), 40.6; cis-(1S,2R), 42.8; trans-(1S,2S), 51.5; trans-(1R,2R), 52.7. The absolute configuration was determined for ethyl cis- and trans-3-methyl-2-phenylcyclopropane-1-carboxylate by comparison of the sign of the optical rotation with literature values.⁴

**References**
$^1$H NMR data of 3

ORTEP View of 3

$^{13}$C NMR data of 3

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