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Tetrahedron: Asymmetry
Tetrahedron: *Asymmetry* 17 (2006) 3084–3090

A chiral phosphepine–olefin rhodium complex as an efficient catalyst for the asymmetric conjugate addition

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Received 21 September 2006; revised 10 November 2006; accepted 13 November 2006
Available online 12 December 2006

Abstract—A monophosphine–olefin was synthesised from a 2,2′-bridged 1,1′-binaphthyl precursor, which served as a chiral bidentate ligand in the Rh catalysed 1,4-additions of arylboronic acids to cycloalkenones and 5,6-dihydro-2*H*-pyran-2-one. Fair yields (64–88%) and high asymmetric inductions (88–98% ee) have been obtained. The crystal structure of a corresponding cationic Rh(I) complex was determined.

1. Introduction

Recently bidentate ligands with phosphine–olefin[1] or olefin–olefin coordination with C_1 symmetry,[2] and olefin–olefin coordination with C_2 symmetry,[3] such as **1**–**4**, have been prepared and applied in asymmetric catalysis showing their potential as chiral modifiers. Rhodium, iridium and palladium complexes have been prepared and, in several cases, the solid state structure was determined. These ligands can be classified according to their origin of chirality (Fig. 1). Either the ligand itself may be chiral forming a chelate with an appropriate transition metal to give a kinetically stable complex with C_1 or C_2 symmetry (**1**–**3**), or an achiral ligand forms a chiral chelate, which has to be subsequently resolved via fractional crystallisation of diastereomeric complexes[2e,3d] **4a** and **4b**. For the synthesis of chiral ligands, various strategies have been applied: suitable ligands are accessible (a) via precursors from the chiral pool,[2a–d] (b) introduction of a chiral group such as menthoxy into a racemic precursor[1a] **1**, (c) asymmetric catalytic transformation of a prochiral precursor[3a] **3** (nine steps from norbornadiene), (d) crystallisation of diastereomeric intermediates[3b] or (e) optical resolution by enantioselective chromatography[1b,c,e,3f] **2**. The preferred asymmetric transformations tested so far were hydrogenations,[1a,e,2e] conjugate addition of organometallic reagents to α,β-unsaturated ketones, aldehydes and esters,[1b,e,2a,c–e,3a,c,d,f] the allylic alkylation of 1,3-diphenylpropenyl acetate,[1c] and the arylation of imines.[3b] In an overwhelming number of cases, both conversions and enantioselectivities were fair to high, but the requirement of working out individual resolution procedures and multistep synthetic sequences for most ligands (if not available from the chiral pool) is still a limitation to their practical usefulness.

We, therefore, set out to design a new chiral phosphine–olefin ligand accessible in a few steps from an inherently chiral precursor and test its efficiency in Rh-catalysed asymmetric 1,4-additions.

2. Results and discussion

2.1. Synthesis

Dinaphthophosphepine **5**, a chiral mono phosphine with (pseudo)-C_2 symmetry, was chosen as an easily modifiable base structure, which can be conveniently prepared from enantiopure 2,2′-dimethyl-1,1′-binaphthyl on a multigram-scale (Scheme 1).

Consequently we attempted the synthesis of **8** by introducing a side arm with an olefin functionality. Stereoselective deprotonation of **6** with *n*-BuLi[4] and treatment with cinnamyl bromide was followed by the deprotection of **7** with Et_2NH to yield (S,S_a,S_P)-**8** in 61% [from (S_a)-**6**]. An alternative approach via the corresponding *P*-sulfide was

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doi:10.1016/j.tetasy.2006.11.022

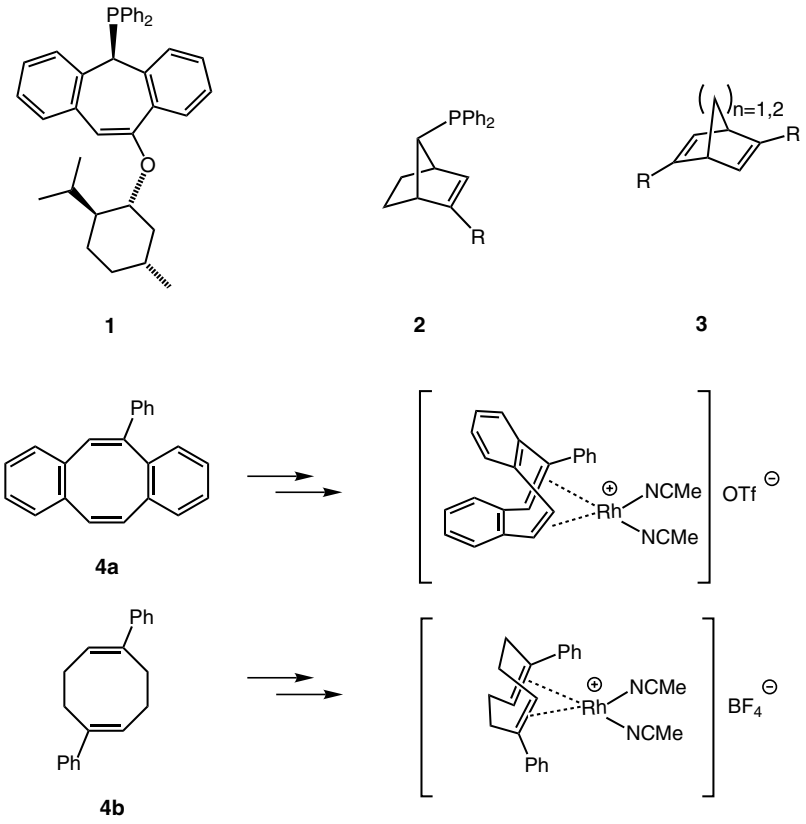
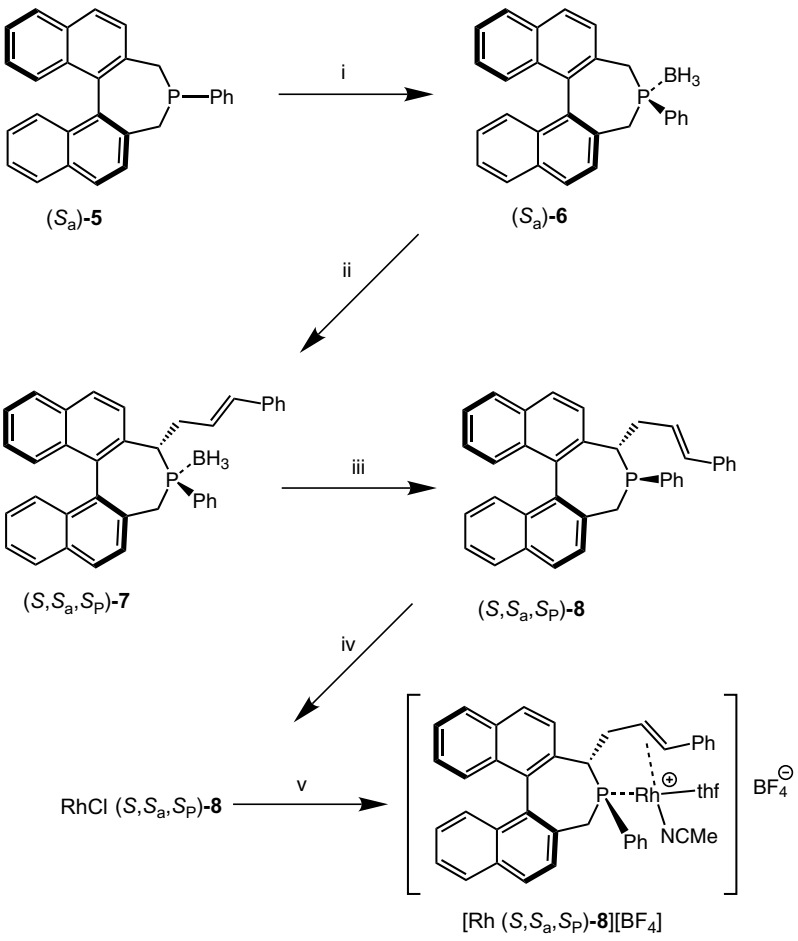


Figure 1.

inadequate, since subsequent desulfurisation with Raney-Ni resulted partly in simultaneous hydrogenation of the double bond. An attempted reduction with $(Me_3Si)_3SiH$/AIBN[5] failed, giving an inseparable mixture consisting mainly of polymerised products. From (S,S_a,S_P)-**8** a neutral rhodium(I) complex was prepared for which a dimeric structure was assumed and which was directly used in the catalysis (see below). A subsequent treatment with $AgBF_4$ in CH_2Cl_2/acetonitrile afforded the tetrafluoroborate complex of **8**. Crystallisation from a mixture of $CHCl_3$/MeOH/THF yielded a solvate having coordinated one molecule each of THF and acetonitrile. The NMR spectra of this sparingly soluble species in CD_2Cl_2 or methanol-d_4 showed P and olefin complexation (in methanol-d_4: ^{31}P NMR δ: 16.43 (s) → 101.62 (d, $J_{RhP} = 197$ Hz), ^1H NMR δ: 5.82/5.60 → 4.28/3.87). While in methanol a single species (>95%) was observed, in CD_2Cl_2 a second species (approx. 30%) appeared also showing signals indicative of olefin coordination. In both cases, no evidence for coordinated solvent was found. Only sharp signals due to free THF and acetonitrile were present and no evidence for a ligand exchange was detected. In contrast, aliphatic and, in part, aromatic signals show pronounced broadening. In solution, the complex is moderately stable and the decomposition took place within a few hours resulting in extensive signal broadening and darkened solutions. We concluded the predominance of a highly unsaturated monomeric Rh(I)–ligand species in solution, weakly stabilised by labile solvent molecules. The X-ray diffraction structure (Fig. 2) showed a 1:1 complex with **8** coordinated to Rh in a bidentate fashion forming a $5\frac{1}{2}$ chelate ring with *P*-phenyl and allyl-phenyl rings in a *syn*-arrangement. Two solvent molecules, acetonitrile and THF, occupying positions *trans* to the olefin and P, correspondingly, are bound to Rh(I) to give a slightly distorted square planar coordination geometry with typical Rh–P and Rh–(HC=CH) distances [2.1732(6) and 2.132(2)/2.110(2) Å, respectively].[6] The complex shows a C30–C31 double bond length of 1.411(3) Å, markedly longer than that of metal-free ethylene [1.337(2) Å],[7] but comparable with those of other rhodium olefin complexes.[8]

2.2. Catalytic experiments

As a test reaction for ligand **8**, the Rh catalysed asymmetric conjugate addition of Ar–$B(OH)_2$ to cycloalkyl enones **9**–**11** and lactone **12** were investigated (Scheme 2).[9] In all cases, the reaction proceeded with fair yield (64–88%) at an elevated temperature (4 h at 50 °C) showing high enantioselectivities of 88–98% ee (Table 1). The level of asymmetric induction is comparable to published results obtained with diolefin and olefin–phosphine ligands, supporting the stability of the catalytically active species in our case. The ease of formation of the P–olefin Rh-chelate from ligand **8**, despite the comparably high degree of conformational freedom of the free ligand (with two rotateable σ-bonds in the 'side arm'), is noteworthy and obviously overbalanced through the formation of a strain free chelate ring (see crystal structure). In contrast, the previously used ligands were either rigid (diolefin ligands[2,3] such as **3** and **4**) or possessed only one rotateable σ-bond (C–PPh_2 in olefin–phosphine ligands[1] such as **1** and **2**). The absolute con-



Scheme 1. Reagents and conditions: (i) BH_3·THF, 0 °C → rt; (ii) *n*-BuLi, −70 → −40 °C; PhCH=CHCH$_2$Br; (iii) Et_2NH/THF, 50 °C; (iv) $[Rh(CH_2{=}CH_2)_2Cl]_2$; (v) $AgBF_4$, MeCN/THF.

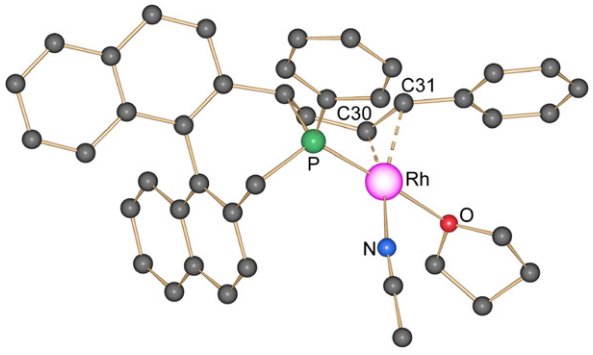
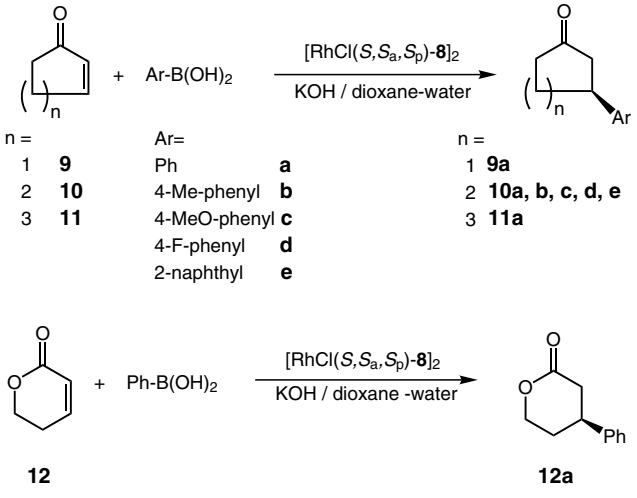


Figure 2. SCHAKAL view of the structure of $[Rh^I(S,S_a,S_P)$-**8**$(CH_3CN)(thf)]^+$ in the tetrafluoroborate salt; hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (°): Rh–P 2.1732(6), Rh–C30 2.110(2), Rh–C31 2.132(2), Rh–O 2.1639(18), Rh–N 2.074(2); P–Rh–C30 85.07(7), P–Rh–C31 86.23(7), N–Rh–O 85.97(8), N–Rh–P 96.39(6), C30–Rh–O 91.10(9), C31–Rh–O 93.53(8)°.



Scheme 2.

figuration of the products is in agreement with the proposed mechanism[10] when assuming a geometry of intermediate *A* (Fig. 3) with olefin coordination in analogy to the crystal structure (Fig. 2). The substrate coordinates with the *si*-side of the double bond *trans* to P since this arrangement results in minimal steric interaction with the phenyl group of the side arm and the binaphthyl moiety. Introduction of the Rh-attached aryl group at the β–C resulted in the formation of products with an (*S*)-configuration.

Table 1. Asymmetric 1,4-addition[a]

Substrate	Ar	Product	% Yield[b]	% ee[c]
9	Ph	**9a**	70	88 (+)
10	Ph	**10a**	88	98 (*S*)
10	4-Me–Ph	**10b**	82	98 (*S*)
10	4-OMe–Ph	**10c**	71	92 (−)
10	4-F–Ph	**10d**	76	94 (+)
10	2-Naphthyl	**10e**	64	97 (*S*)
11	Ph	**11a**	70	91 (*S*)
12	Ph	**12a**	72	90 (+)

[a] Reactions were run in 1,4-dioxane/aqueous KOH with 0.4 mmol of substrate, 3 equiv of boronic acid and 0.5 mol % of [RhCl (S,S_a,S_P)-**8**]$_2$; 4 h at 50 °C.

[b] Isolated yield after preparative TLC.

[c] Determined by chiral HPLC (Chiralpak IA: **9a**, **10b**, **10c**, **10d**, Chiralcel OD-H: **10a**, **10e**, **11a**; Chiralcel OG: **12a**).

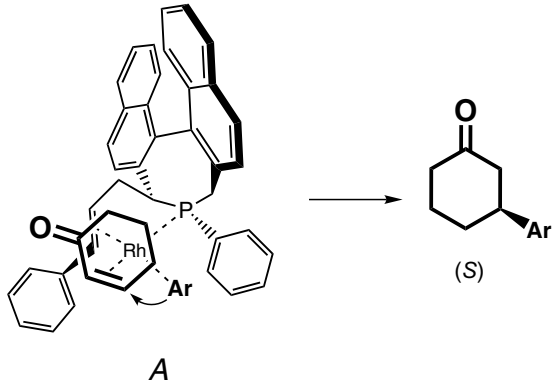


Figure 3. Suggested geometry of the Rh-substrate complex with (S,$S_a$$S_P$)-**8**.

3. Conclusions

In summary we have synthesised a new chiral bidentate ligand with olefin and phosphorus coordination sites in three steps from (*S*)-4-phenyl-4,5-dihydro-3*H*-dinaphtho[2,1-*c*;1′,2′-*e*]phosphepine in a total yield of 39%. As deduced from X-ray structure analysis, the ligand formed a chelate structure in a square planar rhodium complex, which served as an efficient catalyst for asymmetric 1,4-addition reactions. Products could be isolated in a reasonable yield and a high enantiomeric purity (up to 98% ee). The stereoselective and straightforward preparation of ligand **8** opens access to a group of analogous P-olefin ligands with varying substituents at phosphorus and the olefinic terminus. Their investigation and extension to further asymmetric reactions will be part of an ongoing project.

4. Experimental

4.1. General

Melting points: Kofler melting point apparatus, uncorrected. NMR: Bruker AM 400 spectrometer at 400.13 MHz (^{1}H), and 100.61 MHz (^{13}C), respectively, in $CDCl_3$ unless noted otherwise; chemical shifts δ are reported in ppm relative to $CHCl_3$ (7.24 or 77.00 ppm, respectively). Coupling patterns are designated as s(inglet), d(oublet), t(riplet), q(uartet), m(ultiplet), p(seudo) and b(road). $^{13}C\{^1H\}$ NMR spectra are recorded in a *J*-modulated mode; signals are assigned as C, CH_2 and CH_3; undesignated signals refer to CH-resonances. In spectral areas with extensive signal overlapping multiplets could not be identified; these signals of unclear relationship are underlined, ignoring probable multiplet structures. MS: FINNIGAN MAT 8230 EI (70 eV). HRMS: FINNIGAN MAT 8230. For HPLC determination of chiral products a HP 1090 chromatograph equipped with a diode array detector was used. Optical rotations were measured with a Perkin Elmer polarimeter 243 equipped with a 1 dm thermostated cell.

Petroleum ether, dichloromethane and ethyl acetate were distilled, absolute 1,4-dioxane from sodium, THF from sodium benzophenone ketyl, Et_2O and *n*-hexane from $LiAlH_4$; *n*-BuLi was used as 1.6 M solution in *n*-hexane (Aldrich). All the other chemicals were of analytical grade and used without further purification.

4.2. Synthesis

4.2.1. (*S*)-4-Phenyl-4,5-dihydro-3*H*-dinaphtho[2,1-*c*;1′,2′-*e*]-phosphepine borane complex 6. Crude (*S*)-4-phenyl-4,5-dihydro-3*H*-dinaphtho[2,1-*c*;1′,2′-*e*]phosphepine **5** in hexane as obtained from $PhPCl_2$ and (*S*)-2,2′-bis(lithiomethyl)-1,1′-binaphthyl–TMEDA complex, prepared from (*S*)-2,2′-dimethyl-1,1′-binaphthyl[11] (33.4 mmol), *n*-BuLi (100 mmol) and TMEDA (100 mmol) according to Ref. 12 was concentrated to half of its volume. Water (35 mL) was added and CH_2Cl_2 (200 mL) and the aqueous layer extracted with CH_2Cl_2 (2 × 25 mL). The combined organic layers were washed with water and brine and dried over $MgSO_4$. After filtration, evaporation and drying in vacuum, the crude phosphine was dissolved in THF (60 mL) and cooled to 0 °C. To this solution was added dropwise BH_3·THF (40 mL, 40 mmol, 1 M solution in THF) and the reaction was slowly warmed up to rt. After stirring for 2 h, water (4 mL) was added carefully. The mixture was then concentrated and the residue dissolved in CH_2Cl_2 (200 mL). The organic layer was washed with H_2O (2 × 25 mL) and brine and dried over anhydrous Na_2SO_4. Removal of the solvent left the crude product, which was purified by chromatography (SiO_2, petroleum ether/CH_2Cl_2 = 70:30) to afford (*S*)-**6** as a white powder; yield 5.5 g (64% rel to recovered (*S*)-2,2′-dimethyl-1,1′-binaphthyl); mp: 219–225 °C. ^{1}H NMR δ: 7.97 (d, J = 8.3 Hz, 1H); 7.92 (d, J = 8.3 Hz, 2H); 7.83 (d, J = 8.0 Hz, 1H); 7.64 (d, J = 8.6 Hz, 1H); 7.46–7.33 (m, 7H); 7.25–7.19 (m, 3H); 7.10 (d, J = 8.6 Hz, 1H); 7.06 (d, J = 8.6 Hz, 1H); 3.27 (dd, J = 13.4, 16.4 Hz, 1H); 3.05 (dd, J = 8.7, 14.6 Hz, 1H); 3.02 (dd, J = 1.9, 13.1 Hz, 1H), 2.86 (dd, J = 5.2, 14.2 Hz, 1H); 1.3–0.3 (bq, 3H). ^{13}C NMR δ: 133.91 (d, J = 7.7 Hz, C); 133.41 (d, J = 4.5 Hz, C); 133.22 (d, J = 2.1 Hz, C); 132.87 (C); 132.25 (C); 132.24 (C); 132.07 (C); 132.12 (d, J = 9.1 Hz); 131.74 (d, J = 2.9 Hz); 130.80 (d, J = 10.6 Hz, C); 129.90 (d, J = 6.8 Hz, C); 128.97 (d, J = 3.7 Hz); 128.80 (d, J = 2.3 Hz); 128.59 (d, J = 9.1 Hz); 128.41; 128.40; 128.38; 128.37; 128.29; 128.13 (d, J = 2.9 Hz); 127.78 (C); 126.95; 126.59; 126.46;

125.80 (d, $J = 1.4$ Hz, C); 125.67 (d, $J = 1.7$ Hz); 32.38 (d, $J = 31.0$ Hz, CH_2); 29.82 (d, $J = 31.0$ Hz, CH_2). ^{31}P NMR δ: 42.30 (br s) MS (160 °C) m/z (rel%): 402 (15, M^+). HRMS (EI): m/z calcd for $C_{28}H_{24}BP$ 402.1714, obsd 402.1698. $[\alpha]_D^{20} = +106$ (c 1.0, $CHCl_3$).

4.2.2. (*S*,S_a,S_P)-3-Cinnamyl-4-phenyl-4,5-dihydro-3*H*-dinaphtho[2,1-*c*;1′,2′-*e*]phosphepine borane complex 7. To a solution of borane **6** (600 mg, 1.5 mmol) in THF (15 mL) was added dropwise *n*-BuLi (1.3 mL, 2.08 mmol; 1.6 M in hexane) with stirring at −78 °C. The dark red solution was allowed to warm to −40 °C over 2 h and was then again cooled to −78 °C. Cinnamyl bromide (500 mg, 2.5 mmol) dissolved in dry THF (5 mL) was added over 15 min. The mixture was allowed to return to rt and stirring was continued for an additional hour. After quenching with a few drops of water, the mixture was concentrated and the residue was dissolved in CH_2Cl_2 (50 mL). The organic phase was washed sequentially with water and brine and dried over $MgSO_4$. Removal of the solvent left the crude product, which was treated with acetone (20 mL) and sonicated for 10 min. The suspension was filtered and the solid washed with acetone (10 mL) to yield the pure borane complex **7** (563 mg, 71%) as a white solid; mp: 224–227 °C. ^1H NMR δ: 8.02 (d, $J = 8.3$ Hz, 1H); 7.98 (d, $J = 8.3$ Hz, 1H); 7.93 (d, $J = 8.3$ Hz, 1H); 7.82 (d, $J = 8.7$ Hz, 1H); 7.68 (dd, $J = 1.2$, 8.3 Hz, 1H); 7.50–7.33 (m, 7H); 7.30–7.22 (m, 3H); 7.15–7.03 (m, 5H); 6.97–6.93 (m, 2H); 5.73–5.65 (m, 1H); 5.52 (d, $J = 15.9$ Hz, 1H); 3.48 (dd, $J = 13.0$, 16.9 Hz, 1H); 3.15 (ddd, $J = 4.2$, 10.0, 12.7 Hz, 1H); 3.02 (dd, $J = 2.5$, 13.0 Hz, 1H); 2.56–2.51 (m, 1H); 1.49–1.39 (m, 1H); 1.3–0.2 (bq, 3H). ^{13}C NMR δ: 137.14 (C); 134.41 (d, $J = 7.7$ Hz, C); 134.02 (d, $J = 3.8$ Hz, C); 134.00 (C); 133.15 (d, $J = 2.0$ Hz, C); 133.11 (C); 132.77 (C); 132.42 (d, $J = 2.0$ Hz, C); 131.72 (d, $J = 8.5$ Hz); 131.61; 131.58; 131.57; 130.62 (d, $J = 3.5$ Hz); 130.03 (d, $J = 44.3$ Hz, C); 129.10 (d, $J = 3.5$ Hz); 129.93 (d, $J = 5.8$ Hz, C); 128.64; 128.56; 128.34; 128.23; 128.15; 127.92 (d, $J = 14.2$ Hz); 127.06; 126.88; 126.76; 126.35; 126.18; 126.05; 125.86; 125.82; 46.04 (d, $J = 27.4$ Hz); 33.75 (d, $J = 4.5$ Hz, CH_2); 30.82 (d, $J = 33.7$ Hz, CH_2). ^{31}P NMR δ: 42.17 (br s). MS (190 °C) m/z (rel%): 504 (5, M^+-BH_3). HRMS (EI): m/z calcd for $C_{37}H_{29}P$ 504.2007, obsd 504.2003. $[\alpha]_D^{20} = +404$ (c 0.5, $CHCl_3$).

4.2.3. (*S*,S_a,S_P)-3-Cinnamyl-4-phenyl-4,5-dihydro-3*H*-dinaphtho[2,1-*c*;1′,2′-*e*]phosphepine 8. Borane complex **7** (540 mg, 1.04 mmol) was stirred with a degassed mixture of diethylamine (5 mL) and THF (5 mL) at 50 °C for 12 h. After cooling, the solvent was removed under vacuum and MeOH (15 mL) was added and the suspension sonicated for 10 min. The solid was separated and crystallised from toluene/pentane to afford phosphine **8** (461 mg, 86%) as a white solid; mp: 178–180 °C. ^1H NMR δ: 7.91 (d, $J = 8.6$ Hz, 1H); 7.89 (d, $J = 8.6$ Hz, 1H); 7.83 (d, $J = 8.1$ Hz, 1H); 7.69 (d, $J = 8.3$ Hz, 1H); 7.63 (d, $J = 8.6$ Hz, 1H); 7.40–6.96 (m, 16H); 6.90 (d, $J = 8.6$ Hz, 1H); 5.84–5.80 (m, 1H); 5.60 (d, $J = 16.0$ Hz, 1H); 3.03–2.90 (m, 3H); 2.11–2.10 (m, 1H), 1.53–1.48 (m, 1H). ^{13}C NMR δ: 138.86 (C); 137.46; 137.36 (d, $J = 2.7$ Hz, C); 134.39 (d, $J = 5.5$ Hz, C); 132.98 (d, $J = 31.5$ Hz, C); 132.79 (C); 132.78 (C); 132.76 (C); 132.75 (C); 132.58 (C); 131.75 (d, $J = 18.2$ Hz); 130.77; 130.31; 129.44; 129.28; 129.02; 128.71 (d, $J = 1.7$ Hz); 128.39; 128.35; 128.29; 128.26; 128.04; 127.82; 127.10 (d, $J = 2.5$ Hz); 126.76; 126.60; 125.99; 125.90; 125.81; 125.20 (d, $J = 4.6$ Hz); 48.68 (d, $J = 20.8$ Hz); 38.60 (d, $J = 31.4$ Hz, CH_2); 31.86 (d, $J = 16.8$ Hz, CH_2). ^{31}P NMR δ: 16.43 (s). MS (190 °C) m/z (rel%): 504 (97, M^+). HRMS (EI): m/z calcd for $C_{37}H_{29}P$ 504.2007, obsd 504.1996. $[\alpha]_D^{20} = +286$ (c 0.5, $CHCl_3$).

4.2.4. [Rh (*S*,S_a,S_P)-8(thf)CH_3CN][BF_4]. Ligand **8** (25 mg, 0.05 mmol) was dissolved in degassed toluene (0.5 mL). To this was added $[Rh(CH_2{=}CH_2)_2Cl]_2$ (10.7 mg, 0.055 mmol) in toluene (2 mL). The intensively orange-red solution was kept at rt for 1 h. Filtration over Celite and removal of the solvent left the neutral rhodium complex in a quantitative yield as an orange precipitate, which was used for catalytic experiments without purification. The crude complex was dissolved in CH_2Cl_2 (1 mL) and upon the addition of a solution of $AgBF_4$ (11.7 mg, 0.06 mmol) in acetonitrile (0.3 mL), the reaction mixture turned yellow-brown and became turbid. After 0.5 h the precipitated AgCl was separated by filtration over Celite, and the filtrate was evaporated. The residue was dissolved in $CHCl_3$ (3 mL) and MeOH (1 mL). THF was added on top avoiding mixing, and diffusion was allowed to take place at 4 °C over two days. During this time the solution turned pale yellow and crystals suitable for X-ray analysis had formed. ^1H NMR (CD_3OD) δ: 1.60–1.75 (m, 2H); 3.16–3.28 (m, 3H); 3.87 (m, 1H); 4.28 (m, 1H); 7.10 (d, $J = 8.3$ Hz, 1H); 7.14 (d, $J = 8.7$ Hz, 1H); 7.24 (m, 4H); 7.29 (pt, $J = 7.6$ Hz, 1H); 7.36 (d, $J = 8.3$ Hz, 1H); 7.42 (m, 2H); 7.49 (pt, $J = 7.7$ Hz, 1H); 7.52 (pt, $J = 7.5$ Hz, 1H); 7.54–7.62 (m, 3H); 7.73 (br s, 1H); 7.97–8.04 (m, 5H); 8.10 (m, 1H). ^{13}C NMR (CD_3OD) δ: 33.76 (CH_2); 36.90 (CH_2); 44.26 (d, $J = 29$ Hz); 55.99 (br, CH=); 61.70 (br, CH=); 127–135 (CH_{ar}, $C_{quat.ar}$). ^{31}P NMR (CD_3OD) δ: 101.62 (d, $J_{PRh} = 197$ Hz).

4.3. Catalytic experiments (*General procedure*)

To a solution of [RhCl (*S*,S_a,S_P)-**8**]$_2$ (12.8 mg, 20 μmol Rh) in 1,4-dioxane (0.4 mL) was added KOH (0.20 mL, 0.2 mmol; 1 M solution in water) and the resulting solution was stirred for 5 min. After the addition of Ar–$B(OH)_2$ (1.2 mmol) in 1,4-dioxane (1.2 mL) and further stirring for 5 min, this was transferred via teflon cannula to the corresponding cycloalkenone (0.4 mmol) in dioxane (1 mL). After stirring for 4 h at 50 °C the mixture was passed through a pad of silica gel with ethyl acetate and the solvents were removed under vacuum. The residue was purified by preparative TLC on silica gel with petroleum ether/ethyl acetate or petroleum ether/Et_2O.

4.3.1. 3-Phenylcyclopentanone 9a. Colourless oil; 70% yield; 88% ee; Chiralpak IA column (*n*-hexane/2-propanol, 98:2, 1.0 mL/min); t_R: 9.2 min (+), 11.9 min (−). ^1H NMR δ: 7.35–7.28 (m, 2H); 7.25–7.20 (m, 3H); 3.38 (m, 1H); 2.66 (dd, $J = 7.5$, 18.0 Hz, 1H); 2.44–2.22 (m, 4H); 2.02–1.89 (m, 1H). ^{13}C NMR δ: 217.85 (C); 143.04 (C); 128.67; 126.72; 126.70, 45.78 (CH_2); 42.21; 38.85 (CH_2); 31.18

(CH_2). MS (30 °C) *m*/*z* (rel%): 160 (57, M^+). HRMS (EI): *m*/*z* calcd for $C_{11}H_{12}O$ 160.0889, obsd 160.0891.

4.3.2. 3-Phenylcyclohexanone 10a. Colourless oil; 88% yield; 98% ee; Chiralcel OD-H column (*n*-hexane/2-propanol, 98:2, 0.5 mL/min); t_R: 23.7 min (*S*), 25.6 min (*R*). ^1H NMR δ: 7.34–7.30 (m, 2H); 7.25–7.20 (m, 3H); 3.00 (tt, $J = 11.7$, 3.7 Hz, 1H); 2.59 (ddt, $J = 13.9$, 4.5, 1.8 Hz, 1H); 2.52 (ddd, $J = 14.0$, 12.3, 0.8 Hz, 1H); 2.48–2.45 (m, 1H); 2.40–2.37 (m, 1H); 2.17–2.12 (m, 1H); 2.10–2.06 (m, 1H); 1.89–1.72 (m, 2H). ^{13}C NMR δ: 211.35 (C); 144.37 (C); 128.71; 126.72; 126.55, 48.88 (CH_2); 44.72; 41.16 (CH_2); 32.81 (CH_2); 25.54 (CH_2). MS (30 °C) *m*/*z* (rel%): 174 (42, M^+). HRMS (EI): *m*/*z* calcd for $C_{12}H_{14}O$ 174.1045, obsd 174.1049.

4.3.3. 3-(4-Methylphenyl)cyclohexanone 10b. Colourless oil; 82% yield; 98% ee; Chiralpak IA column (*n*-hexane/2-propanol, 98:2, 1.0 mL/min); t_R: 10.7 min (*R*), 11.6 min (*S*). ^1H NMR δ: 7.12–7.09 (m, 4H); 2.96 (m, 1H); 2.55–2.33 (m, 4H); 2.31 (s, 3H); 2.13–2.03 (m, 2H); 1.83–1.72 (m, 2H). ^{13}C NMR δ: 211.14 (C); 141.42 (C); 136.26 (C); 129.32; 126.41; 49.05 (CH_2); 44.36; 41.17 (CH_2); 32.88 (CH_2); 25.52 (CH_2); 20.95 (CH_3). MS (30 °C) *m*/*z* (rel%): 188 (52, M^+). HRMS (EI): *m*/*z* calcd for $C_{13}H_{16}O$ 188.1201, obsd 188.1197.

4.3.4. 3-(4-Methoxyphenyl)cyclohexanone 10c. Colourless oil; 71% yield; 92% ee; Chiralpak IA column (*n*-hexane/2-propanol, 98:2, 1.0 mL/min); t_R: 19.4 min (−), 22.5 min (+). ^1H NMR δ: 7.11 (d, $J = 8.3$ Hz, 2H); 6.84 (d, $J = 8.3$ Hz, 2H); 3.77 (s, 3H); 2.95 (m, 1H); 2.55–2.33 (m, 4H); 2.13–2.02 (m, 2H); 1.81–1.71 (m, 2H). ^{13}C NMR δ: 211.14 (C); 158.29 (C); 136.59 (C); 127.48; 114.04; 55.28 (CH_3); 49.24 (CH_2); 43.98; 41.18 (CH_2); 33.02 (CH_2); 25.49 (CH_2). MS (30 °C) *m*/*z* (rel%): 204 (87.3, M^+). HRMS (EI): *m*/*z* calcd for $C_{13}H_{16}O_2$ 204.1150, obsd 204.1154.

4.3.5. 3-(4-Fluorphenyl)cyclohexanone 10d. Colourless oil; 76% yield; 94% ee; Chiralpak IA column (*n*-hexane/2-propanol, 98:2, 1.0 mL/min); t_R: 14.0 min (+), 15.1 min (−). ^1H NMR δ: 7.15 (dd, $J = 5.1$, 8.5 Hz, 2H); 7.00 (t, $J = 8.5$ Hz, 2H); 2.97 (m, 1H); 2.55–2.32 (m, 4H); 2.15–2.12 (m, 2H); 1.83–1.71 (m, 2H). ^{13}C NMR δ: 210.67 (C); 162.77 (d, $J = 246$ Hz, C); 139.72 (d, $J = 141$ Hz, C); 127.95 (d, $J = 7.8$ Hz); 115.44 (d, $J = 21.7$ Hz); 49.06 (CH_2); 43.99; 41.10 (CH_2); 32.89 (CH_2); 25.38 (CH_2). MS (30 °C) *m*/*z* (rel%): 192 (88, M^+). HRMS (EI): *m*/*z* calcd for $C_{12}H_{13}FO$ 192.0950, obsd 192.0954.

4.3.6. 3-(2-Naphthyl)cyclohexanone 10e. White solid; 64% yield; 97% ee; Chiralcel OD-H column (*n*-hexane/2-propanol, 98:2, 0.4 mL/min); t_R: 64.5 min (*S*), 80.0 min (*R*). ^1H NMR δ: 7.81–7.77 (m, 3H); 7.62 (d, $J = 1.0$ Hz, 1H); 7.47–7.40 (m, 2H); 7.35 (dd, $J = 1.8$, 8.6 Hz, 1H); 3.17 (m, 1H); 2.66–2.60 (m, 2H); 2.47–2.36 (m, 2H); 2.17–2.14 (m, 2H); 1.96–1.90 (m, 1H); 1.83–1.78 (m, 1H). ^{13}C NMR δ: 210.9 (C); 141.74 (C); 136.36 (C); 134.85 (C); 128.35; 127.67; 127.60; 126.18; 125.62; 125.30; 124.73; 48.85 (CH_2); 44.78; 41.80 (CH_2); 32.74 (CH_2); 25.52 (CH_2). MS (30 °C) *m*/*z* (rel%): 224 (55, M^+). HRMS (EI): *m*/*z* calcd for $C_{16}H_{14}O$ 224.1201, obsd 224.1207.

4.3.7. 3-Phenylcycloheptanone 11a. Colourless oil; 70% yield; 91% ee; Chiralcel OD-H column (*n*-hexane/2-propanol, 98:2, 0.5 mL/min); t_R: 22.7 min (*S*), 25.6 min (*R*). ^1H NMR δ: 7.28–7.24 (m, 2H); 7.16–7.10 (m, 3H); 2.90–2.88 (m, 2H); 2.64–2.55 (m, 3H); 2.05–2.00 (m, 3H); 1.73–1.69 (m, 2H); 1.50–1.48 (m, 1H). ^{13}C NMR δ: 213.42 (C); 146.90 (C); 128.63; 126.40; 126.34; 51.25 (CH_2); 43.93; 42.74 (CH_2); 39.19 (CH_2); 29.24 (CH_2); 24.17 (CH_2). MS (30 °C) *m*/*z* (rel%): 188 (100, M^+). HRMS (EI): *m*/*z* calcd for $C_{13}H_{16}O$ 188.1201, obsd 188.1197.

4.3.8. 4-Phenyl-tetrahydro-2*H*-pyran-2-one 12a. Colourless oil; 72% yield; 90% ee; Chiralcel OG column (*n*-hexane/2-propanol, 90:10, 1.0 mL/min); t_R: 36.0 min (−), 40.8 min (+). ^1H NMR δ: 7.36–7.32 (m, 2H); 7.28–7.25 (m, 1H); 7.20–7.18 (m, 2H); 4.48 (ddd, $J = 4.0$, 4.6, 11.2 Hz, 1H); 4.38 (ddd, $J = 3.6$, 10.0, 11.2 Hz, 1H); 3.21 (m, 1H); 2.90 (ddd, $J = 1.8$, 6.0, 17.7 Hz, 1H); 2.62 (dd, $J = 10.7$, 17.7 Hz, 1H); 2.16–2.14 (m, 1H); 2.10–2.00 (m, 1H). ^{13}C NMR δ: 212.26 (C); 135.93 (C); 128.99; 127.24; 126.45; 68.90 (CH_2); 37.49 (CH_2); 37.46; 30.32 (CH_2). MS (30 °C) *m*/*z* (rel%): 176 (100, M^+). HRMS (EI): *m*/*z* calcd for $C_{11}H_{12}O_2$176.0837, obsd 176.0835.

4.4. Crystallographic structure determination

X-ray diffraction measurements were performed on an X8APEXII CCD diffractometer with graphite monochromated Mo Kα radiation, $\lambda = 0.71073$ Å at 100(2) K. Single crystal was positioned at 40 mm from the detector and 2567 frames were measured, each for 10 s over 1° scan width. The data were processed using SAINT software, corrections for absorption were performed with program SADABS.[13] The structure was solved by direct methods and refined by full-matrix least-squares techniques. Non-hydrogen atoms were refined with anisotropic displacement parameters. H atoms were placed in geometrically calculated positions and refined as riding atoms in the subsequent least squares model refinements. The isotropic thermal parameters were estimated to be 1.2 times the values of the equivalent isotropic thermal parameters of the atoms to which hydrogens were bonded. The following computer programs were used: structure solution, SHELXS-97,[14] refinement, SHELXL-97,[15] molecular diagrams, SCHAKAL99,[16] computer: Pentium IV; scattering factors were taken from the literature.[17] Details of crystal data, data collection and refinement are as follows:[18]

[Rh^I(*S*,S_a,S_P)-**9**(CH_3CN)(thf)][BF_4]: $C_{43}H_{40}BF_4NOPRh$, $M_r = 807.45$, orthorhombic, space group $P2_12_12_1$ (no. 19), $a = 10.7746(3)$, $b = 12.3893(4)$, $c = 27.1841(9)$ Å, $V = 3628.8(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.478$ g/cm^3, $\mu = 0.571$ mm^{-1}. Of 129,099 reflections collected up to $\theta_{max} = 30°$, 10,584 were independent, $R_{int} = 0.065$, and 9577 were observed ($I > 2\sigma(I)$); final *R* indices: $R_1 = 0.0352$, $wR_2 = 0.0841$ (all data).

Acknowledgements

P.K. is grateful for a grant provided by the *Fonds zur Förderung der wissenschaftlichen Forschung in Österreich*

(Lise Meitner Grant Nr. M852-N11). We are also thankful to Mr. A. Roller for the collection of X-ray data.

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