# Olefins as Steering Ligands for Homogeneously Catalyzed Hydrogenations

**Pascal Maire, Stephan Deblon, Frank Breher, Jens Geier, Carsten Böhler, Heinz Rüegger, Hartmut Schönberg, and Hansjörg Grützmacher*[a]**

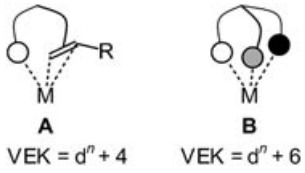
**Abstract:** Iridium(I) complexes containing a (5*H*-dibenzo[*a*,*d*]cyclohepten-5-yl)-phosphane (tropp$^{R}$; R = phosphorus-bound substituent = Ph, Cyc) as a rigid, concave-shaped, mixed phosphane olefin ligand were prepared and tested as catalyst precursors in the hydrogenation of imines. With the complex [Ir(tropp$^{Cyc}$)(cod)]OTf, turnover frequencies (TOFs) of $>6000\ h^{-1}$ were reached in the hydrogenation of *N*-phenyl-benzylidenamine, PhN=CHPh. Lower activities ($TOF > 80\ h^{-1}$) are observed with *N*-phenyl-(1-phenylethylidene)amine, PhN=CMePh. Chiral tropp-type ligands were prepared in few simple steps. Monosubstitution of the olefinic unit in the dibenzo[*a*,*d*]cycloheptenyl moiety with (*R*)- or (*S*)-mentholate gave mixtures of diastereomers that could be separated and isolated in enantiomerically pure form. Iridium(I) complexes with these ligands are rare examples of side-on bonded enolether complexes. In catalytic imine hydrogenations, complete conversion (>98%) was reached in all cases (conditions: $p[H_2] = 50$ bar, $T = 50\,°C$, $t = 2$ h, substrate/catalyst 100:1). The best enantiomeric excess (*ee* = 86% *S* isomer) was reached with PhN=CMePh as substrate and the *R*,*R* form of the (10-menthyloxy-5*H*-dibenzo[*a*,*d*]cyclohepten-5-yl)diphenylphosphane ligand. The iridium(I) complex containing the same phosphane gave a 60% *ee* (*S* isomer) with the enamide N-(1-phenylvinyl)acetamide as substrate (conditions: $p[H_2] = 4$ bar, $T = 50\,°C$, $t = 18$ h, substrate/catalyst = 50:1). These reactions constitute the first examples in which chiral olefins have been used as steering ligands in catalytic enantioselective hydrogenations.

**Keywords:** enantioselectivity · homogeneous catalysis · hydrogenation · imines · iridium · olefins

## Introduction

Many scientists would probably not enthusiastically recommend the use of olefins as steering ligands, especially not in transition-metal-catalyzed hydrogenations of unsaturated bonds. Indeed, olefins are either subject to chemical changes or are kinetically labile place holders for so-called "vacant" coordination sites; in either case they are displaced from the transition metal. However, calculations show that the iridium trihydride olefin complex $[Ir(H)_3(PH_3)_2(C_2H_4)]$ (**I**) is about 65 kJ mol$^{-1}$ more stable than the iridium–alkyl complex $[Ir(H)_2(PH_3)_2(C_2H_5)]$ (**II**), the first intermediate on the hydrogenation pathway taken in olefin insertion into one Ir–H bond. Note that the product state $[IrH(C_2H_6)(PH_3)_2]$ (**III**) is even 130 kJ mol$^{-1}$ higher in energy than **I**, but very labile towards dissociation into $[IrH(PH_3)_2] + C_2H_6$.[1] Consequently, olefin hydrogenation profits from the poor binding quality of alkanes to transition metals, from which they escape by diffusion. When this diffusion process is suppressed, might olefins then be used as steering ligands for catalytic hydrogenations?[2–5]

Olefins have interesting electronic properties (that is, their donor–acceptor properties can be varied over a wide range) and a useful spatial extension for creating asymmetry. As shown in Scheme 1, binding of a bischelate with an unsymmetrically substituted olefin $H_2C{=}CHR$, as in **A**, will create a chiral complex. The alternative formulation of such a metal olefin complex as a metallacyclopropane relates this situation to chiral tripod complexes **B** containing three different donor centers.[6] However, while tripod ligands con-




Scheme 1. Topographical similarity between a bidentate donor-olefin complex **A** with $d^n + 4$ valence electrons and a tripod complex **B** with $d^n + 6$ valence electrons.

[a] P. Maire, S. Deblon, Dr. F. Breher, J. Geier, C. Böhler, H. Rüegger, H. Schönberg, Prof. Dr. H. Grützmacher
Department of Chemistry and Applied Biosciences
ETH-Hönggerberg
Wolfgang-Pauli-Strasse, 8093 Zürich (Switzerland)
Fax: (+41)-1-633-103
E-mail: gruetzmacher@inorg.chem.ethz.ch



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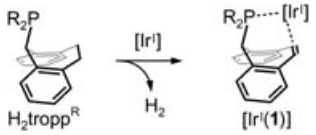
tribute six electrons to the valence electron configuration and often electronically saturate a metal complex, the ligand sphere in **A** acts only as a four-electron donor.

In previous work we reported the easily achieved *dehydrogenation* reaction of the phosphane 5-diphenylphosphanyl-10,11-dihydro-5*H*-dibenzo[*a*,*d*]cycloheptene, $H_2tropp^{Ph}$, with iridium(I) complexes to give quantitative yields of complexes with the unsaturated 5-diphenylphosphanyl-5*H*-dibenzo[*a*,*d*]cycloheptene ($tropp^R$ **1**, R = Ph = phosphorus-bound substituent) as ligand (Scheme 2).[7]

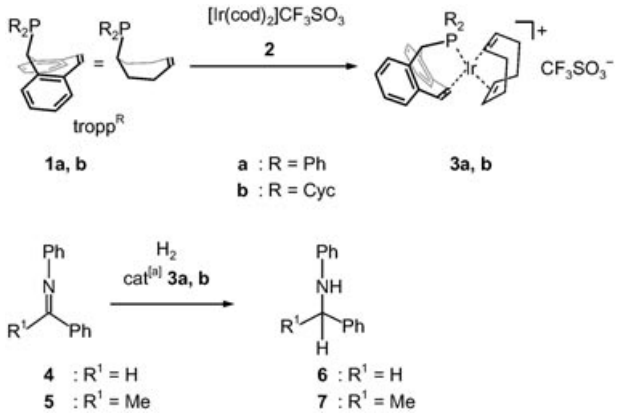



Scheme 2. Dehydrogenation of $H_2tropp^R$ with iridium(I) complexes.

To answer the question motivating this study, iridium tropp complexes were synthesized and tested as catalyst precursors in catalytic hydrogenations.

## Results

The iridium $tropp^R$ complexes **3a** and **3b** were synthesized in a straightforward and quantitative reaction (Scheme 3, top) as deep red crystalline substances. For a first check of




Scheme 3. Synthesis of iridium complexes **3a** and **3b** and catalyzed hydrogenations of imines **4** and **5**. [a] s/c 1000, $p[H_2] = 50$ bar, $T = 50\,^{\circ}C$, [s] = 1 M, THF.

catalytic activity, **3a** was dissolved in a THF/cod mixture (1:1 v/v, cod = 1,5-cyclooctadiene), and under 5 atm $H_2$ complete conversion of cod to cyclooctane was observed. The $C{=}C_{trop}$ bond remained unaffected and the solution with the catalyst could be recycled without loss of activity.

Subsequently, the homogeneously catalyzed hydrogenation of the imines[8a–j] **4** and **5** (Scheme 3, bottom) was investigated, and the results are listed in Table 1.

Excellent activity was found in the hydrogenation of benzylidene aniline **4** to *N*-phenyl-benzylamine **6** with **3b** as the catalyst containing the P,P-di(cyclohexyl)-substituted ligand $tropp^{Cyc}$. A rather low activity—not unusual for imine hydrogenations, however—was observed when phenyl(1-phenylethylidene)amine **5** was hydrogenated with **3a** or **3b** as catalyst, indicating a marked steric effect on the reaction rate.

Table 1. Comparison of TOFs for the hydrogenation of imines **4** and **5** to the corresponding amines **6** and **7** with catalyst precursors **3a** and **3b**.

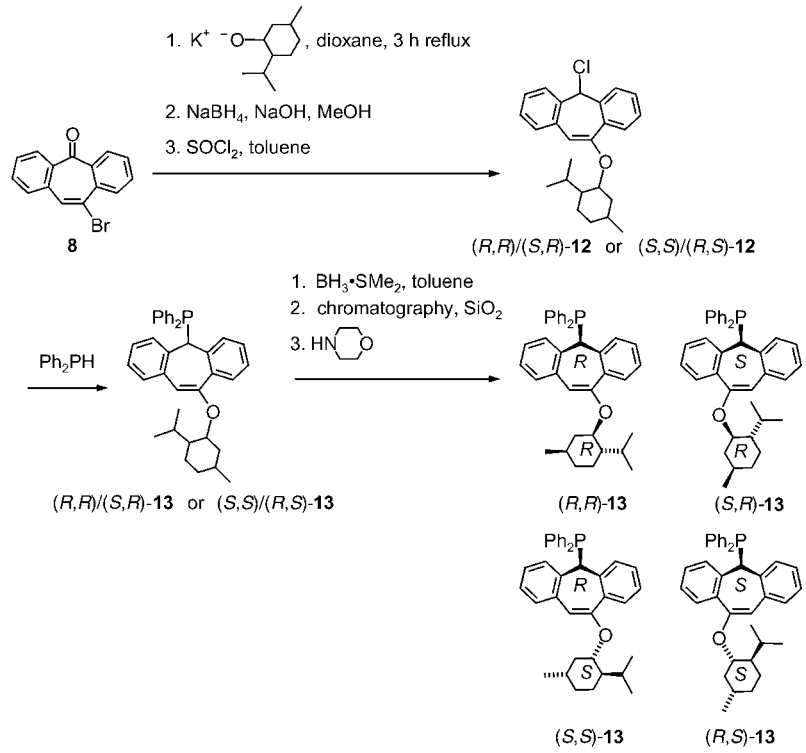
| | cat: **3a** (R = Ph) | cat: **3b** (R = Cyc) |
|---|---|---|
| TOF (**4**→**6**) [$h^{-1}$] | >2000 | >6000 |
| TOF (**5**→**7**) [$h^{-1}$] | 82 | 76 |

Chiral tropp ligands with unsymmetrically substituted C=C units were prepared in a few simple steps (Scheme 4). First, 10-bromodibenzo[*a*,*d*]cyclohepten-5-one (**8**) was transformed with potassium (*R*)-mentholate into 10-[(1*R*)-menthoxy]dibenzo[*a*,d]cyclohepten-5-one (90%), which was converted with $NaBH_4$/MeOH into a mixture of the (5*R*/5*S*)-diastereomers of 10-[(1*R*)-menthoxy]-5*H*-dibenzo[*a*,*d*]cyclohepten-5-ol (94%), and subsequently into a mixture of the diastereoisomers of the chloro compound, (*R*,*R*)-**12** and (*S*,*R*)-**12**. Without further purification, these compounds were treated with diphenylphosphane to yield the mixture of diastereoisomers of the $^{menthoxy}tropp^{Ph}$ phosphanes (*R*,*R*)-**13** and (*S*,*R*)-**13** (81%). To prevent phosphane oxygenation, the diastereomers were converted into the $BH_3$ adducts, and these were separated by column chromatography. The free phosphanes were obtained after deprotection with morpholine and crystallization from acetonitrile, as colorless crystals in enantiomerically pure form (96% (*R*,*R*)-**13** and 95% (*S*,*R*)-**13**). The same reaction sequence with potassium (*S*)-mentholate gave the phosphanes (*R*,*S*)-**13** and (*S*,*S*)-**13**.

The enantiomerically pure tetracoordinated 16-electron complexes (*R*,*R*)-**15** or (*R*,*S*)-**15**, or their enantiomers (*S*,*S*)-**15** and (*S*,*R*)-**15**, respectively (Scheme 5), were obtained quantitatively by treatment of the corresponding $^{menthoxy}tropp^R$ phosphanes **13** with $[Ir(cod)_2]SO_3CF_3$ (**2**). The rhodium complex (*S*,*R*)-**17** was prepared in a similar way (Scheme 5).

As with **3a**, cod was cleanly hydrogenated with complexes **15** as catalyst precursors. Enantioselective hydrogenations were investigated with phenyl(1-phenylethylidene)amine **5** and **18** as substrates. Complete conversion was achieved in all cases under the given conditions. With (*R*,*R*)-**15** as catalyst, the *S*-configured isomer (*S*)-**7** is formed (entry 1, Table 2) and the observed enantiomeric excess (86% *ee*) is in the upper range obtained for this substrate.[5] When the menthoxy substituent is shifted to the other carbon atom of the $C{=}C_{trop}$ unit—that is, the stereochemistry at the 5-position of the tropp ligand is reversed—and (*S*,*R*)-**15** is employed as catalyst, (*S*)-**7** is again obtained, although with a lower *ee*. The *R*-configured amine (*R*)-**7** was obtained with identical *ee* values (entries 3, 4, Table 2) when the enantiomers (*S*,*S*)-**15** and (*R*,*S*)-**15** containing the *S*-configured menthoxy substituent were used as catalysts. This experiment indicates that the complexes **15** are indeed the precursors to the catalytic active species. With *N*-(1-phenylvinyl)acetamide **18** (which has better storage properties than **5**) as sub-



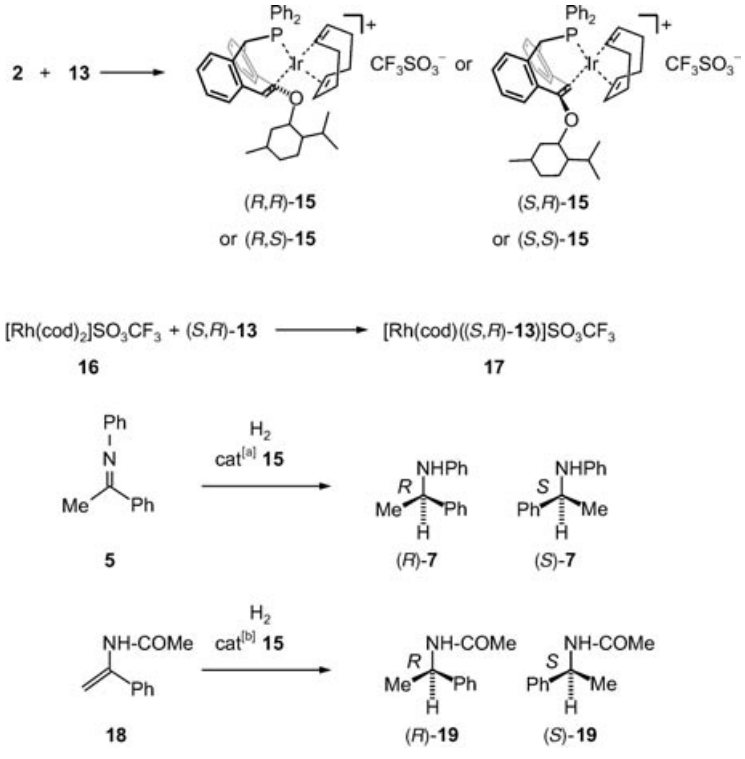

Scheme 4. Syntheses of enantiomerically pure tropp ligands (*R*,*R*)-**13**, (*S*,*R*)-**13**, (*S*,*S*)-**13**, and (*R*,*S*)-**13**. In the designation of the stereochemistry, the configuration at the benzylic carbon in the dibenzo[*a*,*d*]cycloheptene moiety is given first and the configuration at the ether carbon of the menthoxy group second.

strate, the *S*-configured isomer (*S*)-**19** was again obtained as the major product (60% *ee*) with the (*R*,*R*)-configured catalyst (entry 5, Table 2). However, in contrast to the previously described experiments with **5**, the *R*-configured isomer (*R*)-**19** was obtained in 24% *ee* when the diastereomer (*S*,*R*)-**15** served as catalyst precursor (entry 6, Table 2).

The rhodium complex **17** showed no catalytic activity under the given experimental conditions. After prolonged reaction times (days), only decomposition under formation of rhodium black occurred.

## Solid-state and solution structures

**X-ray diffraction studies**: To gain some information about the conformations of the chiral ligands in their non-coordinated and coordinated forms, the




Scheme 5. Enantioselective catalytic imine hydrogenations with the iridium complexes (*R*,*R*)-**15**, (*S*,*R*)-**15**, (*S*,*S*)-**15**, and (*R*,*S*)-**15**. In the designation of the stereochemistry, the configuration at the benzylic carbon in the dibenzo[*a*,*d*]cycloheptene moiety is given first and the configuration at the ether carbon of the menthoxy group second. [a] s/c 100, $p[H_2]=50$ bar, $T=50$ °C. [b] s/c 50, $p[H_2]=50$ bar, $T=50$ °C.

Table 2. Reaction conditions and enantiomeric excesses (*ee*s) obtained in homogeneously catalyzed imine hydrogenations with complexes **15**.

| Entry | Cat. | Solvent | Substrate | *t* [h] | Yield [%][b] /product | % *ee*[c] |
|---|---|---|---|---|---|---|
| 1[a] | (*R*,*R*)-**15** | $CHCl_3$ | **5** | 2 | >98/**7** | 86 (*S*) |
| 2[a] | (*S*,*R*)-**15** | $CHCl_3$ | **5** | 2 | >98/**7** | 45 (*S*) |
| 3 | (*S*,*S*)-**15** | $CHCl_3$ | **5** | 2 | >98/**7** | 86 (*R*) |
| 4 | (*R*,*S*)-**15** | $CHCl_3$ | **5** | 2 | >98/**7** | 45 (*R*) |
| 5 | (*R*,*R*)-**15** | $CHCl_3$ | **18** | 18 | >98/**19** | 60 (*S*) |
| 6 | (*S*,*R*)-**15** | $CHCl_3$ | **18** | 18 | >98/**19** | 24 (*R*) |

[a] Identical results with isolated and in situ prepared catalyst precursors from **2** and (*R*,*R*)-**15** or (*S*,*R*)-**15**. [b] Determined by GC analysis. [c] Determined by GC analysis with a chiral stationary phase (Lipodex E).

structures of the phosphanes (*R*,*R*)-**13** and (*S*,*R*)-**13** and of the iridium complex (*R*,*R*)-**15** were determined by X-ray structure analysis.[9] We did not obtain suitable crystals of (*S*,*R*)-**15**, but the structure of the rhodium complex (*S*,*R*)-**17** was investigated. The results are shown in Figure 1. Structurally characterized examples of vinyl ether complexes of the late transition metals are rare.[10] While the C4=C5$_{trop}$ unit in the complex (*R*,*R*)-**15** binds almost symmetrically to the iridium center (Ir−C4 228(1) pm, Ir−C5 223.1(9) pm), in the rhodium complex **17** the C4−C5 unit of the (*R*,*S*)-**13** diastereomer is bonded at much longer distances and in a highly unsymmetrical fashion to the rhodium center (Rh1−C4 231.6(3) pm, Rh1−C5 306.0(1) pm). The $^{13}C$ NMR data imply that such a slipping of the metal towards the CH of

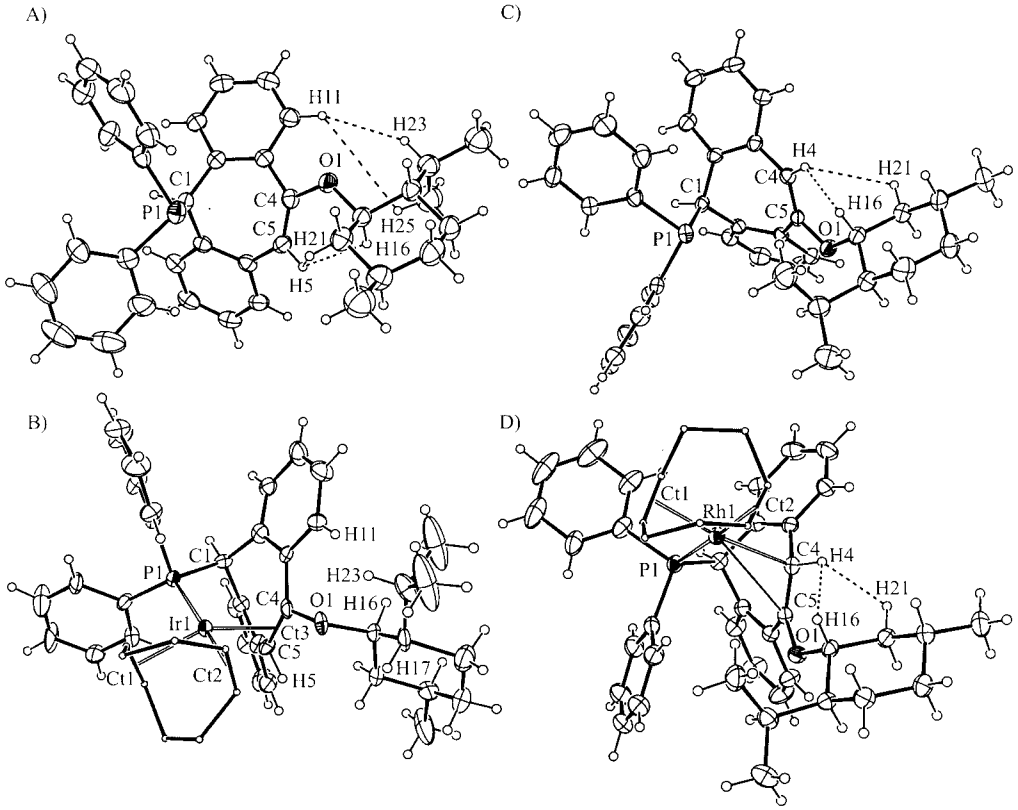



Figure 1. A) Structure of the phosphane (*R*,*R*)-**13**. B) Structure of the iridium(I) complex (*R*,*R*)-**15**. C) Structure of the phosphane (*S*,*R*)-**13**. D) Structure of the rhodium(I) complex **17**. Thermal ellipsoids at 30% probability. Selected bond lengths [pm] and angles [°]. Ct1, Ct2, and Ct3 denote the centroids of the coordinated C=$C_{cod}$ bonds (Ct1, Ct2) or the coordinated C4–C5 bond (Ct3). A) (*R*,*R*)-**13**: P1–C1 190.1(3), C4–C5 132.8(4), C4–O1 137.2(4), O1–C16 143.4(3), H11–H23 ≈250, H11–H25 ≈350, H5–H21 ≈240, H5–H16 ≈200; Σ°(P) 301.5(1). B) (*R*,*R*)-**15**: Ir–P1 226.5(2), Ir–C4 228(1), Ir–C5 223.1(9), Ir–Ct1 204(1), Ir–Ct2 216(1), Ir–Ct3 213(1), P1–C1 187(1), C4–C5 1.46(1), C4–O1 139(1), O1–C16 149(1); P1-Ir-Ct1 93.7(5), Ct1-Ir1-Ct2 83.7(5), Ct2-Ir-Ct3 95.6(5), P1-Ir1-Ct3 92.2(5), C4-O1-C16 116.0(7), Σ°(P) 317.6. C) The average of two independent molecules in the unit cell are given for (*S*,*R*)-**13**: P1–C1 188.8(3), C4–C5 134.0(4), C5–O1 136.4(3), O1–C16 144.1(3), H4–H16 ≈190, H4–H21 ≈265; C5-O1-C16 120.2(2), Σ°(P) 301.8(1). **17**: Rh1–P1 226.9(1), Rh1–C4 231.6(3), Rh1–C5 306.0(1), Rh1–Ct1 201.7(1), Rh1–Ct2 216.5(1), Rh1–Ct3 262.3(1), C4–C5 139.5(4), C5–O1 135.0(3), O1–C16 145.5(3), H4–H16 ≈220, H4–H21 ≈200; P1-Rh1-Ct1 92.6(1), Ct1-Rh1-Ct2 85.2(1), Ct2-Rh-Ct3 101.6(1), Ct3-Rh1-P1 80.4(1), C5-O1-C16 122.8(2), Σ°(P) 315.5(1).

the CH=COR unit may easily happen in all complexes in solution. The coordination shift $\Delta\delta^{13}$C (usually to lower frequency) is marginal for the =COR carbon nucleus (<7 ppm, see data in Table 3), while $\Delta\delta^{13}$C is significantly larger for =*C*H (24–31 ppm).

Table 3. Selected NMR data for the C=$C_{trop}$ units in (*R*,*R*)-**13**, (*S*,*R*)-**13**, (*R*,*R*)-**15** , (*S*,*R*)-**15** , and (*S*,*R*)-**17**.

| $\delta$ | (*R*,*R*)-**13** | (*S*,*R*)-**13** | (*R*,*R*)-**15** | (*S*,*R*)-**15** | (*S*,*R*)-**17** |
|---|---|---|---|---|---|
| =C*H* | 6.40 | 6.47 | 6.78 | 6.78 | 6.66 |
| =*C*H | 105.5 | 108.0 | 74.7 | 80.4 | 84.1 |
| =*C*OR | 154.6 | 152.8 | 152.7 | 146.4 | 155.5 |

**NMR spectroscopy**: With regard to the catalytic reactions, it was of interest to examine the structures in solution and to compare them with the solid-state structures. In the $^1$H NOESY spectra, intense cross-peaks were found for the proton–proton interactions indicated by dashed lines in Figure 1, which indicate that the structures of (*R*,*R*)-**13**, (*S*,*R*)-**13**, and (*S*,*R*)-**17** are essentially retained in solution. Furthermore, only one conformer is observed in each case for the phosphanes (*R*,*R*)-**13** and (*S*,*R*)-**13** and the rhodium(I) complex (*S*,*R*)-**17**. The NMR data for the iridium complex (*S*,*R*)-**15** fit nicely with the solid-state structure of the rhodium complex (*S*,*R*)-**17**; that is, the conformation of the (*S*,*R*)-**13** phosphane ligand is probably very similar in both compounds. For the iridium complex (*R*,*R*)-**15**, however, the NOESY spectrum indicates the presence of two conformers in solution. Only the minor component has the structure shown in Figure 1B, indicated by a weak cross-peak for the H11–H16 interaction. For the major conformer, a strong NOE is seen between the olefinic H5 proton and the methine ether proton H16. While this observation is compatible with a structure in which the menthoxy group has rotated counter-clockwise to a conformation seen in (*S*,*R*)-**15** and **17**, the absence of any contacts between the isopropyl protons to H5 or the cod protons (which are present in (*S*,*R*)-**15** and **17**) make this conformation unlikely. Weak NOEs are observed between the *i*Pr protons and the benzo group proton H11, and this, together with the strong H5–H16 NOE, indicates a structure in which the menthoxy group has rotated clockwise in order to minimize the steric interaction between the *i*Pr group and the Ir(cod) unit.

## Conclusion

It is evident from the above experiments that the unsymmetrical substitution at the C=$C_{trop}$ bond and the stereogenic centers in the menthoxy group have an influence on the stereochemistry in the hydrogenations. The NOESY experiments suggest that the complexes with the (*S*,*R*)-configured ligand **13** are rather rigid and that the *i*Pr group of the menthoxy substituent is in proximity to the metal center. Hence, it may be that the stereochemistry in reactions with the (*S*,*R*)-**13** ligand is controlled by the chirality of the menthoxy group and that the *R* configuration favors the *S* configuration in the product (entry 2, Table 2) or at least diminishes the *ee* for the *R* configuration in the product (entry 6, Table 2). However, the fact that the stereochemistry may be controlled by the configuration at the coordinated C=Ctrop bond is clearly demonstrated by the experiments reported in entries 5 and 6 in Table 2; specifically in complexes with the *R*,*R*-configured ligand, in which the orientation of the menthoxy group is more flexible and, importantly, the *i*Pr group is located away from the metal center. A more detailed analysis must await a better understanding of iridium-catalyzed hydrogenations.

The experiments described in this work were performed in an attempt to expand the classes of ligands known to be usable for homogeneously catalyzed reactions. The question raised at the beginning can be answered in combination with Hayashi's and Carreira's recent results:[3, 4] *yes, olefins can be used as steering ligands in catalysis, even for catalyzed hydrogenations*. The ligands presented here are certainly not the best choice with respect to their performance. Since, however, olefins show an enormous electronic flexibility, like almost no other class of ligands, and furthermore are present as potential binding sites in many natural products not yet explored for the purposes of organometallic chemistry, a large pool of ligands with potentially better properties remains to be explored.

## Experimental Section

**General**: All syntheses were performed under argon by use of standard Schlenk techniques. All solvents were dried and purified by standard procedures and were freshly distilled under argon from sodium/benzophenone (THF), from sodium/diglyme/benzphenone (*n*-hexane, toluene), or from calcium hydride ($CH_2Cl_2$) prior to use. Air-sensitive compounds were stored and weighed in a glovebox (Braun MB 150 B-G system), and reactions on small scales were performed directly in the glovebox. NMR spectra were recorded on Avance DPX 300 or Avance DPX 250 systems. The chemical shifts are given as $\delta$ values and were referenced against tetramethylsilane (TMS) for $^1$H and $^{13}$C, 85% $H_3PO_4$ for $^{31}$P, $BF_3{\cdot}Et_2O$ for $^{11}$B, and $CFCl_3$ for $^{19}$F NMR spectra. Coupling constants *J* are given in Hertz [Hz] as positive values regardless of their real individual signs. The multiplicity of the signals is indicated as s, d, t, q, or m for singlets, doublets, triplets, quartets, or multiplets, respectively. The abbreviation br. is given for broadened signals. Quaternary carbon atoms are indicated as $C_{quart}$, aromatic units as $CH_{ar}$ when not noted otherwise. The olefinic protons and $^{13}$C atoms of the C=$C_{tropp}$ unit in the central seven-membered ring are indicated as $CH_{tropp}$ and $CH_{tropp}$, respectively. IR spectra were measured on a Perkin–Elmer 2000 FT-IR spectrometer with a KBr beamsplitter. The UV/Vis spectra were measured with a UV/Vis/NIR Lambda 19 spectrometer in 0.5 cm quartz cuvettes. Mass spectra were taken on a Finnigan MAT SSQ 7000 in the EI (70 eV) mode.

**Syntheses**

**[Ir(cod)(tropp$^{ph}$)]$CF_3SO_3$ (3a)**: A solution of 5-diphenylphosphanyl-5*H*-dibenzo[*a*,*d*]cycloheptene (tropp$^{ph}$, **1a**,[7a] 188 mg, 0.50 mmol) in $CH_2Cl_2$ (3 mL) was added with vigorous stirring to a solution of [Ir(cod)$_2$]$CF_3SO_3$ (**2**, 278 mg, 0.50 mmol) in $CH_2Cl_2$ (3 ml). The resulting dark brown solution was stirred for an additional 5 min and was then layered with *n*-hexane (10 mL). After one day, the product **3a** started to crystallize as deep red, lustrous needles. Yield: 360 mg (88%). M.p.: 190–195 °C (decomp); $^1$H NMR (300.1 MHz, $CD_2Cl_2$): $\delta$ = 7.64–7.58 (m, 2H; $CH_{ar}$), 7.53–7.43 (m, 2H; $CH_{ar}$), 7.40–7.28 (m, 10H; $CH_{ar}$), 7.15–7.08 (m, 2H; $CH_{ar}$), 6.98–6.86 (m, 2H; $CH_{ar}$), 6.32 (d, $J_{P,H}$ = 0.7 Hz, 2H; $CH_{tropp}$), 5.80 (d, $^2J_{P,H}$ = 14.6 Hz, 1H; $CHP$), 5.57 (brs, 2H; $CH_{cod}$), 4.27 (brs, 2H; $CH_{cod}$), 2.57 (brm, 4H; $CH_{2cod}$), 2.11–1.77 (brm, 4H; $CH_{2cod}$) ppm; $^{13}$C NMR (75.5 MHz, $CD_2Cl_2$): $\delta$ = 136.4 (d, $J_{P,C}$ = 8.2 Hz, 2C; $C_{quart}$), 134.1 (d, $J_{P,C}$ = 9.2 Hz, 4C; $CH_{ar}$), 132.4 (d, $J_{P,C}$ = 1.5 Hz, 2C; $C_{quart}$), 131.7 (d, $J_{P,C}$ = 2.4 Hz, 2C; $CH_{ar}$), 130.2 (d, $J_{P,C}$ = 6.1 Hz, 2C; $CH_{ar}$), 129.7 (d, $J_{P,C}$ = 1.8 Hz, 2C; $CH_{ar}$), 129.5 (2C; $CH_{ar}$), 128.8 (d, $J_{P,C}$ = 10.2 Hz, 4C; $CH_{ar}$), 128.6 (d, $J_{P,C}$ = 1.5 Hz, 2C; $CH_{ar}$), 126.2 (d, $^1J_{P,C}$ = 53.0 Hz, 2C; $C_{ipsoPh}$), 109.4 (d, $J_{P,C}$ = 11.3 Hz, 2C; $CH_{cod}$), 82.7 (2C; $CH_{cod}$), 80.4 (2C; $CH_{tropp}$), 52.1 (d, $J_{P,C}$ = 27.7 Hz, 1C; $CHP$), 32.5 (d, $J_{P,C}$ = 3.0 Hz, 2C; $CH_{2cod}$), 30.3 (brs, 2C; $CH_{2cod}$) ppm; $^{31}$P NMR (121.5 MHz, $CD_2Cl_2$): $\delta$ = 62.4 (s) ppm; IR: $\tilde{\nu}$ = 2921(w), 1482(w), 1435(w), 1259vs ($SO_3^-$), 1223(m), 1155(s), 1098(w), 1028(vs), 898(w), 865(w), 804(w), 749(m), 694(m), 634(s), 572(w), 559(w) cm$^{-1}$; UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ = 320 nm.

**[Ir(cod)(tropp$^{cyc}$)]$CF_3SO_3$ (3b)**: A solution of 5-dicyclohexylphosphanyl-5*H*-dibenzo[*a*,*d*]cycloheptene (tropp$^{cyc}$, **1b**, 195 mg, 0.50 mmol) in $CH_2Cl$ (3 mL) was added with vigorous stirring to a solution of [Ir(cod)$_2$]$CF_3SO_3$ (**2**; 278 mg, 0.50 mmol) in $CH_2Cl_2$ (3 mL). After layering of the reaction solution with *n*-hexane (10 mL), the product **3b** crystallized as deep red needles. Yield: 350 mg (84%). M.p.: 175–179 °C (decomp); $^1$H NMR (300.1 MHz, $CD_2Cl_2$): $\delta$ = 7.81–7.78 (m, 4H; $CH_{ar}$), 7.64–7.36 (m, 4H; $CH_{ar}$), 6.45 (s, 2H; $CH_{tropp}$), 6.24 (d, $^1J_{P,H}$ = 13.0 Hz, 1H; $CHP$), 5.49–5.42 (m, 4H; $CH_{cod}$), 2.54–2.19 (m, 8H; $CH_{2cod}$) 1.75–1.05 (m, 20H; $CH_{2cyc}$), 0.50–0.44 (m, 2H; $CH_{cyc}$) ppm; $^{13}$C NMR (75.5 MHz, $CD_2Cl_2$): $\delta$ = 136.5 (d, $J_{P,C}$ = 6.3 Hz, 2 C; $C_{quart}$), 133.0 (2C; $C_{quart}$), 129.7 (2C; $CH_{ar}$), 129.6 (2C; $CH_{ar}$), 129.3 (d, $J_{P,C}$ = 6.4 Hz, 2C; $CH_{ar}$), 128.8 (2C; $CH_{ar}$), 106.6 (d, $J_{P,C}$ = 10.7 Hz, 2C; $CH_{cod}$), 80.9 (2C; $CH_{tropp}$), 78.5 (2C; $CH_{cod}$), 45.9 (d, $^1J_{P,C}$ = 24.1 Hz, 1C; $CHP$), 37.5 (d, $^1J_{P,C}$ = 24.1 Hz, 2C; $PCH_{cyc}$), 33.5 (d, $J_{P,C}$ = 2.9 Hz, 2C; $CH_{2cyc}$), 30.8 [brs, 2C; $CH_{2cod}$), 29.8 (brs, 2C; $CH_{2cod}$), 28.8 (d, $J_{P,C}$ = 3.7 Hz, 2 C; $CH_{2cyc}$), 27.3 (d, $J_{P,C}$ = 11.1 Hz, 2C; $CH_{2cyc}$), 26.7 (d, $J_{P,C}$ = 9.8 Hz, 2 C; $CH_{2cyc}$), 25.4 (brs, 2C; $CH_{2cyc}$) ppm; $^{31}$P NMR (121.5 MHz, $CD_2Cl_2$): $\delta$ = 66.4 (s) ppm; IR: $\tilde{\nu}$ = 2924(m), 2854(w), 1488(w), 1448(w), 1331(w), 1262(s), 1224(m), 1138(s), 1039(s), 853(w), 803(w), 758(m), 634(s), 572(m) cm$^{-1}$; UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ = 345 nm; MS (FAB, *m*/*z*, %): 689 (100) [*M*−Otf], 581 (10) [*M*−Otf−cod].

**10-[(1*R*)-Menthyloxy]-dibenzo[*a*,*d*]cyclohepten-5-one (9)**: 10-Bromodibenzo[*a*,*d*]cyclohepten-5-one (**8**; 12.00 g, 42.1 mmol)[11] and potassium (*R*)-menthoxylate (8.99 g, 46.3 mmol, freshly prepared from 1.2 equiv (*R*)-menthol and 1.1 equiv potassium at 100 °C in 1,4-dioxane) were dissolved in 1,4-dioxane (150 mL). Gentle warming of the reaction mixture occurred, and it turned reddish-brown. It was then heated to 100 °C and stirred for 3 h. Subsequently, all volatile components were evaporated under vacuum (P = $10^{-2}$ Torr). The residue was dissolved in *tert*-butyl methyl ether (TBME, 250 mL), and the solution was washed with saturated aqueous NaCl. The separated organic phase was dried over $MgSO_4$ and all volatile components were evaporated under reduced pressure to leave a yellow oil, which was purified by flash chromatography (FC) (silica, ethyl acetate (EE)/hexane 1:9). Yield: 13.66 g (90%), yellow oil. Thin-layer chromatography (TC) (silica, EE/hexane: 1/9): $R_f$ = 0.53; $^1$H NMR (300.1 MHz, $CDCl_3$): $\delta$ = 8.09 (dd, *J* = 7.9 Hz, 1.3 Hz, 1H; $CH_{ar}$), 8.02–7.96 (m, 2H; $CH_{ar}$), 7.68–7.34 (m, 5H; $CH_{ar}$), 6.47 (s, 1H; $CH_{tropp}$), 4.19 (ddd, $^3J_{H,H}$ = 10.3 Hz, $^3J_{H,H}$ = 10.3 Hz, $^3J_{H,H}$ = 4.0 Hz, 1H; $OCH$), 2.34–2.24 (m, 2H; $CH_{menthyl}$, $CH_{2menthyl}$), 1.83–0.82 (m, 7H; $CH_{menthyl}$, $CH_{2menthyl}$), 0.98 (d, $^3J_{H,H}$ = 7.0 Hz, 3H; $CH_{3menthyl}$), 0.94 (d, $^3J_{H,H}$ = 6.5 Hz, 3H; $CH_{3menthyl}$), 0.83 (d, $^3J_{H,H}$ = 7.0 Hz, 3H; $CH_{3menthyl}$) ppm; $^{13}$C NMR (62.9 MHz, $CDCl_3$): $\delta$ = 195.0 (C=O), 152.8 (=$CO_{quart}$), 138.8($C_{quart}$), 137.1 ($C_{quart}$), 134.2 ($C_{quart}$), 132.7 ($C_{quart}$), 131.6 ($CH_{ar}$), 131.3 ($CH_{ar}$), 129.5 ($CH_{ar}$), 129.3 ($CH_{ar}$), 129.0 ($CH_{ar}$), 128.7 ($CH_{ar}$), 126.5

($CH_{ar}$), 126.0 ($CH_{ar}$), 107.7 ($CH_{tropp}$), 77.4 ($OCH_{menthyl}$), 48.2 ($CH_{menthyl}$), 39.6 ($CH_{2menthyl}$), 34.5 ($CH_{2menthyl}$), 31.4 ($CH_{menthyl}$), 26.1 ($CH_{menthyl}$), 23.4 ($CH_{2menthyl}$), 22.1 ($CH_{3menthyl}$), 20.9 ($CH_{3menthyl}$), 16.5 ($CH_{3menthyl}$) ppm; IR: $\tilde{\nu}$ = 3064(w), 2955(m), 2923(m), 2869(m), 1707(s), 1648(m), 1620(s), 1594(s), 1558(m), 1447(m), 1386(m), 1369(m), 1301(m), 1251(s), 1200(s), 1130(s), 1085(s), 1040(m), 933(m), 905(m), 826(w), 768(s), 753(s), 700(s); MS (70 eV, *m/z*, %): 361 (65), 360 (74) $[M]^+$, 223 (65), 222 (100), 194 (80), 176 (39), 165 (76), 139 (18), 83 (66), 69 (45), 55 (56).

**(5*R*/*S*)-10-[(1*R*)-Menthyloxy]-5*H*-dibenzo[*a*,*d*]cyclohepten-5-ol ((*R*,*R*)-10 and (*S*,*R*)-10)**: A solution of sodium borohydride (577 mg, 15.25 mmol, 55%) and sodium hydroxide (55 mg, 1.38 mmol, 5%) in water (10 mL) was added to a solution of 10-[(1*R*)-menthyloxy]-5*H*-dibenzo[*a*,*d*]cyclohepten-5-one (**9**) (10.00 g, 27.7 mmol) in MeOH (500 mL). The reaction mixture was stirred for 3 h at room temperature, and was then concentrated under vacuum. The resulting yellow oil was dissolved in $Et_2O$, and this solution was washed with saturated aqueous NaCl. The organic phase was separated, dried over $Na_2SO_4$, and subsequently concentrated to dryness. The resulting yellow oil was purified by medium-pressure chromatography (MPLC) (silica; EE/hexane 1:9), which resulted in a pure, colorless oil containing both diastereoisomers (*R*,*R*)-**10** and (*S*,*R*)-**10** . Yield: 9.42 g (94%); TC (silica, EE/hexane: 1/9): $R_f$ = 0.36; $^1$H NMR (300.1 MHz, $CDCl_3$): $\delta$ = 7.76–7.63 (br m, 3H; $CH_{ar}$), 7.48–7.40 (m, 1H; $CH_{ar}$), 7.35–7.16 (m, 4H; $CH_{ar}$), 6.52 (s, 0.5H; $CH_{tropp}$), 6.42 (s, 0.5H; $CH_{tropp}$), 5.26 (br s, 1H; C*H*P), 4.28 (m, 0.5H; $OCH_{menthy}$), 4.04 (m, 0.5H; $OCH_{menthyl}$), 2.58 (br s, 1H; O*H*), 2.45–2.31 (m, 2H; $CH_{menthyl}$, $CH_{2menthyl}$), 1.84–0.82 (m, 16H; $CH_{menthyl}$, $CH_{2menthyl}$).

The product consists of a 50/50 mixture of both diastereomers. The $^{13}$C resonances are additionally broadened by dynamic exchange between two isomers, which differ in the position of the hydroxy group in a 5-*endo* or 5-*exo* orientation in the central seven-membered ring. A mere listing of the signals without any assignments is given here. $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta$ = 153.8, 153.7, 141.4, 139.4, 131.8, 131.7, 129.4, 127.5, 126.7, 126.4, 126.0, 120.8, 108.0, 103.6, 76.6, 70.6, 48.2, 39.9, 39.6, 34.5, 31.4, 31.4, 26.1, 25.9, 23.4, 23.3, 22.2, 22.2, 21.1, 21.0, 16.5 ppm; IR: $\tilde{\nu}$ = 3419(m), br, 3065(w), 2953(s), 2923(s), 2867(s), 1615(m), 1564(m), 1484(m), 1455(m), 1370(m), 1283(w), 1241(m), 1188(s), 1131(s), 1086(m), 1039(s), 985(m), 970(m), 904(w), 819(w), 767(s), 750(m), 723(s), 650(m) $cm^{-1}$; MS (70 eV, *m/z*, %): 362 (12) $[M]^+$, 224 (96), 207 (30), 195 (51), 179 (100), 178 (73), 165 (48), 152 (15), 83 (35), 69 (16), 55 (41).

**[(5*S*)-10-[(1*R*)-Menthyloxy]-5*H*-dibenzo[*a*,*d*]cyclohepten-5-yl]diphenylphosphane ((*S*,*R*)-13) and [(5*R*)-10-[(1*R*)-menthyloxy]-5*H*-dibenzo[*a*,*d*]-cyclohepten-5-yl]diphenylphosphane ((*R*,*R*)-13)**: A mixture of (*R*,*R*)-**10** and (*S*,*R*)-**10** (3.25 g, 8.97 mmol) was dissolved in toluene (50 mL) and cooled to −15°C. At this temperature, thionyl chloride (1.96 mL, 26.9 mmol, 3 equiv) was added dropwise. The solution was allowed to warm to room temperature and stirred overnight. Subsequently, the excess of thionyl chloride and all solvents were evaporated under vacuum. The residue was dissolved in toluene (10 mL) and subsequently concentrated under vacuum ($P = 10^{-2}$ Torr). This procedure was performed twice. Finally, a mixture of the diastereomeric chlorides (*R*,*R*)-**12** and (*S*,*R*)-**12** was obtained as a sticky yellow oil. This was dissolved in toluene (30 mL), and diphenylphosphane (1.754 g, 9.42 mmol, 1.05 equiv) was added at room temp. The reaction solution was heated for 10 min at 120°C. Subsequently, a saturated aqueous solution of $Na_2CO_3$ (20 mL) was added. The organic layer was separated, and the aqueous phase was extracted twice with toluene (10 mL). The combined organic phases were dried over $Na_2SO_4$, filtered, and concentrated. The raw material was purified by column chromatography (under an argon atmosphere, aluminium oxide N, THF/hexane 1:6, $R_f$ = 0.4). This procedure gave a mixture of the two diastereomers (*R*,*R*)-**13** and (*S*,*R*)-**13** as a colorless oil (3.86 g, 7.27 mmol, 81%).

A borane-dimethylsulfide solution (3.40 mL, 2.0 M in toluene, 6.80 mmol) was added dropwise at −15°C to a mixture of (*R*,*R*)-**13** and (*S*,*R*)-**13** (3.61 g, 6.80 mmol) in toluene (20 mL). The solution was allowed to warm to room temperature and was stirred for one hour. Afterwards the solvent was evaporated under vacuum and both diastereomeric borane-phosphane adducts were separated by FC (silica toluene/hexane 1:1). (*S*,*R*)-**14**: Yield 1520 mg (41%), TC (silica, toluene $R_f$ = 0.71). (*R*,*R*)-**14**: Yield: 940 mg (25%), TC (silica, toluene, $R_f$ = 0.66).

The borane adduct (*S*,*R*)-**14** (1383 mg, 2.54 mmol) was dissolved in morpholine (3 mL), and the solution was stirred for 1 h. The excess of morpholine was then evaporated under vacuum, and the free phosphane was separated from the aminoborane ($BH_3$·morpholine) by filtration over aluminium oxide N (toluene, $R_f > 0.9$). Concentration to dryness and recrystallization of the residue from $CH_3CN$ yielded (*S*,*R*)-**13** (1280 mg, 2.41 mmol, 95%) as colorless crystals. The other diastereomer (*R*,*R*)-**13** was obtained analogously from (*R*,*R*)-**14** (966 mg, 1.77 mmol) in 96% yield (904 mg, 1.70 mmol).

**[(5*S*)-10-[(1*R*)-Menthyloxy]-5*H*-dibenzo[*a*,*d*]cyclohepten-5-yl]diphenylphosphane ((*S*,*R*)-13)**: M.p: 130°C; $^1$H NMR (300.1 MHz, $CDCl_3$): $\delta$ = 7.75 (dd, $J$ = 7.5 Hz, $J$ = 1.7 Hz, 1H; $CH_{ar}$), 7.37–7.09 (m, 14H; $CH_{ar}$), 7.02 (ddd, $J$ = 7.3 Hz, $J$ = 7.3 Hz, $J$ = 1.1 Hz, 1H; $CH_{ar}$), 6.97 (d(br), $J$ = 7.0 Hz, 2H; $CH_{ar}$), 6.47 (s, 1H; $CH_{tropp}$), 4.84 (d, $^2J_{P,H}$ = 5.6 Hz, 1H; C*H*P), 4.28 (ddd, $J$ = 10.4 Hz, $J$ = 10.4 Hz, $J$ = 4.0 Hz, 1H; $OCH_{menthyl}$), 2.73 (d(br), $J$ = 12.3 Hz, 1H; $CH_{2menthyl}$), 2.50 (m, 1H; $CH_{menthyl}$), 1.89–1.79 (m, 2H; $CH_{2menthyl}$), 1.75–1.53 (m, 2H; $CH_{menthyl}$, $CH_{2menthyl}$), 1.33–1.09 (m, 3H; $CH_{menthyl}$, $CH_{2menthyl}$), 1.07 (d, $^3J_{H,H}$ = 6.5 Hz, 3H; $CH_{3menthyl}$), 1.05 (d, $^3J_{H,H}$ = 7.1 Hz, 3H; $CH_{3menthyl}$), 1.00 (d, $^3J_{H,H}$ = 6.9 Hz, 3H; $CH_{3menthyl}$) ppm; $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta$ = 154.3 (d, $J_{C,P}$ = 4.9 Hz, = $CO_{quart}$), 139.3 (d, $J_{C,P}$ = 9.4 Hz; $C_{quart}$), 138.4 (d, $J_{C,P}$ = 7.9 Hz; $C_{quart}$), 137.1 (d, $J_{C,P}$ = 7.6 Hz; $C_{quart}$), 136.8 (d, $J_{C,P}$ = 8.5 Hz; $C_{quart}$), 134.5 (d, $J_{C,P}$ = 4.3 Hz; $C_{quart}$), 133.8 ($CH_{ar}$), 133.7 ($CH_{ar}$), 133.6 ($C_{quart}$), 133.5 ($CH_{ar}$), 133.4 ($CH_{ar}$), 129.7 (d, $J_{C,P}$ = 2.7 Hz; $CH_{ar}$), 129.4 (d, $J_{C,P}$ = 3.3; $CH_{ar}$), 129.1 (d, $J_{C,P}$ = 1.5 Hz; $CH_{ar}$), 129.0 ($CH_{ar}$), 128.3 ($CH_{ar}$), 127.8 (2C; $CH_{ar}$), 127.7 ($CH_{ar}$), 127.7 ($CH_{ar}$), 127.6 ($CH_{ar}$), 127.4 (d, $J_{C,P}$ = 1.4 Hz; $CH_{ar}$), 126.2 ($CH_{ar}$), 126.2 ($CH_{ar}$), 126.1 ($CH_{ar}$), 108.0 (d, $J_{C,P}$ = 5.5 Hz; $CH_{tropp}$), 76.4 ($CHO_{menthyl}$), 56.8 (d, $^1J_{C,P}$ = 20.7 Hz; C*H*P), 48.4 ($CH_{menthyl}$), 40.2 ($CH_{2menthyl}$), 34.7 ($CH_{2menthyl}$), 31.5 ($CH_{menthyl}$), 26.0 ($CH_{menthyl}$), 23.8 ($CH_{2menthyl}$), 22.4 ($CH_{3menthyl}$), 21.0 ($CH_{3menthyl}$), 17.0 ($CH_{3menthyl}$) ppm; $^{31}$P NMR (121.5 MHz, $CDCl_3$): $\delta$ = −14.1 (s) ppm; IR: $\tilde{\nu}$ = 3053(w), 2953(m), 2915(m), 2865(w), 1952(w), 1810(w), 1621(s), 1564(w), 1490(m), 1453(m), 1432(m), 1383(m), 1246(m), 1204(m), 1130(w), 1087(s), 1041(w), 987(w), 915(m), 809(m), 764(m), 741(s), 694(s), 661(m), 642(m), 615(m) $cm^{-1}$; MS (70 V, *m/z*, %): 530 (19) $[M]^+$, 391 (100) $[M-\text{menthyl}]^+$, 345 (6), 207 (74), 183 (14), 178 (28), 108 (6), 83 (25), 69 (15), 55 (46).

**[(5*R*)-10-[(1*R*)-Menthyloxy]-5*H*-dibenzo[*a*,*d*]cyclohepten-5-yl]diphenylphosphane ((*R*,*R*)-13)**: M.p. 147°C; $^1$H NMR (300.1 MHz, $CDCl_3$): $\delta$ = 7.81 (dd, $J$ = 7.6 Hz, $J$ = 1.7 Hz, 1H; $CH_{ar}$), 7.32–7.08 (m, 14H; $CH_{ar}$), 7.02–6.95 (m, 3H; $CH_{ar}$), 6.40 (s, 1H; $CH_{tropp}$), 4.82 (d, $^2J_{P,H}$ = 5.8 Hz, 1H; C*H*P), 4.40 (ddd, $J$ = 10.3 Hz, $J$ = 10.3 Hz, $J$ = 3.8 Hz, 1H; $OCH_{menthyl}$), *2.84 (br d, J* = 12.8 Hz, 1H; $CH_{2menthyl}$), 2.56 (m, 1H; $CH_{menthyl}$), 1.92–1.73 (m, 3H; $CH_{2menthyl}$), 1.72–1.56 (m, 1H; $CH_{menthyl}$), 1.34–1.11 (m, 3H; $CH_{menthyl}$, $CH_{2menthyl}$), 1.10 (d, $^3J_{H,H}$ = 7.0 Hz, 3H; $CH_{3menthyl}$), 1.04 (d, $^3J_{H,H}$ = 6.6 Hz, 3H; $CH_{3menthyl}$), 0.99 (d, $^3J_{H,H}$ = 7.0 Hz, 3H; $CH_{3menthyl}$) ppm; $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta$ = 154.6 (d, $J_{C,P}$ = 5.2 Hz, =$CO_{quart}$), 139.6 (d, $J_{C,P}$ = 9.4 Hz; $C_{quart}$), 138.5 (d, $J_{C,P}$ = 8.2 Hz; $C_{quart}$), 138.2 (d, $J_{C,P}$ = 8.2 Hz; $C_{quart}$), 137.1 (d, $J_{C,P}$ = 8.5 Hz; $C_{quart}$), 134.4 (d, $J_{C,P}$ = 4.6 Hz; $C_{quart}$), 134.0 (d, $J_{C,P}$ = 4.9 Hz; $C_{quart}$), 133.8 ($CH_{ar}$), 133.7 ($CH_{ar}$), 133.5 ($CH_{ar}$), 133.5 ($CH_{ar}$), 129.5 (d, $J_{C,P}$ = 2.7 Hz; $CH_{ar}$), 129.2 (d, $J_{C,P}$ = 3.3, $CH_{ar}$), 129.1 ($CH_{ar}$), 128.8 (d, $J_{C,P}$ = 1.5 Hz; $CH_{ar}$), 128.2 ($CH_{ar}$), 128.2 ($CH_{ar}$), 127.8 ($CH_{ar}$), 127.8 ($CH_{ar}$), 127.7 ($CH_{ar}$), 127.6 ($CH_{ar}$), 127.0 (d, $J_{C,P}$ = 1.4 Hz; $CH_{ar}$), 126.2 ($CH_{ar}$), 126.1 ($CH_{ar}$), 125.9 ($CH_{ar}$), 105.5 (d, $J_{C,P}$ = 5.5 Hz; $CH_{tropp}$), 76.3 ($CHO_{menthyl}$), 56.9 (d, $J_{C,P}$ = 20.7 Hz; C*H*P), 48.1 ($CH_{menthyl}$), 39.9 ($CH_{2menthyl}$), 34.7 ($CH_{2menthyl}$), 31.6 ($CH_{menthyl}$), 26.2 ($CH_{menthyl}$), 23.3 ($CH_{2menthyl}$), 22.3 ($CH_{3menthyl}$), 21.1 ($CH_{3menthyl}$), 16.2 ($CH_{3menthyl}$) ppm; $^{31}$P NMR (121.5 MHz, $CDCl_3$): $\delta$ = −12.8 (s) ppm; IR: $\tilde{\nu}$ = 3058(w), 3016(w), 2956(m), 2920(m), 2867(w), 1965(w), 1618(s), 1566(m), 1490(m), 1450(w), 1435(m), 1386(m), 1245(s), 1208(s), 1160(w), 1132(m), 1089(s), 1043(m), 914(m), 811(m), 772(m), 745(s), 717(m), 696(s), 661(m), 641(m), 615(w) $cm^{-1}$.

**[(5*S*)-10-[(1*R*)-Menthyloxy]-5*H*-dibenzo[*a*,*d*]cyclohepten-5-yl]diphenylphosphane·$BH_3$ ((*S*,*R*)-14)**: $^1$H NMR (300.1 MHz, $CDCl_3$): $\delta$ = 7.74–7.68 (m, 1H; $CH_{ar}$), 7.58–7.06 (m, 17H; $CH_{ar}$), 5.71 (s, 1H; $CH_{tropp}$), 5.14 (d, $^2J_{P,H}$ = 14.6 Hz, 1H; C*H*P), 4.05 (ddd, $J$ = 10.3 Hz, $J$ = 10.3 Hz, $J$ = 3.9 Hz, 1H; $OCH_{menthyl}$), 2.47–2.31 (m, 2H; $CH_{menthyl}$), 1.80–1.71 (m, 2H; $CH_{2menthyl}$), 1.64–1.52 (m, 1H; $CH_{2menthyl}$), 1.51–1.36 (m, 1H; $CH_{menthyl}$), 1.28–0.96 (m, 3H; $CH_{2menthyl}$), 1.00 (d, $^3J_{H,H}$ = 7.0 Hz, 3H; $CH_{3menthyl}$), 0.94 (d, $^3J_{H,H}$ = 6.9 Hz, 3H; $CH_{3menthyl}$), 0.93 (d, $^3J_{H,H}$ = 6.6 Hz, 3H; $CH_{3menthyl}$), 1.4–0.2 (br, 3H; $BH_3$) ppm; $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta$

= 152.8 (=$CO_{quart}$), 135.6 (d, $J_{C,P}$ = 3.9 Hz; $C_{quart}$), 135.1 ($C_{quart}$), 134.8 (d, $J_{C,P}$ = 3.0 Hz; $C_{quart}$), 133.7 ($C_{ar}$), 133.6 ($CH_{ar}$), 132.8 ($CH_{ar}$), 132.7 ($C_{quart}$), 132.5 (d, $J_{C,P}$ = 2.1 Hz; $C_{quart}$), 131.0 ($C_{quart}$), 130.6 (d, $J_{C,P}$ = 2.5 Hz; $CH_{ar}$), 130.4 (d, $J_{C,P}$ = 2.4, $CH_{ar}$), 130.2 (d, $J_{C,P}$ = 6.4, $CH_{ar}$), 129.9 (d, $J_{C,P}$ = 5.2 Hz; $CH_{ar}$), 129.7 ($C_{quart}$), 129.5 ($CH_{ar}$), 129.3 (d, $J_{C,P}$ = 1.8 Hz; $CH_{ar}$), 129.0 ($CH_{ar}$), 128.2 ($CH_{ar}$), 128.0 ($CH_{ar}$), 127.9 ($CH_{ar}$), 127.7 ($CH_{ar}$), 127.6 (d, $J_{C,P}$ = 2.0 Hz; $CH_{ar}$), 127.3 ($CH_{ar}$), 127.2 ($CH_{ar}$), 126.6 ($CH_{ar}$), 108.3 ($CH_{tropp}$), 75.9 ($CHO_{menthyl}$), 56.4 (d, $^1J_{C,P}$ = 25.0 Hz; $CH_{benzyl}$), 48.1 ($CH_{menthyl}$), 38.8 ($CH_{2menthyl}$), 34.6 ($CH_{2menthyl}$), 31.4 ($CH_{menthyl}$), 25.2 ($CH_{menthyl}$), 23.2 ($CH_{2menthyl}$), 22.3 ($CH_{3menthyl}$), 21.3 ($CH_{3menthyl}$), 16.6 ($CH_{3menthyl}$) ppm; $^{31}$P NMR (101.3 MHz, $CDCl_3$): $\delta$ = 25.9 (br) ppm; $^{11}$B NMR (96.3 MHz, $CDCl_3$): $\delta$ = −36.5 (br) ppm; IR: $\tilde{\nu}$ = 3056(w), 2952(m), 2923(m), 2867(m), 2367 m P-$BH_3$, 2343 m P-$BH_3$, 1960(w), 1623(s), 1567(w), 1494(m), 1436(m), 1384(w), 1246(m), 1207(m), 1133(m), 1100(m), 1085(m), 1056(s), 984(w), 971(w), 917(w), 821(w), 746(m), 732(s), 694(s), 608(m) $cm^{-1}$.

**[(5*R*)-10-[(1*R*)-Menthyloxy]-5*H*-dibenzo[*a*,*d*]cyclohepten-5-yl]diphenylphosphane·$BH_3$ ((*R*,*R*)-14)**: $^1$H NMR (300.1 MHz, $CDCl_3$): $\delta$ = 7.84–7.80 (m, 1H; $CH_{ar}$), 7.53–7.06 (m, 17H; $CH_{ar}$), 5.73 (s, 1H; $CH_{tropp}$), 5.12 (d, $^2J_{P,H}$ = 14.7 Hz, 1H; C*H*P), 4.02 (m, 1H; O$CH_{menthyl}$), 2.45–2.29 (m, 1H; $CH_{menthyl}$), 2.16 (brd, $J$ = 12.6 Hz, 1H; $CH_{menthyl}$] 1.80–1.60 (m, 3H; $CH_{2menthyl}$), 1.56–1.41 (m, 1H; $CH_{menthyl}$), 1.19–0.89 (m, 3H; $CH_{2menthyl}$), 1.03 (d, $^3J_{H,H}$ = 6.5 Hz, 3H; $CH_{3menthyl}$), 0.99 (d, $^3J_{H,H}$ = 7.0 Hz, 3H; $CH_{3menthyl}$), 0.76 (d, $^3J_{H,H}$ = 6.9 Hz, 3H; $CH_{3menthyl}$), 1.3–0.2 (br, 3H; $BH_3$) ppm; $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta$ = 154.2 (=$CO_{quart}$), 135.8 (d, $J_{C,P}$ = 4.0 Hz; $C_{quart}$), 135.4 ($C_{quart}$), 134.4 (d, $J_{C,P}$ = 3.3 Hz; $C_{quart}$), 133.6 ($C_{quart}$), 133.4 ($CH_{ar}$), 132.9 ($CH_{ar}$), 132.8 (d, $J_{C,P}$ = 2.4 Hz; $C_{quart}$), 132.7 ($CH_{ar}$), 130.9 ($CH_{quart}$), 130.7 (d, $J_{C,P}$ = 2.5 Hz; $CH_{ar}$), 130.5 (d, $J_{C,P}$ = 2.3, $CH_{ar}$), 130.3 (d, $J_{C,P}$ = 6.1, $CH_{ar}$), 130.3 ($CH_{ar}$), 129.9 (d, $J_{C,P}$ = 5.2 Hz; $CH_{ar}$), 129.6 ($CH_{ar}$), 129.1 (d, $J_{C,P}$ = 2.1 Hz; $CH_{ar}$), 128.3 ($CH_{ar}$), 128.2 ($CH_{ar}$), 128.0 ($CH_{ar}$), 127.8 ($CH_{ar}$), 127.4 (d, $J_{C,P}$ = 2.3 Hz; $CH_{ar}$), 127.3 (d, $J_{C,P}$ = 2.4 Hz; $CH_{ar}$), 127.2 (d, $J_{C,P}$ = 2.4 Hz; $CH_{ar}$), 126.3 ($CH_{ar}$), 104.7 ($CH_{tropp}$), 76.5 ($CHO_{menthyl}$), 56.9 (d, $^1J_{C,P}$ = 25.0 Hz; C*H*P), 48.2 ($CH_{menthyl}$), 40.4 ($CH_{2menthyl}$), 34.4 ($CH_{2menthyl}$), 31.6 ($CH_{menthyl}$), 25.9 ($CH_{menthyl}$), 23.0 ($CH_{2menthyl}$), 22.3 ($CH_{3menthyl}$), 21.2 ($CH_{3menthyl}$), 15.9 ($CH_{3menthyl}$) ppm; $^{31}$P NMR (121.5 MHz, $CDCl_3$): $\delta$ = 25.6 (br) ppm; $^{11}$B NMR (96.3 MHz, $CDCl_3$): $\delta$ = −33.7 (br) ppm; IR: $\tilde{\nu}$ = 3058(w), 2954(m), 2925(m), 2868(m), 2388 m P-$BH_3$, 1981(w), 1621(m), 1568(w), 1494(w), 1436(m), 1385(w), 1248(m), 1209(m), 1135(m), 1086(s), 1056(s), 970(w), 917(w), 820(w), 746(m), 732(s), 694(s), 608(m) $cm^{-1}$; MS (70 eV, $m/z$, %): 544 (53) $[M]^+$, 530 (17) $[M-BH_3]^+$, 391 (100) $[M-\text{menthyl}-BH_3]^+$, 345 (10), 207 (40), 192 (5), 178 (12), 108 (6), 83 (10), 69 (12), 55 (22).

**[Ir(cod)$^{(5S)\text{-}10\text{-}(1R)\text{-}\text{menthyloxy}}$tropp$^{ph}$]$CF_3SO_3$ ((*S*,*R*)-15)**: Compound (*S*,*R*)-**13** (106 mg, 0.20 mmol) and [Ir(cod)$_2$]$CF_3SO_3$ **2** (111 mg, 0.20 mmol) were dissolved in $CH_2Cl_2$ (3 mL). The resulting red–violet solution was layered with *n*-hexane (5 mL), whereupon the complex (*S*,*R*)-**15** precipitated as a red microcrystalline powder. Yield: 180 mg (92%). M.p.: 188°C (decomp); $^1$H NMR (300.1 MHz, $CDCl_3$): $\delta$ = 8.34 (dd, $J$ = 7.8 Hz, $J$ = 1.7 Hz, 1H; $CH_{ar}$), 7.61–7.15 (m, 13H; $CH_{ar}$), 7.02 (dd, $J$ = 7.7 Hz, $J$ = 7.7 Hz, 1H; $CH_{ar}$), 6.89 (d, $J$ = 7.6 Hz, 1H; $CH_{ar}$), 6.78 (d, $J$ = 2.1 Hz, 1H; $CH_{tropp}$), 6.69 (d, $J$ = 7.2 Hz, 1H; $CH_{ar}$), 6.66 (dd, $J$ = 8.6 Hz, $J$ = 1.2 Hz, 1H; $CH_{ar}$), 6.35 (brm, 1H; $CH_{cod}$), 5.84 (d, $^2J_{P,H}$ = 14.3 Hz, 1H; C*H*P), 5.24 (brm, 1H; $CH_{cod}$), 4.92 (ddd, $J$ = 10.3 Hz, $J$ = 10.3 Hz, $J$ = 4.0 Hz, 1H; O$CH_{menthyl}$), 3.77 (brm, 1H; $CH_{cod}$), 3.40 (brm, 1H; $CH_{cod}$), 2.52–2.38 (m, 2H; 1×$CH_{menthyl}$ and 1×$CH_{2cod}$), 2.24–1.47 (m, 12H; 7×$CH_{2cod}$ and 2×$CH_{menthyl}$ and 3×$CH_{2menthyl}$), 1.37–1.24 (m, 1H; $CH_{2menthyl}$), 1.13 (d, $^3J_{H,H}$ = 6.9 Hz, 3H; $CH_{3menthyl}$), 1.02 (d, $^3J_{H,H}$ = 6.8 Hz, 3H; $CH_{3menthyl}$), 0.89–0.71 (m, 2H; $CH_{2menthyl}$), 0.66 (d, $^3J_{H,H}$ = 6.3 Hz, 3H; $CH_{3menthyl}$) ppm; $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta$ = 146.4 (=$CO_{quart}$), 136.6 ($C_{quart}$), 134.3 ($CH_{ar}$), 134.2 ($CH_{ar}$), 134.0 (d, $J_{P,C}$ = 2.1 Hz; $C_{quart}$), 133.2 ($CH_{ar}$), 133.0 ($CH_{ar}$), 132.1 ($CH_{ar}$), 131.9 (d, $J_{P,C}$ = 5.8 Hz; $CH_{ar}$), 131.8 (d, $J_{P,C}$ = 8.5 Hz; $CH_{ar}$), 131.7 ($CH_{ar}$), 131.7 ($C_{quart}$), 130.7 (d, $J_{P,C}$ = 2.7 Hz; $C_{quart}$), 129.3 ($CH_{ar}$), 129.3 ($CH_{ar}$), 129.3 ($CH_{ar}$), 129.2 ($CH_{ar}$), 129.1 ($CH_{ar}$), 129.1 ($CH_{ar}$), 129.0 ($CH_{ar}$), 128.9 (d, $J_{P,C}$ = 2.1 Hz; $CH_{ar}$), 128.7 ($CH_{ar}$), 128.5 ($CH_{ar}$), 128.2 (d, $J_{P,C}$ = 55.7 Hz; $C_{ipsoPh}$), 125.9 (d, $J_{P,C}$= 48.4 Hz; $C_{ipsoPh}$), 106.6 (d, $J_{P,C}$ = 10.4 Hz; $CH_{cod}$), 98.7 (d, $J_{P,C}$ = 11.9 Hz; $CH_{cod}$), 86.3 (O$CH_{menthyl}$), 80.4 ($CH_{tropp}$), 76.8 ($CH_{cod}$), 65.6 ($CH_{cod}$), 57.0 (d, $^1J_{P,C}$ = 24.7 Hz; $CH_{benzyl}$), 49.6 ($CH_{menthyl}$), 39.5 ($CH_{2menthyl}$), 35.4 (d, $J_{P,C}$ = 3.4 Hz; $CH_{2cod}$), 34.1 ($CH_{2menthyl}$), 32.9 ($CH_{2cod}$), 31.1 ($CH_{menthyl}$), 29.9 (d, $J_{P,C}$ = 3.1 Hz; $CH_{2cod}$), 27.4 ($CH_{2cod}$), 25.6 ($CH_{menthyl}$), 23.0 ($CH_{2mentyl}$), 22.1 ($CH_{3menthyl}$), 22.0 ($CH_{3menthyl}$), 16.6 ($CH_{3menthyl}$) ppm; $^{19}$F NMR (282.4 MHz, $CDCl_3$): $\delta$ = −78.4 ppm; $^{31}$P NMR (121.5 MHz, $CDCl_3$): $\delta$ = 69.1 ppm; IR: $\tilde{\nu}$ = 3053(w), 2928(m), 2870(m), 2031(w), 1991(w), 1595(w), 1483(m), 1451(w), 1436(m), 1368(w), 1259(s), 1222(m), 1146(s), 1098(m), 1029(s), 940(w), 900(w), 746(m), 694(m), 668(w), 652(w), 635(s) $cm^{-1}$; UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ = 497 nm.

**[Ir(cod)$^{(5R)\text{-}10\text{-}(1R)\text{-}\text{menthyloxy}}$tropp$^{ph}$]$CF_3SO_3$ ((*R*,*R*)-15)**: Compound (*R*,*R*)-**13** (106 mg, 0.20 mmol) and [Ir(cod)$_2$]$CF_3SO_3$ **2** (111 mg, 0.20 mmol) were dissolved in $CH_2Cl_2$ (3 mL) to give a red–violet solution. This was layered with *n*-hexane (5 mL), whereupon the complex (*R*,*R*)-**15** was obtained as a red microcrystalline powder. Yield: 176 mg (90%). M.p.: >195°C (decomp); $^1$H NMR (300.1 MHz, $CDCl_3$): $\delta$ = 8.00 (dd, $J$ = 8.1 Hz, $J$ = 1.3 Hz, 1H; $CH_{ar}$), 7.49–7.11 (m, 15H; $CH_{ar}$), 7.00 (d, $J$ = 7.6 Hz, 1H; $CH_{ar}$), 6.97 (dd, $J$ = 9.0 Hz, $J$ = 1.4 Hz, 1H; $CH_{ar}$), 6.78 (d, $J$ = 2.4 Hz, 1H; $CH_{tropp}$), 6.02 (brm, 1H; $CH_{cod}$), 5.90 (d, $^2J_{P,H}$ = 13.8 Hz, 1H; C*H*P), 5.41 (brm, 1H; $CH_{cod}$), 4.91 (ddd, $J$ = 10.2 Hz, $J$ = 10.2 Hz, $J$ = 4.2 Hz, 1H; O$CH_{menthyl}$), 3.86 (brm, 1H; $CH_{cod}$), 3.05 (brm, 1H; $CH_{cod}$), 2.52–1.11 (m, 16H; 8$CH_{2cod}$ and 3$CH_{menthyl}$ and 5$CH_{2menthyl}$), 1.05–0.99 (m, 1H; $CH_{2menthyl}$), 1.01 (d, $^3J_{H,H}$ = 6.3 Hz, 3H; $CH_{3menthyl}$), 0.85 (d, $^3J_{H,H}$ = 7.0 Hz, 3H; $CH_{3menthyl}$), 0.79 (d, $^3J_{H,H}$ = 6.9 Hz, 3H; $CH_{3menthyl}$) ppm; $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta$ = 152.7 (d, $J_{P,C}$ = 4.6 Hz; =$CO_{quart}$), 135.9 (d, $J_{P,C}$ = 1.2 Hz; $C_{quart}$), 134.5 ($CH_{ar}$), 134.4 ($CH_{ar}$), 133.4 (d, $J_{P,C}$ = 5.8 Hz; $C_{quart}$), 132.9 ($CH_{ar}$), 132.7 ($CH_{ar}$), 132.5 ($CH_{ar}$), 132.3 (d, $J_{P,C}$ = 3.7 Hz; $C_{quart}$), 131.8 (d, $J_{P,C}$ = 2.4 Hz; $CH_{ar}$), 131.6 (d, $J_{P,C}$ = 2.4 Hz; $CH_{ar}$), 131.3 (d, $J_{P,C}$ = 5.8 Hz; $CH_{ar}$), 130.5 (d, $J_{P,C}$ = 7.6 Hz; $C_{quart}$), 129.5 (d, $J_{P,C}$ = 7.0 Hz; $CH_{ar}$), 129.3 (d, $J_{P,C}$ = 1.8 Hz; $CH_{ar}$), 129.1 ($CH_{ar}$), 129.1 ($CH_{ar}$), 129.0 ($CH_{ar}$), 129.0 ($CH_{ar}$), 128.7 ($CH_{ar}$), 128.7 ($CH_{ar}$), 128.4 (d, $J_{P,C}$ = 2.1 Hz; $CH_{ar}$), 128.4 (d, $J_{P,C}$ = 2.1 Hz; $CH_{ar}$), 128.1 (d, $J_{P,C}$ = 6.7 Hz; $C_{ipsoPh}$), 126.8 (d, $J_{P,C}$ = 51.7 Hz; $C_{ipsoPh}$), 105.7 (d, $J_{P,C}$ = 10.0 Hz; $CH_{cod}$), 97.7 (d, $J_{P,C}$ = 12.5 Hz; $CH_{cod}$), 83.8 (O$CH_{menthyl}$), 74.7 ($CH_{tropp}$), 69.4 ($CH_{cod}$), 67.9 ($CH_{cod}$), 56.8 (d, $^1J_{P,C}$ = 25.3 Hz; C*H*P), 49.9 ($CH_{menthyl}$), 40.9 ($CH_{2menthyl}$), 35.7 (d, $J_{P,C}$ = 3.0 Hz; $CH_{2cod}$), 33.8 ($CH_{2menthyl}$), 32.9 ($CH_{2cod}$), 31.2 ($CH_{menthyl}$), 29.7 (d, $J_{P,C}$ = 3.4 Hz; $CH_{2cod}$), 27.6 ($CH_{2cod}$), 25.7 ($CH_{menthyl}$), 22.7 ($CH_{2menthyl}$), 22.3 ($CH_{3menthyl}$), 21.1 ($CH_{3menthyl}$), 16.5 ($CH_{3menthyl}$) ppm; $^{19}$F NMR (282.4 MHz, $CDCl_3$): $\delta$ = −78.4 ppm; $^{31}$P NMR (121.5 MHz, $CDCl_3$): $\delta$ = 64.8 ppm; IR: $\tilde{\nu}$ = 3063(w), 2933(m), 2871(m), 1982(w), 1594(w), 1485(m), 1438(m), 1261(s), 1222(w), 1147(m), 1099(w), 1031(s), 642(w), 904(m), 841(w), 765(w), 730(m), 697(m), 635(s) $cm^{-1}$; UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ = 497 nm, 453 nm.

**[Rh(cod)$^{(5S)\text{-}10\text{-}(1R)\text{-}\text{menthyloxy}}$tropp$^{ph}$]$CF_3SO_3$ ((*S*,*R*)-17)**: Compound (*S*,*R*)-**13** (106 mg, 0.20 mmol) and [Rh(cod)$_2$]$CF_3SO_3$ **16** (94 mg, 0.20 mmol) were dissolved in $CH_2Cl_2$ (3 mL). The deep red solution was stirred for 1 h at room temperature and was then concentrated under vacuum (P = $10^{-2}$ Torr). The residue was suspended in *n*-hexane (5 mL) with stirring until an orange powder was obtained; this was filtered and dried in vacuum. Yield 145 mg (82%). Crystals suitable for a X-ray analysis were obtained by slow diffusion of hexane into a concentrated solution of (*S*,*R*)-**17** in $CH_2Cl_2$. M.p.: 135°C (decomp); $^1$H NMR (300.1 MHz, $CDCl_3$): $\delta$ = 8.17 (dd, $J$ = 7.3 Hz, $J$ = 2.2 Hz, 1H; $CH_{ar}$), 7.72 (dd, $J$ = 7.9 Hz, $J$ = 1.0 Hz, 1H; $CH_{ar}$), 7.50–7.13 (m, 13H; $CH_{ar}$), 7.02–6.92 (m, 3H; $CH_{ar}$), 6.66 (d, $J$ = 2.7 Hz, 1H; $CH_{tropp}$), 6.38 (brm, 1H; $CH_{cod}$), 5.64 (brm, 1H; $CH_{cod}$), 5.35 (d, $J$ = 14.8 Hz, 1H; C*H*P), 4.82 (ddd, $J$ = 10.5 Hz, $J$ = 10.5 Hz, $J$ = 4.0 Hz, 1H; O$CH_{menthyl}$), 3.96 (brm, 1H; $CH_{cod}$), 3.45 (brm, 1H; $CH_{cod}$), 2.68–1.24 (m, 15H; 8×$CH_{2cod}$, 3×$CH_{menthyl}$, 4×$CH_{2menthyl}$), 1.17 (d, $J$ = 6.9 Hz, 3H; $CH_{3menthyl}$), 1.04 (d, $J$ = 6.9 Hz, 3H; $CH_{3menthyl}$), 0.95–0.78 (m, 2H; $CH_{2menthyl}$), 0.74 (d, $J$ = 6.4 Hz, 3H; $CH_{3menthyl}$) ppm; $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta$ = 155.5 (dd, $J$ = 3.4 Hz, $J$ = 1.8 Hz; $C_{quart}$), 135.2 (dd, $J$ = 3.1 Hz, $J$ = 0.9 Hz; $C_{quart}$), 134.9 (dd, $J$ = 5.6 Hz, $J$ = 1.3 Hz; $C_{quart}$), 133.7 ($CH_{ar}$), 133.6 ($CH_{ar}$), 133.4 ($CH_{ar}$), 133.2 ($CH_{ar}$), 132.5 ($CH_{ar}$), 131.8 (d, $J$ = 2.4 Hz; $CH_{ar}$), 131.7 (d, $J$ = 2.6 Hz; $CH_{ar}$), 131.6 (dd, $J$ = 4.7 Hz, $J$ = 1.0 Hz; $C_{quart}$), 131.4 (d, $J$ = 8.1 Hz; $C_{quart}$), 131.3 (d, $J$ = 5.3 Hz; $CH_{ar}$), 129.9 (dd, $J$ = 45.1 Hz, $J$ = 1.1 Hz; $C_{ipsoPh}$), 129.4–129.2 (7C; $CH_{ar}$), 128.9 ($CH_{ar}$), 128.8 ($CH_{ar}$), 128.7 (d, $J$ = 1.5 Hz; $CH_{ar}$), 127.6 (dd, $J$ = 41.3 Hz, $J$ = 1.8 Hz; $C_{ipsoPh}$), 114.4 (dd, $J$ = 9.3 Hz, $J$ = 5.5 Hz; $CH_{cod}$), 108.7 (dd, $J$ = 9.5 Hz, $J$ = 6.1 Hz; $CH_{cod}$), 86.2 (d, $J$ = 12.5 Hz; $CH_{cod}$), 85.4 (O$CH_{menthyl}$), 84.1 (dd, $J$ = 4.9 Hz, $J$ = 2.3 Hz; $CH_{tropp}$), 80.6 (d, $J$ = 11.9 Hz; $CH_{cod}$), 57.6 (d, $J$ = 18.6 Hz; C*H*P), 49.7 ($CH_{menthyl}$), 39.1 ($CH_{2menthyl}$), 34.3 ($CH_{2cod}$), 34.3 ($CH_{2menthyl}$), 31.2 ($CH_{2cod}$), 31.1 ($CH_{2cod}$), 29.8 ($CH_{menthyl}$), 27.2 ($CH_{2cod}$), 25.9 ($CH_{menthyl}$), 23.4 ($CH_{2menthyl}$), 22.3 ($CH_{3menthyl}$), 22.2

($CH_{3menthyl}$), 17.0 ($CH_{3menthyl}$) ppm; $^{19}$F NMR (282.4 MHz, $CDCl_3$): $\delta$ = −78.4 ppm; $^{31}$P NMR (121.5 MHz, $CDCl_3$): $\delta$ = 85.9 (d, $J_{Rh,P}$ = 163 Hz) ppm; IR: $\tilde{\nu}$ = 2925 (m), 1486 (w), 1435 (m), 1259 (vs), 1147 (s), 1029 (s), 745 (m), 693 (m) $cm^{-1}$; UV/Vis($CHCl_3$): $\lambda_{max}$ = 469 nm.

**Catalyses**: The catalytic experiments were performed in a 60 mL high-pressure steel-vessel (Medimex). For the pressure control, a pressflow control unit (bpc 6002, Büchi) was used. The products in the catalytic experiments were analyzed with a HP 6890 gas chromatograph equipped with a flame-ionization detector (Hewlett–Packard). For the separation of the product mixtures, $H_2$ was used as carrier gas and the following columns were employed: HP-5 crosslinked 5% PH ME SILOXANE (30 m × 320 μm × 0.25 μm). Lipodex E (25 m × 0.25 mm ID) Machery & Nagel.

**Phenyl(1-phenylethyl)amine 7 from phenyl(1-phenylethyliden)amine 5**: The conversion rate was determined on the HP-5 (150 °C isotherm; flow rate: 1.9 mL $H_2$ $min^{-1}$). Retention times: 9.2 min.: phenyl(1-phenylethyl)-amine (**7**); 10.5 min.: phenyl(1-phenylethyliden)amine (**5**). The enantiomeric excess (*ee*) was determined on Lipodex E (110 °C for 1 min., then heating to 150 °C with a rate of 0.6 °C $min^{-1}$; flow rate: 0.9 mL $H_2$ $min^{-1}$.). Retention times: 65.7 min.: (*S*)-**7**; 66.4 min.: (*R*)-**7**.

***N*-(1-Phenylethyl)acetamide (19) from *N*-(1-phenylvinyl)acetamide (18)**: The conversion rate was determined on the HP-5 (150 °C isotherm; flow rate: 1.9 mL $H_2$ $min^{-1}$). Retention times: 3.6 min: *N*-acetyl-1-phenylethyl-amine; 4.5 min: *N*-acetyl-1-phenylethenamine. The enantiomeric excess (*ee*) was determined on Lipodex E (140 °C for 1 min, then heating to 150 °C with a rate of 0.6 °C $min^{-1}$; flow rate: 0.7 mL $H_2$ $min^{-1}$). Retention times: 16.4 min: (*R*)-**19**; 16.9 min: (*S*)-**19**.

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[1] M. T. Benson, T. R. Cundari, *Inorg. Chim. Acta* **1997**, *259*, 91.

[2] This concept has been patented with 5-phosphanyl-[*a*,*d*]dibenzocycloheptenes as ligands: H. Grützmacher, S. Deblon, P. Maire, H. Schönberg, **2002**, DE 101 59 015.6.

[3] For a very recent application of $C_2$-symmetric norbornadiene as ligand to rhodium in catalyzed asymmetric 1,4-additions see: T. Hayashi, K. Ueyama, N. Tokunaga, K. Yoshida, *J. Am. Chem. Soc.* **2003**, *125*, 11508.

[4] For a very recent report on the use of a chiral olefin as ligand in $Ir^I$ complexes for the kinetic resolution of allyl carbonates, see: C. Fischer, C. Defieber, T. Suzuki, E. M. Carreira, *J. Am. Chem. Soc.* **2004**, *126*, 1628.

[5] Olefin hydride complexes are indeed quite stable when the olefin is incorporated within a chelating ligand framework; see for examples: a) C. Böhler, N. Avarvari, H. Schönberg, M. Wörle, H. Rüegger, H. Grützmacher, *Helv. Chim. Acta* **2001**, *84*, 3127; b) S. Hua Liu, X. Huang, Z. Lin, C. Po Lau, G. Jia, *Eur. J. Inorg. Chem.* **2002**, 1697.

[6] For recent examples of enantiomerically pure tripods see: a) G. Brinkmann, R.-M. Pfeifer, C. Rummey, K. Hartner, M. Breuning, *J. Org. Chem.* **2003**, *68*, 6859; b) I. Hegelmann, N. Burzlaff, *Eur. J. Inorg. Chem.* **2003**, 409; c) L. Gade, *Acc. Chem. Res.* **2002**, *35*, 575.

[7] a) J. Thomaier, S. Boulmaâz, H. Schönberg, H. Rüegger, A. Currao, H. Grützmacher, H. Hillebrecht, H. Pritzkow, *New J. Chem.* **1998**, *22*, 947; b) S. Deblon, L. Liesum, *J.* Harmer, H. Schönberg, A. Schweiger, H. Grützmacher, *Chem. Eur. J.* **2002**, *8*, 601.

[8] For selected recent publications see: a) C. J. Cobley, J. P. Henschke, *Adv. Synth. Catal.* **2003**, *345*, 195; b) E. Guiu, B. Muñoz, S. Castillón, C. Claver, *Adv. Synth. Catal.* **2003**, *345*, 169; c) X.-b. Jiang, A. J. Minnaard, B. Hessen, B. L. Feringa, A. L. L. Duchateau, J. G. O. Andrien, J. A. F. Boogers, J. G. de Vries, *Org. Lett.* **2003**, *5*, 1503; d) F. Menges, A. Pfaltz, *Adv. Synth. Catal.* **2002**, *344*, 40; e) H.-U. Blaser, B. Pugin, F. Spindler, A. Togni, *C. R. Chim.* **2002**, *5*, 379; f) D. Xiao, X. Zhang, *Angew. Chem.* **2001**, *113*, 3533; *Angew. Chem. Int. Ed.* **2001**, *40*, 3425; g) T. Ohkuma, M. Kitamura, R. Noyori, in *Catalytic Asymmetric Synthesis (2nd Edition)*, Wiley-VCH, New York, **2000**, 1; h) S. Kainz, A. Brinkmann, W. Leitner, A. Pfaltz, *J. Am. Chem. Soc.* **1999**, *121*, 6421; i) H.-U. Blaser, B. Pugin, F. Spindler, in *Comprehensive Asymmetric Catalysis I–III*, *Vol. 1*, (Eds.: E. N. Jacobsen, A. Pfaltz, H. Yamamoto), Springer, Berlin, **1999**, 247; j) Hydrogenation of enamides: M. J. Burk, Y. M. Wang, J. R. Lee, *J. Am. Chem. Soc.* **1996**, *118*, 5142.

[9] Data collection was on Bruker SMART (CCD) ((*R*,*R*)-**13**, (*S*,*R*)-**13**, (*S*,*R*)-**17**) and STOE IPDS I [(*R*,*R*)-**15**] diffractometers. The structures were solved by Patterson ((*R*,*R*)-**15**) or direct methods ((*R*,*R*)-**13**, (*S*,*R*)-**13**, (*S*,*R*)-**17**), all atoms except hydrogen being refined anisotropically (SHELXTL). In the cases of (*R*,*R*)-**13**, (*S*,*R*)-**13**, and (*S*,*R*)-**17** the data were corrected for absorption by use of the program SADABS. (*R*,*R*)-**13**: $C_{37}H_{39}OP$; crystal size 1.00 × 0.36 × 0.14 mm; orthorhombic, space group $P2_12_12_1$, $a$ = 9.155(2), $b$ = 9.382(2), $c$ = 36.290(9) Å, $V$ = 3117(1) $Å^3$, $Z$ = 4, $\mu$ = 0.12 $mm^{-1}$; $\lambda(Mo_{K\alpha})$ = 0.71073 Å, $T$ = 233 K, $2\theta_{max}/2\theta_{min}$ = 53.08°/2.24°, collected (independent) reflections = 18148 (6387), $R_{int}$ = 0.0758; 332 refined parameters, $R_1$ = 0.0532 for 3345 reflections with $I > 2\sigma$, $wR_2$ = 0.1384 for all data, GooF on $F^2$ = 0.924, Flack x parameter = 0.1(1), max./min. residual electron density = 0.28/−0.22 e $Å^{-3}$. (*S*,*R*)-**13**: $C_{37}H_{39}OP$; crystal size 0.48 × 0.44 × 0.40 mm; monoclinic, space group $P2_1$, $a$ = 9.63(1), $b$ = 29.57(3), $c$ = 10.69(1) Å, $\beta$ = 98.95(2)°, $V$ = 3005(6) $Å^3$, $Z$ = 4, $\mu$ = 0.12 $mm^{-1}$; $\lambda(Mo_{K\alpha})$ = 0.71073 Å, $T$ = 293 K, $2\theta_{max}/2\theta_{min}$ = 52.74°/2.76°, collected (independent) reflections = 19295 (11987), $R_{int}$ = 0.0545; 703 refined parameters, $R_1$ = 0.0424 for 7133 reflections with $I > 2\sigma$, $wR_2$ = 0.0937 for all data, GooF on $F^2$ = 0.814, Flack x parameter = 0.00(7), max./min. residual electron density = 0.14/−0.18 e $Å^{-3}$. (*R*,*R*)-**15**: $C_{46}H_{51}Cl_3F_6IrOP_2$; crystal size 0.30 × 0.27 × 0.21 mm; monoclinic, space group $P2_1$, $a$ = 9.998(2), $b$ = 22.088(4), $c$ = 10.313(2) Å, $\beta$ = 97.23(3)°, $V$ = 2259.4(8) $Å^3$, $Z$ = 2, $\mu$ = 3.26 $mm^{-1}$; $\lambda(Mo_{K\alpha})$ = 0.71073 Å, $T$ = 293 K, $2\theta_{max}/2\theta_{min}$ = 46.50°/4.50°, collected (independent) reflections = 12186 (6166), $R_{int}$ = 0.0447; 536 refined parameters, $R_1$ = 0.0441 for 5641 reflections with $I > 2\sigma$, $wR_2$ = 0.1093 for all data, GooF on $F^2$ = 1.071, Flack x parameter = 0.01(2), max./min. residual electron density = 1.87/−1.97 e $Å^{-3}$. (*S*,*R*)-**17**: $C_{47}H_{53}Cl_2F_3O_4PRhS$; crystal size 0.54 × 0.50 × 0.46 mm; monoclinic, space group $P2_1$, $a$ = 10.181(1), $b$ = 19.492(1), $c$ = 11.926(4) Å, $\beta$ = 106.304(1)°, $V$ = 2271.4(1) $Å^3$, $Z$ = 2, $\mu$ = 0.63 $mm^{-1}$; $\lambda(Mo_{K\alpha})$ = 0.71073 Å, $T$ = 298 K, $2\theta_{max}/2\theta_{min}$ = 56.56°/3.56°, collected (independent) reflections = 13430 (9234), $R_{int}$ = 0.0181; 532 refined parameters, $R_1$ = 0.0303 for 8345 reflections with $I > 2\sigma$, $wR_2$ = 0.0729 for all data, GooF on $F^2$ = 1.023, Flack x parameter = 0.02(2), max./min. residual electron density = 0.28/−0.49 e $Å^{-3}$. CCDC-242539–CCDC-242542 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit @ccdc.cam.ac.uk).

[10] a) $Ru^0$ vinylether (vinyl sulfide) complexes: J. G. Pinas, T. Marumo, Y. Ichikawa, M. Hirano, S. Komiya, *J. Chem. Soc. Dalton Trans.* **2000**, 2613, and lit. cited therein; b) for a dinuclear Rh complex with a special vinyl ether moiety see: R. S. Dickson, G. D. Fallon, F. I. McLure, R. J. Nesbit, *Organometallics* **1987**, *6*, 215.

[11] G. Walker, A. R. Engle, *J. Org. Chem.* **1972**, *37*, 4294.

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