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Chiral Phosphane Alkenes (PALs): Simple Synthesis, Applications in Catalysis, and Functional Hemilability

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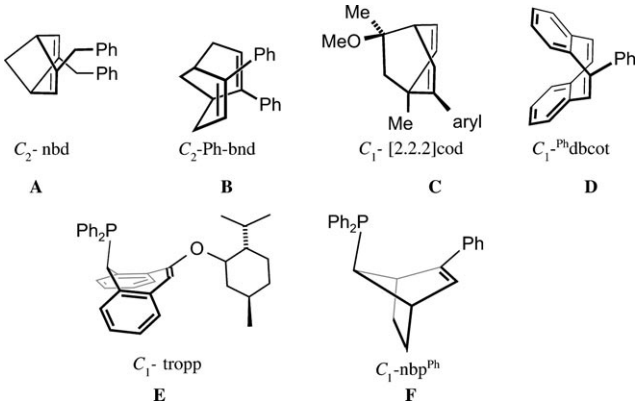
Dedicated to Dr. Herbert Hugl

Abstract: A simple synthesis of a chiral phosphane alkene (PAL) involves: 1) palladium-catalyzed Suzuki coupling of 10-bromo-5*H*-dibenzo[*a*,*d*]cyclohepten-5-ol (**1**) with phenylboronic acid to give quantitatively 10-phenyl-5*H*-dibenzo[*a*,*d*]cyclohepten-5-ol (**2**); 2) reaction of **2** with Ph_2PCl under acidic conditions to give a racemic mixture of the phosphane oxide (10-phenyl-5*H*-dibenzo[*a*,*d*]cyclohepten-5-yl)diphenylphosphane oxide (^{Ph}troppo^{Ph}, **3**), which is separated into enantiomers by using high-pressure liquid chromatography (HPLC) on a chiral column; 3) reduction with trichlorosilane to give the enantiomerically pure phosphanes (*R*)- and (*S*)-(10-phenyl-5*H*-dibenzo[*a*,*d*]cyclohepten-5-yl)diphenylphosphane (^{Ph}tropp^{Ph}, **4**). This highly rigid, concave-shaped ligand serves as a bidentate ligand in Rh^I and Ir^I complexes. Catalysts prepared from $[Rh_2(\mu_2\text{-}Cl)_2(C_2H_4)_4]$ and (*S*)-**4** have allowed the efficient enantioselective 1,4-addition of arylboronic acids to α,β-unsaturated carbonyls (Hayashi–Miyaura reaction) (5–0.1 mol% catalyst, up to 95% *ee*). The iridium complex (*S*,*S*)-[Ir(^{Ph}tropp^{Ph})$_2$]OTf ((*S*,*S*)-**6**; OTf = SO_3CF_3) has been used as a catalyst in the hydrogenation of various nonfunctionalized and functionalized olefins (turnover frequencies (TOFs) of up to 4000 h^{-1}) and moderate enantiomeric excesses have been achieved (up to 67% *ee*). [Ir(^{Ph}tropp^{Ph})$_2$]OTf reversibly takes up three equivalents of H_2. The highly reactive octahedral $[Ir(H)_2(OTf)(CH_2Cl_2)(H_2\text{-}^{Ph}tropp^{Ph})_2]$ could be isolated and contains two hydrogenated monodentate H_2-^{Ph}tropp^{Ph} phosphanes, one CH_2Cl_2 molecule, one triflate anion, and two hydrides. Based on this structure and extensive NMR spectroscopic studies, a mechanism for the hydrogenation reactions is proposed.

Keywords: alkenes · asymmetric catalysis · hydrogenation · iridium · P ligands

Introduction

Alkenes have become recognized as steering ligands in catalysis. Lemaire and co-workers[1] proposed various η^4-1,5-cyclooctadienerhodium(I) and -iridium(I) complexes, $[M(cod)L_2]^+$, to be the active catalysts in transfer hydrogenation reactions.[2] Chiral ligands **A**–**D** in which the stereogenic centers result from asymmetric substitution of a coordinated alkene (Scheme 1) were recently introduced by Hayashi[3] and Carreira[4] and their co-workers as well as by our group[5] and proved to be effective in a wide variety of ho-



Scheme 1. Chiral alkenes used as steering ligands in enantioselective catalysis. nbd = norbornadiene; Ph-bnd = 2,6-diphenylbicyclo[3.3.1]nona-2,6-diene; dbcot = dibenzo[*a*,*e*]cyclooctene; nbp^{Ph} = 7-diphenylphosphanylnorbornene.

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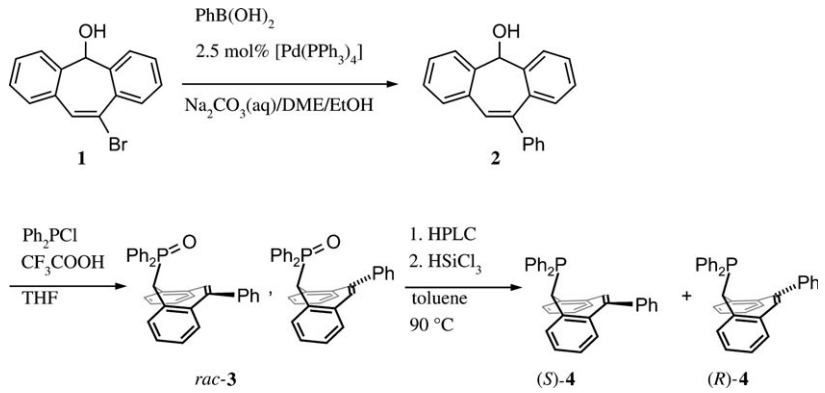
mogeneously catalyzed reactions [1,4-addition of arylboronic acids to α,β-unsaturated carbonyls (Hayashi–Miyaura reaction), allylic alkylation reactions, kinetic racemate resolution of allyl carbonates, and hydrogenation, transfer hydrogenation, and hydroboration reactions].

As we have pointed out, phosphane alkene ligands (PALs) are especially interesting because they are topographically related to tripod ligands (six-electron donors) but serve only as four-electron donors.[6,7] 5-Phosphanyl-5*H*-dibenzo[*a,d*]cycloheptenes, ^{R1}tropp^{R} (R denotes the phosphorus atom, R1 the C=C-bonded substituent) have been introduced as a new class of very rigid concave-shaped PALs.[8] A patent has been granted that describes the utility of this ligand in cyclocarbonylation reactions.[9] We found tropp-type phosphanes to be excellent ligands in the cross-coupling of aryl halides with arylboronic acids (Suzuki–Miyaura coupling)[10] and chiral tropp derivatives **E** have been employed in the iridium-catalyzed enantioselective hydrogenation of imines.[6] Very recently, the use of the chiral PAL ligand **F** in the Rh^{I}-catalyzed enantioselective Hayashi–Miyaura reaction, which gives biologically active compounds, was reported.[11]

In this paper we describe a compact, simple synthesis of an enantiomerically pure PAL, its application in enantioselective catalyses, and, in particular, its function as a hemilabile ligand.[12]

Results and Discussion

Syntheses: In a palladium-catalyzed Suzuki reaction, 10-bromo-5*H*-dibenzo[*a,d*]cyclohepten-5-ol (**1**) was coupled with phenylboronic acid to give 10-phenyl-5*H*-dibenzo-[*a,d*]cyclohepten-5-ol (**2**) on a multigram scale in 97% yield (Scheme 2).[13] The subsequent reaction of **2** with Ph_2PCl under acidic conditions gave the oxophosphorane ^{Ph}troppo^{Ph} (*rac*-**3**), in an Arbuzov-type rearrangement. The enantiomers were very easily separated by using high-pressure liquid chromatography (HPLC) on a cellulose tris(3,5-dimethylphenylcarbamate) (OD-H) column, and subsequent reduction with $HSiCl_3$ under standard conditions gave the phosphanes (*S*)-^{Ph}tropp^{Ph} ((*S*)-**4**) and (*R*)-^{Ph}tropp^{Ph} ((*R*)-**4**) in an excellent overall yield (85% based on **1**).



Scheme 2. Synthesis of chiral PALs (*S*)-^{Ph}tropp^{Ph} ((*S*)-**4**) and (*R*)-^{Ph}tropp^{Ph} ((*R*)-**4**).

The structure of *rac*-**4** was determined by using X-ray crystallography and the resulting structure is displayed in Figure 1.[14]

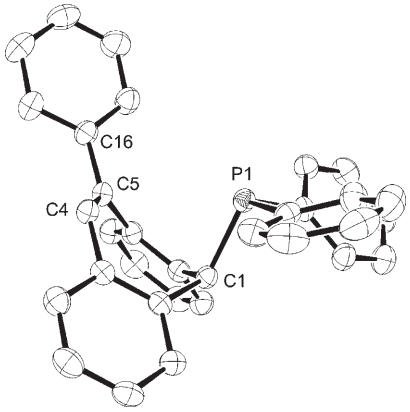
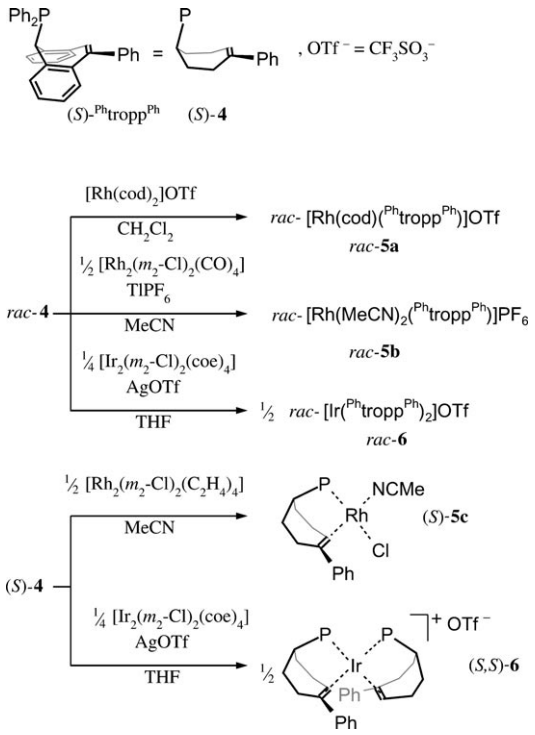


Figure 1. ORTEP view of the *S* enantiomer of **4**. The thermal ellipsoids are drawn at the 50% probability level. The hydrogen atoms have been omitted for clarity. Selected bond lengths [Å]: P1–C1 1.894(2), C4–C5 1.344(2), C4–C16 1.491(2). The bite angle of **4** is 75.5°.

The racemic mixture of ^{Ph}tropp^{Ph} (*rac*-**4**) was allowed to react with a variety of rhodium(I) or iridium(I) precursor complexes (Scheme 3) to give the complexes [Rh(cod)(^{Ph}tropp^{Ph})]OTf (*rac*-**5a**), [Rh(MeCN)$_2$(^{Ph}tropp^{Ph})]PF_6 (*rac*-**5b**), [RhCl(MeCN)(^{Ph}tropp^{Ph})] (*rac*-**5c**), and the bis-tropp complex [Ir(^{Ph}tropp^{Ph})$_2$]OTf, which was obtained as a racemic mixture of the homochiral complexes (*S,S*)-**6** and (*R,R*)-**6**. The ease of the latter reaction is remarkable in view of the steric encumbrance of the free ligand (cone angle ≈240°).

The *S*-configured enantiomer (*S*)-**4** was used to synthesize the chiral complexes (*S*)-**5c** and (*S,S*)-**6**. All the complexes were obtained in excellent yields (90–97%) and are crystalline stable materials. Note that **5a–c** and **6** are examples of very rare triaryl-substituted alkene complexes. NMR spectroscopic data show that the C=C$_{trop}$ unit is coordinated to the rhodium center in **5a–c**. This is, for example, indicated by the significant coordination shift ($\Delta\delta = \delta_{complex} - \delta_{ligand}$) observed for the tertiary =^{13}CH nucleus in (*S*)-**5c** ($\Delta\delta^{CH} = -75.6$ ppm).

In the bis-tropp iridium complex **6**, the C=C double bonds are less strongly bonded ($\Delta\delta^{CH} = -48.6$ ppm) as is also indicated by the results of an X-ray structure analysis (Figure 2, performed on a single crystal containing a race-



Scheme 3. Synthesis of chiral (^{Ph}tropp^{Ph}) Rh^{I} (**5a–c**) and Ir^{I} complexes (**6**). coe = cyclooctene.

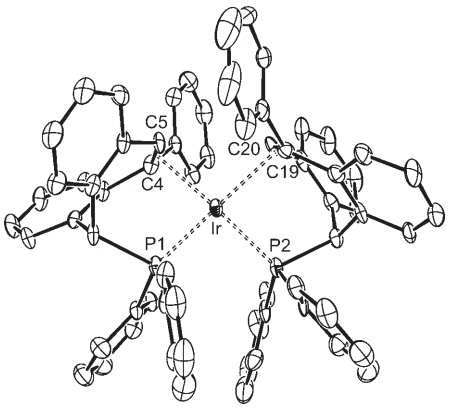
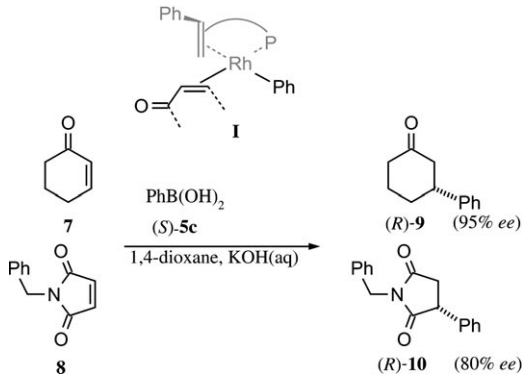


Figure 2. ORTEP plot of (*S*,*S*)-[Ir(^{Ph}tropp^{Ph})$_2$]OTf ((*S*,*S*)-**6**). The thermal ellipsoids are shown at the 30% probability level. The *R*,*R* isomer, the hydrogen atoms, the triflate anion, and two molecules of dichloromethane have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Ir–P1 2.263(3), Ir–P2 2.271(3), Ir–C4 2.40(1), Ir–C5 2.29(1), Ir–C19 2.47(1), Ir–C20 2.34(1), Ir–ct1 2.24(1), Ir–ct2 2.30(1) (ct1 = centroid of C4=C5, ct2 = centroid of C19=C20); P1–Ir–ct1 88.6(1), ct1–Ir–ct2 95.1(1), ct2–Ir–P2 88.6(1).

mic mixture of **6**). The Ir–C bonds are quite long, especially to the quaternary carbon atoms =CPh: Ir1–C4 2.40(1) Å, Ir1–C19 2.47(1) Å.

Both phosphorus centers adopt a *cis* position within the mildly tetrahedrally distorted coordination sphere of the Ir^{I} center ($\varphi = 24°$; the angle at the intersection between the planes running through iridium, phosphorus, and the centroid, ct, of the coordinated C=C bond) and the Ir–P bonds have typical lengths (2.267(4) Å).

Catalyzed 1,4-addition of arylboronic acids to α,β-unsaturated ketones: The enantiomerically pure complex (*S*)-[Rh$_2$(μ_2-OH)$_2$(^{Ph}tropp^{Ph})$_2$] (derived in situ from [Rh$_2$(μ_2-Cl)$_2$(C$_2$H$_4$)$_4$] and (*S*)-**4** in dioxane/KOH/H$_2$O) is the precursor of the enantioselective catalyst for the Hayashi–Miyaura reaction (Scheme 4) and cyclohex-2-enone (**7**) was converted cleanly to 3-phenylcyclohexanone (**9**) (1–5 mol% catalyst, 55 °C,

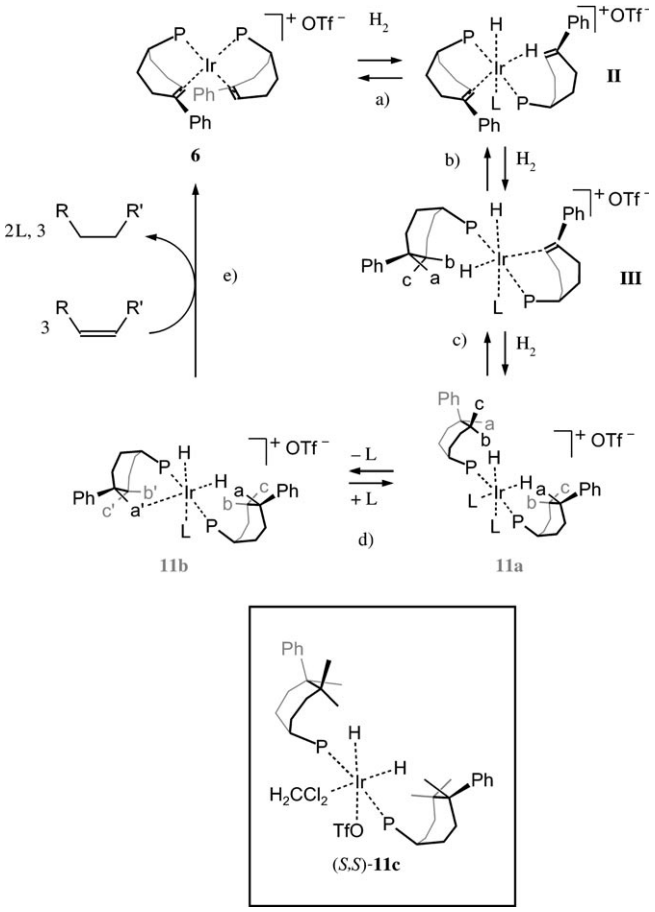


Scheme 4. Enantioselective Hiyashi–Miyaura reactions using (*S*)-[Rh(^{Ph}tropp^{Ph})] complexes as catalysts.

2 h, >85% conversion) and *N*-benzylmaleimide (**8**) (0.1 mol%, 55 °C, 2 h, >98% conversion) to 1-benzyl-3-phenylpyrrolidine-2,5-dione (**10**). In both cases, the *R*-configured products (95% *ee* for (*R*)-**9**, 79% for (*R*)-**10**) were obtained in accord with the suggested intermediate **I** in which the strongly σ-donating phenyl group binds highly stereoselectively in the *trans* position with respect to the π-accepting C=C$_{trop}$ moiety.[3,11,15]

Hydrogenation reactions: We were also interested in the performance of the [M(^{Ph}tropp^{Ph})] complexes as catalysts in hydrogenation reactions. In previous work we showed that a saturated, dihydrogenated dibenzo[*a*,*d*]cycloheptanylphosphane, H$_2$-tropp, which binds as a monodentate ligand via the phosphorus atom, may only be dehydrogenated to a chelating bidentate tropp ligand within the coordination sphere of Rh^{I} and Ir^{I} complexes.[16] We also demonstrated that with strained ligand systems the C=C$_{trop}$ unit may be hydrogenated in Ir^{I} complexes.[17] The Rh^{I} complexes **5a–c** showed no detectable reaction with H$_2$, however, the iridium complex [Ir(^{Ph}tropp^{Ph})$_2$]OTf (**6**) does react readily. Various NMR spectroscopic experiments have allowed us to make some suggestions with respect to the rather complicated reaction sequence that is shown in Scheme 5.

1) In CH$_2$Cl$_2$ as solvent and under conditions in which the H$_2$ concentration in solution is low, two new ^{31}P resonances at $\delta = 62.5$ and 39 ppm were detected, in addition to a resonance from unreacted **6** ($\delta = 52.9$ ppm), which are typical for the κ^1,η^2- and κ^1 binding modes, respectively, of the tropp



Scheme 5. Reaction of **6** with H_2. L stands for loosely bound unspecified ligands (solvent molecules) and a, b, c and a′, b′, c′ denote protons in the hydrogenated ^{Ph}tropp^{Ph} ligand. The racemic mixture of **6** was used for these experiments and only the *S,S* isomer is shown. The five steps (a–e) are mentioned in the main text.

ligand (step a in Scheme 5). The large value of $^2J(P,P) = 316$ Hz indicates that both phosphorus centers are in a *trans* position. Furthermore, a broad resonance at $\delta = -13.5$ ppm in the ^{1}H NMR spectrum indicates the presence of two hydrides. We assigned the structure **II** to this complex. It is likely that another ligand L occupies the sixth coordination site in this Ir^{III} complex and this may be a solvent molecule or the OTf$^-$ counteranion. Exchange of L, a possible mutual displacement of the C=C$_{trop}$ units, and the reversibility of the H_2 addition step (see below) explain the highly fluxional behavior and the broadened NMR spectroscopy resonances that made further characterization of **II** impossible.

2) At slightly higher H_2 concentrations, another species **III** was observed which exhibits two well-resolved doublets in the ^{31}P NMR spectrum at $\delta = 58.2$ and 34.9 ppm with a $^2J(P,P)$ value of 274 Hz (step b in Scheme 5). Again, the chemical shifts indicate that the complex contains one tropp ligand binding in a κ^1,η^2 mode and one ligand coordinated only via the phosphorus atom in a κ^1 mode. The P,P coupling constant indicates that the phosphorus centers adopt a *trans* position. In the ^{1}H NMR spectrum, two well-resolved hydride resonances are observed at $\delta = -13.5$ (ddd, $^2J(P,H) = 27.8$, $^2J(P,H) = 6.2$, $^2J(H,H) = 2.5$ Hz) and -15.3 ppm (ddd, $^2J(P,H) = 18.0$, $^2J(P,H) = 9.8$, $^2J(H,H) = 2.5$ Hz). The coupling constants indicate that the two hydrides adopt a *cis* position with respect to each ^{31}P nucleus and to each other. Two-dimensional ^{13}C{^{1}H} HMQC correlation experiments showed that the ^{1}H signals at 2.80 (H_c), 4.33 (H_b), and 4.82 ppm (H_a) (integrating one proton each) are bonded to sp^3 carbon atoms. The related ^{13}C chemical shifts are 39.8 ppm for CH_bH_c and 48.2 ppm for CH_a. That is, the C=C$_{trop}$ unit of the κ^1-bonded ligand is hydrogenated. The other ^{Ph}tropp^{Ph} ligand is unchanged as is evidenced by the singlet in the ^{1}H NMR spectrum at $\delta = 5.18$ ppm for the olefinic proton in the CH=CPh unit. The corresponding ^{13}C signal appears at 93.5 ppm. These spectroscopic data led us to propose the structure **III** for this compound. Again, an additional ligand L (solvent, OTf$^-$) likely occupies the sixth coordination site in this Ir^{III} *cis*-dihydride complex.

3) At yet higher H_2 concentrations (reached by shaking the reaction mixtures at 1–4 bar H_2), a third species was detected (step c in Scheme 5). At room temperature, a broad singlet at $\delta = 45.0$ ppm was observed in the ^{31}P NMR spectrum and one very broad resonance at -30.52 ppm in the ^{1}H NMR spectrum indicating the presence of hydrides. A two-dimensional ^{13}C{^{1}H} HMQC experiment clearly showed that both C=C$_{trop}$ units are hydrogenated. In the CPhH$_a$–CH$_b$H$_c$ unit, the H_a proton is observed as a broad singlet at $\delta = 3.81$ ppm, H_b exhibits a doublet at $\delta = 3.22$ ppm ($^2J(H_b,H_c) = 15.1$ Hz), and H_c exhibits a doublet of doublets at $\delta = 2.44$ ppm ($^2J(H_b,H_c) = 15.1$, $^3J(H_a,H_c) = 5.5$ Hz). Each signal integrates for two protons. The ^{13}C NMR spectrum shows a resonance at $\delta = 39.9$ ppm for the CH_bH_c carbon atom and at $\delta = 47.3$ ppm for the CH_a unit. The observed line broadening in the ^{31}P and ^{1}H NMR spectra indicate dynamic phenomena. Notably, in a two-dimensional ^{1}H{^{1}H} NOESY correlation experiment, exchange between H_a, H_b, and the hydrides was observed. This finding gives a first indication that the hydrogenation of the C=C$_{trop}$ units is reversible. On the basis of these spectroscopic data, we propose structure **11a** for this complex. Again, labile solvent molecules or the OTf$^-$ anion likely complete the coordination sphere of this Ir^{III} dihydride diphosphane complex and their exchange causes the NMR resonances to broaden.

4) Decreasing the temperature of solutions of **11a** from 298 to 190 K led to significant but reversible changes in the NMR spectra. A new species, **11b**, was reversibly formed (Scheme 5, step d). In the ^{1}H NMR spectrum, the broad resonance at about -30 ppm at 298 K is replaced by two multiplets at -29.12 and -26.33 ppm ($^2J(P,H) = 14.5$, $^2J(H,H) = 9.9$ Hz). The coupling constants indicate that, again, both hydrides are in a *cis* position with respect to the phosphorus nuclei and to each other. Two separated sets of signals for H_b, H_c, H_{benz} and $H_{b'}$, $H_{c'}$, $H_{benz'}$ are observed and demonstrate the nonequivalence of the hydrogenated tropp ligands, H_2-^{Ph}tropp^{Ph}, at 190 K (H_{benz} denotes the benzylic proton in the α position to the phosphorus atom; the nonequivalence of the ligands is also clearly seen in the ^{13}C NMR spectrum).

In a $^{31}P\{^1H\}$ HMQC experiment, long-range coupling of $H_{a'}$ to the phosphorus nuclei was observed. These spectroscopic data suggest that **11b** results from **11a** by the substitution of one ligand L by an agostic Ir–$H_{a'}$ interaction. A mutual H_a/$H_{a'}$ displacement is an obvious dynamic process and the likely reason why these protons are observed as a broadened singlet. That only a singlet at $\delta = 49.0$ ppm is observed in the ^{31}P NMR spectrum of **11b** is likely due to the fact that both phosphorus nuclei are fortuitously isochronous.

The structures shown in Scheme 5, especially of **11a**, are strongly supported by the results of a single-crystal X-ray analysis of the yellow complex **11c** (Figure 3), which was obtained by slow diffusion of *n*-hexane into a hydrogen-saturated solution of **11a**.[15] All structural features deduced from the NMR spectra are observed in the structure of **11c**. That is, two hydrogenated, very bulky H_2-^{Ph}tropp^{Ph} ligands (cone angle $\approx$270°) bind via the phosphorus centers to an iridium(III) center and reside in the *trans* positions of the octahedral coordination sphere. The two hydrides H1 and H2 (placed in calculated positions) are in *cis* positions with respect to the phosphorus centers and to each other. The remaining two coordination sites in the basal plane are occupied by one of the oxygen atoms of the triflate anion (Ir–O 2.260(6) Å) and one of the chlorine atoms of a CH_2Cl_2 molecule. The structure shows only minor distortions from an ideal octahedral form. Complex **11c** is only the second example of an iridium–methylene chloride complex and the long Ir···Cl distance (2.551(3) Å) indicates that the CH_2Cl_2 is loosely bound.[18]

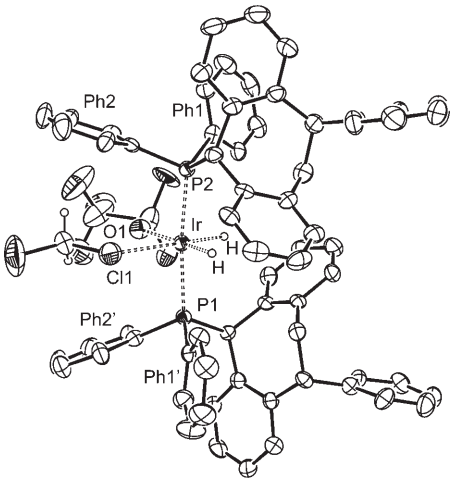
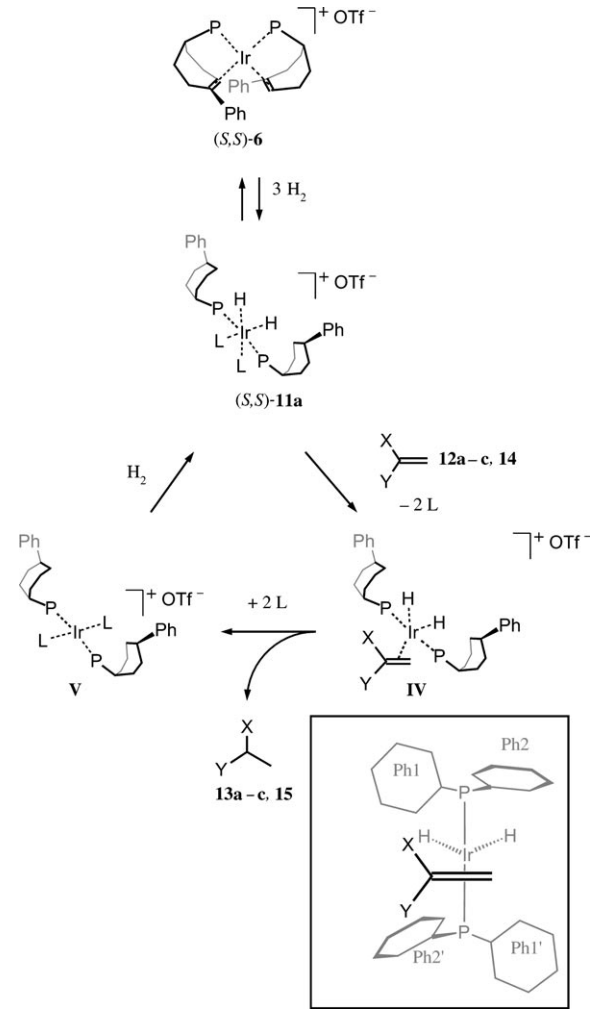


Figure 3. ORTEP plot of (*S*,*S*)-[Ir(H)$_2$(OTf)(CH_2Cl_2)(H_2-^{Ph}tropp^{Ph})$_2$] (**11c**); thermal ellipsoids are shown at the 30% probability level. The *R*,*R* isomer, the hydrogen atoms of the H_2-^{Ph}tropp^{Ph} ligands, and a molecule of CH_2Cl_2 have been omitted for clarity. The hydrogen atoms bonded to the iridium are shown in calculated positions. Selected bond lengths [Å] and angles [°]: Ir1–P1 2.315(2), Ir–P2 2.313(2), Ir–Cl1 2.550(3), Ir–O1 2.260(6); O1–Ir–P2 92.1(2), O1–Ir–P1 94.7(2), P2–Ir–P1 172.7(1), O1–Ir–Cl1 88.2(2), P2–Ir–Cl1 93.5(1), P1–Ir–Cl1 89.2(1).

5) The complexes **11a–c** are highly reactive. When solutions of **11a** were repeatedly purged with argon at room temperature, the starting complex **6** was formed after some time and when simple alkenes like 1-octene or cyclooctene were added as hydrogen scavengers, **6** was recovered in >90% yield (Scheme 5, step e). That is, the hydrogenation of the C=C_{trop} bonds in **6** is fully reversible and **11c** is able to deliver the three equivalents of hydrogen initially taken up in the hydrogenation reactions.

Enantioselective hydrogenation reactions: Therefore **11a–c** are efficient catalysts for the hydrogenation of alkenes and at 1 bar of H_2, room temperature, and with a substrate-to-catalyst ratio (S/C) of 4000, 1-octene and cyclooctene are converted to octane and cyclooctane with turnover frequencies (TOFs) of >4000 and 3500 h^{-1}, respectively.[19] The efficacy of the enantiomerically pure complex (*S*,*S*)-**6** was tested under comparable conditions in the enantioselective hydrogenation of itaconic acid (**12a**) and its esters **12b**,**c** and **14** (Scheme 6 and Table 1). These substrates have previously been found difficult to hydrogenate with iridium complexes.[20]

By using S/C = 10000, an 85% conversion of the dimethyl ester **12b** to dimethyl succinate **13b** was achieved after 2 h,



Scheme 6. Proposed mechanism for the catalytic hydrogenation of alkenes with (*S*,*S*)-**6** as catalyst precursor. L stands for loosely bound unspecified ligands (solvent molecules).

Table 1. Substituents X,Y in functionalized olefins and *ee*'s in enantioselective hydrogenation reactions with catalyst (*S*,*S*)-**6**.

	X	Y	*ee* [%] (configuration)
12, **13a**	CH_2COOH	COOH	30 (*R*)
12, **13b**	CH_2COOMe	COOMe	60 (*R*)
12, **13c**	CH_2COO*n*Bu	COO*n*Bu	67 (*R*)
14, **15**	NHCOMe	COOMe	39 (*S*)

with an enantiomeric excess (*ee*) of 60%. With the same S/C ratio, the free acid **12a** (39% conversion) and the *n*-butyl ester **12c** (23% conversion) were found to have lower activities and the products **13a** and **13c** were obtained with 30 and 67% *ee*, respectively (see also Table 2 in the Experimental Section). The α-dehydroamino acid ester **14** was converted with a conversion of >99% to **15** at S/C=100, but at lower catalyst loadings the activity drops to give 23% (S/C=4000) or 7% conversion (S/C=10000). The enantioselectivity remained unchanged at a moderate 39% *ee* in favor of the *S*-configured isomer.

A model explaining the preference for the formation of the *R* isomers of **13a–c** and the *S* isomer of **15** is shown at the bottom of Scheme 6 and was constructed on the basis of the structure of the $[Ir(H)_2(H_2\text{-}^{Ph}tropp^{Ph})_2]$ fragment of **11c**. We assume that in the reactive conformation of intermediate **IV**, the C=C bond of the substrate lies in the plane with the hydrides in the C_2-symmetric bipyramidal structure of the catalyst. The sterically more demanding X group (CH_2COOR for **12a–c**, NHCOMe for **14**) is expected to be more comfortably placed in the relatively open space below the phenyl group Ph1 which is coplanar with the P–Ir–P vector. This assumption is also in accord with the increase in *ee* in the order R=H<R=Me<R=*n*Bu observed for the itaconate esters **12a–c**. Rapid oxidative addition of H_2 to the intermediate **V**, a solvated bis-phosphane iridium complex with the monodentate phosphanes in *trans* positions, completes the catalytic cycle.

Conclusion

In the reactions described in this work, PALs served as functional hemilabile ligands in the catalytic hydrogenation of alkenes. Classical hemilabile ligands stabilize a reactive metal fragment through a rapid intramolecular "on"–"off" equilibrium,[12] $[M(\kappa^2\text{-}D\cap Z)]\rightleftharpoons[M(\kappa^1\text{-}D\cap Z)]$ (D=inert donor, Z=labile donor), but their chemical composition remains intact. This is not the case with PALs in hydrogenation reactions. When the activation barriers involved in the chemical transformation of the ligand are sufficiently high, an advantage of such chemically functional hemilabile behavior may be that the substrate does not have to compete with the intramolecular donor Z for the vacant coordination sites at the (catalytically) reactive metal site.

Experimental Section

General techniques: All syntheses were performed in dried glassware under argon using standard Schlenk techniques. Solvents were freshly distilled from sodium/benzophenone (THF), sodium/tetraglyme/benzophenone (hexane, toluene), or calcium hydride (dichloromethane) prior to use. Air-sensitive compounds were stored and weighed in an argon-filled glove box (Braun MB 150 B-G system) and small-scale reactions were performed directly in the glove box. 10-Bromo-5*H*-dibenzo[*a*,*d*]cyclohepten-5-one was synthesized from dibenzosuberenone following a reported procedure.[21]

Characterization: NMR spectra were recorded with Bruker Avance 500, 300, or 250 spectrometers. The chemical shifts (δ) were measured according to procedures set out by IUPAC and are expressed in ppm relative to tetramethylsilane (TMS) for ^1H and ^{13}C NMR spectra and H_3PO_4 for ^{31}P NMR spectra.[22] The exception is for ^{103}Rh, with the frequency reference $\Xi=3.16$ MHz. Coupling constants *J* are given in hertz (Hz) as absolute values unless specifically stated otherwise. Where a first-order analysis is appropriate, the multiplicity of the signals is indicated as s, d, t, q, or m for singlets, doublets, triplets, quartets, or multiplets, respectively. Otherwise the spin systems are specified explicitly. The abbreviation br is given for broadened signals. Quaternary carbon atoms are indicated as C_{quat}, quaternary aromatic carbon atoms as C_{ar}, and aromatic units as CH_{ar} and CH_{ar} unless noted otherwise.

X-ray crystallographic measurements were performed by using a Bruker SMART Apex and CCD1k as well as with Stoe IPDS I and IPDS II area-detector diffractometers. Refinement was carried out using SHELXL-97[26].

IR spectra were recorded with a Perkin–Elmer-Spectrum 2000 FTIR-Raman spectrometer equipped with a KBr beam splitter (range 500–4000 cm^{-1}). Solution spectra were measured in a 0.5 mm KBr cell; for solid compounds the ATR technique was applied. The absorption bands are described as follows: strong (s), very strong (vs), medium (m), weak (w), or broad (br).

UV/Vis spectra were measured with the UV/Vis Lambda 19 spectrometer in 0.5 cm quartz cuvettes (range 200–600 nm).

The mass spectra of organic compounds were recorded on a Finnigan MAT SSQ 7000 mass spectrometer.

Gas chromatograms were recorded with a HP Series 6890 gas chromatograph on an Agilent 19091J-413 HP-5 5% phenyl methyl siloxane column (30.0 m, 320 μm, 0.25 μm) or on a Lipodex-E MN 723368.25 chiral column (25.0 m, 259 μm, 0.21 μm).

Melting points were determined with a Büchi melting-point apparatus and are uncorrected. Samples were prepared in open-glass capillaries.

Syntheses and spectroscopic data

*10-Bromo-5*H*-dibenzo[*a,d*]cyclohepten-5-ol (^{Br}tropOH)* (***1***): A 500 mL round-bottomed flask was charged with 10-bromo-5*H*-dibenzo[*a*,*d*]cyclohepten-5-one (20.0 g, 70 mmol) and MeOH (200 mL). The solution was cooled to 0°C and subsequently $NaBH_4$ (1.3 g, 35 mmol) and a solution of NaOH (140 mg, 3.5 mmol) in water (5 mL) was added. The reaction mixture was allowed to warm to room temperature and stirred for 18 h. H_2O (100 mL) was added to the mixture, leading to the precipitation of **1**. Filtration and crystallization from a Et_2O/*n*-hexane (1:2) gave 19.9 g (99% yield) of colorless crystals.

M.p. 126–131°C; ^1H NMR (300.1 MHz, $CDCl_3$, 25°C, TMS): $\delta=2.46$ (br s, 1H; O*H*), 5.36 (br s, 1H; CH_{benz}), 7.20–7.35 (m, 4H; $CH_{ar}+CH_{olefin}$), 7.39–7.50 (m, 3H; CH_{ar}), 7.62–7.90 ppm (m, 3H; CH_{ar}); $^{13}C\{^1H\}$ NMR (300.1 MHz, $CDCl_3$, 25°C, TMS): $\delta=70.3$ (br; CH_{benz}), 121.0 (br; CH_{ar}), 121.5 (br; CH_{ar}), 126.4 (br; CH_{ar}), 126.7 (br; CH_{ar}), 127.3 (br; CH_{ar}), 129.0 (br; CH_{ar}), 130.17 (s; CH_{ar}), 131.4 (br; C_{quat}), 132.1 (br; C_{quat}), 133.8 (br; C_{quat}), 141.1 (br; C_{quat}), 141.8 ppm (br; C_{quat}). The signal for the fifth quaternary carbon was not observed.

*10-Phenyl-5*H*-dibenzo[*a,d*]cyclohepten-5-ol (^{Ph}tropOH)* (***2***): A 250 mL round-bottomed flask was charged with **1** (4.0 g, 13.9 mmol) and dimethoxyethane (DME) (100 mL). $Pd(OAc)_2$ (93 mg, 0.4 mmol), Ph_3P (349 mg, 1.3 mmol), a degassed aqueous solution of Na_2CO_3 (9 mL, 2 M),

and $PhB(OH)_2$ (2.0 g, 16.6 mmol) were added to this solution. The reaction mixture was stirred under reflux for 18 h. Then, H_2O (30 mL) was added and **2** was extracted with AcOEt (3×30 mL). The combined organic phases were dried with Na_2SO_4, filtered, and all volatile materials were removed under reduced pressure. The resulting solid was purified by using flash chromatography (AcOEt/*n*-hexane 2:8) to give 3.9 g (97% yield) of the pure product.

M.p. 122–124°C; ^{1}H NMR (250.1 MHz, $CDCl_3$, 25°C, TMS): δ=2.61 (br s, 1H; O*H*), 5.44 (s, 1H; CH_{benz}), 7.05–7.95 ppm (br m, 14H; CH_{ar}, CH_{olefin}); ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$, 25°C, TMS): δ=70.9 (br; *C*H$_{benz}$), 120.9 (br; *C*H$_{ar}$), 125.9 (br; *C*H$_{ar}$), 126.1 (br; *C*H$_{ar}$), 127.72 (*C*H$_{ar}$), 127.9 (br; *C*H$_{ar}$), 128.34 (*C*H$_{ar}$), 128.45 (*C*H$_{ar}$), 128.92 (*C*H$_{ar}$), 129.1 (br, *C*H$_{ar}$), 129.97 (br; *C*H$_{ar}$), 132.4 (br; C_{quat}), 133.6 (br; C_{quat}), 141.8 (br; C_{quat}), 142.6 (br; C_{quat}), 143.3 (br; C_{quat}), 143.57 ppm (C_{quat}); MS (70 eV): *m*/*z* (%): 284.0 (100) [M^+], 255.0 (44), 207.0 (29) [M^+−Ph], 179.0 (41).

*(10-Phenyl-5*H*-dibenzo[*a,d*]cyclohepten-5-yl)diphenylphosphane oxide (^{Ph}tropo^{Ph}) (**3**)*: A 150 mL Schlenk tube was charged with **2** (3.8 g, 13.0 mmol) and THF (70 mL). CF_3COOH (3.0 g, 27 mmol) and freshly distilled Ph_2PCl (3.1 g, 14.3 mmol) were added to this solution. The reaction mixture was then stirred at room temperature for 20 h. The reaction was quenched with a saturated aqueous $NaCl/Na_2CO_3$ solution (40 mL). The phosphine oxide *rac*-**3** was then extracted with THF (3×20 mL). The organic phase was dried with Na_2SO_4, filtered, and the volatile materials removed under reduced pressure. The colorless oil was purified by using flash chromatography on silica gel (AcOEt/*n*-hexane 6:4) to provide a colorless solid in 97% yield (6.3 g).

The two enantiomers were separated by preparative high-performance liquid chromatography (HPLC) (OD-H (cellulose triphenylcarbamate) column; flow rate: 0.8 mL min^{-1}; eluent: *n*-hexane/isopropanol 98:2; retention times: (*R*)-**3**: 8.0 min, $[\alpha]_D^{20}$=−27.8; (*S*)-**3**: 10.4 min, $[\alpha]_D^{20}$=20.9).

M.p. 95–100°C; ^{1}H NMR (250.1 MHz, $CDCl_3$, 25°C, TMS): δ=5.20 (d, ^2J(P,H)=13.9 Hz, 1H; CH_{benz}), 6.53 (s, 1H; CH_{ar}), 6.98–7.60 (m, 20H; CH_{ar}), 7.28 (s, 1H; CH_{olefin}), 7.87 ppm (t, J=8.9 Hz, 2H; CH_{ar}); ^{13}C{^{1}H} NMR (62.9 MHz, $CDCl_3$, 25°C, TMS): δ=59.5 (d, ^1J(P,C)=62.9 Hz; *C*H$_{benz}$), 127.2 (d, J(P,C)=2.3 Hz; *C*H$_{paraP}$), 127.5 (d, ^2J(P,C)=11.5 Hz; *C*H$_{orthoP}$), 128.3 (d, J(P,C)=1.1 Hz; *C*H$_{ar}$), 128.5 (d, ^2J(P,C)=11.5 Hz; *C*H$_{orthoP}$), 129.1 (d, J(P,C)=0.8 Hz; *C*H$_{ar}$), 129.5 (s; *C*H$_{ar}$), 130.0 (d, J(P,C)=2.7 Hz; *C*H$_{ar}$), 130.4 (d, ^3J(P,C)=7.3 Hz; *C*H$_{metaP}$), 130.6 (d, J(P,C)=1.9 Hz; *C*H$_{ar}$), 130.9 (s; *C*H$_{olefin}$), 131.1 (d, J(P,C)=5.0 Hz; *C*H$_{ar}$), 131.3 (s; *C*H$_{ar}$), 131.3 (d, J(P,C)=2.7 Hz; *C*H$_{ar}$), 132.9 (d, ^1J(P,C)=96.3 Hz; C_{ipsoP}), 135.4 (d, J(P,C)=3.5 Hz; $C_{olefintrop}$), 135.5 (d, ^1J(P,C)=94.2 Hz; C_{ipsoP}), 136.4 (d, J(P,C)=8.9 Hz; C_{ar}), 136.5 (d, J(P,C)=8.6 Hz; C_{ar}), 137.8 (d, J(P,C)=3.8 Hz; C_{ar}), 144.3 (s; C_{ar}), 144.3 ppm (s; C_{ar}); ^{31}P{^{1}H} NMR (101.3 MHz, $CDCl_3$, 25°C, H_3PO_4): δ=26.4 ppm (s); MS (70 eV): *m*/*z* (%): 468.3 (18) [M^+], 267.2 (100) [^{Ph}trop$^+$], 77.1 (<4) [$C_6H_5^+$]; ATR IR (neat): $\tilde{\nu}$=3052–3016 (w; CH stretch), 1597 (w), 1490 (s), 1436 (vs), 1186 (m; P=O stretch), 1112 (s), 695 (vs), 551 cm^{-1} (vs).

*(10-Phenyl-5*H*-dibenzo[*a,d*]cyclohepten-5-yl)diphenylphosphane (^{Ph}tropp^{Ph}) (**4**)*: A 250 mL Schlenk tube was charged with (*S*)-**3** (2.0 g, 4.3 mmol) and toluene (100 mL). $HSiCl_3$ (11.5 g, 85.0 mmol) was added to this solution. The reaction mixture was warmed to 90°C and stirred for 18 h. The reaction was quenched with a degassed 20% aqueous NaOH (6.3 M) solution (70 mL) and then the phosphane was extracted with toluene (3×20 mL). The organic phase was dried with Na_2SO_4 and filtered under the exclusion of air. The volatile materials were removed under reduced pressure and the phosphane was crystallized from CH_2Cl_2/*n*-hexane (1:5). After 18 h at room temperature, 1.75 g (90% yield) of colorless crystals of (*S*)-**4** precipitated.

M.p. 175–180°C; ^{1}H NMR (300.1 MHz, $CDCl_3$, 25°C, TMS): δ=4.91 (d, ^2J(P,H)=5.9 Hz; CH_{benz}), 6.90 (s; CH_{ar}), 6.93 (s; CH_{ar}), 7.00–7.23 (m, 9H; CH_{ar}), 7.29 (s, 1H; CH_{olefin}), 7.30–7.35 (m, 2H; CH_{ar}), 7.37–7.57 ppm (m, 10H; CH_{ar}); ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$, 25°C, TMS): δ=56.9 (d, ^1J(P,C)=20.0 Hz; *C*H$_{benz}$), 125.9 (s; *C*H$_{paraP}$), 126.3 (s; *C*H$_{paraP}$), 127.4 (s; *C*H$_{ar}$), 127.7 (d, ^3J(P,C)=6.7 Hz; *C*H$_{metaP}$), 127.9 (s; *C*H$_{ar}$), 128.1 (d, ^3J(P,C)=6.7 Hz; *C*H$_{metaP}$), 128.3 (s; *C*H$_{ar}$), 128.6 (s; *C*H$_{ar}$), 129.0 (s; *C*H$_{ar}$), 129.6 (d, J(P,C)=3.0 Hz; *C*H$_{trop}$), 129.7 (d, J(P,C)=1.8 Hz; *C*H$_{trop}$), 129.8 (d, J(P,C)=3.2 Hz; *C*H$_{trop}$), 130.7 (d, J(P,C)=1.7 Hz; *C*H$_{trop}$), 133.5 (d, ^2J(P,C)=19.6 Hz; *C*H$_{orthoP}$), 133.9 (d, ^2J(P,C)=20.7 Hz; 2*C*H$_{orthoP}$), 135.2 (d, ^4J(P,C)=4.3 Hz; $C_{olefintrop}$), 136.7 (d, ^4J(P,C)=4.7 Hz; *C*H$_{olefintrop}$), 137.9 (d, ^1J(P,C)=20.0 Hz; C_{ipsoP}), 138.3 (d, ^1J(P,C)=20.7 Hz; C_{ipsoP}), 139.4 (d, J-(P,C)=7.8 Hz; C_{trop}), 140.5 (d, J(P,C)=9.4 Hz; C_{trop}), 144.0 (s; C_{trop}), 144.0 (s; C_{trop}), 144.6 ppm (s; C_{ar}); ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, 25°C, H_3PO_4): δ=−13.8 ppm (s); MS (70 eV): *m*/*z* (%): 452.3 (5) [M^+], 267.2 (100) [^{Ph}trop$^+$], 183.1 (15) [Ph_2P^+], 77.1 (<4) [$C_6H_5^+$]; ATR IR (neat): $\tilde{\nu}$=3054–3011 (w; CH stretch), 1481 (s), 1430 (s; C=C stretch), 1095 (w), 1025 (w), 774 (s), 739 (vs), 695 cm^{-1} (vs).

*[Rh(cod)(^{Ph}tropp^{Ph})]OTf (**5a**)*: A solution of *rac*-**4** (0.08 g, 0.17 mmol) in CH_2Cl_2 (1 mL) was added dropwise to a solution of $[Rh(cod)_2]OTf$ (0.08 g, 0.17 mmol) in CH_2Cl_2 (2 mL). The red solution was stirred for 30 min at room temperature and then the volatile materials were removed under reduced pressure. The red solid was dissolved in CH_2Cl_2 and layered with *n*-hexane. After 18 h at room temperature, 0.13 g (90% yield) of red crystals were isolated.

M.p. 170–175°C; ^{1}H NMR (300.1 MHz, $CDCl_3$, 25°C, TMS): δ=1.42 (m, 1H; CH_{cod}), 1.65–1.87 (m, 2H; CH_{cod}), 1.99 (m, 1H; CH_{cod}), 2.22–2.67 (m, 4H; CH_{cod}), 3.70 (d, ^3J(P,H)=6.1 Hz, 1H; C$H_{olefincod}$), 3.83 (d, ^3J-(P,H)=5.3 Hz, 1H; C$H_{olefincod}$), 4.48 (s, 1H; C$H_{olefincod}$), 5.35 (d, ^2J(P,H)=14.9 Hz, 1H; CH_{benz}), 6.35 (s, 1H; C$H_{olefincod}$), 6.90 (d, J=7.9 Hz, 1H; CH_{ar}), 7.10 (d, ^3J(P,H)=4.4 Hz, 1H; H$_{olefintrop}$), 7.05–7.56 (m, 17H; CH_{ar}), 7.63 (s, 2H; CH_{ar}), 7.82 (d, J=7.9 Hz, 1H; CH_{ar}), 7.85–7.95 ppm (m, 2H; CH_{ar}); ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$, 25°C, TMS): δ=25.9 (s; *C*H$_{2,cod}$), 28.5 (s; *C*H$_{2,cod}$), 31.4 (s; *C*H$_{2,cod}$), 34.5 (s; *C*H$_{2,cod}$), 56.3 (d, ^1J-(P,C)=21.6 Hz; *C*H$_{benz}$), 82.7 (d, ^2J(P,C)=11.2 Hz; *C*H$_{olefincod}$), 92.6–92.9 (m; *C*H$_{olefincod}$+*C*H$_{olefintrop}$), 111.6 (s; *C*H$_{olefincod}$), 116.6 (s; *C*H$_{olefincod}$), 126.8 (d, ^1J(Rh,C)=1.5 Hz; $C_{olefintrop}$), 127.4 (s; *C*H$_{ar}$) 127.9 (d, ^4J(P,C)=1.7 Hz; *C*H$_{paraP}$), 128.1 (s; *C*H$_{ar}$), 128.9 (d, ^2J(P,C)=10.0 Hz; *C*H$_{orthoP}$), 129.3 (d, ^2J(P,C)=10.0 Hz; *C*H$_{orthoP}$), 129.5 (d, ^1J(P,C)=6.2 Hz; C_{ipsoP}), 130.2 (s; *C*H$_{ar}$), 130.3 (d, ^1J(P,C)=5.8 Hz; C_{ipsoP}), 130.5–130.9 (m; *C*H$_{ar}$+C_{ar}), 131.1 (s; *C*H$_{ar}$), 131.6 (d, ^3J(P,C)=2.9 Hz; *C*H$_{metaP}$), 132.1 (d, ^3J-(P,C)=2.9 Hz; *C*H$_{metaP}$), 132.5 (s; *C*H$_{ar}$), 132.8 (d, J(P,C)=10.0 Hz; *C*H$_{trop}$), 133.4 (d, J(P,C)=9.5 Hz; *C*H$_{trop}$), 134.0 (s; C_{trop}), 134.6 (d, ^2J-(P,C)=7.5 Hz; C_{trop}), 135.1 (d, ^2J(P,C)=7.0 Hz; C_{trop}), 141.9 ppm (s; C_{ar}); ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, 25°C, H_3PO_4): δ=79.1 ppm (d, ^1J-(Rh,P)=163.2 Hz); ^{103}Rh NMR (12.6 MHz, $CDCl_3$, 25°C): δ=377.1 ppm (d, ^1J(Rh,P)=163.2 Hz); UV/Vis (THF): λ=283.9 nm; ATR IR (neat): $\tilde{\nu}$=3049 (w; CH stretch), 2916–2841 (m; CH stretch), 1486 (m), 1436 (m; CC stretch), 1259 (s), 1148 (s), 1028 (vs), 764 (s), 697 (vs), 635 cm^{-1} (vs).

*[Rh(CH$_3$CN)$_2$(^{Ph}tropp^{Ph})]PF$_6$ (**5b**)*: A 10 mL Schlenk tube was charged with $[Rh_2(\mu_2\text{-}Cl)_2(CO)_4]$ (40 mg, 0.10 mmol), *rac*-**4** (93 mg, 0.20 mmol), $TlPF_6$ (72 mg, 0.20 mmol), and CH_3CN (3 mL). Immediate evolution of CO and precipitation of white TlCl were observed. The resulting orange suspension was then filtered through dry Celite. The filtrate was concentrated under reduced pressure yielding an orange solid which was washed with *n*-hexane to give 156 mg of **5b** (95% yield).

M.p. 152–157°C; ^{1}H NMR (300.1 MHz, CD_3CN, 25°C, TMS): δ=5.80 (d, ^2J(P,H)=15.9 Hz, 1H; CH_{benz}), 6.97–7.06 (m, 2H; CH_{ar}), 7.23 (d, ^2J-(Rh,H)=2.9 Hz, 1H; C$H_{olefintrop}$), 7.18–7.68 (m, 17H; CH_{ar}), 7.74–7.91 ppm (m, 4H; CH_{ar}); ^{13}C{^{1}H} NMR (75.5 MHz, CD_3CN, 25°C, TMS): δ=52.1 (d, ^1J(P,C)=24.4 Hz; *C*H$_{benz}$), 96.2 (br s; *C*H$_{olefintrop}$), 117.3 (s; C_{CH_3CN}), 122.7 (br s; $C_{olefintrop}$), 127.6 (s; *C*H$_{ar}$), 128.4 (s; *C*H$_{ar}$), 128.7 (d, ^3J-(P,C)=10.7 Hz; *C*H$_{metaP}$), 128.7 (s; *C*H$_{ar}$), 129.0 (d, ^3J(P,C)=11.0 Hz; *C*H$_{metaP}$), 129.7 (d, J(P,C)=6.4 Hz; *C*H$_{trop}$), 129.9 (s; *C*H$_{ar}$), 130.0 (s; *C*H$_{ar}$), 130.1 (s; *C*H$_{ar}$), 130.2 (s; *C*H$_{ar}$), 130.6 (s; *C*H$_{ar}$), 131.1 (s; *C*H$_{ar}$), 131.7 (d, J(P,C)=2.6 Hz; *C*H$_{trop}$), 132.3 (d, J(P,C)=2.7 Hz; *C*H$_{trop}$), 132.7 (d, ^2J(P,C)=9.7 Hz; *C*H$_{orthoP}$), 134.5 (d, ^2J(P,C)=11.0 Hz; *C*H$_{orthoP}$), 135.6 (d, ^1J(P,C)=29.3 Hz; C_{ipsoP}), 135.5 (s; C_{trop}), 135.8 (d, ^1J(P,C)=29.0 Hz; C_{ipsoP}), 137.0 (s; C_{trop}), 142.1 ppm (s; C_{ar}); ^{31}P{^{1}H} NMR (121.5 MHz, CD_3CN, 25°C, H_3PO_4): δ=−144.4 (sept, ^1J(P,F)=706.5 Hz, 1P; PF_6), 93.8 ppm (d, ^1J(Rh,P)=158.2 Hz); ^{103}Rh NMR (12.6 MHz, CD_3CN, 25°C): δ=596.2 ppm (dd, ^1J(Rh,P)=158.2, ^2J(Rh,H)=2.9 Hz); UV/Vis (THF): λ=284.0 nm; ATR IR (neat): $\tilde{\nu}$=3049–2929 (w; CH stretch), 1575 (w), 1484 (m), 1436 (m), 1285 (br s), 1099 (m), 831 (vs), 741 (s), 697 cm^{-1} (s).

*[Rh$_2$(μ_2-Cl)$_2$(^{Ph}tropp^{Ph})$_2$] and [RhCl(MeCN)(^{Ph}tropp^{Ph})] (**5c**)*: A mixture of $[Rh_2(\mu_2\text{-}Cl)_2(C_2H_4)_4]$ (9 mg, 23 μmol) and (*S*)-**4** (21 mg, 46 μmol) in

THF (1 mL) was stirred for 1 h at room temperature. The solvent was removed and $[Rh_2(\mu_2\text{-}Cl)_2(^{Ph}tropp^{Ph})_2]$ was precipitated from CH_2Cl_2/*n*-hexane (1:5) as an orange powder (25 mg, 93 %). The NMR spectra were recorded in CD_3CN, which caused the formation of $[RhCl(CD_3CN)(^{Ph}tropp^{Ph})]$.

^{1}H NMR (300.1 MHz, $CDCl_3$, 5 % CD_3CN, 25 °C, TMS): $\delta = 4.81$ (d, $^2J(P,H) = 14.1$ Hz, 1H; CH_{benz}), 5.26 (s, 1H; $CH_{olefintrop}$), 6.75–7.00 (m, 5H; CH_{ar}), 7.05–7.50 (m, 14H; CH_{ar}), 7.70 (d, $J(H,H) = 7.5$ Hz; CH_{ar}), 8.05 (m, 2H; CH_{ar}), 8.43 ppm (d, $J(H,H) = 7.1$ Hz; CH_{ar}); $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$, 5 % CD_3CN, 25 °C, TMS): $\delta = 51.4$ (d, $J(P,C) = 25.7$ Hz; CH_{benz}), 61.1 (d, $J(P,C) = 14.0$ Hz; $CH_{olefintrop}$), 126.5 (br; CH_{ar}), 126.0 (CH_{ar}), 126.3 (d, $J(P,C) = 1.2$ Hz; CH_{ar}), 126.6 (d, $J(P,C) = 1.2$ Hz; CH_{ar}), 127.4 (CH_{ar}), 127.5 (CH_{ar}), 127.6 (CH_{ar}), 127.8 (CH_{ar}), 127.9 (CH_{ar}), 128.8 (d, $J(P,C) = 1.2$ Hz; CH_{ar}), 129.0 (d, $J(P,C) = 6.1$ Hz; CH_{ar}), 129.2 (d, $J(P,C) = 6.4$ Hz; CH_{ar}), 129.7 (d, $J(P,C) = 2.1$ Hz; CH_{ar}), 130.1 (br; CH_{ar}), 130.3 (d, $J(P,C) = 2.9$ Hz; CH_{ar}), 133.1 (d, $J(P,C) = 9.4$ Hz; CH_{ar}), 134.9 (d, $J(P,C) = 10.2$ Hz; CH_{ar}), 135.3 (m; C_{ar}), 135.6 (m; C_{ar}), 140.4 (m; C_{ar}), 140.8 (m; C_{ar}), 148.0 ppm (C_{ar}). The quaternary olefinic carbon atom was not observed. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$, 5 % CD_3CN, 25 °C, H_3PO_4): $\delta = 99.3$ ppm (d, $J(Rh,P) = 197$ Hz).

*[Ir(^Phtropp^Ph)_2]OTf (**6**)*: A solution of (*S*)-**4** (403 mg, 0.89 mmol) in THF (5 mL) was added dropwise to a solution of $[Ir_2(\mu_2\text{-}Cl)_2(coe)_4]$ (200 mg, 0.22 mmol) in THF (5 mL). The mixture was stirred for 1 h until the color of the solution changed from deep red to a very intense dark red. AgOTf (114 mg, 0.45 mmol) was added and the mixture was stirred for an additional 5 h. The suspension was then filtered and the filtrate was concentrated under reduced pressure. The resulting solid was dissolved in CH_2Cl_2 and layered with *n*-hexane. After 20 h at room temperature, 540 mg (97 % yield) of dark-red crystals were obtained.

M.p. 168–173 °C; ^{1}H NMR (300.1 MHz, CD_2Cl_2, 25 °C, TMS): $\delta = 5.18$ (m, $^2J(P,H) + {}^4J(P',H) = 14.0$ Hz, 2H; CH_{benz}), 6.10 (d, $J = 7.0$ Hz, 2H; CH_{ar}), 6.27 (t, $J = 8.8$ Hz, 2H; CH_{ar}), 6.33 (s, 2H; $CH_{olefintrop}$), 6.44–6.75 (m, 10H; CH_{ar}), 6.89–7.92 ppm (m, 32H; CH_{ar}); $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2, 25 °C, TMS): $\delta = 57.3$ (m, $^1J(P,C) + {}^3J(P',C) = 27.6$ Hz; CH_{benz}), 88.1 (t, $^2J(P,C_{cis}) + {}^2J(P,C_{trans}) = 10.6$ Hz; $CH_{olefintrop}$), 115.0 (t, $^2J(P,C_{cis}) + {}^2J(P,C_{trans}) = 6.6$ Hz; $C_{olefintrop}$), 126.5 (s; CH_{ar}), 127.3–127.6 (m; $CH_{orthoP} + CH_{ar}$), 127.8 (s; CH_{ar}), 128.2 (s; CH_{ar}), 128.3 (d, $J(P,C) = 1.4$ Hz; CH_{ar}), 128.5 (s; CH_{ar}), 129.0 (s; CH_{ar}), 129.1 (d, $^2J(P,C) = 13.8$ Hz; CH_{orthoP}), 129.3 (s; CH_{ar}), 129.6 (s; CH_{ar}), 129.8 (s; CH_{ar}), 130.9 (s; CH_{ar}), 131.3 (s; CH_{ar}), 132.3 (t, $^3J(P,C) = 4.3$ Hz; CH_{metaP}), 133.9 (t, $^3J(P,C) = 4.8$ Hz; CH_{metaP}), 134.3 (s; CH_{ar}), 135.2 (d, $J(P,C) = 4.1$ Hz; C_{trop}), 135.3 (d, $J(P,C) = 3.7$ Hz; C_{trop}), 135.6 (d, $^1J(P,C) = 12.3$ Hz; C_{ipsoP}), 137.0 (d, $J(P,C) = 0.9$ Hz; C_{trop}), 143.3 ppm (d, $J(P,C) = 0.9$ Hz; C_{ar}); $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2, 25 °C, H_3PO_4): $\delta = 52.9$ ppm (s); UV/Vis (THF): $\lambda = 368.5$ nm; ATR IR (neat): $\tilde{\nu} = 3053$ (m; CH stretch), 1575 (w), 1481 (m), 1439 (m; CC stretch), 1263 (s), 1136 (s), 1030 (s), 694 (s), 635 (s), 514 cm^{-1} (s).

*[Ir(H)_2(L_2)(H_2-^Phtropp^Ph)_2] **11a,b** (L = CH_2Cl_2 and/or OTf and/or agostic-H)*: Compound *rac*-**6** (20 mg, 0.016 mmol) was dissolved in CD_2Cl_2 (0.4 mL) in a resealable J-young NMR tube. The tube was cooled in liquid N_2 and the argon atmosphere was replaced with 1 bar of H_2. Upon warming to room temperature (**CAUTION**: the tube was under approximately 4 bar of H_2), the sample was vigorously shaken and the color of the solution gradually changed from deep red to yellow. The selected chemical shifts for **11a** listed below were assigned on the basis of two-dimensional $^{13}C\{^1H\}$ HMQC, HMBC, and $^{31}P\{^1H\}$ COSY NMR experiments.

^{1}H NMR (500.2 MHz, CD_2Cl_2, 25 °C, TMS): $\delta = -30.52$ (brs, 2H; $H_{hydride}$), 2.44 (dd, $^2J(H,H) = 15.1$, $^3J(H,H) = 5.5$ Hz, 2H; CH_c), 3.22 (d, $^2J(H,H) = 15.1$ Hz, 2H; CH_b), 3.81 (brs, 2H; CH_a), 5.58 (s, 2H; CH_{ar}), 5.61 (d, $^2J(P,H) = 14.4$ Hz, 1H; CH_{benz}), 7.07 (br, 2H; CH_{orthoP}), 7.45 ppm (br, 2H; CH_{orthoP}); ^{13}C NMR (125.8 MHz, CD_2Cl_2, 25 °C, TMS): $\delta = 39.9$ (s, 1C; CH_{CHbHc}), 47.3 (s, 1C; CH_{CHa}), 58.6 ppm (d, $^1J(P,C) = 60.6$ Hz, 1C; CH_{benz}); $^{31}P\{^1H\}$ NMR (202.5 MHz, CD_2Cl_2, 25 °C, H_3PO_4): $\delta = 45.0$ ppm (s).

Compound **11b** was formed in CD_2Cl_2 from **11a** at low temperatures. The selected chemical shifts given below were assigned on the basis of $^{13}C\{^1H\}$ HMQC, HMBC, and $^{31}P\{^1H\}$ COSY experiments at 190 K.

^{1}H NMR (500.2 MHz, CD_2Cl_2, −83 °C, TMS): $\delta = -29.12$ (q, $^2J(P,H) = 14.5$, $^2J(H,H) = 9.9$ Hz, 1H; $H_{hydride}$), −26.33 (q, $^2J(P,H) = 14.5$, $^2J(H,H) = 9.9$ Hz, 1H; $H_{hydride}$), 1.98 (d, $J = 13.5$ Hz, 1H; $CH_{c'}$), 2.15 (d, $J = 12.8$ Hz, 1H; CH_c), 3.01 (d, $J = 10.4$ Hz, 1H; $CH_{b'}$), 3.19 (d, $J = 10.7$ Hz, 1H; CH_b), 3.33 (s, 2H; $CH_{a'} + CH_a$), 5.50 (brs, 1H; $CH_{benz'}$), 5.67 ppm (brs, 1H; CH_{benz}); ^{13}C NMR (125.8 MHz, CD_2Cl_2, −83 °C, TMS): $\delta = 39.5$ (s, 1C; $CH_{CHb'Hc'}$), 40.7 (s, 1C; CH_{CHbHc}), 47.1 (s, 1C; $CH_{CHa+CHa'}$), 55.9 (1C; CH_{benz}), 56.7 ppm (1C; $CH_{benz'}$); $^{31}P\{^1H\}$ NMR (202.5 MHz, CD_2Cl_2, −83 °C, H_3PO_4): $\delta = 49.0$ ppm (s).

Catalyses

*1,4-Addition of PhB(OH)_2 to cyclohex-2-enone (**7**)*: A solution of $[Rh_2(\mu_2\text{-}Cl)_2(C_2H_4)_4]$ (10 mg, 26 μmol) and (*S*)-**4** (24 mg, 53 μmol) in 1,4-dioxane (3 mL) was stirred for 15 min at room temperature and then KOH (0.3 mL of a 1.7 M solution, 0.5 mmol) was added and the mixture stirred for a further 5 min. $PhB(OH)_2$ (370 mg, 3.0 mmol) was added to the resulting orange solution and after 5 min of stirring cyclohex-2-enone (**7**) (103 mg, 1.0 mmol) was added. The mixture was kept at 55 °C for 2 h whereby the conversion was followed by GC (capillary HP-5: 90 °C for 3 min, then heating to 180 °C at a rate of 3 °C min^{-1}; flow rate: 1.6 mL H_2 min^{-1}; retention times: **7**: 2.93 min; **9**: 18.6 min). Under these conditions, the following conversions were obtained for various catalyst loadings: 5 mol %: 86 %; 3 mol %: 81 %; 1 mol %: 51 %. From the experiment with 5 mol % catalyst loading the product was isolated as follows: addition of saturated aqueous $NaHCO_3$ (5 mL), extraction with *tert*-butyl methyl ether (TBME; 3 × 10 mL), drying with $MgSO_4$, and concentration under reduced pressure left a brown oil that was purified by using flash chromatography (silica gel, hexane/TBME 1:0.6) to provide 420 mg of **9** as a slightly yellow oil (yield 82 %).

The enantiomeric excess (*ee* 92–95 %) was determined by chiral HPLC (Chiralcel OD-H; eluent: *n*-hexane/*i*PrOH 98:2; retention times: (*R*)-**9**: 26.3 min; (*S*)-**9**: 31.3 min). The major product had the *R* configuration, as judged by a comparison with the reported optical rotation: $[\alpha]_D^{20} = +17.3$ ($c = 0.75$ in $CHCl_3$).[23]

*1,4-Addition of PhB(OH)_2 to N-benzylmaleimide (1-benzylpyrrole-2,5-dione) (**8**)*: A solution of $[Rh_2(\mu_2\text{-}Cl)_2(C_2H_4)_4]$ (5 mg, 13 μmol) and (*S*)-**4** (13 mg, 28 μmol) in 1,4-dioxane (2.5 mL) was stirred for 15 min at room temperature and then KOH (0.25 mL of a 1.0 M solution, 0.25 mmol) was added. The mixture was stirred for a further 5 min. Subsequently $PhB(OH)_2$ (185 mg, 1.5 mmol) was added to the orange solution and then, after 5 min of stirring, *N*-benzylmaleimide (**8**) (97 mg, 0.5 mmol) was added. The mixture was kept at 55 °C for 2 h. GC analysis (capillary HP-5: 90 °C for 3 min, then heating to 180 °C at a rate of 4 °C min^{-1}; flow rate: 1.6 mL H_2 min^{-1}; retention times: **8**: 23.1 min; **10**: 34.1 min) of the crude reaction mixture indicated complete conversion (> 98 %). Saturated aqueous $NaHCO_3$ (5 mL) was then added. Extraction with TBME (3 × 10 mL), drying with $MgSO_4$, and concentration under reduced pressure gave a brown oil which was purified by using flash chromatography (silica gel, hexane/TBME 1:0.8) to provide 1-benzyl-3-phenylpyrrolidine-2,5-dione (**10**) as a colorless solid (isolated yield: 93 %). Complete conversion within 2 h at 55 °C was also observed with a catalyst loading of only 0.1 mol %.

The enantiomeric excess *ee* (80 %) was determined by means of chiral HPLC (Chiralcel OD-H: *n*-hexane/*i*PrOH 90:10; retention times: (*S*)-**10**: 21.1 min; (*R*)-**10**: 25.3 min). The major product had the *R* configuration, as judged by a comparison with the reported optical rotation:[24] $[\alpha]_D^{20} = -50.1$ ($c = 0.82$ in $CHCl_3$).

*Hydrogenation of itaconic acid (2-methylenesuccinic acid) (**12a**)*: Under the conditions specified in Table 2, a 50 mL Teflon-sealed Schlenk tube was charged with a mixture of itaconic acid (131 mg, 1.00 mmol), the solvent (0.6 mL) (see Table 2), and catalyst (*S,S*)-**6** in CH_2Cl_2 (0.5 mL) (for S/C ratios see Table 2). This mixture was frozen in liquid N_2. The reaction flask was evacuated and purged with 1 bar of H_2. Upon warming to room temperature, whereby the pressure of H_2 increased to about 2.5 bar, the color of the solution changed from dark brown to pale yellow. After 2 h of stirring the solution at room temperature, the conversion was checked with ^{1}H NMR spectroscopic analysis by integration of representative signals of **12a** and **13a** in $[D_6]$DMSO.

Table 2. Solvent, reaction time, S/C ratio, conversion, and *ee* for the catalyzed hydrogenation reactions of **12a–c** and **14** using (*S*,*S*)-**6** as catalyst at a hydrogen pressure of ≈2.5 bar and $T = 298$ K.

Entry	Solvent	t [min]	S/C ratio	Conversion [%]	*ee* [%]
reactions with itaconic acid (**12a**)					
1	MeOH	120	200	>99	30
2	THF	120	200	>99	21
3	MeOH	120	4000	74	23
4	MeOH	120	10000	39	n.d.[a]
reactions with 2-methylenesuccinic acid dimethyl ester (**12b**)					
5	CH_2Cl_2	60	4000	90	60
6	CH_2Cl_2	1200	10000	85	60
reactions with 2-methylenesuccinic acid dibutyl ester (**12c**)					
7	CH_2Cl_2	120	200	>99	67
8	CH_2Cl_2	120	500	>99	n.d.[a]
9	CH_2Cl_2	120	2000	>99	58
10	CH_2Cl_2	120	10000	23	n.d.[a]
reactions with 2-acetamidoacrylic acid methyl ester (**14**)					
11	CH_2Cl_2	120	100	>99	39
12	CH_2Cl_2	120	4000	23	39
13	CH_2Cl_2	120	10000	7	39

[a] n.d. = not determined.

The enantiomeric excess was determined by using the corresponding 2-methylsuccinic acid dimethyl ester (**13b**), which was obtained by methylation of **13a** with $TMSCHN_2$ in MeOH/benzene, by GC (chiral capillary: Lipodex-E, 70 °C, heating rate: 1 °C min^{-1}; final temperature: 110 °C; flow rate: 0.8 mL H_2 min^{-1}; retention times: (*S*)-**13b**: 18.6 min; (*R*)-**13b**: 19.2 min; **12b**: 23.7 min).[25] The major isomer had the *R* configuration.

*Hydrogenation of dimethyl itaconate (2-methylenesuccinic acid dimethyl ester) (**12b**)*: Under the conditions specified in Table 2, a 300 mL Teflon-sealed Schlenk tube was charged with **12b** (entry 5: 316 mg, 2 mmol; entry 6: 790 mg, 5 mmol), CH_2Cl_2 (9.5 mL), and (*S*,*S*)-**6** (0.5 mL of a 1 mM solution in CH_2Cl_2). The solution was frozen in liquid N_2 and the argon atmosphere replaced by 1 bar of H_2. Upon warming to room temperature, whereby the pressure of H_2 increased to about 2.5 bar, the solution changed from dark red to colorless. After the indicated reaction times, yields and enantioselectivities were determined by using GC.

The configuration of the major product was *R* (by comparison with a sample of (*R*)-2-methylsuccinic acid dimethyl ester purchased from Fluka).

*Hydrogenation of dibutyl itaconate (2-methylenesuccinic acid dibutyl ester) (**12c**)*: Under the conditions specified in Table 2, a 50 mL Teflon-sealed Schlenk tube was charged with dibutyl itaconate (**12c**) (242 mg, 1.0 mmol), CH_2Cl_2 (0.5 mL), and various amounts of (*S*,*S*)-**6** (50 μmol, 20 μmol, 5 μmol, 1 μmol, entries 7–10) in CH_2Cl_2 (0.5 mL). The mixture was frozen in liquid N_2 and the flask evacuated and purged with 1 bar of H_2. Upon warming to room temperature, the color of the solution changed from dark brown to pale yellow. After 2 h of stirring the solution at room temperature, the conversion was checked by ^{1}H NMR spectroscopic analysis by integration of representative signals of **12c** and **13c** in $CDCl_3$. In one experiment (entry 7), the solvent was evaporated and the resulting orange oil was distilled at 0.02 mbar to provide 2-methylsuccinic acid dibutyl ester as a colorless liquid (isolated yield: 224 mg, 92%).

^{1}H NMR (300.1 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 0.86$ (t, ^3J(H,H) = 7.4 Hz, 6H; CH_3(Bu)), 1.17 (d, ^3J(H,H) = 7.1 Hz, 3H; CH_3), 1.21–1.36 (m, 4H; CH_2(Bu)), 1.42–1.55 (m, 4H; CH_2(Bu)), 2.29 (dd, ^2J(H,H) = 16.5, ^3J(H,H) = 5.7 Hz, 1H; CH_2), 2.82 (dd, ^2J(H,H) = 16.5, ^3J(H,H) = 8.5 Hz, 1H; CH_2), 2.95–3.08 (m, 1H; CH), 4.00–4.13 ppm (m, 2H; OCH_2(Bu)); ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 13.5$ (CH_3(Bu)), 16.9 (CH_3), 19.1 (CH_2(Bu)), 30.7 (CH_2(Bu)), 35.9 (CH), 37.6 (CH_2), 64.0 (OCH_2(Bu)), 64.1 (OCH_2Bu), 171.3 (C=O), 174.6 ppm (C=O).

To determine the enantiomeric excess, **13c** was converted into **13a** by saponification with KOH/H_2O in boiling EtOH which was subsequently methylated with $TMSCHN_2$ to give **13b**. The resulting product **13b** was analyzed by means of GC (for conditions, see above), showing an enantiomeric excess of 58–67%. The *R* configuration was the major isomer to be obtained.

*Hydrogenation of 2-acetamidoacrylic acid methyl ester (**14**)*: Under the conditions specified in Table 2, a 50 mL Teflon-sealed Schlenk tube was charged with 2-acetamidoacrylic acid methyl ester **14** (143 mg, 1.0 mmol), CH_2Cl_2 (1.5 mL), and various amounts of (*S*,*S*)-**6** (100 μmol, 2.5 μmol, 1 μmol, entries 11–13) in CH_2Cl_2 (0.5 mL). The mixture was frozen in liquid N_2 and the flask evacuated and purged with 1 bar of H_2. Upon warming to room temperature, the color of the solution changed from dark brown to pale yellow. After 2 h of stirring the solution at room temperature, yields and enantioselectivities were determined by means of GC (chiral capillary: Lipodex-E; 80 °C (3 min); heating rate: 3 °C min^{-1}; final temperature: 170 °C; flow rate: 0.8 mL H2 min^{-1}; retention times: (*S*)-**15**: 23.2 min; (*R*)-**15**: 23.8 min; **14**: 22.6 min).

The configuration of the major product was *S* (by comparison with a sample of *N*-acetyl-D-alanine methyl ester (*R*)-**15** purchased from Bachem).

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[13] We applied a slightly modified procedure which gives **1** in a quantitative (>97%) isolated yield; see the Experimental Section for details.
[14] Crystal structure of (*S*)-**4**: $C_{33}H_{25}P$; orthorhombic; space group $P2_12_12_1$; $a=11.4415(7)$, $b=13.6491(9)$, $c=15.3552(9)$ Å; $V=2398(1)$ Å^3; $Z=4$; $\rho_{calcd}=1.253$ Mg m^{-3}; crystal dimensions $0.58\times0.51\times0.32$ mm; Bruker SMART Apex diffractometer; $Mo_{K\alpha}$ radiation; 200 K; $2\theta_{max}=56.56°$; 19578 reflections, 5965 independent ($R_{int}=0.0223$), direct methods; full-matrix least-squares refinement versus F^2 with SHELXTL (version 6.12) and SHELXL-97; 307 parameters, 0 restraints; $R_1=0.0389$ and wR_2 (all data) $=0.0971$; max/min residual electron density $=0.313/-0.191$ e Å^{-3}. Crystal structure of (*S*,*S*)-**6**: $C_{67}H_{50}F_3IrO_3P_2S$; monoclinic; space group $P2_1/n$; $a=21.465(5)$, $b=14.328(3)$, $c=22.546(5)$ Å; $\beta=114.37(1)°$; $V=6316(2)$ Å^3; $Z=4$; $\rho_{calcd}=1.489$ Mg m^{-3}; crystal dimensions $0.31\times0.22\times0.18$ mm; Bruker SMART Apex diffractometer; $Mo_{K\alpha}$ radiation; 200 K; $2\theta_{max}=43.94°$; 26029 reflections, 7679 independent ($R_{int}=0.0526$); direct methods; full-matrix least-squares refinement versus F^2 with SHELXTL (version 6.12) and SHELXL-97; 714 parameters; 923 restraints; $R_1=0.0751$ and wR_2 (all data) $=0.2135$; max/min residual electron density $=4.110/-1.673$ e Å^{-3}. Crystal structure of (*S*,*S*)-**11c**: $C_{68}H_{58}Cl_2F_3IrO_3P_2S$; monoclinic; space group $P2_1/c$; $a=25.555(4)$, $b=10.265(2)$, $c=25.414(4)$ Å; $\beta=109.14(1)°$; $V=6298(1)$ Å^3; $Z=4$; $\rho_{calcd}=1.500$ Mg m^{-3}; crystal dimensions $0.4\times0.2\times0.1$ mm; Bruker SMART PLATFORM diffractometer equipped with CCD Detector; $Mo_{K\alpha}$ radiation; 293 K; $2\theta_{max}=39.56°$; 32855 reflections, 5689 independent ($R_{int}=0.1092$); direct methods; empirical absorption correction SADABS (version 2.03); full-matrix least-squares refinement versus F^2 with SHELXTL (version 6.12); 748 parameters; 984 restraints; $R_1=0.0418$ and wR_2 (all data) $=0.0897$; max/min residual electron density $=0.79/-0.51$ e Å^{-3}. CCDC-285365 ((*S*)-**4**), CCDC-284999 ((*S*,*S*)-**6**), and CCDC-285000 ((*S*,*S*)-**11c**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
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