DOI: 10.1002/adsc.200800221

Chiral Bis(*N*-arylamino)phosphine-oxazolines: Synthesis and Application in Asymmetric Catalysis

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Received: April 11, 2008; Published online: August 19, 2008

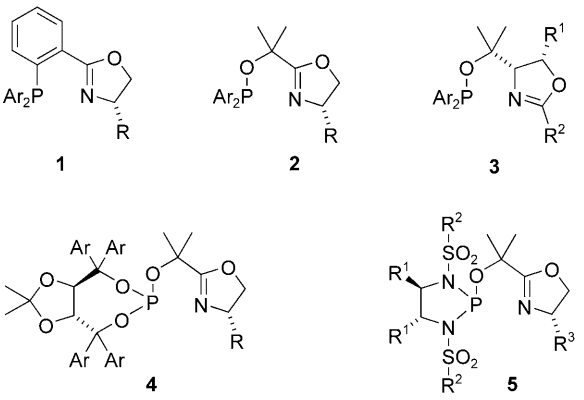
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.200800221.

Abstract: *N*-Arylation or *N*-alkylation of chiral 1,2-diamines followed by ring closure with phosphorus trichloride (PCl_3) and subsequent coupling with an oxazoline alcohol resulted in a new class of N,P ligands. The corresponding iridium tetrakis[3,5-bis(trifluormethyl)phenyl]borate (BAr_F) complexes were found to be efficient catalysts for the enantioselective hydrogenation of unfunctionalized olefins and α,β-unsaturated carboxylic esters.

Keywords: alkenes; asymmetric hydrogenation; homogeneous catalysis; iridium; N,P ligands

Introduction

Iridium complexes with chiral N,P ligands have emerged as efficient catalysts for the asymmetric hydrogenation of unfunctionalized alkenes and certain classes of functionalized olefins for which no suitable chiral catalysts were available before.[1–5] After initial studies of iridium catalysts based on phosphinooxazolines **1** (PHOX ligands),[6] we and others developed many further chiral oxazoline ligands, such as phosphinites **2** and **3**,[7] which have considerably extended the application range of Ir-catalyzed asymmetric hydrogenation (for non-oxazoline-based ligands, see refs.[1–3,5]). As further variations of this structural motif we reported phosphite-oxazolines **4** and bis(*N*-sulfonylamino)phosphine-oxazolines **5**.[8] Although Ir complexes of ligands **5** gave high enantioselectivites in the hydrogenation of unfunctionalized olefins, their activity was low, and consequently, only low conversions were achieved. In view of the encouranging enantioselectivities, we decided to study additional structural variants of these ligands with *N*-aryl instead of *N*-sulfonamido groups, to see if a more electron-rich P atom would have a positive effect on catalytic activity. Herein, we describe the synthesis of a series of bis(*N*-arylamino)phosphine-oxazolines and their use in the iridium-catalyzed hydrogenation of unfunctionalized olefins and α,β-unsaturated carboxylic esters.

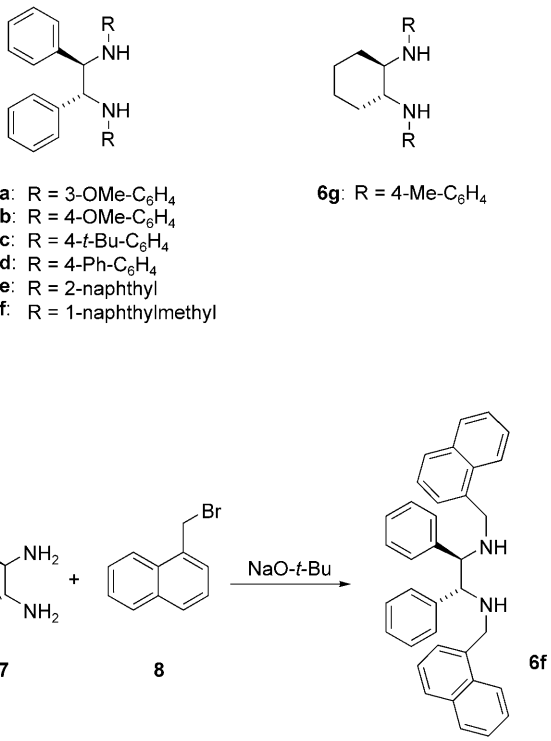


Results and Discussion

Synthesis of Bis(*N*-arylamino)phosphine-oxazolines

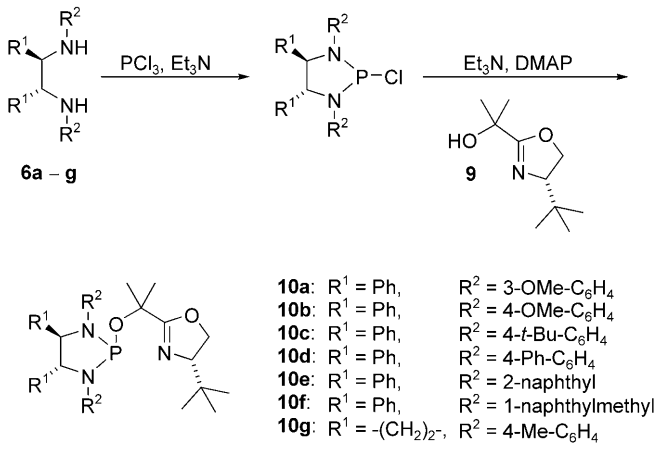
The synthesis of ligands **6a–g** started from commercially available, enantiomerically pure 1,2-diphenylethylenediamine and 1,2-diaminocyclohexane. Amination according to the procedure of Wagaw and Buchwald[9] led to the arylated diamines **6a–e,g** in 31–99% yield.

For the synthesis of the arylmethyl-substituted diamine **6f** an alternative route was chosen: 1-methylnaphthalene was converted to its brominated product **8** in 95% yield,[10] which was reacted with diamine **7** and sodium *tert*-butoxide to give the desired alkylated diamine **6f** (Scheme 1).



Scheme 1. Synthesis of diamine **6f**.

The secondary amines **6a–g** were treated with phosphorus trichloride and triethylamine at −78 °C in toluene and slowly warmed to room temperature overnight. Slow warming was essential to suppress the formation of by-products. After filtration of the suspension and removal of the solvent, yellow solids were obtained and characterized by ^{1}H and ^{31}P NMR spectroscopy. These air- and moisture-sensitive *P*-chlorodiazaphospholidines were directly converted into the corresponding N,P ligands **10a–g** by stirring with triethylamine, DMAP and oxazoline alcohol **9** overnight in moderate to good yields of 38–64% (Scheme 2). In one case (R^2 = 2-naphthyl) the yield was only 11%, possibly due to steric hindrance. These ligands were found to be air-stable solids, which can be stored at room temperature for several months without decomposition.



Scheme 2. Synthesis of bis(*N*-arylamino)phosphine-oxazoline ligands **10a–g**.

Attempts to prepare analogous ligands from other secondary diamines such as (1*R*,2*R*)-diphenylethylene-1,2-diamine substituted at the nitrogen atoms with 2-methoxyphenyl or 1-naphthyl groups, or (*R*)-2,2′-bis[(4-methoxyphenyl)amino]-1,1′-binaphthalene failed. The corresponding ligands could not be isolated, although in the first two cases, NMR spectroscopy indicated that the cyclic chlorophosphine had actually formed.

Structural information about the bis(*N*-arylamino)-phosphine-oxazolines ligands geometry could be obtained from a crystal structure of an Rh complex derived from a phenyloxazoline analogue of ligand **10g** (Figure 1).[11] Addition of the ligand to a solution of $[Rh(COD)Cl]_2$ followed by anion exchange from Cl^- to PF_6^- afforded the complex in good yield. Slow recrystallization from ethyl acetate/cyclohexane at −18 °C yielded orange needles suitable for X-ray analysis.

The diazaphospholidine ring of the ligand adopts a nearly planar conformation. The tolyl groups shield the coordination sphere next to the phosphorus atom. These structural features are similar to those of the bis(*N*-sulfonylamino)phosphine-oxazolines **5**, implying

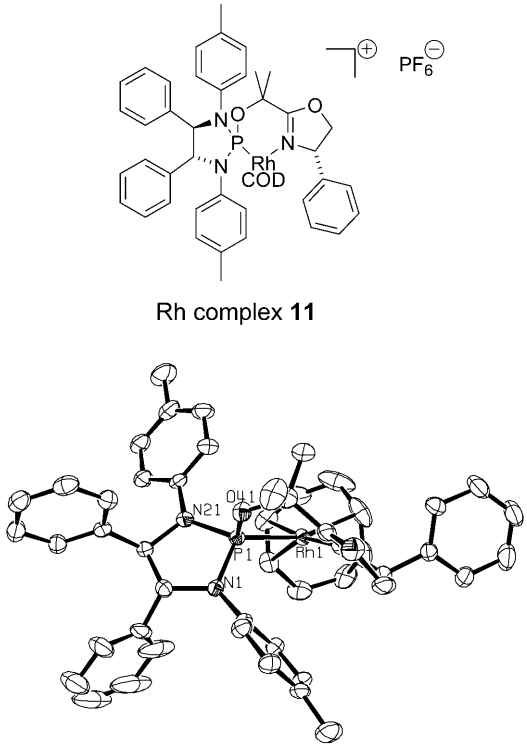
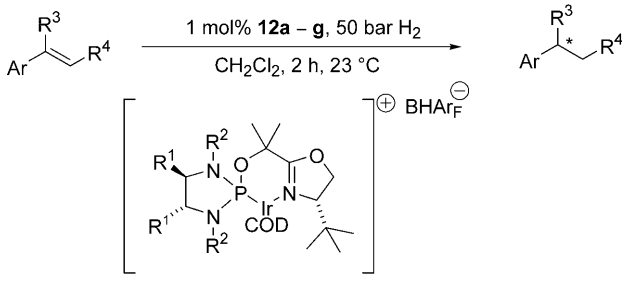


Figure 1. Crystal structure of Rh complex **11** derived from a phenyloxazoline analogue of ligand **10g**.

that substitution of the electron-withdrawing arylsulfonamide groups of ligand **5** with the more electron-donating arylamino groups of ligand **10** alters mainly the electronic rather than the steric properties of the ligand.

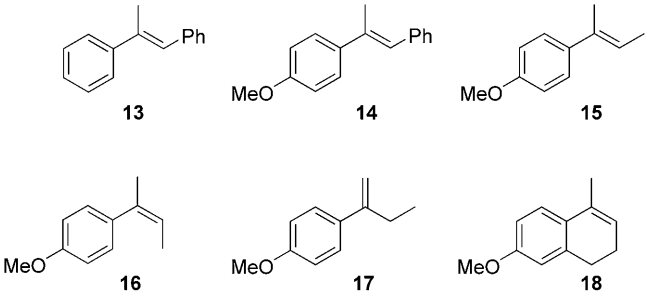
Iridium-Catalyzed Hydrogenation

Iridium complexes of bis(*N*-arylamino)phosphine-oxazoline ligands **10a–g** were synthesized using our standard protocol: a solution of $[Ir(COD)Cl]_2$ and the N,P ligand in dichloromethane was heated under reflux followed by ion exchange by treatment with $NaBAr_F$ (sodium tetrakis[3,5-bis(trifluormethyl)phenyl]borate) in a two-phase dichloromethane-water system. Subsequent chromatography on a silica gel column afforded the desired iridium complexes **12a–g** in good yields. These complexes were then tested as catalysts in the hydrogenation of unfunctionalized olefins **13–18**, using 1 mol% of catalyst in dichloromethane at room temperature for 2 h under 50 bar hydrogen pressure (Scheme 3). Lower catalyst loading or reduction of hydrogen pressure resulted in incomplete conversions and lower enantioselectivities.



12a: R^1 = Ph, R^2 = 3-OMe-C_6H_4
12b: R^1 = Ph, R^2 = 4-OMe-C_6H_4
12c: R^1 = Ph, R^2 = 4-*t*-Bu-C_6H_4
12d: R^1 = Ph, R^2 = 4-Ph-C_6H_4
12e: R^1 = Ph, R^2 = 2-naphthyl
12f: R^1 = Ph, R^2 = 1-naphthylmethyl
12g: R^1 = -$(CH_2)_2$-, R^2 = 4-Me-C_6H_4

Scheme 3. Iridium-catalyzed hydrogenations of unfunctionalized olefins.



In the hydrogenation of (*E*)-1,2-diphenylpropene **13**, catalysts **12b** and **12g** derived from diphenylethylenediamine and cyclohexanediamine, respectively, showed the highest enantioselectivity (>99% *ee*) (see Table 1, entries 1 and 2). Catalysts **12c–e** also exerted high enantiocontrol of >98% *ee* (see Supporting Information). The 3-methoxyphenyl-substituted complex **12a** and the 1-naphthylmethyl-substituted complex **12f** led to inferior enantiomeric excesses of 95% and 88%. In comparison to the analogous tosylated ligand **5a**[8] [R^1 = -$(CH_2)_4$-, R^2 = 4-tolyl, R^3 = *tert*-butyl, 15% conversion, 94% *ee*], these new N,P ligands showed higher enantiocontrol and activity. Similar trends were also observed with the coresponding 4-methoxy-substituted substrate **14** (see entries 3, 4 and Supporting Information).

Table 1. Enantioselective hydrogenations of olefins with catalysts **12a–g**.

Entry	Substrate	Catalyst	Conversion [%][a]	*ee* [%][b]
1	**13**	**12b**	>99	>99 (*R*)
2	**13**	**12g**	>99	>99 (*R*)
3	**14**	**12b**	>99	>99 (*R*)
4	**14**	**12g**	>99	>99 (*R*)
5	**15**	**12c**	>99	93 (*R*)
6	**15**	**12d**	>99	94 (*R*)
7	**16**	**12f**	>99	88 (*S*)
8	**17**	**12f**	>99	70 (*S*)
9	**18**	**12a**	>99	82 (*S*)
10	**18**	**12b**	>99	82 (*S*)
11	**18**	**12e**	>99	83 (*S*)
12	**18**	**12f**	>99	82 (*S*)

[a] Determined by GC.
[b] Determined by GC or HPLC using chiral columns.

(*E*)- and (*Z*)-2-aryl-2-butenes are more demanding substrates which usually react with lower enantiocontrol than the corresponding methylstilbenes **13** and **14**.[1–8] With (*E*)-2-(4-methoxyphenyl)-2-butene **15** the best results were achieved with ligands **12c** and **12d** with up to 94% *ee* (Table 1, entries 5 and 6), which exceed the enantioselectivities achieved with PHOX ligand **1a** (>99% conversion, 81% *ee*) and the tosylated ligand **5a** (65% conversion, 84% *ee*).[8]

For the corresponding (*Z*)-isomer **16**, complex **12f** with 1-naphthylmethyl substituents proved to be the best catalyst affording 88% *ee*, whereas all other complexes gave inferior results (52 and 79% *ee*) (see Table 1, entry 7 and Supporting Information).

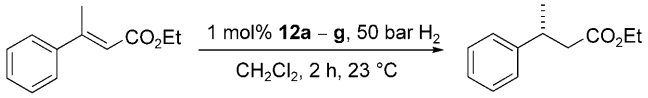
Complex **12f** was also the best catalyst for the reduction of 2-(4-methoxyphenyl)butene **17** (entry 8) with an enantiocontrol of 70% *ee*. A clear decrease in enantioselectivity to 14% *ee* was observed by using ligand **12g** with a 1,2-diaminocyclohexane backbone instead of the (1*R*, 2*R*)-diphenylethylene-1,2-diamine backbone (see Supporting Information).

Using 6-methoxy-1-methyl-3,4-dihydronaphthalene **18** as substrate a similar trend could be observed. Independently of the substitution pattern of the *N*-aryl substituents, all catalysts (**12a**, **12b**, **12e** and **12f**) based on the 1,2-diphenylethylene-1,2-diamine framework showed enantioselectivites between 82–83% *ee*. Only complex **12g**, with a cyclohexane-1,2-diamine backbone, gave a lower *ee* of 72% (see Table 1, entries 9–12 and Supporting Information). In comparison, the related tosylated ligand **5a** gave very poor results for this substrate (>99% conversion, 18% *ee*).

Hydrogenation of *N*-(1-*p*henylethylidene)aniline, (*E*)-2-methyl-3-phenylprop-2-enol and 3-methylcyclohexenone resulted in low enantioselectivities (see Supporting Information).

α,β-Unsaturated carboxylic acids can be reduced with high enantioselectivity using Ru catalysts.[12,13] For analogous esters only a few suitable catalytic systems have been reported so far. The best results have been achieved by semicorrin cobalt complexes[14] using sodium borohydride as reducing agent, and with certain iridium complexes.[4,5b,7,16] Complexes **12a–g** proved to be very efficient catalysts for this class of substrate. In the hydrogenation of ethyl β-methylcinnamate **19** excellent enantioselectivities of up to 98% *ee* were obtained (Table 2).

Table 2. Enantioselective Ir-catalyzed hydrogenation of ethyl β-methylcinnamate **19**.[a]

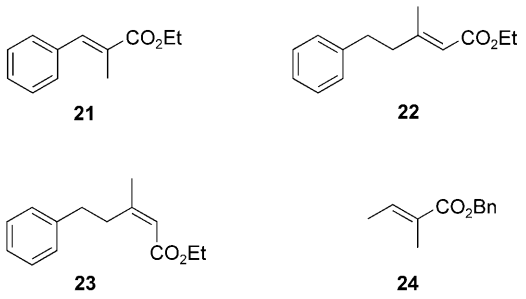


19 (*R*)-**20**

Entry	Catalyst	Conversion [%][b]	*ee* [%][c]
1	**12a**	94	97 (*R*)
2	**12b**	>99	97 (*R*)
3	**12c**	>99	98 (*R*)
4	**12d**	>99	96 (*R*)
5	**12e**	>99	97 (*R*)
6	**12f**	97	90 (*R*)
7	**12g**	>99	96 (*R*)

[a] All reactions were carried out with 1 mol% of catalyst in CH_2Cl_2 at 50 bar H_2 at 23 °C for 2 h.
[b] Determined by GC.
[c] Determined by GC or HPLC using chiral columns.

Ethyl α-methylcinnamate **21** reacted with lower but still respectabele enantioselectivity (Table 3). In this case, catalysts **12a** and **12b** gave the best results with up to 88% *ee*. These values are comparable to the enantioselectivities reported for the hydrogenation of the corresponding free acid with a ruthenium(H_8-BINAP) catalyst.[13b] In comparison, PHOX ligand **1a** afforded only 3% *ee* for this substrate.



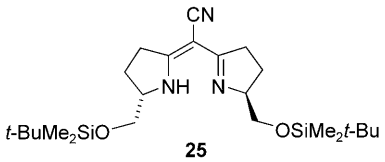
21 **22** **23** **24**

Table 3. Enantioselective Ir-catalyzed hydrogenation of α,β-unsaturated esters **21**–**24**.[a]

Entry	Substrate	Catalyst	Conversion [%][b]	*ee* [%][c]
1	**21**	**12a**	71	88 (*S*)
2	**21**	**12b**	95	88 (*S*)
3	**22**	**12a**	>99	88 (*S*)[17]
4	**22**	**12c**	>99	88 (*S*)
5	**22**	**12e**	>99	88 (*S*)
6	**22**	**12g**	>99	88 (*S*)
7	**23**	**12b**	>99	90 (*R*)
8	**24**	**12e**	>99	72 (*S*)[18]

[a] All reactions were carried out with 1 mol% of catalyst in CH_2Cl_2 at 50 bar H_2 at 23 °C for 2 h.
[b] Determined by GC.
[c] Determined by GC or HPLC using chiral columns.

For (*E*)- and (*Z*)-ethyl 3-methyl-5-phenylpent-2-enoates **22** and **23** the highest enantioselectivities so far have been achieved with a cobalt complex derived from the semicorrin ligand **25** (94% *ee* for **22** and **23**).[14]



25

Iridium catalysts **12a**, **12c**, **12e**, and **12g** all gave 88% *ee* in the hydrogenation of (*E*)-ester **22** (Table 3, entries 3 to 6). (*Z*)-Ester **23** reacted with somewhat higher enantioselectivity of 90% *ee* with catalyst **12b**, whereas complexes **12d** and **12g** gave 86% and 83% *ee*. In comparison, PHOX ligand **1a** led to 72% and 78% *ee* for (*E*)- and (*Z*)-ester **22** and **23**, respectively (see Supporting Information).

The benzyl ester of (*E*)-tiglic acid **24** afforded only moderate enantioselectivities of up to 72% *ee* with catalyst **12e** (Table 3, Entry 8), whereas up to 90% *ee* was reported for the hydrogenation of the corresponding free acid with a BINAP-like ligand derived from equilenin.[15]

Conclusions

Bis(*N*-arylamino)phosphine-oxazolines have proved to be efficient ligands for the iridium-catalyzed asymmetric hydrogenation of unfunctionalized olefins and, particularly, α,β-unsaturated carboxylic esters. Our results show that these ligands form more reactive iridium catalysts than the previously reported *N*-sulfonyl derivatives. Crystal structure data indicate that the two ligand classes possess sterically similar coordination spheres, implying that the higher reactivity primarily results from an electronic influence of the more electron-rich phosphorus atom of the *N*-aryl-substituted ligands rather than from steric effects. In view of the modular nature and easy synthesis from readily available chiral precursors, these ligands should also prove useful for other applications in asymmetric catalysis.

Experimental Section

Typical Procedures for the Bis-Arylation of Chiral Diamines

(1*R*,2*R*)-1,2-*N*,*N*′-Bis(3-methoxyphenylamino)-1,2-diphenylethane (6a): $Pd_2(dba)_3$ (0.05 equiv.) and *rac*-BINAP (0.10 equiv.) were premixed in toluene (20 mL mmol^{-1} diamine) for one hour at room temperature. 3-Bromoanisole (1.8 equiv.) and sodium *tert*-butoxide (2.8 equiv.) were added and the solution stirred for further 30 min. After adding (1*R*,2*R*)-(+)-1,2-diphenyl-1,2-ethanediamine (1 equiv.) the reaction mixture was refluxed for 4 h and after cooling to room temperature hydrolyzed with water. The solution was filtered and dried over Na_2SO_4. The solvent was evaporated and the residue was purified by chromatography [5×10 cm, hexane/ethyl acetate (10:1 to 5:1)] and recrystallization (CH_2Cl_2/hexane) to give the product as a white solid; yield: 80%.

1-(Bromomethyl)naphthalene (8): 1-Methylnaphthalene (1.4 g, 10 mmol) was dissolved in dry benzene (100 mL) and NBS (1.79 g, 10 mmol) and catalytic amounts of AIBN were added. The reaction mixture was heated at 80 °C for 2.5 h. After cooling to room temperature the reaction mixture was filtered through Celite and the solvent evaporated. The residue was purified by chromatography [hexane/ethyl acetate (5:1)] and subsequent recrystallization (pentane/dichloromethane) to give the product as a colorless solid; yield: 2.11 g (95%).

(1*R*,2*R*)-*N*,*N*′-Bis[(1-naphthyl)methyl]-1,2-diphenylethane-1,2-diamine (6f): (1*R*,2*R*)-Diphenylethylene-1,2-diamine **7** (740 mg, 3.5 mmol) was dissolved in toluene (50 mL) and NaO-*t*-Bu (978 mg, 9.8 mmol) was added. After stirring for 1.5 h at room temperature, 1-(bromomethyl)-naphthalene **8** (1.40 g, 6.3 mmol) was added and the reaction mixture heated under reflux for 2 h. After cooling to room temperature the mixture was quenched with water (5 mL), the phases were separated and the combined organic phases dried over $MgSO_4$. The residue obtained after evaporation of the solvent was purified by chromatography [hexane/ethyl acetate (10:1)] to give the product as a pale yellow solid; yield: 39%.

General Procedure for the Synthesis of Ligands 10a–g

(4*R*,5*R*)-1,3-Bis(3-methoxyphenyl)-2-{2-[(*S*)-4-*tert*-butyl-4,5-dihydrooxazol-2-yl]propan-2-yl}-4,5-diphenyl[1,3,2]diazaphospholidine (10a): Triethylamine (4.2 equiv.) was dissolved in toluene (1.8 mL mmol^{-1}) and cooled to −78 °C. Freshly distilled phosphorus trichoride (2.1 equiv.) and a suspension of diamine **6a** (1 equiv.) in toluene (10 mL mmol^{-1}) were added and the reaction mixture was allowed to slowly warm to room temperature overnight. After filtration under argon and removal of the solvent under high vacuum, the residue was dissolved in toluene (7.4 mL mmol^{-1}) and cooled to −78 °C. A solution of NEt_3 (10 equiv.) and DMAP (1.02 equiv.) in toluene (1 mL mmol^{-1}) was added very slowly dropwise followed by a solution of the oxazoline alcohol **9** (1 equiv.) in toluene (3 mL mmol^{-1}). The reaction mixture was allowed to slowly warm to room temperature overnight. After column chromatography (4×10 cm, hexane/ethyl acetate, 5/1) the desired product was obtained as white solid; yield: 61%.

General Procedure for the Synthesis of Iridium Complexes of Ligands 12a–g

Ligand (1 equiv.) and $[Ir(COD)Cl]_2$ (0.5 equiv.) were dissolved in dichloromethane (36 mL mmol^{-1}) and heated under reflux for 1 h. After cooling to room temperature $NaBAr_F$ (1.5 equiv.) and water (11 mL mmol^{-1}) were added and the reaction mixture was stirred vigorously for 20 min. The phases were separated and the aqueous phase was extracted twice with dichloromethane. The combined organic phases were washed with water and the solvent was evaporated. The residue was purified by chromatography (dichloromethane, 4×10 cm) to give the product.

Rhodium Complex 11

Ligand **10g** (150 mg, 0.240 mmol) and $[Rh(COD)Cl]_2$ (61 mg, 124 mmol) were dissolved in dichloromethane (1.3 mL) and stirred for two hours at room temperature. Ammonium hexafluorophosphate (57 mg, 0.350 mmol) was added and the reaction mixture was stirred overnight. The suspension was washed with water (4 mL) and the solvent evaporated. Crystals suitable for X-ray analysis were obtained by recrystallization from ethyl acetate/cyclohexane at −18 °C.

General Procedure for Ir-Catalyzed Hydrogenation

The alkene (1 equiv.) and Ir complex (1 mol%) were dissolved in CH_2Cl_2 (10 mL mmol^{-1} substrate) in a high-pressure autoclave (without exclusion of oxygen), pressurized to 50 bar with hydrogen and stirred for 2 h at room temperature. The solvent was removed and the residue was suspended in heptane, filtered through a syringe filter (CHROMAFIL O-20/15 MS PTFE 0.2 μm, Macherey–Nagel) and the filtrate was directly used for GC and chiral HPLC analysis to determine the conversion and enantiomeric excess (for analytical procedures and data, see refs.[7b,c]).

Analytical characterization data for all compounds are available in the Supporting Information.

Acknowledgements

Financial support by the Swiss National Science Foundation and the Federal Commission for Technology and Innovation (KTI Project No 5189.2 KTS) is gratefully acknowledged.

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