Highly Efficient Synthesis of (Phosphinodihydrooxazole)-(1,5-cyclooctadiene) Iridium Complexes

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A highly efficient one-pot procedure for the synthesis of complexes of the type $[\text{Ir}(\text{COD})(\text{Phox})]\text{X}$, where Phox is a (chiral) phosphinoxazoline ligand, $\text{X} = \text{PF}_6$ or $\text{B}[(3,5-(\text{CF}_3)_2\text{C}_6\text{H}_3)]_4$ (BARF), is developed. Former reported syntheses demanded the isolation of pure ligands by column chromatography, but the ligands tend to adsorb irreversibly on silica. Moreover, the chromatography has to be performed with careful exclusion of air. The present method avoids this difficulties. The yields of the syntheses are comparable with those starting from the pure ligands. The method is also suitable for the preparation of complexes of the type $[\text{Rh}(\text{COD})(\text{Phox})]\text{BARF}$ and $[\text{Rh}(\text{Phox})_2]\text{BARF}$.

Key words: Iridium, Rhodium, Chiral Ligand, Homogeneous Catalysis, Heterocycles

Introduction

Chiral phosphinodihydrooxazole complexes of iridium are valuable catalysts which are used in homogeneous enantioselective hydrogenation. In a pioneering work of A. Lightfoot, P. Schnider and A. Pfaltz, complexes of type **4** (see Scheme 2) were shown to catalyze enantiospecific hydrogenation of stilbenes and styrenes [1]. Imines were also hydrogenated with high enantioselectivity [2]. Enantioselective hydrogenation, catalyzed by these complexes, could also be carried out in supercritical CO_2 [3,4]. Recently, we have found a new reaction for the homogeneous hydrogenation of electron-deficient alkenes, catalyzed by complexes of the type $[\text{Ir}(\text{COD})(\text{P}^*\text{N})]\text{BARF}$ (COD stands for 1,5-cyclooctadiene, BARF for tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, P^*N for a κ^2 -*P,N*-coordinated ligand) in the presence of ethyldiisopropylamine [5].

Current methods for the syntheses of these complexes comprise the syntheses of the ligands, their isolation and purification (*via* column chromatography), followed by complexation on iridium (Scheme 1).

According to the push-pull phosphinylation mechanism [6], method 1 [7] requires an excess of phosphine, which prevents crystallization of the ligand, which thus must be separated by column chromatography. In our hands, method 1 was reproducible up to chromatogra-

Scheme 1. Methods for the synthesis of phox ligands and the corresponding iridium complexes.

phy. Ligand **3c** (Scheme 2) has been described as an air-stable compound [8], but in our experiments this was not the case. The chromatography must be performed strictly under nitrogen on deoxygenated sorbents using deoxygenated eluent, otherwise the phosphine oxide derived from **3c** is detected by ^{31}P NMR. The main problem was the irreversible adsorption of the ligand on silica, neutral or basic alumina, such that it remained in the column even when triethylamine was added to the eluent. The irreversible adsorption lowered the yield of the ligand to 20–30 %. Method 2 [9] gave the desired phosphinoxazolines with a best GC

Scheme 2. One-pot synthesis of complexes of the type $[\text{Ir}(\text{COD})(\text{Phox})]\text{X}$. Reagents and conditions: i: 1.1 eq. $n\text{BuLi}$, Et_2O , 5 min or MTBE, 30 min (for **1g**, **1i**), r. t.; ii: 1 eq., stirring in Et_2O at r. t. or reflux in MTBE, 10 h (**2**); iii: $[\text{Ir}(\text{COD})\text{Cl}]_2$, CH_2Cl_2 , 2–4 h, reflux; iv: NaBARF or KPF_6 , CH_2Cl_2 , 1–4 h.

yield of 20 %, and hence was not further explored. According to ref. [10], method 3 gives impure ligand, and hence chromatography is necessary. Methods 4 [7], 5 [11], 6 [12] and 7 [13, 14] also require column chromatography.

Results and Discussion

In order to obtain the required complexes we developed the following one-pot procedure (Scheme 2). The preparation of the ligand has also been simplified compared to that in ref. [7]. Although the possibility of complexation of impure ligand was indicated in the literature, the particular procedure was either not described [15], or the crude ligand was only filtered through a plug of silica gel [16].

Chiral 2-(2-fluorophenyl)-4-*R*-4,5-dihydrooxazoles **2** are normally synthesized from aminoalcohols, the latter being derivatives of natural and synthetic chiral amino acids (except **2h**). Although it would be possible to synthesize the complex **2b** in enantiomerically pure form from chiral alaninol, for our purposes (the above mentioned DIPEA-activated Ir-catalyzed hydrogenation) we needed only a racemic complex.

Compounds **4** are insensitive to oxygen and moisture and could be purified by column chromatography (preferably those with BARF as anion) or precipita-

tion by ether (those with the PF_6^- anion). The complexes are colored which makes monitoring of the column chromatography extremely simple, because there is no need of fraction collecting.

The identity of the synthesized complexes was confirmed by ^1H , ^{13}C and ^{31}P NMR spectra and by HRMS ESI/FT-ICR. Compounds **4c** [1, 15], **4f** [1, 15], **4i** [15] and **4l** [15] are described in the literature, but the NMR spectra for **4i** and **4l** have not been reported.

n-Butyllithium was used to deprotonate the diaryl- or dialkylphosphines. Although according to ref. [17] the use of *s*-BuLi is preferred, it does not result in a better yield of complex **4**. The use of THF is avoided in the ligand preparation (except **4m**). THF is known to slowly react with lithium diphenylphosphide [18–20], thus decreasing the yield of the desired ligand. Sterically unhindered diphenylphosphine and hindered di-*o*-tolyl-, dixylyl- and dicyclohexylphosphine readily enter in the phosphinylation reaction, giving the corresponding ligands and complexes, but hindered phosphines must be deprotonated during 30 min in MTBE, and then refluxed overnight with fluoroxazoline **2c** (otherwise the conversion of **2c** is incomplete). Lithium di-*tert*-butylphosphide, bis(trimethylsilyl)phosphide and phospholan-1-ide failed to enter in this reaction, *i. e.* ligand formation was not detected.

Scheme 3. Synthesis of pure **4i**. Scheme 4. Preparation of the Rh complexes **5** and **6**.

Complex **4i** and dicyclohexylphosphine oxide are coeluted by dichloromethane and could not be separated even by hexane-dichloromethane gradient chromatography. The analytically pure complex **4i** was synthesized from **4l** (Scheme 3). The latter was purified by precipitation with ether from a dichloromethane solution.

Complex **4g** was obtained in impure form. All attempts to purify it by gradient chromatography (hexane-dichloromethane or hexane-chloroform) were unsuccessful. The complex with PF_6^- as counter-ion was also obtained in an impure state, and the above-mentioned strategy with anion exchange was not applicable for **4g**. However, the formation of **4g** was proven by its mass spectrum.

Being successful in the synthesis of the Ir complexes, we checked the possibility of synthesizing the analogous Rh complexes (Scheme 4). With 1 eq. of ligand and for 1 eq. of Rh, complex **5** was synthesized. COD bound to Rh is more labile than that bound to Ir, therefore an excess of ligand yielded complex **6**.

Because of the strong *trans*-effect of the phosphorus atom, the ligands in complex **6** are expected to be *cis*-arranged. The iminic carbon gives rise to a triplet of doublets in the ^{13}C NMR spectrum, and this multiplicity

is only possible for a *cis*-arrangement ($^3J_{\text{CCCCP}} \approx 4.4$ Hz, $^3J_{\text{CNRhP}} \approx 4.4$ Hz, $^2J_{\text{CNRh}} \approx 1.5$ Hz). The fine structure was seen only on a 100 MHz instrument (Varian ^{UNITY} INOVA), while the ^{13}C NMR spectrum, acquired on a 150 MHz (Bruker Avance DRX600) spectrometer, showed a broad singlet. The carbons 1-C, 3''-CH, 1''-C and 2''-CH (numbering is shown in Fig. 1, Experimental Section) of complex **6** give rise to pseudo-triplets in the ^{13}C NMR spectrum representing $\text{AXX}'\text{Z}$ spin systems ($\text{A} = ^{13}\text{C}$, $\text{X}, \text{X}' = ^{31}\text{P}$, $\text{Z} = \text{Rh}$).

Using this protocol, (4*S*)-2-(2-(diphenylarsino)-phenyl)-4-isopropyl-4,5-dihydrooxazole (**7**) was synthesized from the oxazoline **2c** and lithium diphenylarsinide. The complexes $[\text{Ir}(\text{COD})(\text{7})]\text{BARF}$ and $[\text{Ir}(\text{COD})(\text{7})]\text{PF}_6$ were found to be inherently unstable at r. t. and were detected only by mass spectrometry. The complex $[\text{Ir}(\text{COD})(\text{7})]\text{BARF}$ was a weak hydrogenation catalyst of stilbene, that is why its research was discontinued.

The NMR spectra of complexes **4–6** are complicated because the signals in the proton spectra are not fully resolved (in both aromatic and aliphatic parts), and the chirality makes the atoms of phenyl rings and of COD magnetically nonequivalent. With the help of 2D techniques (HMBC, HSQC, COSY, TOCSY, ROESY and *J*-resolved) most assignments could be made. Not resolved multiplets (nrm) are inherent for the ^1H NMR spectra of these complexes. Although the shifts of individual peaks are indistinguishable in 1D spectra, the precise ^1H NMR shifts could be established from HSQC and HMBC experiments. 2D spectra were not measured for compounds **4c** and **4f**, because their spectra are in agreement with the ones found in the literature.

Complex **4e** has very interesting spectral properties. While the other compounds show a sharp ^{31}P NMR singlet, **4e** shows two broad singlets at $\delta = +16.1$ and $+8.5$ ppm in CDCl_3 . The conformational stability known for tri-*o*-tolylphosphine [21] forced us to examine high-temperature ^{31}P NMR spectra of this compound. At 140 °C and higher temperatures the solution of **4e** in 1,2,4-trichlorobenzene shows a sharp singlet at $\delta = +12.5$ ppm (line width 53.4 Hz), whereas on cooling this singlet begins to broaden, and at 60 °C two broadened singlets appear. The approximate coalescence temperature in this solvent is 80 °C. The ^1H NMR spectrum of this compound accordingly shows only broad lines. The complex reacts with DMSO when heated at 140 °C. Therefore a resolved ^1H NMR spectrum of this compound which is in fast

conformational equilibrium cannot be obtained. However, cooling to $-40\text{ }^{\circ}\text{C}$ gave sharp peaks in the ^1H , ^{13}C and ^{31}P NMR spectra. Based on the relative integral intensity of the ^{31}P NMR signals (recorded without proton decoupling), the relative concentration of conformers at $-40\text{ }^{\circ}\text{C}$ is 1 : 0.75 (at $\delta = +16.1$ and $+8.5$ ppm, respectively). A full assignment of the NMR spectra of this complex cannot be achieved, since broad peaks in 1D NMR experiment result in low cross peaks in HSQC and HMBC spectra.

Further proof of the identity of complexes **4–6** is provided by the mass spectra (with isotopic clusters) and the ability of the synthesized compounds to perform hydrogenation of stilbene under 100 bar of hydrogen in dichloromethane or toluene solution (except **6**). As expected, the hydrogenation of stilbene in toluene was inhibited by ethyldiisopropylamine [15, 22, 23].

Conclusion

By using an easy synthetic procedure, complexes of the general formula $[\text{Ir}(\text{COD})(\text{Phox})]\text{BARF}$ and $[\text{Ir}(\text{COD})(\text{Phox})]\text{PF}_6$ were synthesized without isolation of the air-sensitive free ligands. By using this method two complexes of rhodium (**5** and **6**) were also synthesized. For compounds not fully characterized in the literature, full assignments of the NMR spectra were carried out. Complex **4e** was found to exist as a mixture of two stable conformers at r. t.

Experimental Section

If not stated otherwise, solvents were dried and degassed by distillation over Na/K alloy (or CaH_2 for dichloromethane) in nitrogen atmosphere and stored under nitrogen. Diphenylphosphine was obtained from MCAT as a gift. $[\text{Ir}(\text{COD})\text{Cl}]_2$ was purchased from Chempur or obtained from Umicore as a gift. The other compounds were purchased from Sigma-Aldrich, Fluka, Acros, ABCR, and Fluorochem, or synthesized by known procedures: NaBARF [24], oxazolines [7]. GC/MS was performed on an HP GC/MS 5890/5972 instrument (EI, 70 eV) equipped with a Phenomenex Zebron ZB-5 column ($30\text{ m} \times 0.25\text{ mm} \times 0.25\text{ }\mu\text{m}$). Helium was used as carrier gas. HRMS ESI/FT-ICR spectra were recorded on a Bruker APEX II FT/ICR instrument with a 7 Tesla magnet in positive polarization. Rotation angles were measured on a Perkin-Elmer 241 polarimeter with 5 sec integration time. We used chloroform, stabilized with 1 % of ethanol (Acros) for measurement of the rotation angles. NMR spectra were recorded on Bruker Avance DRX600 (600 MHz), Jeol JNM-LA 400 (400 MHz), or Varian $^{\text{UNITY}}$ INOVA 400 (400 MHz) instruments. Refer-

Fig. 1. Atom numbering for compounds **4–6**, used for the assignment of NMR spectra.

ence standards are: TMS (internal) for ^1H and for ^{13}C NMR, 85 % H_3PO_4 (external) for ^{31}P NMR, $\text{Et}_2\text{O} \cdot \text{BF}_3$ (external) for ^{11}B NMR, CFCl_3 (internal) for ^{19}F NMR. “Nrm” stands for not resolved multiplet. In order to define the arrangement of ligands, the ^{13}C NMR spectrum of complex **6** was obtained using special parameters (spectral width $+175 - -5$ ppm, 256000 points, acquisition time 7.0736 sec, relaxation delay 1 sec) on a $^{\text{UNITY}}$ INOVA 400 instrument. The numbering of atoms for compounds **4–6**, used for assignment of the NMR spectra, is shown in Fig. 1 (2' and 6', 3' and 5', 2'' and 6'' as well as 3'' and 5'' are inequivalent only for complexes **4e**, **4g** and **4h**).

All complexes bearing the BARF counter-ion, have shown the following signals in NMR spectra: ^1H NMR (CDCl_3 , 600 MHz): $\delta = 7.54$ (br s, 4 H, 4- H_{BARF}), 7.74 (br s, 8 H, 2- H_{BARF}). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 150 MHz): $\delta = 117.50$ (br s, 4- CH_{BARF}), 124.55 (q, $J = 273$ Hz, CF_3), 128.9 (br q, $J = 30$ Hz, 3- C_{BARF}), 134.81 (br s, 2- CH_{BARF}), 161.72 (q 1 : 1 : 1 : 1, $J = 50.5$ Hz, 1- C_{BARF}). ^{19}F NMR (CDCl_3 , 376 MHz): $\delta = -62.8$. ^{11}B NMR (CDCl_3 , 128 MHz): $\delta = -6.9$.

CAUTION. All diarylphosphines, dialkylphosphines, lithium diaryl- and dialkylphosphides, and all ligands **3** are very toxic and pyrophoric compounds. All operations must be carried out strictly under inert gas in a well-ventilated fume hood or in a glovebox.

Synthesis of bis(2,6-dimethylphenyl)phosphine oxide

In 50 mL of absolute Et_2O , 2,6-dimethylbromobenzene (18.506 g, 0.1 mol) and magnesium (2.674 g, 0.11 mol) were mixed in a nitrogen atmosphere. One crystal of iodine was added, and the mixture was heated by a heatgun. After the formation of the Grignard reagent had started, the mixture was refluxed for 3 h until the magnesium was dissolved. The mixture was cooled to *ca.* $-100\text{ }^{\circ}\text{C}$ with liquid nitrogen, and diethyl phosphite (3.8 mL, 0.03 mol) was added. The mixture was warmed to r. t. and refluxed overnight (*ca.* 10 h), cooled and poured into 200 mL of 1N aqueous HCl. The layers were separated, the aqueous phase washed with dichloromethane (5×100 mL), the united organic phases were dried with

Na₂SO₄, filtered, and evaporated. The residue was recrystallized from EtOAc to give white crystalline dioxylphosphine oxide (4.768 g, 61 %). The substance is moderately air-stable even in solution, but should be stored in the crystalline state in a nitrogen-filled glovebox. – ¹H NMR (CDCl₃, 400 MHz): δ = 2.44 (s, 12 H, Me), 7.04 (s, 4 H, 3-H), 7.29 (br t, *J* = 7 Hz, 2 H, 4-H), 8.61 (d, *J* = 478 Hz, 1 H, PH). – ¹³C NMR (CDCl₃, 100 MHz): δ = 20.74 (d, *J* = 8.0 Hz), 129.32 (d, *J* = 98 Hz), 129.71 (d, *J* = 9.6 Hz), 131.81 (d, *J* = 2.4 Hz), 141.77 (d, *J* = 10.4 Hz). – ³¹P NMR (CDCl₃, 161 MHz): δ = +10.88 (d, *J* = 478 Hz).

Synthesis of bis(2,6-dimethylphenyl)phosphine (**1g**)

Compound **1g** was synthesized with a yield of 69 % from bis(2,6-dimethylphenyl)phosphine oxide by stirring at 70 °C with triisobutylaluminum in toluene for 48 h, by the known procedure [25]. White crystals. – ¹H NMR (C₆D₆, 400 MHz): δ = 2.22 (s, 12 H, CH₃), 5.26 (d, *J* = 231 Hz, 1 H, PH), 6.83 (dd, *J* = 7.4 Hz, *J* = 2.3 Hz, 4 H, 3-H), 6.97 (t, *J* = 7.4 Hz, 2 H, 4-H). – ¹³C{¹H} NMR (C₆D₆, 100 MHz): δ = 22.93 (d, *J* = 10.4 Hz, CH₃), 128.48 (s, 4-C), 128.63 (d, *J* = 2.4 Hz, 3-C), 133.38 (d, *J* = 17.7 Hz, 1-C), 142.56 (d, *J* = 12.0 Hz, 2-C). – ³¹P NMR (C₆D₆, 161 MHz): δ = –91.60 (d, *J* = 231 Hz).

Synthesis of *rac*-2-(acetoxymino)-3,3-dimethyl-2,3-dihydro-1*H*-inden-1-yl acetate

A three-necked 1 L flask equipped with a reflux condenser was charged with a solution of 2-(hydroxymino)-3,3-dimethyl-2,3-dihydro-1*H*-inden-1-one [26] (18.4 g, 97 mmol, recrystallized from toluene) in 460 mL of methanol (under nitrogen) and cooled to –20 °C. NaBH₄ (16.56 g, 438 mmol) was added, and the mixture was stirred for 1 h with cooling (the reaction is so vigorous, that reflux begins), then for 10 h in an ice bath. The mixture was evaporated *in vacuo* and suspended in 368 mL of pyridine (with vigorous shaking under nitrogen). Acetic anhydride (184 mL) was added, and vigorous shaking continued, resulting in a violet color which changed to yellow within 30 sec. After 12 h the mixture was evaporated *in vacuo*, and the residue was triturated in 800 mL of water to give crude *rac*-2-(acetoxymino)-3,3-dimethyl-2,3-dihydro-1*H*-inden-1-yl acetate. It was recrystallized from a mixture toluene/hexane (1 : 3) to give white crystals with a yield of 70 %.

Synthesis of *rac*-*cis*-2-amino-3,3-dimethyl-2,3-dihydro-1*H*-inden-1-ol

A three-necked 100 mL flask equipped with a reflux condenser was charged with a solution of *rac*-2-(acetoxymino)-3,3-dimethyl-2,3-dihydro-1*H*-inden-1-yl ac-

etate (1 g, 3.63 mmol) in 20 mL THF (under nitrogen) and cooled to –20 °C. The borane-dimethylsulfide complex (94 %, Acros, 1.4 mL, 14.72 mmol) was added, and the mixture was heated and refluxed for 3 h, then cooled to –20 °C, and 1*N* HCl (3.4 mL) was added under air which resulted in refluxing. After cooling, the mixture was poured into 2*N* KOH and five times extracted with CH₂Cl₂. The organic extracts were dried with Na₂SO₄, filtered and evaporated, giving pure white *rac*-*cis*-2-amino-3,3-dimethyl-2,3-dihydro-1*H*-inden-1-ol. This substance is very unstable and epimerizes upon storage, and should be used within 2–3 d. The method can be scaled up to 20 g of *rac*-2-(acetoxymino)-3,3-dimethyl-2,3-dihydro-1*H*-inden-1-yl acetate. Although in the original article [27] the use of the borane-THF complex is described, this leads to a mixture, where the target compound was not detected. A communication with Atsushi Sudo (author of article [27]) revealed that the borane-dimethylsulfide complex should be used.

Synthesis of (3*aR*,8*bS*)-2-(2-fluorophenyl)-4,4-dimethyl-4,8*b*-dihydro-3*aH*-indeno[2,1-*d*]oxazole (**2h**)

rac-*cis*-2-Amino-3,3-dimethyl-2,3-dihydro-1*H*-inden-1-ol was resolved as described in the literature [27]. In absolute dioxane under nitrogen (1*S*,2*R*)-2-amino-3,3-dimethyl-2,3-dihydro-1*H*-inden-1-ol (1.665 g, 9.4 mmol) and NEt₃ (2.6 mL, 19 mmol) were dissolved. With cooling to 0 °C, 2-fluorobenzoyl chloride (1.2 mL, 9.9 mmol) was added, and the mixture was stirred for 8 h at r. t. SOCl₂ (13.4 mL, 184.7 mmol) was added (cooling to 0 °C), and the mixture was stirred for 2 h, then evaporated *in vacuo* at r. t. The residue was suspended in 5*N* NaOH and extracted five times with CH₂Cl₂. After drying of the extracts with Na₂SO₄, filtration and evaporation of the solvent the residue was redissolved in absolute Et₂O. Na₂SO₄ (3.4 g, 23.9 mmol) and NaOH dust (Aldrich, 3.4 g, 85 mmol) were added, and the mixture was stirred for 48 h at r. t. in a sealed flask. Water was added, and the organic layer was separated. Adsorption on silica with subsequent column chromatography on 200 g of silica (Et₂O-pentane 2 : 3) gave crystalline off-white (3*aR*,8*bS*)-2-(2-fluorophenyl)-4,4-dimethyl-4,8*b*-dihydro-3*aH*-indeno[2,1-*d*]oxazole (**2h**) with a yield of 30 %. Unfortunately, the target compound is only a by-product. The formula of the main product, which is less polar and elutes first from the column, was not assigned. The spectral properties of **2h** correspond to those published [28].

General procedure A for the synthesis of **4a**–**e**, **4f**, **4k** and **4j**

Diphenylphosphine (**1a**) (61 mg, 0.33 mmol, for complexes **4a**–**d**, **4k**, **4j**) or di(*o*-tolyl)phosphine (**1e**) (71 mg, 0.33 mmol, for complexes **4e**, **4f**) was dissolved in diethyl ether (4 mL), and *n*-BuLi (1.6 M solution in hexane, 0.21 mL,

0.33 mmol) was added at r.t., and the yellow mixture was stirred for 5 min. Oxazoline (**2a–d**, **2k**, 0.3 mmol) was added to the reaction mixture, and the reaction mixture was stirred overnight. At this point, gas chromatography with a mass-sensitive analyzer was performed, which showed a conversion of **2** of over 90 % into ligand **3**. The mixture was evaporated in a stream of nitrogen. $[\text{Ir}(\text{COD})\text{Cl}]_2$ (100.8 mg, 0.15 mmol) and CH_2Cl_2 (3 mL) were added to the residue, and the mixture was refluxed for 2 h and cooled. The anion exchange can be carried out in air. The procedure can be scaled up to 400 mg of $[\text{Ir}(\text{COD})\text{Cl}]_2$. The complexes of this type (with various anions) are found to be unstable in toluene on storage (toluene being metallated).

Exchange of Cl by BARF

NaBARF (292 mg, 0.33 mmol) was added to the reaction mixture with stirring at r.t. for 1–3 h. The exchange could be monitored by TLC on silica gel eluting with dichloromethane (R_f of $[\text{Ir}(\text{COD})\text{Cl}(\text{Phox})]$ is 0, that of $[\text{Ir}(\text{COD})(\text{Phox})]\text{BARF}$ is 0.75–1). Then silica gel (1 g) was added, and the mixture was evaporated under vacuum at r.t. This silica was placed on top of the column filled with 20 g of silica gel, and the desired colored complex was eluted with CH_2Cl_2 . The eluant was evaporated *in vacuo* (without heating), and the complex was dried in a vacuum (10^{-2} mbar).

Exchange of Cl by PF_6

A solution of KPF_6 (184 mg, 1 mmol) in water (2 mL) was added to the reaction mixture. The two-phase system was vigorously stirred for 2 h, the exchange being monitored with TLC on silica gel with CH_2Cl_2 -MeOH (20 : 1) as eluent. The organic layer was separated, and the aqueous residue was extracted 5 times with CH_2Cl_2 . Combined organic extracts were dried over Na_2SO_4 , filtered and evaporated at r.t. The residue was redissolved in a minimum amount of CH_2Cl_2 , and the target complex was precipitated with 100 mL of Et_2O , filtered, washed off from the filter with CH_2Cl_2 , evaporated at r.t. and dried in a vacuum (10^{-2} mbar).

(2-(2-(Diphenylphosphino)phenyl)-4,5-dihydrooxazole)-(η⁴-1,5-cyclooctadiene)iridium(I) tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (**4a**)

Yield: 74 %. Red crystals. Unstable on storage at r.t. even in crystalline form (should be stored at -20°C). – ^1H NMR (CDCl_3 , 600 MHz): δ = 1.93 (m, 2 H, a-4- H_{COD} and a-8- H_{COD}), 2.05 (m, 2 H, a-3- H_{COD} and a-7- H_{COD}), 2.26 (m, 4 H, e-3- H_{COD} , e-4- H_{COD} , e-7- H_{COD} , e-8- H_{COD}), 3.16 (br s, 2 H, 5- and 6- H_{COD}), 4.09 (t, J = 10 Hz, 2 H, NCH_2), 4.48 (t, J = 10 Hz, 2 H, OCH_2), 5.08 (br s, 2 H, 1- and 2- H_{COD}), 7.43 (dd, J = 11.4 Hz, J = 8.2 Hz, 4 H, 2'-H), 7.49 (m, 6 H, 3-, 4- and 3'-H), 7.60 (m, 3 H, 5-

and 4'-H), 8.05 (m, 1 H, 6-H), and the signals of BARF. – $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 150 MHz): δ = 32.13 (d, J = 3.4 Hz, 4- and 8- CH_2COD), 29.70 (3- and 7- CH_2COD), 54.55 (NCH_2), 64.28 (5- and 6- CH_{COD}), 68.39 (OCH_2), 95.14 (d, J = 11.5 Hz, 1-2 and 2- CH_{COD}), 126.20 (d, J = 60 Hz, 1'-C), 128.68 (d, J = 8.8 Hz, 1-C), 129.36 (d, J = 9.9 Hz, 3'-CH), 129.39 (d, J = 46.1 Hz, 2-C), 132.15 (d, J = 1.6 Hz, 5-CH), 132.47 (d, J = 2.4 Hz, 4'-CH), 133.23 (d, J = 9.9 Hz, 3-CH), 133.35 (d, J = 8.0 Hz, 6-CH), 133.89 (d, J = 6.9 Hz, 4-CH), 134.18 (d, J = 12.1 Hz, 2'-CH), 165.68 (d, J = 8.0 Hz, $\text{N}=\text{C}$), and the signals of BARF. – ^{31}P NMR (CDCl_3 , 161 MHz): δ = +16.1. – HRMS ESI/FT-ICR: isotope cluster 630–634, found (calcd.): 630.1679, 66 % (630.1671, 60 %); 631.1721, 21 % (633.1728, 31 %); 631.1856, 12 % (631.1704, 19 %); 632.1688, 100 % (632.1694, 100 %); 633.1714, 33 % (633.1728, 31 %); 634.1739, 7 % (634.1761, 5 %).

Racemic (2-(2-(diphenylphosphino)phenyl)-4-methyl-4,5-dihydrooxazole)-(η⁴-1,5-cyclooctadiene)iridium(I) tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (**4b**)

Yield: 80 %. Red crystals. Very stable on storage at r.t. even in CDCl_3 solution (6 month). – ^1H NMR (CDCl_3 , 600 MHz): δ = 1.05 (d, J = 5.7 Hz, Me), 1.47 (nrm, 1 H, a-4- H_{COD}), 1.65 (nrm, 1 H, a-8- H_{COD}), 2.03 (nrm, 1 H, e-4- H_{COD}), 2.06 (nrm, 1 H, e-8- H_{COD}), 2.45 (nrm, 3 H, a-7- H_{COD} and 3- H_{COD}), 2.53 (nrm, 1 H, e-7- H_{COD}), 3.14 (br m, 1 H, 5- H_{COD}), 3.36 (br m, 1 H, 6- H_{COD}), 4.18 (dd, J = 9.0 Hz, J = 3.9 Hz, 1 H, OCH_2), 4.27 (br s, 1 H, NCHMe), 4.46 (d, J = 9.0 Hz, 1 H, OCH_2), 4.97 (br s, 2 H, 1- and 2- H_{COD}), 7.14 (dd, J = 11.3 Hz, J = 6.6 Hz, 2 H, 2'-H), 7.41 (nrm, 1 H, 3-H), 7.46 (nrm, 2 H, 3'-H), 7.47 (nrm, 1 H, 4'-H), 7.48 (nrm, 2 H, 3''-H), 7.55 (nrm, 1 H, 4''-H), 7.60 (nrm, 4 H, 4-, 5- and 2''-H), 8.07 (m, 1 H, 6-H), and the signals of BARF. – $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 150 MHz): δ = 23.16 (Me), 26.47 (8- CH_2COD), 28.59 (4- CH_2COD), 32.22 (3- CH_2COD), 36.06 (7- CH_2COD), 61.52 (NCHMe), 63.80 (6- CH_{COD}), 63.92 (5- CH_{COD}), 74.24 (OCH_2), 93.54 (d, J = 13.2 Hz, 1- CH_{COD}), 96.49 (d, J = 12.1 Hz, 2- CH_{COD}), 117.5 (br s, 4- CH_{BARF}), 121.81 (d, J = 58.3 Hz, 1'-C), 128.65 (d, J = 29.7 Hz, 2-C), 128.98 (d, J = 11.0 Hz, 3'-CH), 129.12 (d, J = 50.6 Hz, 1''-C), 129.60 (d, J = 11.0 Hz, 3''-CH), 129.70 (d, J = 15.4 Hz, 1-C), 132.23 (d, J = 3.3 Hz, 4'-CH), 132.25 (br s, 5-CH), 132.70 (d, J = 2.2 Hz, 4''-CH), 133.11 (d, J = 9.9 Hz, 2'-CH), 133.39 (br s, 3-CH), 133.46 (d, J = 7.7 Hz, 6-CH), 133.99 (d, J = 6.6 Hz, 4-CH), 134.96 (d, J = 12.1 Hz, 2''-CH), 163.73 (d, J = 6.6 Hz, $\text{N}=\text{C}$), and the signals of BARF. – ^{31}P NMR (CDCl_3 , 161 MHz): δ = +17.6. – HRMS ESI/FT-ICR: isotope cluster 644–648, found (calcd.): 644.1833, 57 % (644.1827, 60 %); 645.1880, 18 % (645.1861, 19 %); 646.1851, 100 % (646.1851, 100 %); 647.1901, 34 % (647.1884, 33 %); 648.1949, 6 % (648.1918, 5 %).

((4*S*)-2-(2-(Diphenylphosphino)phenyl)-4-isopropyl-4,5-dihydrooxazole)-(η⁴-1,5-cyclooctadiene)iridium(I) tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (**4c**)

Yield: 81 % (best yield found in literature is 91 % [3]). Red crystals. Very stable on storage at r.t. even in CDCl₃ solution (6 month).

((4*S*)-2-(2-(Diphenylphosphino)phenyl)-4-*tert*-butyl-4,5-dihydrooxazole)-(η⁴-1,5-cyclooctadiene)iridium(I) tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (**4d**)

Yield: 79.7 %. Red crystals. Very stable on storage at r.t. even in CDCl₃ solution (6 month). – [α]_D²¹ = –155 (c = 0.105, CHCl₃). – ¹H NMR (CDCl₃, 600 MHz): δ = 0.63 (s, 9 H, Me), 1.43 (nrm, 1 H, a-4-H_{COD}), 1.6 (nrm, 1 H, a-8-H_{COD}), 2.0 (nrm, 2 H, e-4- and e-8-H_{COD}), 2.47 (nrm, 2 H, a-3- and a-7-H_{COD}), 2.40 (nrm, 1 H, e-3-H_{COD}), 2.55 (nrm, 1 H, e-7-H_{COD}), 3.04 (br s, 1 H, NOE with 7.11 ppm, 5-H_{COD}), 3.5 (br s, 1 H, NOE with 7.46 ppm, 6-H_{COD}), 3.94 (dd, *J* = 9.4 Hz, *J* = 2.6 Hz, NCH*t*Bu), 4.32 (t, *J* = 9.4 Hz, 1 H, OCH₂), 4.58 (dd, *J* = 9.4 Hz, *J* = 2.6 Hz, 1 H, OCH₂), 4.95 (br m, 2 H, 1- and 2-H_{COD}), 7.11 (br m, 2 H, 2'-H), 7.32 (nrm, 1 H, 3-H), 7.43 (nrm, 2 H, 3'-H), 7.46 (nrm, 2 H, 2''-H), 7.49 (nrm, 1 H, 4'-H), 7.50 (nrm, 2 H, 3''-H), 7.55 (nrm, 1 H, 4''-H), 7.62 (nrm, 2 H, 4- and 5-H), 8.20 (m, 1 H, 6-H), and the signals of BARF. – ¹³C{¹H} NMR (CDCl₃, 150 MHz): δ = 25.09 (Me), 25.51 (8-CH₂COD), 28.16 (4-CH₂COD), 32.70 (3-CH₂COD), 34.42 (CMe₃), 36.8 (7-CH₂COD), 62.74 (5-CH₂COD), 63.37 (6-CH₂COD), 69.82 (OCH₂), 74.47 (NCH*t*Bu), 93.28 (d, *J* = 13.8 Hz, 1-CH₂COD), 97.57 (d, *J* = 10.3 Hz, 2-CH₂COD), 122.31 (d, *J* = 57.4 Hz, 1'-C), 127.61 (d, *J* = 48.2 Hz, 2-C), 128.83 (d, *J* = 10.3 Hz, 3'-CH), 129.12 (d, *J* = 13.8 Hz, 1-C), 129.60 (d, *J* = 51.6 Hz, 1''-C), 129.70 (d, *J* = 11.5 Hz, 3''-CH), 132.09 (4'-CH), 132.58 (d, *J* = 1.6 Hz, 5-CH), 132.62 (4''-CH), 133.19 (d, *J* = 10.3 Hz, 2'-CH), 133.98 (d, *J* = 8.0 Hz, 6-CH), 134.20 (d, *J* = 14.9 Hz, 2''-CH), 134.23 (d, *J* = 6.9 Hz, 4-CH), 134.93 (d, *J* = 2.4 Hz, 3-CH), 164.03 (d, *J* = 4.6 Hz, N=C), and the signals of BARF. – ³¹P NMR (CDCl₃, 161 MHz): δ = +17.5. – HRMS ESI/FT-ICR: isotope cluster 686–690, found (calcd.): 686.2380, 53 % (686.2297, 60 %); 687.2416, 13 % (687.2330, 21 %); 688.2323, 100 % (688.2320, 100 %); 689.2315, 44 % (689.2354, 36 %); 690.2344, 5 % (690.2387, 6 %).

((4*S*)-2-(2-(Di(*o*-tolyl)phosphino)phenyl)-4-isopropyl-4,5-dihydrooxazole)-(η⁴-1,5-cyclooctadiene)iridium(I) tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (**4e**)

Yield: 85 %. Red crystals. Very stable on storage at r.t. even in CDCl₃ solution (6 month). – [α]_D²⁰ = –97 (c = 0.13, CHCl₃). – ³¹P NMR (1,2,4-trichlorobenzene, 161 MHz, 140 °C): δ = +12.5. – ¹H NMR (CDCl₃, 600 MHz, r.t., full assignment is not possible): δ = 0.05 (br s, 3 H), 0.87 (br s, 3 H, Me), 1.41 (br s, 1 H, Me), 1.58 (br m, 1 H), 1.95 (br

s, 1 H) 2.04 (br m, 2 H, CHMe₂ and e-3-H_{COD}), 2.31 (br s, 1 H), 2.35 (s, 6 H, 2'-Me and 2''-Me), 2.42 (br m, 2 H, e-8-CH₂COD), 3.30 (br s, 2 H, 5- and 6-H_{COD}), 4.15 (br s, 1 H, OCH₂), 4.32 (t, *J* = 9.54 Hz, 1 H, OCH₂), 4.43 (br s, 1 H, NCH), 4.68 (br q, *J* = 6.7 Hz, NOE with 2.05 ppm, 1 H, 1-CH₂COD), 4.98 (br s, 1 H, 2-CH₂COD), 7.21 (br s, 2 H, 6'-H), 7.37 (br s, 2 H, 3'-H), 7.43 (br s, 2 H, 4'-H), 7.58 (br s, 3 H, 3-, 4- and 5-H), 8.09 (br m, 1 H, 6-H), and the signals of BARF. – ¹³C{¹H} NMR (CDCl₃, 150 MHz, r.t., assignment is not possible): δ = 12.31, 13.26, 18.71, 24.0, 27.90, 29.71, 31.17, 32.41, 21.97, 35.30, 36.16, 68.18, 70.32, 68.9, 94.6, 127.08 (d, *J* = 8 Hz), 129.51, 132.11, 132.46 (d, *J* = 8 Hz), 132.62, 133.66, 133.71, 133.81 (d, *J* = 8 Hz), 135.3, 163.88, and the signals of BARF. – ³¹P NMR (CDCl₃, 161 MHz, r.t.): 8.54 (br s, 0.9 P), 16.14 (br s, 1 P). – ¹H NMR (CDCl₃, 400 MHz, –40 °C): δ = –0.09 (d, *J* = 6.64 Hz, 1 H), 0.12 (d, *J* = 6.6 Hz, 1.6 H), 0.84 (d, *J* = 7 Hz, 1.3 H), 0.92 (d, *J* = 6.6 Hz, 1.8 H), 1.37 (br s, 1.2 H), 1.55 (br s, 1.3 H), 1.85–2.04 (br m, 4.9 H), 2.22–2.57 (br m, 8.6 H), 2.82 (br s, 0.4 H), 3.15 (br s, 0.4 H), 3.28–3.39 (br m, 1.65 H), 4.1–4.2 (br m, 0.9 H), 4.32–4.44 (br m, 1.3 H), 4.50 (br d, *J* = 7 Hz, 0.6 H), 4.67 (br s, 1 H), 4.93–5.08 (br m, 0.9 H), 6.63 (m, 0.8 H), 6.91 (m, 0.7 H), 7.07 (m, 0.7 H), 7.18–7.26 (m, 1.7 H), 7.34–7.70 (m, 12 H), 8.07 (br m, 1 H), 9.07 (m, 0.5 H), and the signals of BARF. – ¹³C{¹H} NMR (CDCl₃, 150 MHz, –40 °C): δ = 11.94, 13.26, 18.69, 23.45 (br s), 23.79 (d, *J* = 8 Hz), 24.67 (d, *J* = 5.7 Hz), 25.32, 26.77 (d, *J* = 8 Hz), 27.36, 27.67, 29.70 (br s), 32.12, 32.24, 32.27, 33.06, 35.38 (br s), 36.23 (br s), 64.07, 65.04, 66.42, 67.51, 67.81, 68.05, 69.66, 69.88, 88.31 (d, *J* = 12.6 Hz), 89.20 (br d, *J* = 13.8 Hz), 94.03 (d, *J* = 10.3 Hz), 94.76 (br d, *J* = 9.2 Hz), 117.51 (d, *J* = 57.0 Hz), 117.67, 120.39 (d, *J* = 53.9 Hz), 125.99, 126.31 (d, *J* = 4.6 Hz), 126.43, 126.77, 126.84 (d, *J* = 4.6 Hz), 126.99 (d, *J* = 6.9 Hz), 127.07 (d, *J* = 8.0 Hz), 127.70 (d, *J* = 12.6 Hz), 127.68, 128.29 (d, *J* = 19.5 Hz), 129.17, 131.7–132.4 (m), 133.2–133.7 (m), 133.89, 134.38, 135.83, 140.57 (d, *J* = 9.2 Hz), 141.51 (d, *J* = 9.2 Hz), 142.60, 142.70, 140.80, 143.45, 163.16 (d, *J* = 4.6 Hz), 163.76 (d, *J* = 8.0 Hz), and the signals of BARF. – ³¹P NMR (CDCl₃, 161 MHz, –40 °C): δ = 8.21 (s, 0.75 P), 15.75 (s, 1 P). – HRMS ESI/FT-ICR: isotope cluster 644–648, found (calcd.): 700.2441, 51 % (700.2453, 60 %); 701.2434, 17 % (701.2487, 22 %); 702.2472, 100 % (702.2477, 100 %); 703.2477, 34 % (703.2510, 37 %); 704.2539, 6 % (703.2510, 7 %).

((4*S*)-2-(2-(Di(*o*-tolyl)phosphino)phenyl)-4-*tert*-butyl-4,5-dihydrooxazole)-(η⁴-1,5-cyclooctadiene)iridium(I) tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (**4f**)

Yield: 83 % (best yield found in literature is 72 % [15]). Orange crystals, very stable on storage at r.t. even in CDCl₃ solution (6 month).

((4*S*)-2-(2-(Diphenylphosphino)phenyl)-4-isopropyl-4,5-dihydrooxazole)-(η⁴-1,5-cyclooctadiene)iridium(I) hexafluorophosphate (**4j**)

Yield: 78 % (best yield found in literature is 82 % [2]). Red crystals. Unstable on storage in solution, but stable in crystalline state, can be stored at r. t., but better at –20 °C.

(2-(2-(Diphenylphosphino)phenyl)-4,4-dimethyl-4,5-dihydrooxazole)-(η⁴-1,5-cyclooctadiene)iridium(I) tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (**4k**)

Yield: 68 %. Red crystals. Very unstable even in crystalline state. Should be stored at –20 °C. – ¹H NMR (CDCl₃, 600 MHz): δ = 1.31 (s, 6 H, Me), 1.82 (nrm, 2 H, a-3- and a-7-H_{COD}), 2.01 (nrm, 2 H, e-3- and e-7-H_{COD}), 2.22 (nrm, 4 H, 4- and 8-H_{COD}), 3.27 (br s, 2 H, 5- and 6-H_{COD}), 3.87 (s, 2 H, OCH₂), 5.40 (br s, 2 H, 1- and 2-H_{COD}), 7.31 (br s, 4 H, 2''- and 3''-H), 7.44 (nrm, 1 H, 3-H), 7.48 (nrm, 3 H, 2'- and 4''-H), 7.54 (br s, 5 H, 4'-H and 4-H_{BARF}), 7.59 (nrm, 3 H, 5- and 3'-H), 7.60 (nrm, 1 H, 4-H), 7.84 (m, 1 H, 6-H), and the signals of BARF. – ¹³C{¹H} NMR (CDCl₃, 150 MHz): δ = 27.81 (Me), 29.70 (br s, 4- and 8-CH₂COD), 31.90 (br s, 3- and 7-CH₂COD), 61.72 (5- and 6-CH₂COD), 73.12 (OCH₂), 82.47 (NMe₂), 93.64 (d, *J* = 13.2 Hz, 1- and 2-CH_{COD}), 125.29 (d, *J* = 41.7 Hz, 2-C), 125.74 (d, *J* = 60.4 Hz, 1'-C), 129.52 (4''-CH), 129.28 (d, *J* = 11.0 Hz, 2''-CH), 129.91 (d, *J* = 62.6 Hz, 1''-C), 131.23 (d, *J* = 5.5 Hz, 1-C), 131.71 (br s, 3-CH), 131.90 (d, *J* = 7.7 Hz, 6-CH), 131.99 (5-CH), 132.53 (4'-CH), 133.39 (d, *J* = 6.6 Hz, 3C, 4-CH and 3'-CH), 134.07 (br s, 4C, 2'- and 3''-CH), 165.49 (d, *J* = 7.8 Hz, N=C), and the signals of BARF. – ³¹P NMR (CDCl₃, 161 MHz): δ = +21.8. – HRMS ESI/FT-ICR: isotope cluster 658–662, found (calcd.): 658.1974, 51 % (658.1984, 60 %); 659.2018, 17 % (659.2017, 20 %); 660.2012, 100 % (660.2007, 100 %); 661.2029, 32 % (661.2041, 34 %); 662.2083, 2 % (662.2074, 5 %).

((3*aR*,8*bS*)-2-(2-(Diphenylphosphino)phenyl)-4,4-dimethyl-4,8*b*-dihydro-3*aH*-indeno[2,1-*d*]oxazole)-(η⁴-1,5-cyclooctadiene)iridium(I) tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (**4h**)

Diphenylphosphine (61 mg, 0.33 mmol) was dissolved in diethyl ether (1 mL), and *n*-BuLi (1.6 M solution in hexane, 0.21 mL, 0.33 mmol) was added in order to generate lithium diphenylphosphide. Then **2h** (84 mg, 0.3 mmol) was added. After stirring overnight the generated ligand was allowed to react with [Ir(COD)Cl]₂ and NaBARF as described in the general procedure A.

Yield: 79.6 %. Red crystals. Very stable on storage at r. t. even in CDCl₃ solution (6 month). – [α]_D²¹ = 0 (*c* = 0.105, CHCl₃), [α]₅₄₆²¹ = +156 (*c* = 0.105, CHCl₃). – ¹H NMR (CDCl₃, 600 MHz, r. t.): δ = 0.76 (s, 3 H, Me), 1.41 (s, 3 H, Me), 1.47 (nrm, 1 H, a-7-H_{COD}), 1.72 (nrm, 1 H, a-3-H_{COD}),

2.01 (nrm, 1 H, e-7-H_{COD}), 2.12 (nrm, 1 H, e-3-H_{COD}), 2.42 (nrm, 1 H, a-8-H_{COD}), 2.49 (nrm, 1 H, a-4-H_{COD}), 2.52 (nrm, 1 H, e-8-H_{COD}), 2.63 (nrm, 1 H, e-4-H_{COD}), 3.03 (br s, 1 H, NOE with 7.10 ppm, 6-H_{COD}), 3.54 (br s, 1 H, NOE with 7.42 ppm, 5-H_{COD}), 4.69 (d, *J* = 8.5 Hz, 1 H, NCH), 5.12 (m, 1 H, NOE with 4.69 ppm, 1-H_{COD}), 5.16 (m, 1 H, 2-H_{COD}), 6.17 (d, *J* = 8.5 Hz, 1 H, OCH), 7.03 (d, *J* = 7.6 Hz, 1 H, 2'''-H), 7.10 (dd, *J* = 11.5 Hz, *J* = 7.6 Hz, 2 H, 2''-H), 7.24 (br d, *J* = 8.2 Hz, 1 H, 3-H), 7.28 (m, 1 H, 4'''-H), 7.37 (t, *J* = 7.6 Hz, 1 H, 3'''-H), 7.38 (nrm, 1 H, 4'-H), 7.42 (nrm, 5 H, 2'-, 6'- and 3'''- and 4''-H), 7.47 (m, 3 H, 3'-, 5'- and 5'''-H), 7.56 (t, *J* = 7.6 Hz, 1 H, 4-H), 7.61 (t, *J* = 7.6 Hz, 1 H, 5-H), 8.31 (ddd, *J* = 8.2 Hz, *J* = 4.1 Hz, *J* = 1.1 Hz, 1 H, 6-H), and the signals of BARF. – ¹³C{¹H} NMR (CDCl₃, 150 MHz): δ = 26.8 (Me), 31.2 (Me), 25.7 (d, *J* = 2.3 Hz, 3-CH₂COD), 28.1 (7-CH₂COD), 32.5 (8-CH₂COD), 36.2 (4-CH₂COD), 49.5 (CMe₂), 62.9 (5-CH_{COD}), 63.9 (6-CH_{COD}), 79.09 (NCH), 87.8 (OCH), 91.2 (d, *J* = 13.7 Hz, 2-CH_{COD}), 96.8 (d, *J* = 10.0 Hz, 1-CH_{COD}), 123.00 (d, *J* = 58.5 Hz, 1''-C), 123.12 (2'''-CH), 126.30 (5'''-CH), 127.59 (d, *J* = 48.2 Hz, 2-C), 128.51 (4'''-CH), 128.77 (2'- and 6'-CH), 128.99 (d, *J* = 51.6 Hz, 1'-C), 129.58 (d, *J* = 13.8 Hz, 1-C), 129.64 (d, *J* = 11.5 Hz, 3''-CH), 131.82 (3'''-CH), 132.10 (d, *J* = 2.3 Hz, 5'-CH), 132.44 (d, *J* = 2.3 Hz, 3'-CH), 132.52 (d, *J* = 2.3 Hz, 5-CH), 133.21 (d, *J* = 10.3 Hz, 2''-CH), 133.23 (6''-CH), 133.94 (d, *J* = 11.5 Hz, 6-CH), 133.99 (4'-CH), 134.05 (4''-CH), 134.11 (d, *J* = 6.9 Hz, 4-CH), 135.35 (s, 3-CH), 150.87 (1'''-CH), 163.97 (d, *J* = 5.7 Hz, C=N), and the signals of BARF. – ³¹P NMR (CDCl₃, 161 MHz): δ = +16.5. – HRMS ESI/FT-ICR: isotope cluster 746–750, found (calcd.): 746.2302, 54 % (746.2297, 60 %); 747.2313, 22 % (747.2330, 25 %); 748.2293, 100 % (748.2320, 100 %); 749.2287, 43 % (749.2354, 41 %); 750.2255, 9 % (750.2387, 8 %).

General procedure B for the synthesis of **4g**, **4i** and **4l**

A two-necked 10 mL flask was charged with liquid dicyclohexylphosphine (**1i**, 65 mg, 0.33 mmol) or solid dixylphosphine (**1g**, 80 mg, 0.33 mmol) as described in general procedure A. Abs. MTBE (4 mL) was added, and the diarylphosphine was dissolved. *n*-BuLi (1.6 M solution in hexane, 0.21 mL, 0.33 mmol) was added at r. t., and the

yellow (for **1g**) or colorless (for **1i**) mixture was stirred for 30 min. Liquid oxazoline **2c** (62 mg, 0.3 mmol) was added to the reaction mixture. The mixture was refluxed for 12 h and cooled. At this point gas chromatography with mass-sensitive analyzer showed a conversion of **2c** of over 80 % into the ligand **3**. The mixture was evaporated in a stream of nitrogen. $[\text{Ir}(\text{COD})\text{Cl}]_2$ (100.8 mg, 0.15 mmol) and CH_2Cl_2 (3 mL) were added to the residue, and the mixture was refluxed for 4 h. After cooling the anion exchange (to BARF or PF_6) was performed according to the general procedure A.

((4*S*)-2-(2-(*Bis*(2,6-dimethylphenyl)phosphino)phenyl)-4-isopropyl-4,5-dihydrooxazole)-(η^4 -1,5-cyclooctadiene)iridium(I) tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (**4g**)

Yield: 66.9 %. This complex was catalytically active in stilbene hydrogenation, but impure. It could not be purified even by gradient column chromatography (hexane-dichloromethane). Yellow crystals, unstable even in crystalline state. Should be stored at -20°C . $-\alpha_{\text{D}}^{21} = -19$ ($c = 0.12$, CHCl_3), $[\alpha]_{546}^{21} = -48$ ($c = 0.12$, CHCl_3). $-\text{}^1\text{H}$ NMR (CDCl_3 , 600 MHz, r.t.): $\delta = 0.48$ (d, $J = 6.7$ Hz, 3 H, Me_{IPr}), 1.01 (d, $J = 6.7$ Hz, 3 H, Me_{IPr}), 1.85 (s, 3 H, 6''-Me), 2.00 (s, 3 H, 2''-Me), 2.22 (s, 3 H, 2'-Me), 2.50 (m, 1 H, CHMe_2), 3.19 (m, 1 H, 5- H_{COD}), 3.29 (m, 1 H, 6- H_{COD}), 4.40 (br d, $J = 8.1$ Hz, 2 H, OCH_2), 4.63 (br td, $J = 8.1$ Hz, $J = 2.5$ Hz, 1 H, NCH), 4.70 (m, NOE with 3.29 ppm, with 1.76 ppm, 1 H, 2- H_{COD}), 5.24 (m, 1 H, NOE with 2.5 ppm, 4.63 ppm, 1- H_{COD}), 6.86 (br s, 1 H, 4'-H), 7.05 (nrm, 2 H, 3'- and 5'-H), 7.15 (nrm, 2 H, 3''- and 5''-H), 7.37 (nrm, 1 H, 4''-H), 7.55 (t, $J = 7.5$ Hz, 1 H, 5-H), 7.66 (t, $J = 7.5$ Hz, 1 H, 4-H), 8.05 (dd, $J = 10.3$ Hz, $J = 7.5$ Hz, 1 H, 3-H), 8.27 (t, $J = 7.5$ Hz, 1 H, 6-H), and the signals of BARF, CH_2COD and 6'-Me are not distinguishable, since the compound is not pure. $-\text{}^{13}\text{C}\{\text{}^1\text{H}\}$ NMR (CDCl_3 , 150 MHz): $\delta = 7.53$ (6'-Me), 13.78 (Me_{IPr}), 19.01 (Me_{IPr}), 22.78 (2C, 2'-Me and 2''-Me), 26.73 (6''-Me), 29.94 (CHMe_2), 44.66 (6- CH_{COD}), 66.90 (5- CH_{COD}), 67.04 (OCH_2), 79.38 (d, $J = 23.8$ Hz, 1- CH_{COD}), 81.75 (NCH), 103.05 (s, 2- CH_{COD}), 123.42 (d, $J = 16.5$ Hz, 3'-CH), 126.00 (d, $J = 12.8$ Hz, 1-C), 126.28 (d, $J = 56.82$ Hz, 1''-C), 129.76 (d, $J = 47.7$ Hz, 2-C), 130.32 (d, $J = 7.3$ Hz, 4'-CH), 130.51 (d, $J = 88.0$ Hz, 1'-C), 130.74 (d, $J = 7.3$ Hz, 3''-CH), 130.76 (d, $J = 12.8$ Hz, 6'-CMe), 131.14 (d, $J = 7.3$ Hz, 5''-CH), 131.48 (s, 4''-CH), 131.68 (s, 5'-CH), 131.82 (5-CH), 131.98 (d, $J = 7.3$ Hz, 4-CH), 134.85 (d, $J = 7.3$ Hz, 6-CH), 135.53 (s, 3-CH), 140.35 (d, $J = 9.2$ Hz, 2''-CMe), 141.27 (d, $J = 9.2$ Hz, 6''-CMe), 141.45 (d, $J = 1.6$ Hz, 2'-CMe), 163.8 (d, $J = 5.5$ Hz, $\text{N}=\text{C}$), and the signals of BARF, CH_2COD are not distinguishable, since the compound is not pure. $-\text{}^{31}\text{P}$ NMR (CDCl_3 , 161 MHz): $\delta = +20.8$. $-\text{HRMS}$ ESI/FT-ICR: isotope cluster 728–732, found (calcd.): 728.2704, 78 % (728.2766, 60 %); 729.2763,

28 % (729.2800, 23 %); 730.2783, 100 % (730.2790, 100 %); 731.2773, 36 % (731.2823, 39 %); 732.2912, 5 % (732.2857, 7 %).

((4*S*)-2-(2-(Dicyclohexylphosphino)phenyl)-4-isopropyl-4,5-dihydrooxazole)-(η^4 -1,5-cyclooctadiene)iridium(I) tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (**4i**)

Yield: 70 %. This complex was catalytically active in stilbene hydrogenation, but contaminated with dicyclohexylphosphine oxide, and the contaminant could not be removed even by gradient column chromatography (hexane-dichloromethane). The synthesis of analytically pure **4i** is described below.

((4*S*)-2-(2-(Dicyclohexylphosphino)phenyl)-4-isopropyl-4,5-dihydrooxazole)-(η^4 -1,5-cyclooctadiene)iridium(I) hexafluorophosphate (**4l**)

Yield: 68 %. Red crystals. Very unstable on storage even as crystals at r.t. (stable for 1 d). Should be stored at -20°C . $-\alpha_{\text{D}}^{19} = -136$ ($c = 0.11$, CHCl_3). $-\text{}^1\text{H}$ NMR (CDCl_3 , 600 MHz, r.t.): $\delta = 0.80$ (d, $J = 6.6$ Hz, 3 H, Me), 1.08 (d, $J = 6.9$ Hz, 3 H, Me), 1.15–1.4 (nrm, 8 H, Cy), 1.4–1.5 (nrm, 2 H, Cy), 1.70–1.95 (nrm, 10 H, Cy), 1.61 (nrm, 1 H, a-4- H_{COD}), 1.66 (nrm, 1 H, a-8- H_{COD}), 2.07 (nrm, 2 H, CHMe_2 and e-8- H_{COD}), 2.13 (nrm, 2 H, e-4- H_{COD} and 1'-H), 2.29 (nrm, 1 H, a-3- H_{COD}), 2.49 (nrm, 4 H, e-3- H_{COD} , 7- H_{COD} and 1''-H), 3.69 (br s, 1 H, 5- H_{COD}), 4.15 (br s, 1 H, 6- H_{COD}), 4.32 (m, 1 H, NCH), 4.62 (d, $J = 5.9$ Hz, 2 H, OCH_2), 4.74 (m, NOE with 2.07, 4.32 and 4.62 ppm, 1 H, 1- H_{COD}), 5.13 (br s, NOE with 4.32 and 4.62 ppm, 1 H, 2- H_{COD}), 7.67 (pseudo-t, $J = 7.8$ Hz, 1 H, 5-H), 7.78 (m, 2 H, 3- and 4-H), 8.31 (dd, $J = 7.9$ Hz, $J = 2.9$ Hz, 1 H, 6-H). $-\text{}^{13}\text{C}\{\text{}^1\text{H}\}$ NMR (CDCl_3 , 150 MHz): $\delta = 14.84$ (Me), 19.26 (Me), 25.87 (Cy), 26.03 (Cy), 26.09 (8- CH_2COD), 26.94 (d, $J = 8.0$ Hz, Cy), 27.02 (d, $J = 9.2$ Hz, Cy), 27.13 (d, $J = 11.5$ Hz, Cy), 27.32 (d, $J = 9.2$ Hz, Cy), 28.12 (d, $J = 3.4$ Hz, Cy), 29.11 (Cy), 29.44 (4- CH_2COD), 29.98 (Cy), 30.65 (Cy), 31.65 (3- CH_2COD), 32.09 (d, $J = 27.5$ Hz, 1''-CH), 32.96 (CHMe_2), 36.15 (7- CH_2COD), 41.95 (d, $J = 26.4$ Hz, 1'-CH), 59.86 (5- CH_{COD}), 61.92 (6- CH_{COD}), 68.20 (OCH_2), 70.19 (NCH), 89.90 (d, $J = 11.5$ Hz, 1- CH_{COD}), 95.46 (d, $J = 11.5$ Hz, 2- CH_{COD}), 126.80 (d, $J = 35.6$ Hz, 2-C), 129.45 (d, $J = 9.2$ Hz, 1-C), 131.74 (d, $J = 2.3$ Hz, 5-CH), 132.43 (d, $J = 1.2$ Hz, 3-CH), 133.87 (d, $J = 5.7$ Hz, 4-CH), 134.07 (d, $J = 8.0$ Hz, 6-CH), 164.34 (d, $J = 5.7$ Hz, $\text{N}=\text{C}$). $-\text{}^{31}\text{P}$ NMR (CDCl_3 , 161 MHz): $\delta = +10.1$ (ligand), -143.7 (sep, $J = 714$ Hz, PF_6). $-\text{}^{19}\text{F}$ NMR (CDCl_3 , 376 MHz): $\delta = -73.6$ (d, $J = 714$ Hz). $-\text{HRMS}$ ESI/FT-ICR: isotope cluster 684–688, found (calcd.): 684.3051, 54 % (684.3079, 60 %); 685.3070, 17 % (685.3113, 21 %); 686.3089, 100 % (686.3103, 100 %); 687.3071, 33 % (687.3136, 35 %); 688.3137, 5 % (688.3170, 6 %).

((4*S*)-2-(2-(Dicyclohexylphosphino)phenyl)-4-isopropyl-4,5-dihydrooxazole)-(η⁴-1,5-cyclooctadiene)iridium(I) tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (**4i**) from **4l**

4l (50 mg, 0.06 mmol) and NaBARF (54 mg, 0.061 mmol) were dissolved in CH₂Cl₂ (5 mL). The anion exchange was monitored by TLC on silica gel eluting with CH₂Cl₂. *R_f* of **4l** is 0, that of **4i** is 0.9. Within 2 h the mixture was adsorbed on silica gel and chromatographed on silica gel (10 g) according to the general procedure A. Yield: 71 %. Red crystals. Stable on storage in crystalline form at r. t. for at least 1 week. Nevertheless, it should be stored at −20 °C. −[α]_D¹⁹ = −48 (*c* = 0.135, CHCl₃). ¹H NMR (CDCl₃, 600 MHz, r. t.): δ = 0.77 (d, *J* = 6.4 Hz, 3 H, Me), 1.00 (d, *J* = 7.0 Hz, 3 H, Me), 1.19–1.35 (nrm, 8 H, Cy), 1.37–1.50 (nrm, 2 H, Cy), 1.66–1.93 (nrm, 10 H, Cy), 1.61 (nrm, 2 H, a-4- and a-8-H_{COD}), 2.01 (nrm, 1 H, e-8-H_{COD}), 2.07 (m, 1 H, CHMe₂), 2.14 (nrm, 1 H, e-4-H_{COD}), 2.07 (nrm, 1 H, a-7-H_{COD}), 2.22 (nrm, 1 H, 1'-H), 2.23 (nrm, 1 H, a-3-H_{COD}), 2.38 (nrm, 1 H, e-3-H_{COD}), 2.46 (nrm, 1 H, e-7-H_{COD}), 2.47 (nrm, 1 H, 1''-H), 3.72 (br s, 5-CH_{COD}), 4.16 (dt, *J* = 8.8 Hz, *J* = 2.9 Hz, 1 H, NCH), 4.19 (br s, 1 H, 6-CH_{COD}), 4.32 (t, *J* = 9.4 Hz, 1 H, OCH₂), 4.55 (dd, *J* = 9.4 Hz, *J* = 2.9 Hz, 1 H, OCH₂), 4.66 (m, NOE with 4.16, 2.07, 0.77 ppm, 1 H, 1-H_{COD}), 4.86 (br s, NOE with 4.16 ppm, 1 H, 2-H_{COD}), 7.55 (m, 1 H, 5-H), 7.66 (t, *J* = 7.6 Hz, 1 H, 4-H), 7.74 (br s and d, *J* = 8.8 Hz, 9 H, 2-H_{BARF} and 3-H), 8.21 (dd, *J* = 10.6 Hz, *J* = 2.4 Hz, 1 H, 6-H), and the signals of BARF. ¹³C{¹H} NMR (CDCl₃, 150 MHz): δ = 14.53 (Me), 19.16 (Me), 25.76 (Cy), 26.00 (2C, Cy and 8-CH₂COD), 26.91 (d, *J* = 9.2 Hz, Cy), 26.99 (d, *J* = 9.2 Hz, Cy), 27.12 (d, *J* = 11.5 Hz, Cy), 27.37 (d, *J* = 10.3 Hz, Cy), 28.23 (d, *J* = 2.3 Hz, Cy), 29.18 (Cy), 29.43 (4-CH₂COD), 30.18 (Cy), 30.68 (Cy), 31.57 (3-CH₂COD), 32.20 (d, *J* = 28.7 Hz, 1''-C), 32.87 (CHMe₂), 36.04 (d, *J* = 3.5 Hz, 7-CH₂COD), 42.18 (d, *J* = 27.5 Hz, 1'-C), 60.82 (5-CH_{COD}), 62.92 (6-CH_{COD}), 67.87 (OCH₂), 70.27 (NCH), 89.43 (d, *J* = 13.8 Hz, 1-CH_{COD}), 94.14 (d, *J* = 10.3 Hz, 2-CH_{COD}), 127.04 (d, *J* = 35.6 Hz, 2-C), 129.16 (d, *J* = 11.5 Hz, 1-C), 131.84 (5-CH), 132.38 (s, 3-CH), 134.03 (d, *J* = 6.9 Hz, 6-CH), 133.94 (d, *J* = 5.7 Hz, 4-CH), 164.4 (d, *J* = 5.8 Hz, N = C), and the signals of BARF. ³¹P NMR (CDCl₃, 161 MHz): δ = +10.4. ¹H NMR (CDCl₃, 600 MHz, r. t.): δ = 1.44 (nrm, 1 H, a-4-H_{COD}), 1.57 (nrm, 1 H, a-8-H_{COD}), 2.01 (nrm, 1 H, e-8-H_{COD}), 2.05 (nrm, 1 H, e-4-H_{COD}), 2.41 (nrm, 1 H, a-7-H_{COD}), 2.47 (nrm, 1 H, a-3-H_{COD}), 2.52 (nrm, 1 H, e-3-H_{COD}), 2.53 (nrm, 1 H, e-7-H_{COD}), 3.21 (s, 1 H, NOE with 7.14 ppm, 5-H_{COD}), 3.38 (s, 1 H, 6-H_{COD}), 3.72 (m, 2 H, OCH₂), 4.13 (m, 1 H, NCH), 4.68 (br s, 1 H, 2-H_{COD}), 4.82 (s, 1 H, NOE with 4.13 ppm, 1-H_{COD}), 5.68 (d, *J* = 3.5 Hz, CHOH), 7.14 (br s, 2 H, 2'-H), 7.26 (s under signal of CHCl₃, 2'''-H), 7.44 (nrm, 1 H, 3-H), 7.46 (nrm, 1 H, 4'''-H), 7.47 (nrm, 3 H, 4'- and 3'''-H), 7.49 (nrm, 2 H, 3'-H), 7.57 (nrm, 1 H, 4''-H), 7.58 (nrm, 2 H, 3''-H), 7.65 (nrm, 2 H, 2''-H), 7.66 (nrm, 1 H, 4-H), 7.70 (nrm, 1 H, 5-H), 8.31 (m, 1 H, 6-H), and the signals of BARF, OH-exchanged. ¹³C{¹H} NMR (CDCl₃, 150 MHz): δ = 26.37 (8-CH₂COD), 28.52 (4-CH₂COD), 32.24 (7-CH₂COD), 36.15 (3-CH₂COD), 64.12 (5-CH_{COD}), 64.42 (6-CH_{COD}), 64.54 (OCH₂), 74.27 (NCH), 83.33 (CHOH), 93.76 (d, *J* = 13.8 Hz, 1-CH_{COD}), 97.08 (d, *J* = 11.5 Hz, 2-CH_{COD}), 121.20 (d, *J* = 58.5 Hz, 1'-C), 124.85 (2'''-CH), 128.51 (d, *J* = 48.2 Hz, 2-C), 128.63 (d, *J* = 12.6 Hz, 1-C), 129.15 (d, *J* = 11.5 Hz, 3'-CH), 129.75

(1*S*)-((4*S*)-2-(2-(Diphenylphosphino)phenyl)-4,5-dihydrooxazol-4-yl)(phenyl)methanol-(η⁴-1,5-cyclooctadiene)iridium(I) tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (**4m**)

2m (41.3 mg, 0.152 mmol) was dissolved in 5 mL of abs. Et₂O. To this solution KPh₂ (0.5 N solution in THF,

Aldrich, 0.64 mL, 0.32 mmol) was added at r. t. The mixture was stirred overnight at r. t. Degassed water (a few drops) was added, and all volatiles (including diphenylphosphine) were removed *in vacuo* (10^{−2} mbar) with heating (60 °C). The residue was redissolved in abs. CH₂Cl₂ (5 mL). A ³¹P NMR spectrum of this solution showed one signal at δ = −6 ppm (consistent with ref. [29]). [Ir(COD)Cl]₂ (50 mg, 0.0744 mmol) was added to this solution, which was stirred at r. t. for 2 h (refluxing leads to decomposition of the target complex). A ³¹P NMR spectrum of this solution showed one singlet at δ = +20 ppm. From this point work was continued in air. NaBARF (135 mg, 0.152 mmol) was added, and the mixture was stirred for 2 h. The mixture was adsorbed on 1 g of silica gel, and column chromatography was performed on 20 g of silica gel according to the general procedure A with the mixture CH₂Cl₂-hexane (2 : 1). The first spot represented some by-products, whereas the more polar second spot represented the title compound. Yield: 34 %. Red crystals. Very unstable even in crystalline state at r. t., should be stored at −20 °C or below. In CDCl₃ solution, decomposition begins within 1 h. −[α]_D²⁵ = −113 (*c* = 0.11, CHCl₃). ¹H NMR (CDCl₃, 600 MHz, r. t.): δ = 1.44 (nrm, 1 H, a-4-H_{COD}), 1.57 (nrm, 1 H, a-8-H_{COD}), 2.01 (nrm, 1 H, e-8-H_{COD}), 2.05 (nrm, 1 H, e-4-H_{COD}), 2.41 (nrm, 1 H, a-7-H_{COD}), 2.47 (nrm, 1 H, a-3-H_{COD}), 2.52 (nrm, 1 H, e-3-H_{COD}), 2.53 (nrm, 1 H, e-7-H_{COD}), 3.21 (s, 1 H, NOE with 7.14 ppm, 5-H_{COD}), 3.38 (s, 1 H, 6-H_{COD}), 3.72 (m, 2 H, OCH₂), 4.13 (m, 1 H, NCH), 4.68 (br s, 1 H, 2-H_{COD}), 4.82 (s, 1 H, NOE with 4.13 ppm, 1-H_{COD}), 5.68 (d, *J* = 3.5 Hz, CHOH), 7.14 (br s, 2 H, 2'-H), 7.26 (s under signal of CHCl₃, 2'''-H), 7.44 (nrm, 1 H, 3-H), 7.46 (nrm, 1 H, 4'''-H), 7.47 (nrm, 3 H, 4'- and 3'''-H), 7.49 (nrm, 2 H, 3'-H), 7.57 (nrm, 1 H, 4''-H), 7.58 (nrm, 2 H, 3''-H), 7.65 (nrm, 2 H, 2''-H), 7.66 (nrm, 1 H, 4-H), 7.70 (nrm, 1 H, 5-H), 8.31 (m, 1 H, 6-H), and the signals of BARF, OH-exchanged. ¹³C{¹H} NMR (CDCl₃, 150 MHz): δ = 26.37 (8-CH₂COD), 28.52 (4-CH₂COD), 32.24 (7-CH₂COD), 36.15 (3-CH₂COD), 64.12 (5-CH_{COD}), 64.42 (6-CH_{COD}), 64.54 (OCH₂), 74.27 (NCH), 83.33 (CHOH), 93.76 (d, *J* = 13.8 Hz, 1-CH_{COD}), 97.08 (d, *J* = 11.5 Hz, 2-CH_{COD}), 121.20 (d, *J* = 58.5 Hz, 1'-C), 124.85 (2'''-CH), 128.51 (d, *J* = 48.2 Hz, 2-C), 128.63 (d, *J* = 12.6 Hz, 1-C), 129.15 (d, *J* = 11.5 Hz, 3'-CH), 129.75

(3'''-CH), 129.82 (d, $J = 53.9$ Hz, 1''-C), 130.04 (3''-CH), 130.18 (4'''-CH), 130.40 (4'-CH), 132.46 (4''-CH), 132.59 (5-CH), 132.99 (d, $J = 14.5$ Hz, 2'-CH), 133.84 (s, 3-CH), 133.86 (d, $J = 8.0$ Hz, 6-CH), 134.41 (d, $J = 12.6$ Hz, 3C, 4- and 2''-CH), 136.93 (1'''-C), 164.67 (d, $J = 5.7$ Hz, N=C), and the signals of BARF. – ^{31}P NMR (CDCl_3 , 161 MHz): $\delta = +16.9$. – HRMS ESI/FT-ICR: isotope cluster 736–740, found (calcd.): 736.2111, 54 % (736.2090, 60 %); 737.2136, 23 % (737.2123, 23 %); 738.2131, 100 % (738.2113, 100 %); 739.2160, 36 % (739.2146, 39 %), 740.2230, 5 % (740.2180, 7 %).

((4S)-2-(2-(Diphenylphosphino)phenyl)-4-isopropyl-4,5-dihydrooxazole)-(η^4 -1,5-cyclooctadiene)rhodium(I) tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (5)

According to the general procedure A, with $[\text{Rh}(\text{COD})\text{Cl}]_2$. Yield: 86 %. Yellow crystals. Stable in CDCl_3 solution at -20°C for at least 2 weeks. Should be stored at -20°C in crystalline form. – $[\alpha]_{\text{D}}^{21} = -41$ ($c = 0.11$, CHCl_3). – ^1H NMR (CDCl_3 , 600 MHz, r.t.): $\delta = -0.15$ (d, $J = 6.6$ Hz, 3 H, Me), 0.80 (d, $J = 7.0$ Hz, 3 H, Me), 1.85 (nrm, 1 H, a-4- H_{COD}), 1.95 (nrm, 2 H, CHMe_2 and a-8- H_{COD}), 2.13 (nrm, 1 H, e-4- H_{COD}), 2.19 (nrm, 1 H, e-8- H_{COD}), 2.45 (nrm, 1 H, a-3- H_{COD}), 2.50 (nrm, 1 H, a-7- H_{COD}), 2.69 (nrm, 1 H, e-3- H_{COD}), 2.79 (nrm, 1 H, e-7- H_{COD}), 3.51 (br s, NOE with 7.05 ppm, 1 H, 5- H_{COD}), 3.59 (br s, NOE with 7.05, 7.68 ppm, 1 H, 6- H_{COD}), 3.79 (br d, $J = 8.7$ Hz, 1 H, NCH), 4.29 (t, $J = 9.4$ Hz, 1 H, OCH_2), 4.33 (dd, $J = 9.4$ Hz, $J = 3.5$ Hz, 1 H, OCH_2), 5.27 (br s, 2 H, 1- and 2- H_{COD}), 7.05 (nrm, 2 H, 2'-H), 7.33 (br dd, $J = 9.0$ Hz, $J = 7.0$ Hz, 1 H, 3-H), 7.41 (t, $J = 7.2$ Hz, 2 H, 3'-H), 7.50 (br s, 3 H, 4'- and 3''-H), 7.56 (nrm, 1 H, 4''-H), 7.61 (nrm, 2 H, 4- and 5-H), 7.68 (nrm, 2 H, 2''-H), 8.09 (m, 1 H, 6-H), and the signals of BARF. – $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 150 MHz): $\delta = 12.29$ (Me), 18.79 (Me), 26.33 (8- CH_2COD), 28.65 (4- CH_2COD), 30.70 (3- CH_2COD), 32.44 (CHMe_2), 35.33 (7- CH_2COD), 67.74 (OCH_2), 70.90 (NCH), 77.61 (d, $J = 11.5$ Hz, 6- CH_{COD}), 79.05 (d, $J = 12.6$ Hz, 5- CH_{COD}), 105.52 (dd, $J = 11.5$ Hz, $J = 8.0$ Hz, 1- CH_{COD}), 107.66 (dd, $J = 9.2$ Hz, $J = 6.9$ Hz, 2- CH_{COD}), 117.45 (br s, 4''-CH), 124.33 (d, $J = 49.3$ Hz, 1'-C), 128.52 (d, $J = 40.2$ Hz, 2-C), 128.54 (d, $J = 14.9$ Hz, 1-C), 129.03 (d, $J = 10.3$ Hz, 3'-CH), 129.13 (1''-C), 129.80 (d, $J = 10.3$ Hz, 3''-CH), 131.81 (d, $J = 2.3$ Hz, 4'-CH), 132.20 (d, $J = 2.3$ Hz, 5-CH), 132.64 (d, $J = 2.3$ Hz, 4-CH), 132.86 (d, $J = 10.3$ Hz, 2'-CH), 133.64 (d, $J = 8.0$ Hz, 6-CH), 133.72 (d, $J = 13.8$ Hz, 3-CH), 134.46 (d, $J = 12.6$ Hz, 2''-CH), 163.81 (d, $J = 8.0$ Hz, N=C), and the signals of BARF. – ^{31}P NMR (CDCl_3 , 161 MHz): $\delta = +30.7$ (d, $J = 154.1$ Hz). – HRMS ESI/FT-ICR: isotope cluster 584–586, found (calcd.): 584.1588, 100 % (584.1590, 100 %); 585.1596, 32 % (585.1623, 35 %); 586.1613, 5 % (586.1657, 6 %).

cis-Bis-((4S)-2-(2-(diphenylphosphino)phenyl)-4-isopropyl-4,5-dihydrooxazole)rhodium(I) tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (6)

Synthesized from **2c** (84 mg, 0.405 mmol), **1a** (84 mg, 0.451 mmol), *n*-BuLi (0.28 mL, 0.451 mmol), $[\text{Rh}(\text{COD})\text{Cl}]_2$ (40 mg, 0.081 mmol), and NaBARF (144 mg, 0.162 mmol) according the general procedure A. After anion exchange the mixture was adsorbed on silica gel and the solvents evaporated. The column (20 g of silica gel) was packed with silica with the adsorbed complex placed on top. The column was first eluted with *ca.* 100 mL of hexane in order to remove cyclooctadiene, then with CH_2Cl_2 . Yield: 81.6 %; brown crystals, unstable at r.t. even in crystalline form, should be stored at -20°C . – $[\alpha]_{\text{D}}^{21} = -687$ ($c = 0.115$, CHCl_3). – ^1H NMR (CDCl_3 , 600 MHz, r.t.): $\delta = 0.44$ (d, $J = 6.8$ Hz, 3 H, Me), 1.09 (d, $J = 6.8$ Hz, 3 H, Me), 2.09 (m, CHMe_2), 3.85 (m, 1 H, NCH), 4.39 (m, 2 H, OCH_2), 6.87 (br s, 4 H, 2'- and 3'-H), 6.96 (br m, 1 H, 3-H), 7.12 (t, $J = 7.5$ Hz, 1 H, 4'-H), 7.33 (t, $J = 7.5$ Hz, 2 H, 3''-H), 7.42 (nrm, 1 H, 4''-H), 7.45 (nrm, 1 H, 4-H), 7.49 (nrm, 1 H, 5-H), 7.53 (nrm, 2 H, 2''-H), 7.96 (br d, $J = 7.5$ Hz, 6-H), and the signals of BARF. – $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 150 MHz): $\delta = 16.06$ (Me), 20.69 (Me), 32.46 (CHMe_2), 69.25 (OCH_2), 73.47 (NCH), 127.97 (br s, 3'-CH), 128.11 (t, $J = 6.9$ Hz, 1-C), 128.34 (t, $J = 4.6$ Hz, 3''-CH), 129.69 (4'-CH), 130.41 (5-CH), 130.76 (t, $J = 20.7$ Hz, 1''-C), 131.18 (4''-CH), 131.41 (br s, 6-CH), 132.52 (br s, 2'-CH), 132.71 (s, 3-CH), 132.92 (br s, 4-CH), 134.43 (dd, $J = 20.7$ Hz, $J = 17.2$ Hz, 2-C), 134.72 (t, $J = 5.7$ Hz, 2''-CH), 163.63 (s, N=C), and the signals of BARF, 1'-C is not identified, since the broad signal at 6.87 ppm shows no cross peaks in an HMBC spectrum. – ^{31}P NMR (CDCl_3 , 161 MHz): $\delta = +49.3$ (d, $J = 174.8$ Hz). – HRMS ESI/FT-ICR: isotope cluster 849–852, found (calcd.): 849.2263, 100 % (849.2246, 100 %); 850.2285, 49 % (850.2280, 52 %); 851.2387, 10 % (851.2313, 13 %).

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