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 \([\text{Ir(COD)(Phox)}]X\), where Phox is a (chiral) phosphinooxazoline ligand, \(X = \text{PF}_6\) or \(\text{B[(3,5-(CF}_3\text{)2C}_6\text{H}_3)]}_4\) (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 \([\text{Rh(COD)(Phox)}]\text{BARF}\) and \([\text{Rh(Phox)}]_2\)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 CO2 [3,4]. Recently, we have found a new reaction for the homogeneous hydrogenation of electron-deficient alkenes, catalyzed by complexes of the type \([\text{Ir(COD)}(\text{P}^\text{N})]\text{BARF}\) (COD stands for 1,5-cyclooctadiene, BARF for tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, \(\text{P}^\text{N}\) for a \(\kappa^2-P,N\)-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 chromatography. 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, 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 phosphinooxazolines with a best GC

Scheme 1. Methods for the synthesis of phox ligands and the corresponding iridium complexes.
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 2h 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 precipitation 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 \(^1\)H, \(^1^3\)C and \(^3^1\)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 phosphinyla-
tion reaction, giving the corresponding ligands and complexes, but hindered phosphines must be deprotonated during 30 min in MTBE, and then refluxed overnight with fluoroazoline 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.
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 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 ($J_{CCCP} \approx 4.4$ Hz, $J_{CNRP} \approx 4.4$ Hz, $J_{CNRB} \approx 1.5$ Hz). The fine structure was seen only on a 100 MHz instrument (Varian Unity 500), 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 AXX'Z spin systems (A = $^{13}$C, X,X' = $^{31}$P, Z = Rh).

Using this protocol, (4S)-2-(2-(diphenylarsino)phenyl)-4-isopropyl-4,5-dihydrooxazole (7) was synthesized from the oxazoline 2c and lithium diphenylarsinide. The complexes [Ir(COD)(7)]BARF and [Ir(COD)(7)]PF$_6$ were found to be inherently unstable at r. t. and were detected only by mass spectrometry. The complex [Ir(COD)(7)]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 $^1$H NMR spectra of these complexes. Although the shifts of individual peaks are indistinguishable in 1D spectra, the precise $^1$H 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 $^1$H NMR spectrum of this compound accordingly shows only broad lines. The complex reacts with DMSO when heated at 140 °C. Therefore a resolved $^1$H NMR spectrum of this compound which is in fast
conformational equilibrium cannot be obtained. However, cooling to −40 °C gave sharp peaks in the $^1$H, $^{13}$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 °C is 1:0.75 (at δ = +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 [Ir(COD)(Phox)]BARF and [Ir(COD)(Phox)]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. [Ir(COD)Cl]$_2$ was purchased from Chempur or obtained from Umicore as a gift. The other compounds were purchased from Sigma-Aldrich, Fluka, Acros, ABCR, 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 m $\times$ 0.25 mm $\times$ 0.25 µm). 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 UNITY NOVA 400 (400 MHz) instruments. Reference standards are: TMS (internal) for $^1$H and for $^{31}$C NMR, 85% H$_3$PO$_4$ (external) for $^{31}$P NMR, Et$_2$O - BF$_3$ (external) for $^{19}$F NMR. “Nmm” 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 UNITYNOVA 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: $^1$H NMR (CDCl$_3$, 600 MHz): $\delta = 7.54$ (br s, 4 H, 4-H$_{BARF}$), 7.74 (br s, 8 H, 2-H$_{BARF}$), −$^{13}$C($^1$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, dialkylyphosphines, lithium diaryl- and dialkylyphosphides, 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)phosphoxide

In 50 mL of absolute Et$_2$O, 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 °C with liquid nitrogen, and diethylphosphite (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
Na$_2$SO$_4$, filtered, and evaporated. The residue was recrystallized from EtOAc to give white crystalline dixylylphosphine 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. – 31PN M R(CD$_2$Cl$_2$, 161 MHz): $\delta = 2.44$ (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 (CD$_2$Cl$_2$, 100 MHz): $\delta = 20.74$ (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 (CD$_2$Cl$_2$, 161 MHz): $\delta = +10.88$ (d, $J = 478$ Hz).

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

Compound Ig was synthesized with a yield of 69% from bis(2,6-dimethylphenyl)phosphine oxide by stirring at 70 °C with trisobutylaluminum in toluene for 48 h, by the known procedure [25]. White crystals. – 31PN M R(CD$_2$Cl$_2$, 400 MHz): $\delta = 2.22$ (s, 12 H, CH$_2$), 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 NMR (CD$_2$Cl$_2$, 100 MHz): $\delta = 22.93$ (d, $J = 10.4$ Hz, CH$_3$), 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 (CD$_2$Cl$_2$, 161 MHz): $\delta = +91.60$ (d, $J = 231$ Hz).

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

A three-necked 1 L flask equipped with a reflux condenser was charged with a solution of 2-(hydroxyimino)-inden-1-yl acetate. It was recrystallized from toluene and dried with Na$_2$SO$_4$, filtered, and evaporated, giving pure white rac-cis-2-aminomethyl-3,3-dimethyl-2,3-dihydro-1H-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 (3aR,8bS)-2-(2-fluorophenyl)-4,4-dimethyl-4,8b-dihydro-3aH-indeno[2,1-d]oxazole (2h)**

rac-cis-2-Amino-3,3-dimethyl-2,3-dihydro-1H-inden-1-ol was resolved as described in the literature [27]. In absolute dioxane under nitrogen (15,2R)-2-amino-3,3-dimethyl-2,3-dihydro-1H-inden-1-ol (1.665 g, 9.4 mmol) and $\text{NEt}_3$ (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. $\text{SOCl}_2$ (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 5N NaOH and extracted five times with $\text{CH}_2\text{Cl}_2$. After drying of the extracts with Na$_2$SO$_4$, filtration and evaporation of the solvent the residue was redissolved in absolute Et$_2$O. Na$_2$SO$_4$ (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 (Et$_2$O-pentane 2:3) gave crystalline off-white (314 mg, 200 mL). The mixture was triturated in 800 mL of water to give crude rac-2-(acetoxyimino)-3,3-dimethyl-2,3-dihydro-1H-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-1H-inden-1-ol**

A three-necked 100 mL flask equipped with a reflux condenser was charged with a solution of rac-2-(acetoxyimino)-3,3-dimethyl-2,3-dihydro-1H-inden-1-yl acetate (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 1N HCl (3.4 mL) was added under air which resulted in refluxing. After cooling, the mixture was poured into 2N KOH and five times extracted with CH$_2$Cl$_2$. The organic extracts were dried with Na$_2$SO$_4$, filtered and evaporated, giving pure white rac-cis-2-amino-3,3-dimethyl-2,3-dihydro-1H-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-(acetoxyimino)-3,3-dimethyl-2,3-dihydro-1H-inden-1-yl acetate. The organic extracts were dried with Na$_2$SO$_4$, filtered and evaporated, giving pure white rac-cis-2-amino-3,3-dimethyl-2,3-dihydro-1H-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-(acetoxyimino)-3,3-dimethyl-2,3-dihydro-1H-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.

**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% to ligand 3. The mixture was evaporated in a stream of nitrogen. [Ir(COD)Cl]₂ (100.8 mg, 0.15 mmol) and CH₂Cl₂ (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 [Ir(COD)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 (Rf of [Ir(COD)Cl(Phox)] is 0, that of [Ir(COD)(Phox)]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 CH₂Cl₂. The eluant was evaporated in vacuo, and the complex was dried in a vacuum (10⁻² mbar).

**Exchange of Cl by PF₆⁻**

A solution of KPF₆ (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 CH₂Cl₂-MeOH (20 : 1) as eluent. The organic layer was separated, and the aqueous residue was extracted 5 times with CH₂Cl₂. Combined organic extracts were dried over Na₂SO₄, filtered, and evaporated at r.t. The residue was redissolved in a minimum amount of CH₂Cl₂, and the target complex was precipitated with 100 mL of Et₂O, filtered, washed off from the filter with CH₂Cl₂, evaporated at r.t. and dried in a vacuum (10⁻² mbar).

(2-((2-(Diphenylphosphino)phenyl)-4-methyl-4,5-dihydrooxazol-4-yl)-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 CDCl₃ solution (6 month). – ¹H NMR (CDCl₃, 600 MHz): δ = 1.93 (m, 2 H, a-4-HCOD and a-8-HCOD), 2.05 (m, 2 H, a-3-HCOD and a-7-HCOD), 2.26 (m, 4 H, e-3-HCOD, e-4-HCOD, e-7-HCOD, e-8-HCOD). 3.16 (br s, 2 H, 5- and 6-HCOD), 4.09 (t, J = 10 Hz, 2 H, NCH₂), 4.48 (t, J = 10 Hz, 2 H, OCH₂), 5.08 (br s, 2 H, 1- and 2-HCOD), 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 – ¹³C¹H NMR (CDCl₃, 150 MHz): δ = 32.13 (d, J = 3.4 Hz, 4- and 8-CH₂COD), 29.70 (3- and 7-CH₂COD), 54.55 (NCH₂), 64.28 (5- and 6-CH₂COD), 68.39 (OCH₂), 95.14 (d, J = 11.5 Hz, 1- and 2-CH₂COD), 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, 2'-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, N = C), and the signals of BARF. – 31P NMR (CDCl₃, 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 CDCl₃ solution (6 month). – ¹H NMR (CDCl₃, 600 MHz): δ = 1.05 (d, J = 5.7 Hz, Me), 1.47 (nrm, 1 H, a-4-HCOD), 1.65 (nrm, 1 H, a-8-HCOD), 2.03 (nrm, 1 H, e-4-HCOD), 2.06 (nrm, 1 H, e-8-HCOD), 2.45 (nrm, 3 H, a-7-HCOD and 3-HCOD), 2.53 (nrm, 1 H, e-7-HCOD), 3.14 (br m, 1 H, 5-HCOD), 3.36 (br m, 1 H, 6-HCOD), 4.18 (dd, J = 9.0 Hz, J = 3.9 Hz, 1 H, OCH₂), 4.27 (br s, 1 H, NCH₂Me), 4.46 (d, J = 9.0 Hz, 1 H, OCH₂), 4.97 (br s, 2 H, 1- and 2-HCOD), 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. – ¹³C¹H NMR (CDCl₃, 150 MHz): δ = 23.16 (Me), 26.47 (8-CH₂COD), 28.59 (4-CH₂COD), 32.22 (3-CH₂COD), 36.06 (7-CH₂COD), 61.52 (NCH₂Me), 63.80 (6-CH₂COD), 63.92 (5-CH₂COD), 74.24 (OCH₂), 93.54 (d, J = 13.2 Hz, 1-COD), 96.49 (d, J = 12.1 Hz, 2-COD), 117.5 (br s, 4-CH₂COD), 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, N = C), and the signals of BARF. – 31P NMR (CDCl₃, 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 %).
V. Semeniuchenko et al. - (Phosphonidihydroxazole) (1,5-cyclooctadiene) Iridium Complexes

\[(4S)-2-(2-(Di(o-tolyl)phosphino)phenyl)-4-tert-butyl-4,5-dihydroxazole)-(\eta^4-1,5-cyclooctadiene)iridium(I)\] 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).

\[(4S)-2-(2-(Diphenylphosphino)phenyl)-4-isopropyl-4,5-dihydroxazole)-(\eta^4-1,5-cyclooctadiene)iridium(I)\] 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).
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(2-(Diphenylphosphino)phenyl)-4,4-dimethyl-4,5-dihydrooxazole)-(η⁴-1,5-cyclooctadiene)iridium(I) hexafluorophosphate (4j)

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, 3 H, Me), 1.82 (nmr, 2 H, a-3- and a-7-HCOD). 2.01 (nmr, 2 H, e-3- and e-7-HCOD). 2.22 (nmr, 4 H, 4- and 8-HCOD), 3.27 (br s, 2 H, 5- and 6-HCOD). 3.87 (s, 2 H, OCH₂), 5.40 (br s, 2 H, 1- and 2-HCOD), 7.31 (br s, 4 H, 2′- and 3′-H). 7.44 (nmr, 1 H, 3-H). 7.48 (nmr, 3 H, 2′- and 4′-H). 7.54 (br s, 5 H, 4′-H and 4′-HBARF). 7.59 (nmr, 3 H, 5- and 3′-H). 7.60 (nmr, 1 H, 4-H). 7.84 (nmr, 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-CH₂COD). 125.29 (d, J = 47.7 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 %).

(3aR,8bS)-2-(2-(Diphenylphosphino)phenyl)-4,4-dimethyl-4,6-dihydro-3aH-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 CDC₃ solution (6 month). – 1H NMR (CDC₃, 600 MHz, r.t.): δ = 0.156 (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 (nmr, 1 H, a-7-HCOD). 1.72 (nmr, 1 H, a-3-HCOD).

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

A two-necked 10 mL flask was charged with liquid di-cyclohexylphosphine (Ii, 65 mg, 0.33 mmol) or solid dicyclohexylphosphine (Ig, 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 i) 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. [Ir(COD)Cl]2 (100.8 mg, 0.15 mmol) and CH2Cl2 (3 mL) were added to the residue, and the mixture was refluxed for 12 h. After cooling the oil exchange (to BARF or PF6) was performed according to the general procedure A.

(4S)-2-(2-(Bis(2,6-dimethylphenyl)phosphino)phenyl)-4-iso-propyl-4,5-dihydroxazole-(η4-1,5-cyclooctadiene)iridium(I) tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (4g)

Yield: 66.9 %. This complex was catalytically active in stillbene 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. −[31P NMR (CDCl3, 150 MHz); δ = 7.53 (6′-Me), 13.78 (MeP), 19.01 (MeP), 22.78 (2C, 2′-Me and 2′-Me), 26.73 (6′-Me), 29.94 (CHMe2), 44.66 (6-CH2CD), 66.90 (5-CH2CD), 67.04 (OCH2), 79.38 (d, J = 23.8 Hz, 1CH2), 81.75 (CCH), 103.05 (s, 2-CH2), 123.42 (d, J = 16.5 Hz, 3′-CH), 126.00 (d, J = 12.8 Hz, 1-C), 126.28 (d, J = 56.8 Hz, 1′-C), 129.76 (d, J = 47.1 Hz, 3′-C), 130.32 (d, J = 7.3 Hz, 4′-CH), 150.51 (d, J = 88.0 Hz, 1′-C), 130.74 (d, J = 7.3 Hz, 3′-CH), 131.06 (d, J = 12.8 Hz, 6′-CH), 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), 135.55 (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 = 6 Hz, 2′-CMe), 163.85 (d, J = 5.5 Hz, N = C), and the signals of BARF, CH2COD are not distinguishable, since the compound is not pure. −[31P NMR (CDCl3, 161 MHz); δ = +20.8. −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 %).}

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

Yield: 70 %. This complex was catalytically active in stillbene 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.

(4S)-2-(2-(Dicyclohexylphosphino)phenyl)-4-isopropyl-4,5-dihydroxazole-(η4-1,5-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. −[31P NMR (CDCl3, 160 MHz); δ = 0.11 (s, CH3), −1H NMR (CDCl3, 600 MHz, r.t.): δ = 0.80 (d, J = 6.6 Hz, 3 H, Me), 1.08 (d, J = 6.9 Hz, 3 H, Me), 1.15 – 1.4 (nmr, 8 H, Cy), 1.4 – 1.5 (nmr, 2 H, Cy), 1.70 – 1.95 (nmr, 10 H, Cy), 1.61 (nmr, 1 H, a-4-HCy), 1.66 (nmr, 1 H, a-8-HCy), 2.07 (nmr, 2 H, CHMe2 and e-8-HCy), 2.13 (nmr, 2 H, e-4-HCy and e-1′-H), 2.29 (nmr, 1 H, a-3-HCy), 2.49 (nmr, 4 H, e-3-HCy, 7-Hcy and 1′-H), 3.69 (br s, 1 H, 1′-Hcy), 4.15 (br s, 1 H, 6-Hcy), 4.32 (m, 1 H, NC), 4.62 (d, J = 5.9 Hz, 2 H, OCH2), 4.74 (m, NOE with 20.7, 4.32 and 6.22 ppm, 1 H, 1′-Hcy), 5.13 (br s, NOE with 4.32 and 6.42 ppm, 1 H, 2-Hcy), 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), −[31P NMR (CDCl3, 150 MHz); δ = 14.84 (Me), 19.26 (Me), 25.87 (Cy), 26.03 (Cy), 26.09 (4-CH2CD), 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-CH2CD), 29.98 (Cy), 30.65 (Cy), 31.65 (3-CH2CD), 32.09 (d, J = 27.5 Hz, 1′-CH), 32.96 (CHMe2), 36.15 (7-CH2CD), 41.95 (d, J = 26.4 Hz, 1′-CH), 59.86 (5-CH2CD), 61.92 (6-CH2CD), 68.20 (OCH2), 70.19 (NCH), 89.90 (d, J = 11.5 Hz, 1-CHCy), 95.46 (d, J = 11.5 Hz, 2-CHCy), 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-C), 132.43 (d, J = 1.2 Hz, 3-C), 133.87 (d, J = 5.7 Hz, 4-C), 134.07 (d, J = 8.0 Hz, 6-C), 164.34 (d, J = 5.7 Hz, N = C). −[31P NMR (CDCl3, 161 MHz); δ = +10.1 (ligand), −134.7 (sep, J = 714 Hz, PF6). −[31P NMR (CDCl3, 376 MHz); δ = −73.6 (d, J = 714 Hz). −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 %).
1.93 (nrm, 10 H, Cy), 1.61 (nrm, 2 H, a-4- and a-8-H COD), 1.19 – 1.35 (nrm, 8 H, Cy), 1.37 – 1.50 (nrm, 2 H, Cy), 1.66 – 1.89 (d, J = 10.6 Hz, 1 H, 4-H), 2.07 (nrm, 1 H, a-7-H COD), 2.22 (nrm, 1 H, 4′-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-CH2(COD)), 4.33 (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-HCOD), 4.86 (br s, NOE with 4.16 ppm, 1 H, 2-HCOD). 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-HBARF and 3-H), 8.21 (dd, J = 10.6 Hz, J = 2.4 Hz, 1 H, 6-H), and the signals of BARF. – 19F NMR (CDCl3, 150 MHz): ‘δ = 14.54 (Me), 19.16 (Me), 25.76 (Cy), 26.00 (2C, Cy and 8-CH2(COD)), 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-CH2(COD)), 30.18 (Cy), 30.68 (Cy), 31.57 (3-CH2(COD)), 32.20 (d, J = 28.7 Hz, 1 H, 2-HCOD), 32.87 (CH2(CH3)), 36.04 (d, J = 3.5 Hz, 7-CH2(COD)), 42.18 (d, J = 27.5 Hz, 1′-C), 60.82 (5-CH2(COD), 62.92 (6-CH2(COD), 67.87 (OCH2), 70.27 (NCH), 89.43 (d, J = 13.8 Hz, 1-CH2(COD)), 94.14 (d, J = 10.3 Hz, 2-CH2(COD)), 127.04 (d, J = 35.6 Hz, 2-C), 129.16 (d, J = 11.5 Hz, 1-C), 131.84 (5-C), 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. – HRMS ESI/FT-ICR: isotope cluster 684 – 688, found (calcd.): 684.3045, 54% (684.3079, 60 %); 685.3143, 19% (685.3113, 21 %); 686.3098, 100% (686.3103, 100 %); 687.3043, 34% (687.3163, 35 %); 688.3145, 8% (688.3170, 6 %).

(1S)-(1S)-2-(2-(Diphenylphosphino)phenyl)-4,5-dihydrooxazole-4-yl[phenyl)methyl-1η5-1,5-cyclooctadiene-iridium(1) 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 KPPh2 (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. Degased 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)Cl2] (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. – 31P NMR (CDCl3, 150 MHz): δ = -113 (c = 0.11, CHCl3). – 1H NMR (CDCl3, 600 MHz, r.t.): δ = 1.44 (nrm, 1 H, a-4-HCOD), 1.57 (nrm, 1 H, a-8-HCOD), 2.01 (nrm, 1 H, e-4-HCOD), 2.05 (nrm, 1 H, e-8-HCOD), 2.41 (nrm, 1 H, a-7-HCOD), 2.47 (nrm, 1 H, a-3-HCOD), 2.52 (nrm, 1 H, e-3-HCOD), 2.53 (nrm, 1 H, e-7-HCOD), 3.21 (s, 1 H, NOE with 7.14 ppm, 5-HCOD), 3.38 (s, 1 H, 6-CH2(COD), 3.72 (m, 2 H, OCH2), 4.13 (m, 1 H, NCH), 4.68 (br s, 1 H, 2-HCOD), 4.82 (s, 1 H, NOE with 4.13 ppm, 1-HCOD), 5.68 (d, J = 3.5 Hz, CHO2), 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. – 19F NMR (CDCl3, 150 MHz): δ = 26.37 (8-CH2(COD)), 28.52 (4-CH2(COD)), 32.24 (7-CH2(COD)), 36.15 (3-CH2(COD)), 64.12 (5-CH2(COD)), 64.42 (6-CH2(COD)), 74.54 (OCH2), 74.72 (NCH), 83.33 (CHO2), 93.76 (d, J = 13.8 Hz, 1-CH2(COD)), 97.08 (d, J = 11.5 Hz, 2-CH2(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
According to the general procedure A with \([\text{Rh(COD)}\text{Cl}_2]\). 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. \(-^1\text{H NMR}\) (CDCl$_3$, 600 MHz, \(\tau\)): \(\delta = -0.15\) (d, \(J = 6.6\) Hz, 3H, Me), 0.80 (d, \(J = 7.0\) Hz, 3H, Me), 1.85 (nmr, 1H, a-4-HCD), 1.95 (nmr, 2H, C(\text{Me}2) and a-8-HCD), 2.13 (nmr, 1H, e-4-HCD), 2.19 (nmr, 1H, e-8-HCD), 2.45 (nmr, 1H, a-3-HCD), 2.50 (nmr, 1H, a-7-HCD), 2.69 (nmr, 1H, e-3-HCD), 2.79 (nmr, 1H, e-7-HCD), 3.51 (br s, NOE with 7.05 ppm, 1H, 5-HCD), 3.59 (br s, NOE with 7.05 ppm, 1H, 5-HCD), 7.36 (br d, \(J = 8.7\) Hz, 1H, NCH), 4.29 (t, \(J = 9.4\) Hz, 1H, OCH$_2$), 4.33 (dd, \(J = 9.4\) Hz, \(J = 5.3\) Hz, 1H, OCH$_2$), 5.27 (br s, 2H, 1- and 2-HCD), 7.05 (nmr, 2H, 2-\(\alpha\)), 7.33 (br dd, \(J = 9.0\) Hz, \(J = 7.0\) Hz, 1H, 3-\(\alpha\)), 7.41 (t, \(J = 7.2\) Hz, 2H, 3-\(\beta\)), 7.50 (br s, 3H, 4- and 5-\(\beta\)), 7.56 (nmr, 1H, 4-\(\beta\)), 7.61 (nmr, 2H, 4- and 5-\(\alpha\)), 7.68 (nmr, 2H, 2-\(\alpha\)), 8.09 (nm, 1H, 6-H), and the signals of BARF. \(-^{13}\text{C NMR}\) (CDCl$_3$), 150 MHz: \(\delta = 12.9\) (Me), 18.79 (Me), 26.33 (8-CH$_2$COD), 28.65 (4-CH$_2$COD), 30.70 (3-CH$_2$COD), 32.44 (CHMe$_2$), 35.33 (7-CH$_2$COD), 67.74 (OCH$_2$), 70.90 (NCH), 77.61 (d, \(J = 11.5\) Hz, 6-CH$_2$COD), 79.05 (d, \(J = 12.6\) Hz, 5-CH$_2$COD), 105.52 (dd, \(J = 11.5\) Hz, \(J = 8.0\) Hz, 1-CH$_2$COD), 107.66 (dd, \(J = 9.2\) Hz, \(J = 6.9\) Hz, 2-CH$_2$COD), 117.45 (br s, 4$^2$-CH), 124.33 (d, \(J = 49.3\) Hz, 1$^3$-C), 128.52 (d, \(J = 40.2\) Hz, 2$^\alpha$), 128.54 (d, \(J = 14.9\) Hz, 1-\(\alpha\)), 129.03 (d, \(J = 10.3\) Hz, 3-\(\alpha\)), 129.13 (1$^3$-C), 129.80 (d, \(J = 10.3\) Hz, 3$^3$-C), 131.81 (d, \(J = 2.3\) Hz, 4$^3$-C), 132.20 (d, \(J = 0.7\) Hz, 5$^3$-C), 132.64 (d, \(J = 2.3\) Hz, 4-CH), 132.86 (d, \(J = 10.3\) Hz, 2$^3$-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, 4$^\alpha$-C), 163.81 (d, \(J = 8.0\) Hz, N=\(\alpha\)), and the signals of BARF. \(-^{31}\text{P NMR}\) (CDCl$_3$), 161 MHz: \(\delta = +0.30\) (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-\(\{(4S)-2\{(2\{(diphenylphosphino)phenyl\})-4-isopropyl-4,5-dihydrooxazole\}\}\)-(4,4,5,5-tetrakis(3,5-bis(trifluoromethyl)phenyl)borate \(\delta\) (d, \(J = 6.8\) Hz, 3H, Me), 1.09 (d, \(J = 6.8\) Hz, 3H, Me), 2.09 (m, C(\text{Me}2)), 3.85 (m, 1H, NCH), 4.39 (m, 2H, OCH$_2$), 6.87 (br s, 4H, 2$^\gamma$- and 3$^\gamma$-H), 6.96 (br m, 1H, 3-\(\alpha\)), 7.12 (t, \(J = 7.5\) Hz, 1H, 3$^\gamma$-H), 7.33 (t, \(J = 7.5\) Hz, 2H, 3$^\gamma$-H), 7.42 (nmr, 1H, 4$^\gamma$-H), 7.45 (br m, 1H, 4-\(\alpha\)), 7.49 (nmr, 1H, 5-\(\alpha\)), 7.53 (2H, 2$^\alpha$, 7.96 (br d, \(J = 7.5\) Hz, 6-H), and the signals of BARF. – $^{13}\text{C}$ \(\delta\) (d, \(J = 6.9\) Hz, 1-\(\alpha\)), 128.34 (t, \(J = 4.6\) Hz, 3$^\alpha$-CH), 129.69 (4$^\alpha$-CH), 130.41 (5-CH), 130.76 (t, \(J = 20.7\) Hz, 1$^\gamma$-C), 131.18 (4$^\gamma$-CH), 131.41 (br s, 6-CH), 132.52 (br s, 2$^\gamma$-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$^\alpha$-CH), 163.63 (s, N=\(\alpha\)), and the signals of BARF, 1$^\gamma$-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): \(\delta = +0.49\) (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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