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An efficient method for the synthesis of enantiopure phosphine–imidazoline ligands: application to the Ir-catalyzed hydrogenation of imines

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Abstract—Phosphine–imidazoline ligands **8**, and the derivatives **16** and **17**, which have electron-withdrawing or electron-donating groups in the aminic nitrogen, were synthesized from 2-aryl-imidazolines, which have previously been obtained from dithioesters. The coordination of ligand **8** to Ir(I) was studied and the molecular structure of the [Ir(η^4-COD)**8**]BF_4 (COD = 1,5-cyclooctadiene) determined through X-ray diffraction. The in situ prepared Ir(I)/phosphine–imidazoline catalysts were tested in the asymmetric hydrogenation of ketimines in order to evaluate the influence of the electronic parameters of the ligand on the catalytic reaction.

1. Introduction

Chiral metal complexes containing oxazoline derivative ligands are efficient catalysts in asymmetric reactions.[1] Although ligands carrying an imidazoline unit are structurally very similar to oxazoline ligands, they have not received as much attention.[2] Ligands **2** (Fig. 1) are some examples of the chiral imidazoline ligands that have been used in catalysis, specifically in the iridium-catalyzed reduction of unfunctionalized alkenes. In several cases, ee's were higher than when phosphine–oxazoline ligands **1** were used.[3] Ligands **3** were used in the palladium-catalyzed copolymerization of CO/styrene,[4] and ligands **4** in the ruthenium-catalyzed Diels–Alder reaction,[5] and in the diethylzinc addition to aldehydes,[6] and ligands **2** were used in the Heck reaction.[7]

The imidazoline ring has been synthesized with a variety of methods.[8] More specifically, imidazoline derivatives bearing a 2-substituted aromatic group have been prepared by condensation of a diamine with aryl imidoesters (Scheme 1a).[7,9,10] However, this procedure usually provides only moderate yields.[4,5,11] Casey and co-workers have published an improved method that allows imidazoline derivatives to be obtained from enantiopure

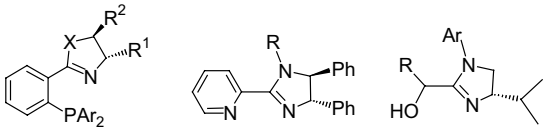
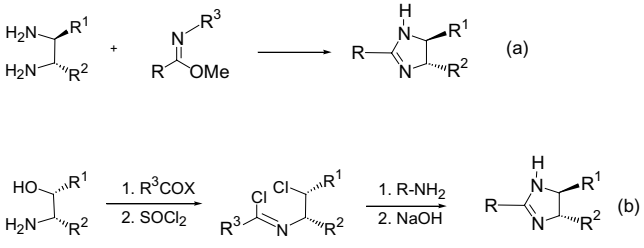


Figure 1.



Scheme 1.

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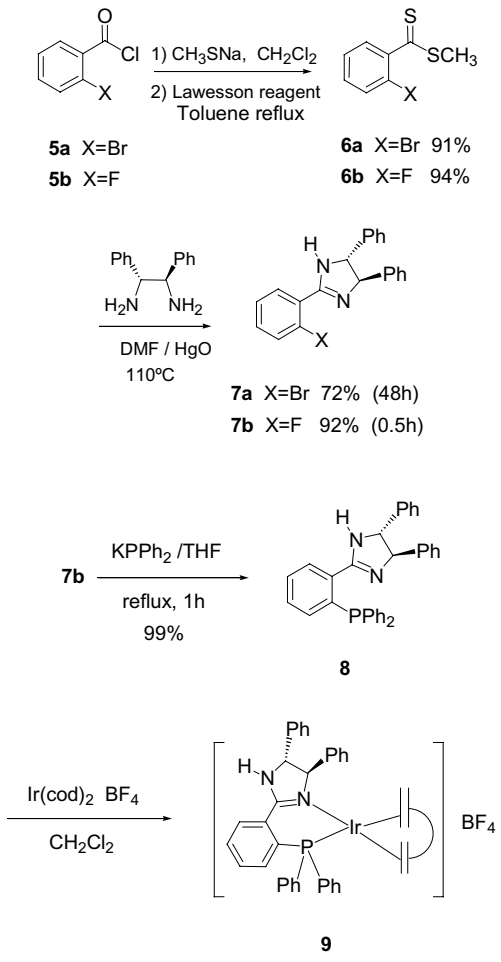
aminoalcohols. The process involves the conversion of aminoalcohols into *N*-chloroethylimidoyl chlorides, which are further reacted with amines and treated in basic medium to afford the enantiopure imidazolines (Scheme 1b).[6,12]

Developing efficient catalysts for the enantioselective conversion of prochiral imines to the corresponding chiral amines is a major research target.[13] Although the enantioselective hydrogenation of alkenes and ketones has been successful with several catalytic systems using phosphorus ligands, the hydrogenation of imines requires further investigation, with high enantioselectivities only being obtained in a few cases.[14,15]

Ligands containing heteroatoms other than phosphorus have occasionally been used successfully in the metal-catalyzed reduction of C=N.[16] Pfaltz and co-workers[17] reported enantioselectivities as high as 89% in the reduction of acyclic imines when cationic Ir(I) complexes with diphenylphosphinooxazolines **1** were used (R = ^{i}Pr, Ar = *o*-Me–Ph, Fig. 1). This is one of the most successful examples of cationic precursors in the asymmetric hydrogenation of imines and it prompted us to try using phosphine–imidazoline ligands in the iridium-catalyzed enantioselective reduction of prochiral imines.

Here we report a new and efficient procedure for synthesizing chiral imidazolines based on the reaction of dithioesters with enantiopure diamines, the synthesis of phosphino imidazoline ligand **8**, the corresponding iridium complex and its behavior as a catalyst precursor in the hydrogenation of imines.



Scheme 2.

2. Results and discussion

Dithioesters **6a** and **b** were prepared from benzoyl chlorides **5a** and **5b**, which have a bromine or fluorine atom at the *ortho*-position. Thus, the reaction of **5a** and **b** with sodium methanethiolate afforded 2-halo-thiobenzoic acid (*S*)-methyl esters in almost quantitative yields, which were subsequently treated with Lawesson's reagent to give dithioesters **6a** and **b** in excellent yields (Scheme 2).[18]

Condensation of dithioesters **6a** and **b** with (1*R*,2*R*)-diphenylethylene diamine in the presence of HgO gave 2-aryl-imidazolines **7a** and **b**.[7] The driving force of the reaction is the precipitation of HgS.[19] Therefore, compounds **7a** and **b** were synthesized from **5a** and **b** with an overall yield of 65% and 86%, respectively.

The phosphino moiety was introduced starting from **7b** following reported procedures.[9d,20] We then reacted **7b** with Ph_2PK in refluxing THF for an hour, which afforded the phosphine–imidazoline ligand **8** in 99% yield.[7] The reaction of ligand **8** with $[Ir(\eta^4\text{-COD})_2]BF_4$ (COD = cyclooctadiene) in dichloromethane gave the complex $[Ir(\eta^4\text{-COD})\mathbf{8}]BF_4$ **9**. The FAB MS analysis of **9** showed peaks at *m*/*z* 783.1 and 675.0, corresponding to M^+ of cation $[Ir(\eta^4\text{-COD})\mathbf{8}]^+$, and the loss of cyclooctadiene (M^+-COD).

The ^{1}H NMR spectra of complex **9** showed signals for the methylene protons of the cyclooctadiene ligand at the expected chemical shift (1.25–2.38 ppm).[21] The olefinic protons of COD had two sets of signals. Two olefinic protons appeared as broad peaks at 4.14–5.12 ppm, and the other two olefinic protons appeared at 2.77–3.41 ppm.[3] In the $^{13}C\{^1H\}$ NMR spectra, the C=N was shifted to a higher chemical shift than the corresponding resonance in the free ligand. This observation is strong evidence of an M–N coordination.[22] The $^{31}P\{^1H\}$ NMR spectra of **9** (15.5 ppm) displayed a singlet shifted to higher chemical shift than in the free ligand **8** (−10.3 ppm), which confirmed that the phosphorus atom was coordinated to the metal center.[17c,d]

The analysis of the single crystal X-ray structure of **9** confirmed the expected organometallic nature of the compound. The elementary cell of crystal of **9** contains two independent molecules (A and B), which have the same chirality and are related by pseudosymmetry. The structures obtained are shown in Figure 2. The independent molecules differ in the conformation of the phosphorus atom, which can be located on the left or the right of the plane of the imidazole ring.

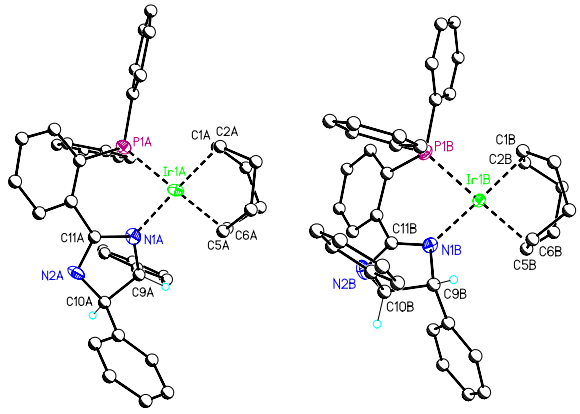


Figure 2. Crystal structure of **9** (molecule A left and B right). Hydrogen atoms, except those attached to chiral atoms, are omitted for clarity.

The coordination geometry of the iridium atom in both molecules is square planar, since the midpoints of the double bonds of the COD ligands, the metal, and the P and N atoms all lie on a plane (main deviation from plane molecule A: 0.0264 Å and molecule B: 0.0035 Å).[16b] The phenyl substituents on the phosphorus adopt a pseudoequatorial and a pseudoaxial position as expected by comparison with the Ir–phosphine–oxazoline[17c,d,23] and Ir–phosphine–imidazoline complexes.[3]

The Ir–N distance [molecule A: 2.084(11) Å; molecule B: 2.095(11) Å] is shorter than the Ir–P distance [molecule A: 2.267(4) Å; molecule B: 2.279(4) Å].[24] The distance from the metal to the midpoint of the C(5)=C(6) double bond *trans* to P [molecule A: 2.083(15) Å; molecule B: 2.102(12) Å] is significantly longer than the distance from the metal to the midpoint of the C(1)=C(2) double bond *trans* to N [molecule A: 2.010(13) Å; molecule B: 1.992(13) Å]. This indicates a clear *trans* effect, which is also observable for similar Ir/NP and Pd/NP[24] complexes. In both molecules, the rings of the chelating ligand (phenyl and imidazoline rings) are not coplanar, but slightly tilted, as indicated by the torsion angle of −27.0° (in molecule A) and 45.2° (in molecule B). These values are similar to those reported by Pfaltz and co-workers for a similar iridium complex.[3]

The absolute configuration for both molecules was determined with *R*(C(9)); *R*(C(10)).[25] Table 1 shows a selection of bond lengths and angles for molecules A and B of complex **9**.

Table 1. Selected bond distances (Å) and angles (°) for complex **9**

	Molecule A	Molecule B
Ir(1)···[C(1)–C(2)]	2.010(13)	1.992(13)
Ir(1)···[C(5)–C(6)]	2.083(15)	2.102(12)
Ir(1)–N(1)	2.084(11)	2.095(11)
Ir(1)–P(1)	2.267(4)	2.279(4)
C(1)–C(2)	1.368(17)	1.378(17)
C(5)–C(6)	1.34(2)	1.373(19)
N(1)–C(11)	1.337(17)	1.291(16)
N(2)–C(11)	1.323(15)	1.340(14)
N(1)–Ir(1)-P(1)	87.0(3)	84.8(3)

We then explored the catalytic behavior of Ir(I)/phosphine–imidazoline catalysts with systems generated in situ from $[Ir(\eta^4\text{-COD})Cl]_2$ or $[Ir(\eta^4\text{-COD})_2]BF_4$ and **8** in order to evaluate the influence of the catalytic precursor.

Three different imines were chosen as model substrates: the acyclic imines *N*-(phenylethylidene)benzylamine **10** and *N*-(phenylethylidene)aniline **11**, and the cyclic imine 6,7-dimethoxy-1-methyl-3,4-dihydroisoquinoline **14**, in which the geometry of the C=N double bond is fixed in the *E*-configuration (Scheme 3).

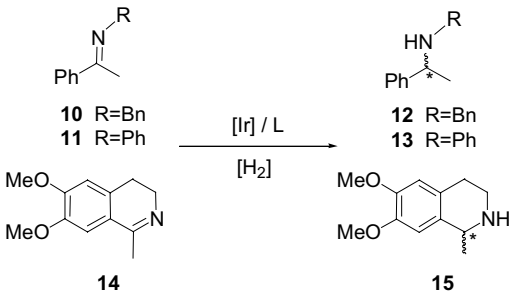
For the reduction of acyclic imines **10** and **11**, the catalytic systems prepared in situ and based on $[Ir(\eta^4\text{-COD})_2]BF_4$/**8** provided better activity than the precursors based on the dinuclear $[Ir(\eta^4\text{-COD})Cl]_2$/**8** (Table 2, entries 2 and 4 vs 1 and 3), although enantioselectivity was negligible for imine **10** and very low for imine **11**.

In the hydrogenation of imine **10**, and in addition to the secondary amine **12**, hydrogenolysis products were also detected, because of the cleavage of the nitrogen–benzylic bond, which decreased selectivity[26] (Table 2, entries 1 and 2).

It has been reported that using additives in the hydrogenation of imines improves the enantioselectivity,[27,28] mainly when neutral precursors are used. However, in our case the cationic precursors provide better conversions, and we decided to explore the role of additives with these precursors.

Many authors have reported the advantages of using additives,[29] particularly iodine, although there are also examples of the use of amines or alcohols with both rhodium- and iridium–phosphine systems.[27a,29b] Nevertheless, additives do not always have a beneficial role; the Ir-BINAP catalyst, for instance, is not affected by the addition of iodide.[30]

Suitable halides,[31] or other additives, which can coordinate to the vacant site of the iridium complex must be selected to improve the enantioselectivity in the hydrogenation of imines.[27,32,33] We selected iodine, tetrabutylammonium iodide, benzylamine, and phthalimide as additives in the hydrogenation of **11**.



Scheme 3.

Table 2. Hydrogenation of imines **10**, **11** and **14** with the catalytic system [Ir(η^4-COD)**8**]BF_4[a]

Entry	Imine	Ligand	Precursor	Additive	Conv (%)	Selec (%)[b]	Ee (%)[c]
1	**10**	**8**	[Ir(η^4-COD)Cl]$_2$	—	27	28	9 (+)
2	**10**	**8**	[Ir(η^4-COD)$_2$]BF_4	—	48	64	3 (+)
3	**11**	**8**	[Ir(η^4-COD)Cl]$_2$	—	2	100	22 (−)
4	**11**	**8**	[Ir(η^4-COD)$_2$]BF_4	—	100	100	15 (−)
5	**11**	**8**	[Ir(η^4-COD)$_2$]BF_4	Bu_4NI	6	100	24 (+)
6	**11**	**8**	[Ir(η^4-COD)$_2$]BF_4	I_2	100	100	0
7	**11**	**8**	[Ir(η^4-COD)$_2$]BF_4	Phthalimide	99	100	12 (−)
8	**11**	**8**	[Ir(η^4-COD)$_2$]BF_4	$BnNH_2$	92	99	13 (−)
9[d]	**14**	**8**	[Ir(η^4-COD)$_2$]BF_4	—	32	100	34 (−)

[a] 1 mol% [Ir], 1.25 mol% ligand, 4 mol% additive, 70 bar H_2, CH_2Cl_2, 25 °C, 16 h.
[b] Selectivity = % of amine in the total products obtained.
[c] No absolute configuration was determined.
[d] 60 bar H_2, 18 h.

The addition of Bu_4NI induced a sharp decrease in the conversion and promoted the formation of the opposite enantiomer (Table 2, entry 5), whereas adding I_2 to the catalytic system gave racemic products (Table 2, entry 6). Hence, the cationic Ir(I)/phosphine–imidazoline/I^- systems did decrease the enantioselectivity of the process. This behavior has already been reported by Pfaltz and co-workers[17c] in the reduction of C=N with cationic Ir(I)/diphenylphosphino-oxazolines catalysts, in which the addition of Bu_4NI also decreased the ee and reversed the configuration of the final product.

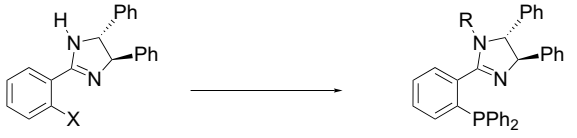
The addition of phthalimide or benzylamine did not have a strong influence on either conversion or enantioselectivity (Table 2, entries 7, 8). The catalytic systems Ir(I)/**8**/amine afforded complete conversions, demonstrating that in this particular case the strong coordinative amines are not poison for the catalyst.

Four different metal precursors were tested, [M(η^4-COD)Cl]$_2$ and [M(η^4-COD)$_2$]BF_4 (M = Ir and Rh) in the reduction of cyclic imine **14**. Conversions were very low (<10%) with both rhodium precursors and the neutral iridium precursor. The hydrogenation of **14** with the catalytic system [Ir(COD)$_2$]BF_4/**8** in the same reaction conditions as the imines **10** and **11**, provided a modest conversion and an ee of 34% (entry 9).

It has been shown that modifying the electronic properties of ligands can have dramatic effects on the enantioselectivity in metal-catalyzed reactions.[34] An important difference (apart from the basicity) between the oxazoline and imidazoline ring is that the imidazoline unit makes it possible to introduce a variety of substituents into the aminic nitrogen, which modify its electronic properties (Fig. 3). We have demonstrated the strong influence of the substituent at the aminic nitrogen on the structure of palladium complexes and in the stereoselectivity of CO/styrene copolymerization.[4] A remarkable influence of the electronic effects in the ligand in the enantioselectivity of the diethylzinc addition to aldehydes,[6] and in the Heck reaction has also been observed.[7]

Accordingly, we decided to prepare diphenylphosphine–imidazoline derivatives with donor or withdrawing groups at the aminic nitrogen. Initially, we reacted **7b** with NaH/BnBr to obtain the benzyl derivative, which was slightly impure due to some the starting material. The reaction of this mixture with $KPPh_2$ provided **17** in moderate yield (Scheme 4). We tried the reaction of **8** with NaH/BnBr to obtain **17** obtaining similar results. Several unsuccessful attempts at purifying **17** were made and the final product contained traces of the starting material. Reaction of **8** with trifluoroacetic anhydride provided **16** in excellent yield.

Reduction of **10** with the catalytic system [Ir(COD)$_2$]BF_4/**16** also afforded moderate yields and selectivities, the ee being very low (Table 3, entries 1 and 2). Also in this case, cationic precursors gave better conversions than neutral ones (Table 3, entries 2 and 4 vs 1 and 3).



7b X=F
8 X=PPh_2

16 R=CF_3
17 R=Bn

Scheme 4.

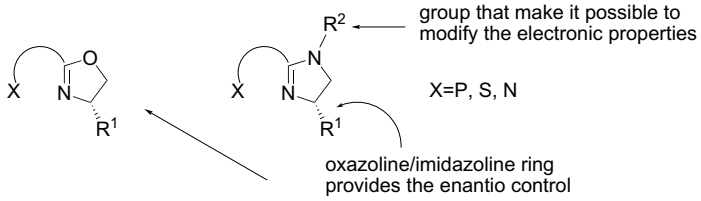


Figure 3.

Table 3. Hydrogenation of imines **10**, **11** and **14** with the catalytic system [Ir(η^4-COD)**16**,**17**]BF_4[a]

Entry	Imine	Ligand	Precursor	Additive	Conv (%)	Selec (%)[b]	Ee (%)[c]
1	**10**	**16**	[Ir(η^4-COD)Cl]$_2$	—	44	38	11 (+)
2	**10**	**16**	[Ir(η^4-COD)$_2$]BF_4	—	75	83	5 (+)
3	**11**	**16**	[Ir(η^4-COD)Cl]$_2$	—	14	100	14 (−)
4	**11**	**16**	[Ir(η^4-COD)$_2$]BF_4	—	100	100	51 (−)
5	**11**	**16**	[Ir(η^4-COD)$_2$]BF_4	Bu_4NI	81	100	27 (+)
6	**11**	**16**	[Ir(η^4-COD)$_2$]BF_4	I_2	100	100	4 (+)
7	**11**	**16**	[Ir(η^4-COD)$_2$]BF_4	Phthalimide	100	100	48 (−)
8	**11**	**16**	[Ir(η^4-COD)$_2$]BF_4	$BnNH_2$	100	99	24 (−)
9[d]	**14**	**16**	[Ir(η^4-COD)$_2$]BF_4	—	42	100	26 (−)
10	**14**	**17**	[Ir(η^4-COD)$_2$]BF_4	—	23	100	9 (−)

[a] 1 mol% [Ir], 1.25 mol% ligand, 4 mol% additive, 70 bar H_2, CH_2Cl_2, 25 °C, 16 h.
[b] Selectivity = % of amine in the total products obtained.
[c] No absolute configuration was determined.
[d] 60 bar H_2, 18 h.

However, when ligand **16** was used, imine **11** was reduced with total conversion and selectivity with the enantiomeric excess being 51% (entry 4). Interestingly, when the withdrawing group CF_3CO was introduced at the iminic nitrogen, the ee increased from 15% (Table 2, entry 4) to 51% (Table 3, entry 4).

Studies in the hydrogenation of enamidoacids using phosphorus ligands have shown that the ee increases when electron-donating groups are present in the ligand. This has been attributed to the fact that electron-rich phosphines, and phosphinites, increase the rate of the oxidative addition (usually the rate limiting step) in the less stable diastereomer by increasing the energy level of the d_{yz} orbital.[34a,b] In the case of imine hydrogenation with ligands **8**, **16**, and **17** we observed an increase in the enantioselectivity when withdrawing groups were used. A mechanism of imine hydrogenation with iridium complexes based on kinetic studies suggests that the rate limiting step is the first hydride transfer to give the η^1-N–Ir intermediate.[35] Possible reasons to explain the results obtained can be the stabilization of the η^1-N–Ir bond, and/or conformational changes in the ligand induced by the trifluoroacetyl group. In fact, the imidazoline and the phenyl group are not coplanar (see Fig. 2), and the torsion angle must be influenced by the substituent at the aminic nitrogen.

Additives have a similar influence to that of the catalytic system [Ir(COD)$_2$]BF_4/**8** (Table 2, entries 5–8, Table 3 entries 5–8). Thus, the addition of tetrabutylammonium iodide decreased the conversion, although less so than with ligand **8**, and inverted the sign of the main enantiomer obtained. The use of iodine provided the racemate while the phthalimide did not have a strong influence on either conversion or enantioselectivity. The catalytic systems Ir(I)/**16**/amine afforded complete conversions. However, a considerable decrease in the ee was observed when benzylamine was added (Table 3, entry 8).

Reduction of imine **14** with the catalytic system [Ir(η^4-COD)$_2$]BF_4/**16** gave a modest conversion and an ee lower than that obtained with ligand **8** (Table 3, entry 9).[27] In this case, we tested the catalytic system [Ir(η^4-COD)$_2$]BF_4/**17** that contained the most electron-rich ligand, which gave a very low ee (entry 10).

3. Conclusions

In conclusion, we have established a very efficient procedure for synthesizing 2-aryl-imidazolines by reacting aryldithioesters with chiral diamines. These imidazolines were used in the synthesis of phosphine–imidazoline ligands **8**, **16**, and **17**.

Catalytic systems formed in situ by the iridium precursor [Ir(η^4-COD)$_2$]BF_4 in the presence of the phosphine–imidazoline ligands **8**, **16**, and **17**, hydrogenate acyclic and cyclic imines provided moderate ee's. In general, the additives had a negative effect on the enantioselectivity of the cationic iridium catalyst based on NP ligands, although the catalyst did not lose its activity when strong coordinative compounds such as amines were added. The electronic properties of the imidazoline moiety, determined by the substituent on the amine group, strongly influence the enantioselectivity obtained in the reduction of imine **11**.

4. Experimental

All reactions were carried out under an argon atmosphere using standard Schlenk techniques. Solvents were distilled and degassed prior to use. ^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$, and $^{19}F\{^1H\}$ NMR spectra were recorded on a Varian Gemini spectrometer at 300 and 400 MHz. Chemical shifts were reported relative to tetramethylsilane for ^1H and $^{13}C\{^1H\}$ as internal reference, H_3PO_4 85% for $^{31}P\{^1H\}$, and trichlorofluoromethane for $^{19}F\{^1H\}$ as external references. Elemental analyses were carried out on a Carlo Erba Microanalyser EA 1108. VG-Autospect equipment was used for FAB mass spectral analyses with 3-nitrobenzylalcohol as matrix. EI mass spectra were obtained on an HP 5989 A spectrometer at an ionizing voltage of 70 eV. Optical rotations were measured on a Perkin–Elmer 241 MC polarimeter. Melting points were determined in an open capillary tube with a Tottoli-Büchi 510 melting point apparatus and are uncorrected. Single hydrogenation reactions were carried out in a Berghof or Parr 100 mL stainless steel autoclave and multi-screening hydrogenations were performed in a home-made 96-microtiter plate in Bayer AG (Leverkusen–Germany). The catalytic reactions

were monitored by GC on a Hewlett–Packard 5890A. Conversion was measured in an Ultra-2 (5% diphenylsilicone/95% dimethylsilicone) column (25 m × 0.2 mm Ø). The enantiomeric excesses were measured directly in the reaction crude by NMR or gas chromatography. *N*-(Phenylethylidene) benzylamine **12** was determined by ^{1}H NMR (with mandelic acid as the resolution agent) or by GC, after derivation into the trifluoroacetamide compound, in a β-cyclodextrin phase. The enantiomeric excess of *N*-(phenylethylidene)aniline **13** and 6,7-dimethoxy-1-methyl-3,4-dihydroisoquinoline imine **15** was determined by CC, after derivation into the acetamide compound, in a MN, Hydrodex–6-TBDM (25 m × 0.25 mm × 0.25 m) column.

4.1. Synthesis of 2-bromo-dithiobenzoic acid (*S*)-methyl ester 6a

2-Bromobenzoylchloride (186 μL, 1.42 mmol) was added dropwise at 0 °C to a suspension of 0.12 g (1.6 mmol) of methanethiolate sodium salt with 1.5 mL of dichloromethane. After 1 h at room temperature, the reaction mixture was quenched with water (5 mL). After several extractions with dichloromethane, the combined organic layers were dried and concentrated to afford 2-bromothiobenzoic acid (*S*)-methyl ester as a yellow liquid (0.325 g), which was used without purification in the next step. Next, Lawesson's reagent (2 g, 5.4 mmol) was added under argon to a solution of 2-bromo-thiobenzoic acid (*S*)-methyl ester (0.325 g, 1.4 mmol) in dry toluene (17 mL) and the mixture heated to reflux. The reaction was monitored by TLC. When no starting material could be detected (ca. 24 h), the reaction mixture was allowed to cool and filtered. The solid was washed with toluene and the combined toluene solutions were evaporated, and purified by flash column chromatography (hexane/ethyl acetate 10:1) to afford 318 mg (91% yield for the two steps) of compound **6a** as a red liquid. ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.57 (m, 1H, arom.), 7.35–7.20 (m, 3H, arom.), 2.78 (s, 3H, CH_3); ^{13}C NMR (100.6 MHz; $CDCl_3$) δ 230.4 (C=S), 147.7 (C, arom.), 133.6 (CH, arom.), 130.4 (CH, arom.), 128.2 (CH, arom.), 127.4 (CH, arom.), 118.6 (C, arom.), 20.9 (CH_3).

4.2. Synthesis of 2-fluoro-dithiobenzoic acid *S*-methyl ester 6b

Using a procedure that was identical to that for **6a**, 2-fluorobenzoylchloride (1.9 mL, 15.5 mmol) was added dropwise at 0 °C to a suspension of sodium methanethiolate salt (1265 g, 17 mmol) in 15 mL of dichloromethane. 2-Fluoro-thiobenzoic acid (*S*)-methyl ester was obtained as a yellow liquid (2.6 g), which was used without purification in the next reaction step. Next, Lawesson's reagent (13.9 g, 37.5 mmol) was added under argon to a solution of 2-fluoro-thiobenzoic acid (*S*)-methyl ester (2.6 g, 15.2 mmol) in dry toluene (17 mL) and the mixture was heated to reflux for 24 h to give compound **6b** as a red liquid (2.76 g, 94% for the two steps). The obtained product was pure enough to be used in the next reaction without purification. ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.56 (m, 1H, arom.), 7.34 (m, 1H, arom.), 7.13–7.03 (m, 2H, arom.), 2.71 (s, 3H, CH_3); ^{13}C NMR (100.6 MHz; $CDCl_3$) δ 224.2 (C=S), 157.3 (d, ^1J(C–F) 253.1 Hz, C, arom.), 134.5 (d, ^2J(C–F) 12.4 Hz, C, arom.), 132 (d, ^3J(C–F) 8.5 Hz, CH, arom.), 129.5 (CH, arom.), 123.9 (d, ^3J(C–F) 3.7 Hz, C, arom.), 116.3 (d, ^2J(C–F) 22.2 Hz, CH, arom.), 20.9 (CH_3).

4.3. Synthesis of (4*R*,5*R*)-2-(2-bromo-phenyl)-4,5-diphenyl-4,5-dihydro-1*H*-imidazole 7a[7]

A solution of **6a** (914 mg, 3.7 mmol) in dimethylformamide (4 mL) was added to a suspension of (1*R*,2*R*)-diphenylethylenediamine (786 mg, 3.7 mmol) and red mercury(II) oxide (814 mg, 3.7 mmol) in dimethylformamide (9 mL) at room temperature and vigorously stirred. The solution was heated at 110 °C for 48 h. Then, the reaction mixture was filtered, concentrated under reduced pressure, and purified by flash column chromatography (hexane/ethyl acetate 1:7) to afford 1 g (72% yield) of compound **3a** as a white powder. Mp = 148–150 °C. $[\alpha]_D^{20}$ = +60.1 (c = 1.07, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (m, 1H, arom.), 7.59–7.57 (m, 1H, arom.), 7.35–7.24 (m, 12H, arom.), 4.83 (s, 2H, CH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 163.1 (C=N), 143.2 (CH, arom.), 133.4 (CH, arom.), 132.6 (C, arom.), 131.5 (CH, arom.), 131.4 (CH, arom.), 129.2 (C, arom.), 128.7 (CH, arom.), 128.4 (CH, arom.), 127.6 (CH, arom.), 127.1 (CH, arom.), 126.8 (CH, arom.), 121.1 (C, arom.), 75.3 (CH). Elemental analysis: Calcd for $C_{21}H_{17}BrN_2$: C, 67.34; H, 4.58; N, 7.44. Found: C, 67.22; H, 4.60; N, 7.46.

4.4. Synthesis of (4*R*,5*R*)-2-(2-fluoro-phenyl)-4,5-diphenyl-4,5-dihydro-1*H*-imidazole 7b[7]

Using a procedure that was identical to that for **7a**, starting from **6b** (326 mg, 1.75 mmol), dimethylformamide (3 mL), (1*R*,2*R*)-diphenylethylenediamine (407 mg, 1.92 mmol), and red mercury(II) oxide (414 mg, 1.9 mmol) in dimethylformamide (2 mL) were reacted at 110 °C for 30 min. Work-up of the reaction mixture afforded compound **7b** (509 mg, 92%). $[\alpha]_D^{20}$ = +48.5 (c = 0.811, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (dt, 1H, J = 7.6 Hz, J = 1.6 Hz, arom.), 7.49–7.12 (m, 13H, arom.), 5.99 (s, 1H, NH), 4.89 (s, 2H, CH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 162.1 (C=N), 159.4 (d, ^1J = 32.9 Hz, C, arom.), 143.3 (C, arom.), 132.6 (d, ^3J = 9.15 Hz, CH, arom.), 131.3 (d, ^4J = 2.3 Hz, CH, arom.), 128 (CH, arom.), 127.5 (CH, arom.), 126.6 (CH, arom.), 124.6 (d, ^3J = 3.1 Hz, CH, arom.), 117.6 (d, ^2J = 10.6 Hz, C, arom.), 116.1 (d, ^2J = 23.6 Hz, CH, arom.); δ_F (376.5 MHz; solvent $CDCl_3$; standard $CFCl_3$) −114.2 (m); m/z 316 (M^+, 11.3%), 239 (1.28), 211 (100); HRMS: m/z, $C_{21}H_{17}N_2F$ calculated: 316.1376, Found: 316.1365. Elemental analysis: Calcd for $C_{21}H_{17}FN_2$: C, 79.72; H, 5.42; N, 8.85. Found: C, 80.10; H, 5.32; N, 8.95.

4.5. Synthesis of (4*R*,5*R*)-2-(2-diphenylphosphanyl-phenyl)-4,5-diphenyl-4,5-dihydro-1*H*-imidazole 8[7]

Compound **7b** (150 mg, 0.475 mmol) was added to a solution of potassium diphenylphosphide (1.04 mL,

0.522 mmol, 0.5 M in tetrahydrofuran) and the resulting mixture heated at 60 °C for 1 h. The reaction crude was then poured into water and extracted twice with dichloromethane. The organic layer was dried with anhydrous $MgSO_4$ and purified by column chromatography under argon (hexane/ethyl acetate 1:1) to give compound **8** as a white foam (226 mg, 99%). $[\alpha]_D^{20} = -19.2$ ($c = 0.57$, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (m, 1H, arom.), 7.32–7.11 (m, 22H, arom.), 6.80 (m, 1H, arom.), 5.86 (br s, 1H, NH), 4.73 (m, 1H, CH), 4.48 (m, 1H, CH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 164.2 (C=N), 143.3–126.7 (arom), 80.3 (CH), 71.3 (CH); ^{31}P NMR (161.9 MHz, $CDCl_3$, standard H_3PO_4 85%) δ −10.3; MS: *m/z* 482 (M^+, 3.78%), 405 (9.61), 301 (100), 222 (3.59); HRMS (EI): *m/z*, $C_{33}H_{27}N_2P$ Calculated 482.1912, Found 482.1911. Elemental analysis: Calcd for $C_{33}H_{27}N_2P$: C, 82.14; H, 5.64; N, 5.81. Found: C, 82.17; H, 5.48; N, 5.29.

4.6. Synthesis of [Ir(η^4-COD)(8)]BF_4 9

A solution of **8** (81.7 mg, 0.17 mmol) in dry and degassed dichloromethane (3 mL) was added dropwise to a chilled (−80 °C) solution of [Ir(η^4-COD)$_2$]BF_4 (70 mg, 0.141 mmol) in dry and degassed dichloromethane (3.5 mL). The solution was allowed to warm to 0 °C and stirred for 30 min. Then, ethyl ether (30 mL) was added to precipitate the desired product **9** as a pale red orange solid (119 mg, 97%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50–6.70 (m, 24H, CH arom.), 4.93 (m, 1H, CH), 4.85 (m, 2H, CH, COD), 4.66 (m, 1H, CH), 2.90 (m, 1H, CH, COD), 2.77 (m, 1H, CH, COD), 2.37 (m, 1H, CH_2, COD), 2.14 (m, 1H, CH_2, COD), 2.03 (m, 3H, CH_2, COD), 1.67 (m, 1H, CH_2, COD), 1.48 (m, 2H, CH_2, COD); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 162.2 (C=N), 141.9–125.4 (arom.), 95.6 (CH, COD), 93.2 (CH, COD), 78.8 (CH), 67.5 (CH), 59.8 (CH, COD), 59.5 (CH, COD), 34.4 (CH_2, COD), 31.5 (CH_2, COD), 29,8 (CH_2, COD), 27.5 (CH_2, COD); ^{31}P NMR (161.9 MHz, $CDCl_3$, standard H_3PO_4 85%) 15.5; *m/z* 783.1 (M^+, 100%). HRMS L-SIMS: *m/z*, $[C_{41}H_{39}N_2PIr]^+$ Calculated 783.2480, Found 783.2467.

4.7. Crystal structure determination of complex 9

Single crystals of **9** were recrystallized under inert conditions from 2-butanone at room temperature. An orange crystal plate with the dimensions $0.20 \times 0.20 \times 0.01$ mm^3 was used to take the measurements. The crystal structure for **9** was determined using a Siemens P4 diffractometer equipped with a SMART-CCD-1000 area detector, a MACScience Co rotating anode with MoK radiation, a graphite monochromator, and a Siemens low temperature device LT2 ($T = -120$ °C). The measurements were made in the range 1.70–31.55° for θ. Fullsphere data collection omega and phi scans. Programs used: Data collection Smart V. 5.060 (BrukerAXS 1999), data reduction Saint+Version 6.02 (Bruker AXS 1999) and absorption correction SADABS (Bruker AXS 1999). The crystal structure solution for **9** in the space group $P2_1$ was achieved using the direct methods implemented in SHELXTL Version 5.10 (Sheldrick, Universtität Göttingen (Germany), 1998) and visualized using the XP program. The missing atoms were subsequently located by difference Fourier synthesis and added to the atom list. The elementary cell contains two independent molecules of complex **9** related by pseudosymmetry. Least-squares refinement on F2 using all measured intensities was carried out with the program SHELXTL Version 6.10 (Sheldrick, Universtität Göttingen (Germany), 2000). All nonhydrogen atoms were refined, including anisotropic displacement parameters. The benzene ring C12A–C17A is disordered, without effects on the chirality, in two positions with a ratio 81:19. Hydrogen atoms were invariably placed in geometrically optimized positions and forced to ride on the atom to which they are attached. A structure solution in the centrosymmetrical space group $P2_1/c$ is also possible and leads after refinement to a single molecule in the elementary cell with disorder at the phenyl rings attached to the chiral centers (C12–C17 and C18–C23). The occupancy of the disordered atoms is 50:50. By solving and refining the structure in the centrosymmetrical space group $P2_1/c$ the absolute configuration cannot be determined and the R_1 value is much higher. The structure solution in the chiral space group $P2_1$ should be preferred. The structure determination was repeated a second time with a new crystal and the results were the same as those of the first crystal measured.

4.8. Crystal data

$(C_{41}H_{39}BF_4N_2PIr) \times 2$, $M = 869.72$, monoclinic, space group $P2_1$ (no. 4), $a = 13.8464(7)$ Å, $b = 13.5639(6)$ Å, $c = 19.0698(8)$ Å, $\beta = 98.779(2)°$, $V = 3539.6(3)$ Å^3, $Z = 2$, $\rho_{calc.} = 1.632$ g cm^{-3}, $\mu = 3.871$ mm^{-1}, $F(000) = 1728$, Reflections collected = 52,629, independent reflections [R(int)] = 22,446 [0.1091], observed reflections Fo > 4σ (Fo) = 7380, Data/restraints/parameters = 22,446/43/896, goodness-of-fit on $F^2 = 0.864$, final R_1 [I > 2σ(I)] = 0.0661, final wR_2 [all data] = 0.1336, absolute structure parameter: −0.003(10). CCDC No. 230095.

4.9. Synthesis of (4*R*,5*R*)-1-trifluoroacetyl-2-(2-diphenylphosphanyl-phenyl)-4,5-diphenyl-4,5-dihydro-1*H*-imidazole 16

A total of 45 μL (0.31 mmol) of trifluoroacetic anhydride was added to a solution of 100 mg (0.207 mmol) of **8** and 60 μL of triethylamine in 1 mL of anhydrous dichloromethane. The solvent was removed after 1 h and the residue purified by silica gel column chromatography under argon (hexane/ethyl acetate 5:1) to give compound **16** as a white solid (102.8 mg, 86%). ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.60 (ddd, $J = 8$ Hz, $J = 4.4$ Hz, $J = 3$ Hz, 1H, arom.), 7.47 (dt, $J = 7.6$ Hz, $J = 0.8$ Hz, 1H, arom.), 7.41–7.20 (m, 19H, arom.), 7.11 (ddd, $J = 7.6$ Hz, $J = 4$ Hz, $J = 0.8$ Hz, 1H, arom.), 7.15 (t, $J = 1.2$ Hz, 1H, arom.), 7.00 (d, $J = 2.4$ Hz, 1H, arom.), 5.28 (d, $^3J = 4.6$ Hz, 1H, CH), 5.16 (d, $^3J = 4.6$ Hz, 1H, CH); ^{13}C NMR (100.6 MHz; $CDCl_3$) δ 165.8 (C=N), 155.1 (d, $^2J_{C-F} = 39.8$ Hz, C=O), 141–125 (arom), 115.4 (d, $^1J_{C-F} = 289.1$ Hz, CF_3), 81.4 (CH), 70.0 (CH); δ_P (161.9 MHz; solvent $CDCl_3$; standard H_3PO_4 85%) −11.8; δ_F (376.5 MHz; solvent $CDCl_3$; standard $CFCl_3$)

−71.7. Elemental analysis: Calcd for $C_{35}H_{26}F_3N_2OP$: C, 72.66; H, 4.53; N, 4.84. Found: C, 72.63; H, 4.34; N, 4.71.

4.10. Synthesis of (4*R*,5*R*)-1-benzyl-2-(2-diphenylphosphanyl-phenyl)-4,5-diphenyl-4,5-dihydro-1*H*-imidazole 17

A solution of 125 mg (0.395 mmol) of **7b** in 1 mL of anhydrous tetrahydrofuran was added to a cooled solution (0 °C) of 17.4 mg (0.43 mmol) of NaH (60% in oil suspension) and 0.5 mL of anhydrous tetrahydrofuran. The mixture was stirred for 30 min and then benzyl bromide (47 μl, 0.395 mmol) added dropwise. After 3 h, the reaction was stopped by adding a few drops of methanol. Purification by column chromatography (hexane/ethyl acetate 3:1) gave compound **4** as a pale yellow solid (88.5 mg, 55%). Several attempts of purification were unsuccessful, and the final product contained 5% of starting material. This mixture was added to a solution of potassium diphenylphosphide (0.5 M in tetrahydrofuran) (0.5 mL, 0.239 mmol) and heated at 60 °C for 1 h. The reaction crude was then poured into water and extracted twice with dichloromethane. The organic layer was dried with anhydrous $MgSO_4$ and purified by column chromatography under argon (hexane/ethyl acetate 3:1) to give compound **17** as a white solid (68 mg, 54%). Several attempts of purification were unsuccessful and the final product contained traces of **7b**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (m, 1H, arom.), 7.44 (m, 1H, arom.), 7.38–7.10 (m, 25H, arom.), 6.90 (m, 2H, arom.), 4.93 (d, ^3J = 9.8 Hz, CH), 4.44 (d, ^3J = 9.8 Hz, CH), 4.28 (d, ^2J = 17 Hz, CH_2), 3.70 (d, ^2J = 17 Hz, CH_2); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 164.9 (C=N), 143.9–126.8 (arom), 78.8 (CH), 72.8 (CH), 49.3 (CH_2); ^{31}P NMR (161.9 MHz, $CDCl_3$) δ −12.3; *m*/*z* 481 (100), 91 (26.11).

4.11. General procedure for the Ir-catalyzed hydrogenation of imines

$[Ir(\eta^4\text{-COD})Cl]_2$ (0.022 mmol) or $[Ir(\eta^4\text{-COD})_2]BF_4$ (0.045 mmol) was dissolved in 10 mL of dry, degassed CH_2Cl_2 in a Schlenk tube. The phosphine–imidazoline ligand (0.055 mmol) was then added, followed by the corresponding imine (4.4 mmol for a 100:1 imine:Ir ratio). The solution was transferred under argon to the autoclave via a syringe. The reaction mixture was stirred at room temperature under 70 bar of H_2 pressure.

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