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ARTICLE

P-Trifluoromethyl ligands derived from *Josiphos* in the Ir-catalysed hydrogenation of 3,4-dihydroisoquinoline hydrochlorides

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The synthesis of mono *P*-trifluoromethyl and therefore P-stereogenic Xyliphos-derived ligands **5** and their application in the Ir-catalyzed enantioselective hydrogenation of 1-substituted 3,4-dihydroisoquinolinium species (DHIQ) is reported. The ligands were prepared following previous procedures involving the reaction of a bistrifluoromethylphosphine with lithiated (*R*)-Ugi amine **1**. Chloroiridium(I) cyclooctadiene precatalysts containing these new partially electron-poor ligands **9** were found to be poorly active in the hydrogenation of free 1-phenyl-3,4-dihydroisoquinoline **12a**. However, the corresponding hydrochloride **12a**□HCl was smoothly reduced at 55-60 °C and 100 bar hydrogen pressure. The (S_P)-configured ligand (S_P)-**5** yielded significantly higher enantioselectivity in hydrogenation experiments than its P-stereoisomeric counterpart (R_P)-**5**. These new ligands were subsequently applied in the hydrogenation of a series of different 1-substituted 3,4-DHIQ chlorides **12a-l**□HCl. Good to excellent enantioselectivity was observed for substrates bearing relatively large substituents in position 1, reaching 96% *ee* for 1-Ph-DHIQ chloride **12a**□HCl without the help of any additives. Furthermore, an interesting counter ion effect was found with chloride being best and hexafluorophosphate very detrimental to enantioselectivity.

Introduction

Hundreds of alkaloids and other biologically active natural products bearing the 1,2,3,4-tetrahydroisoquinoline (THIQ) motif as integral building block are known.[1] Apart from this, THIQs may serve as valuable intermediates in the synthesis of more complex structures, e.g. morphine.[2] Before 2006, stereoselective approaches to THIQs mainly relied on diastereoselective reaction steps, the use of chiral auxiliaries, or the resolution of racemates.[3]

Enantioselective reduction of heteroarenes and unsaturated heterocycles, aiming for chiral piperidines, THIQs, tetrahydroquinolines, and related compounds, constituted an unsolved problem for a long time. Poor activity and enantioselectivity rendered most catalytic systems inefficient. Quinolines have meanwhile become readily amenable substrates, the enantioselective hydrogenation of pyridines, isoquinolines, and 3,4-dihydroisoquinolines (DHIQ), however remaining challenging up to date.[4] The activity of most homogeneous catalysts in the hydrogenation of these underivatized substrates is low and it was reasoned that the product coordinates to the catalyst thereby deactivating it.[5]

Zhou and co-workers reported in 2006 high activity and enantioselectivity in the Ir-catalyzed hydrogenation of 1- and 2-substituted isoquinolines and quinolines, respectively. Stoichiometric amounts of chloroformates were added to the reaction mixture, forming *in situ* iminium carbamates. These are activated towards reduction and the corresponding products are obtained as carbamates that are incapable of forming stable complexes with the catalyst.[5] Similar approaches, applying tosyl chloride or benzyl halides, were reported subsequently for isoquinolines and 3,4-dihydroisoquinolines.[6,7] Zhang and co-workers reduced a series of 1-substituted DHIQs with excellent enantioselectivity applying a dinuclear iodide bridged iridium(III) hydride complex of f-binaphane in the presence of elemental iodine.[8] Ružič and co-workers reported optimized conditions for the asymmetric Ir-catalyzed hydrogenation of 1-phenyl-3,4-dihydroisoquinolinium chloride, **12a**□HCl, reaching full conversion and up to 97% *ee* in the presence of 1-2 equivalents of phosphoric acid.[9] Mashima *et al.* reported the hydrogenation of 1-, 3-, and 1,3-substituted isoquinolinium chlorides applying dinuclear chloride-bridged Ir(III) hydride complexes of Difluorphos (Scheme 1).[10] Another promising approach applied oxidizing additives (iodine, BCDMH) in the hydrogenation of free 3,4-disubstituted isoquinolines, significantly increasing the activity of the catalytic system.[11] Particularly in the last very few years, numerous reports about Ru-catalyzed enantioselective transfer hydrogenation of 3,4-dihydroisoquinolines emerged.[12-14]

A remarkable number of C_1 symmetric bidentate ligands with electronically strongly differing ligating atoms were successfully applied in the hydrogenation of C=N bonds.[15-17] However, C_2-symmetric axially-chiral ligands were almost exclusively applied in the hydrogenation of the above discussed substrate classes so far. Hence, interest arose about the performance of Josiphos-derived *P*-trifluoromethyl ligands, previously reported by our group.[18]

Electron-poor P-stereogenic phosphines are known to withstand rather high reaction temperatures without epimerization. This may be conveniently explained by an altered hybridization of the phosphorus atom. Bent stated that "Atomic s-character

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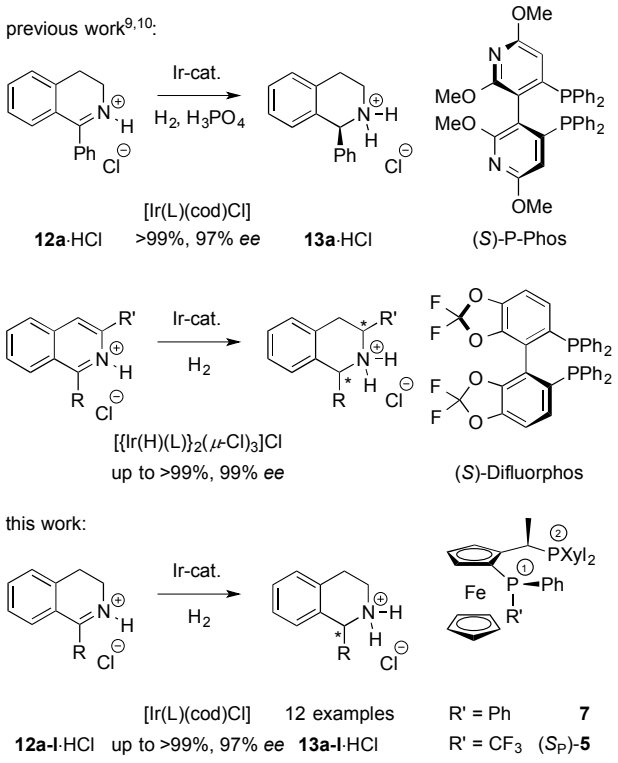
concentrates in orbitals directed toward electropositive substituents. Or, atomic p-character concentrates in orbitals toward electronegative substituents".[19] Hence, electron-withdrawing substituents on phosphines lead to an increased s-character of the lone pair. Assuming that the inversion of the phosphine proceeds via a trigonal planar transition state, the energetically low lying lone pair of high s-character has to rehybridize to pure p-character for inversion and has therefore to overcome this additional energy penalty. However, reduced electron density on π-acceptors, such as e.g. phenyl substituents bearing trifluoromethyl groups, lower the barrier for inversion due to stabilization of the fully occupied p-orbital during the transition state, as already thoroughly investigated by Mislow.[20] It has, however, to be noted that an alternative inversion mechanism was proposed for strongly electron-poor phosphines to proceed via a T-shaped transition state.[21-23]

We disclose herein the first successful application of *P*-trifluoromethyl Josiphos-derived ligands in the enantioselective hydrogenation of various 1-substituted 3,4-dihydroisoquinolines hydrochlorides, **12a-l**·HCl.



Scheme 1 Hydrogenation of 1-substituted isoquinolinium and 3,4-dihydroisoquinolinium chlorides applying iridium(I) precatalysts.

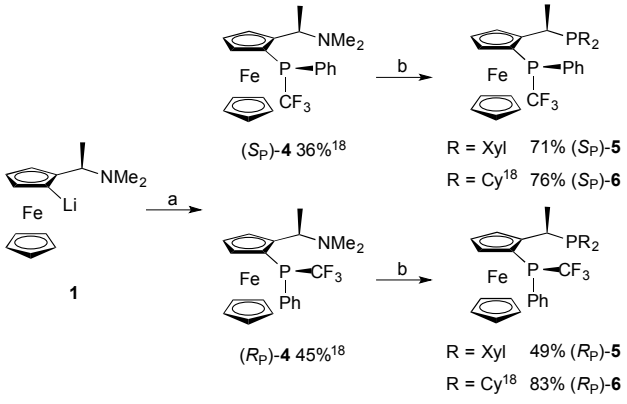
Results and discussion

Ligand Synthesis and Characterization

P-Monotrifluoromethyl and therefore P1-stereogenic Josiphos-derived ligands were prepared adapting the synthetic protocol previously reported from our laboratory (Scheme 2).[18] When a bistrifluoromethylphosphine is treated with lithiated (*R*)-Ugi amine (**1**) as a nucleophile one of the trifluoromethyl substituents acts as a leaving group. The diastereoselectivity of this substitution step varies with the steric bulk of the third substituent on the bistrifluoromethylphosphine. Relatively small residues like phenyl or 2-naphthyl lead usually to a ca. 1:1 mixture of diastereoisomers. In strong contrast to this, only moderately larger substituents such as *o*-tolyl or mesityl, lead to high diastereoselectivity favoring the sterically less congested S_P-configured product (S_P:R_P >10:1). However, the diastereoisomeric phosphinoaminoferrocenes products may be conveniently separated by column chromatography. The last synthetic step follows the synthetic procedure to parent Josiphos **8**, i.e. heating the phosphinoaminoferrocene in acetic acid with the corresponding secondary phosphine.[24,25]

Due to the strongly electron-withdrawing effect of the CF_3 group, no epimerization of the stereogenic phosphine occurred at or below 90°C in all cases under study. However, heating the reaction mixture in acetic acid at reflux overnight, leads to some appreciable epimerization and the resulting mixture is difficult to purify. A comparable situation had been observed for more electron-rich stereogenic phosphines bearing a stereogenic diarylferrocenyl phosphine, where up to 20% of the epimer was formed at 100 °C.[26]

Surprisingly, all Josiphos-derived ligands bearing a dicyclohexylphosphine moiety on the stereogenic side chain in combination with the electron-poor phosphine attached to the Cp, turned out to be oxygen sensitive even as solids. The oxide impurity could neither be separated nor could the oxidized PCy_2 moiety be reduced by conventional methods. Therefore, further studies focused on ligands bearing a bis(3,5-dimethylphenyl)phosphino group on the ethyl side chain, denoted as Xyliphos-derived ligands (**5**).



a) $PhP(CF_3)_2$ (**2**) Et_2O, 0 °C, chromatography.[18] b) Xyl_2PH (**3**) or Cy_2PH, AcOH, 90 °C, crystallization

Scheme 2 Synthesis of Xyliphos- and Josiphos-derived P1-trifluoromethylated ligands **5** and **6.**

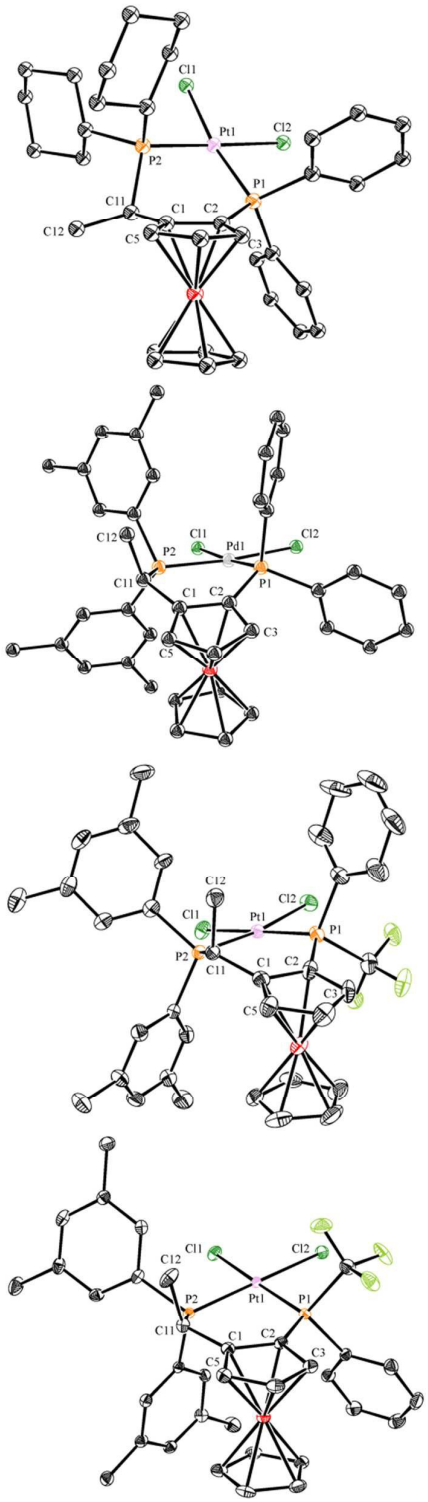


Fig. 1 ORTEPIII plots of investigated Xyliphos-derived $PtCl_2$ complexes **11** and related complexes for comparison. From top: $[Pt((R,S)\text{-Josiphos})Cl_2]$[25], $[Pd((R,S)\text{-Xyliphos})Cl_2]$[27], $[Pt((S_P,R,S)\text{-Ph}(CF_3)\text{-Xyliphos})Cl_2]$, $[(S_P)\text{-}\mathbf{11}]$ and $[Pt((R_P,R,S)\text{-Ph}(CF_3)\text{-Xyliphos})Cl_2]$, $[(R_P)\text{-}\mathbf{11}]$.

Model Pt(II) chloride complexes **11** of the new trifluoromethyl Xyliphos-derived ligands **5** were obtained upon treatment of the ligand with $[Pt(cod)Cl_2]$ in a halogenated solvent. The desired product was conveniently isolated as single crystals by slow diffusion of an alkane into the solution of the complex. X-ray crystallography revealed that both P-stereoisomers strongly resemble each other in the solid state. The trifluoromethyl phosphine forms, as expected, significantly shorter bonds to Pt due to reinforced back-donation and changes in hybridization of the affected phosphorus atom. Figure 1 illustrates the solid state structure and Table 1 provides some characteristic structural parameters of such complexes.

Table 1 Conformational descriptors of complexes containing Josiphos-type ligands

	$[Pt(8)Cl_2]$[d]	$[Pd(7)Cl_2]$[e]	(S_P)-11[f]	(R_P)-11[g]
α1[a]	-19.12 °	-88.07 °	-68.82 °	-54.30 °
α2[b]	-20.30 °	74.01 °	85.05 °	72.90 °
P1-Pt(Pd)	2.237 Å	2.214 Å	2.2130 Å	2.2205 Å
P2-Pt(Pd)	2.248 Å	2.255 Å	2.2332 Å	2.2510 Å
Incl.	28.92 °	-14.85 °	-8.72 °	2.70 °
P1-Pt(Pd)-P2	95.19 °	93.59 °	95.77 °	95.96 °
Plan.[c]	359.96°	359.69°	360.21°	359.61°

[a]C3-C2-P1-R_{exo}. [b]C5-C1-C11-C12. [c]Sum of the four bond angles around Pt/Pd as a measure of distortion of planarity. [d]$[Pt((R,S)\text{-Josiphos})Cl_2]$, CSD-RefCode WIJKEF[25]. [e]$[Pd((R,S)\text{-Xyliphos})Cl_2]$, CSD-RefCode XIKTAN[27]. [f]CSD-number 1000085. [g]CSD-number 1000084.

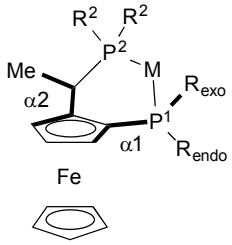


Fig. 2 The torsion angles α1 and α2 used in describing conformational properties complexes containing Josiphos derived ligands.[28]

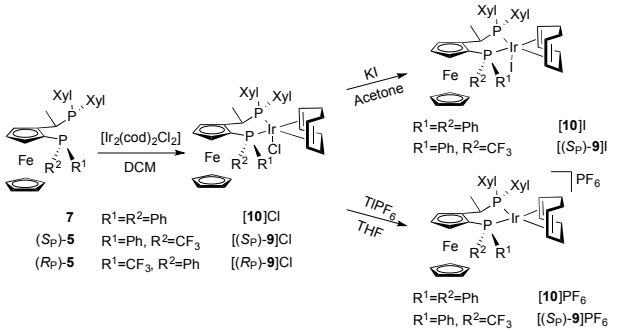
Complexes of all aryl-substituted Josiphos-type phosphine ligands ($P2R_2$ and $P1R_2$, R=aryl) strongly deviate from a conformational point of view compared to P2-alkyl-substituted compounds. All-aryl substituted ligands, like Xyliphos (**7**), usually display a stereogenic $CHCH_3$ fragment with a C-C vector roughly parallel to the ferrocene axis in their complexes, thus giving a pseudo axial methyl group (α2 angles close to 90°, see Fig. 2). Conversely, P2-alkyl-substituted phosphines, like parent Josiphos (**8**), lead to a pseudo equatorial orientation of the methyl group (α2 close to 0° or negative). An analogous, though less pronounced effect can be observed for the α1 torsion angles. Although the origin of this distinct conformational differentiation is not clear, P-CF_3 groups show conformational characteristics similar to those of all aryl-substituted ligands.

NMR spectroscopic features such as chemical shifts and coupling constants can be used to assess the electronic nature of coordinated phosphines.[29] As an example, phosphorus platinum ($^1J_{PPt}$) coupling constants are usually of the order of kHz and span a fairly broad range, allowing for subtle distinctions between similar complexes. Electron-rich phosphines tend to show lower coupling constants to platinum than their electron-poor counterpart. Some of these data are provided in Table 2.

Table 2 NMR Pt-P coupling constants as a measure of phosphine electronic properties

Compound	$^1J_{P\text{-}Pt}$ P1	$^1J_{P\text{-}Pt}$ P2
[Pt(**8**)Cl_2][25]	3552 Hz	3559 Hz
[Pt(**7**)Cl_2][30]	3500 Hz	3630 Hz
[(S_P)-**11**]	3742 Hz	3440 Hz
[(R_P)-**11**]	3740 Hz	3416 Hz

By comparing the Pt-P coupling constants of the partially electron-poor ligand complexes **11** with the ones of complex [Pt(**7**)Cl_2], containing the parent ligand, the electron-poor character of the trifluoromethyl phosphines becomes clear. Furthermore, from an electronic point of view, no significant difference between P-stereoisomeric ligands become apparent.



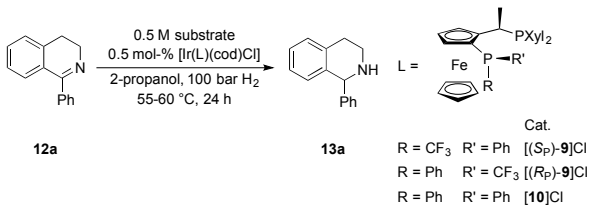
Scheme 3 Complexation of the parent and the new ligands to $[Ir_2(cod)_2Cl_2]$ with subsequent counter ion exchange.

Catalytic applications

[Ir(L)(cod)Cl] precatalysts [**9**]Cl and [**10**]Cl were conveniently prepared by stirring a slight excess of $[Ir_2(cod)_2Cl_2]$ with ligand **5** or **7** in DCM, respectively (Scheme 3). These precatalysts can be handled under ambient atmosphere as a solid but should be stored under an inert atmosphere. The parent ligand **7** and its iridium(I) cyclooctadiene complexes [**10**]Cl were isolated following reported procedures.[31]

1-Phenyl-3,4-dihydroisoquinoline **12a** was first screened as the free base in enantioselective Ir-catalyzed hydrogenations, using complexes [**9**]Cl and [**10**]Cl as catalyst precursors. Under such conditions, both poor catalytic activities and disappointingly low enantioselectivities were observed (Table 3)

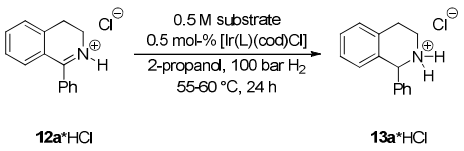
Table 3 Reduction of free DHIQs under high hydrogen pressure using Ir(I) precatalysts [**9**]Cl and [**10**]Cl



Entry	Catalyst	Conv.[a] %	Yield[a] %	*ee* %[b]
1	[(S_P)-**9**]Cl	25	25	30 (+)
2	[(R_P)-**9**]Cl	18	18	16 (-)
3	[**10**]Cl	78	79	21 (+)

[a]Determined by ^{1}H NMR applying an internal standard, ns=1, ds=0. [b]Determined by HPLC. The polarimetric sign corresponds to the hydrochloride.

Table 4 Performance of *P*-trifluoromethyl Josiphos- and Xyliphos-derived ligands in the reduction of 1-Ph-DHIQ chloride **12a**·HCl



Entry	Ligand / Complex	Yield %	% *ee*
1[9]	(*R*,*S*)-Josiphos **8**	60	30 (+)[a]
2[9]	(*S*)-P-Phos	>99	97 (-)[b]
3	(S_P)-CF_3-Josiphos / [(S_P)-**6**]	>99	50 (-)[c]
4	(R_P)-CF_3-Josiphos / [(R_P)-**6**]	98	64 (+)[c]
5	(R_P)-Xyliphos / [(R_P)-**9**]Cl	>99	23 (-)
6	(S_P)-Xyliphos / [(S_P)-**9**]Cl	>99	96 (-)

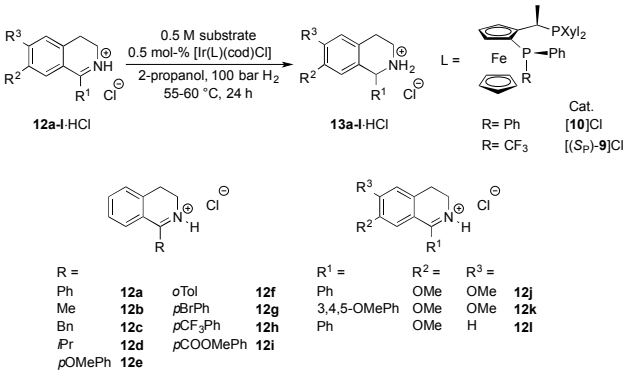
[a]Conditions 2.3 mol-% precat. formed *in situ* from $[Ir_2(cod)_2Cl_2]$ and the ligand, 50 °C, 30 bar, DCE, 3h. [b]S/C >1000/1, precat. formed *in situ* from $[Ir_2(cod)_2Cl_2]$ and (*S*)-P-Phos, 60 °C, 20 bar, THF, 1-2 equiv. H_3PO_4. [c]Precat. formed *in situ* from $[Ir_2(cod)_2Cl_2]$ and the ligand, 1.0 mol-%.

Activation of the substrate and concomitant product derivatization by protonation significantly increased the activity and enantioselectivity of the applied catalytic system. Ružič and co-workers previously examined the parent ligand Josiphos (**8**) under comparable conditions but found still poor activity and enantioselectivity in the hydrogenation of 1-Ph-DHIQ chloride **12a**·HCl (Table 4, entry 1). The *P*-trifluoromethyl ligands of Josiphos-type **6** led to more active catalysts but the enantioselectivity was still rather low (entry 3 and 4). The two diastereoisomeric complexes [(R_P)-**9**]Cl and [(S_P)-**9**]Cl turned out to give comparably active catalysts and constituted a distinct pair of mismatched and matched combinations of absolute configurations, respectively. While the former led to a poor 23% ee, the catalyst containing the S_P configured ligand afforded the opposite enantiomer of the

product in quantitative yield and in 96% enantioselectivity (entries 5-6). Note that these reactions do not require any additives.

The reaction conditions were subsequently further optimized for 1-phenyl-3,4-dihydroisoquinolinium chloride **12a**·HCl using [(S_P)-**9**]Cl as catalyst precursor. 2-Propanol turned out to be the optimal choice as solvent. At room temperature and 100 bar hydrogen pressure, the catalyst's activity was poor (24 h, 14% yield). In contrast, at 55-60 °C and 100 bar hydrogen pressure full conversion was observed after 2-3 hours. The reaction pressure could be lowered to 50 bar or even below without any negative influence on activity, however at the cost of a slightly decreased enantioselectivity. Moreover, at ambient hydrogen pressure and 55-60 °C conversion was slow and the catalyst showed rapid deactivation (5 h, ~30% conversion, 92% *ee*). In a control experiment with the activated catalyst under argon atmosphere, it could be clearly ruled out that the solvent serves as hydrogen source for transfer hydrogenation.

Table 5 Screening of Xyliphos-derived ligand (S_P)-**5** in comparison with the parent ligand **7**



Entry		[(S_P)-**9**]Cl Yield[a] %	[**10**]Cl Yield[a] %	[(S_P)-**9**]Cl % *ee*[b]	[**10**]Cl % *ee*[b]
1	**12a**	>99	>99	96 (-)	84 (-)
2	**12b**	>99	>99	28 (+)[c]	50 (+)[c]
3	**12c**	>99	>99	35 (-)	38 (-)
4	**12d**	>99	>99	93 (+)	85 (+)
5	**12e**	>99	>99	89 (-)	90 (-)
6	**12f**	90[d]	90[d]	94 (-)[e]	95 (-)[e]
7	**12g**	>99	>99	89 (-)	83 (-)
8	**12h**	98	>99	91 (-)	82 (-)
9	**12i**	98	>99	92 (-)	82 (-)
10	**12j**	98	>99	34 (-)	46 (-)
11	**12k**	>99	89	57 (+)	33 (+)
12	**12l**	98	97	75 (+)	77 (+)

[a]Determined by ^{1}H NMR of the hydrochloride, ns=1 ds=0, with internal standard. [b]Determined by chiral HPLC of the free crude base. The sign of optical rotation was determined for the hydrochloride. [c]Determined as (*R*)-menthyl carbamate by GC [d]Substrates purity revealed only 90% in absence of identifiable impurities by ^{1}H NMR and HPLC. [e]*ee* determined as acetamide derivative.

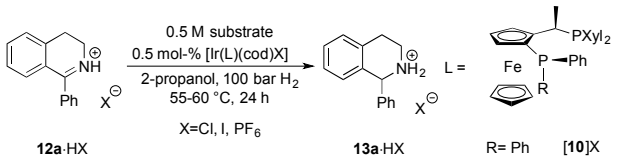
The optimized conditions for the enantioselective hydrogenation of 1-phenyl-3,4-dihydroisoquinoline hydrochloride (**12a**·HCl) were subsequently applied in screening experiments, reducing a series of different 1-substituted 3,4-dihydroisoquinolinium chlorides, **12a-l**·HCl. All investigated DHIQ and THIQ chlorides are poorly soluble in 2-propanol at room temperature and were used as suspensions corresponding to approximately 0.5 M solutions.

The THIQ chlorides **13a-l**·HCl may easily be recrystallized from polar solvents, as already shown by Ružič and co-workers for 1-Ph-THIQ chloride **13a**·HCl.[9] Corresponding reaction products can be treated with almost any aqueous base, liberating the free product without any erosion of enantiopurity.

The results in Table 5 indicate that the *P*-trifluoromethyl ligand (S_P)-**5** performs better than the parent ligand in the hydrogenation of substrates bearing sterically bulky substituents in position 1 (Ph/*i*Pr vs. Me/Bn, entries 1 and 4 vs. entries 2 and 3), though a clear trend is difficult to extract. Furthermore, electron-rich DHIQ cores seem to have a detrimental effect on the enantioselectivity (entry 1 vs. entries 5, 10-12).

In the course of these studies interest arose concerning counter ion effects in connection with the partially electron-poor nature of the new ligands.[32,33] We therefore prepared cationic precatalysts with differing counter ions X and tested them in the enantioselective hydrogenation of corresponding 1-phenyl-3,4-dihydroisoquinolinium salts of the same anion (**12a**·HX).

Table 6 Counter ion effect in the hydrogenation of corresponding 1-Ph-dihydroisoquinolinium species



Entry	Precatalyst	X	Yield[a] %	% *ee*
1	[(S_P)-**9**]Cl	Cl	99	96 (-)
2	[**10**]Cl	Cl	99	84 (-)
3	[(S_P)-**9**]PF_6	PF_6	28	12 (+)
4	[**10**]PF_6	PF_6	43	3 (-)
5	[(S_P)-**9**]I	I	99	82 (-)
6	[**10**]I	I	99	93 (-)

[a]Determined by ^{1}H NMR with internal standard.

For Ir(I) complexes containing either iodide, chloride, or hexafluorophosphate an increasing degree of dissociation of the anion is expected in polar solvents. Thus, iodo complexes often form five-coordinate species, while the corresponding chloro and PF_6^- derivatives are extensively or completely dissociated. Furthermore, the electron-withdrawing CF_3 group in the new ligands may favor ion pairing by virtue of a depleted electron density at the metal center. Thus, counterion effects on activity and enantioselectivity may be anticipated. Indeed, as shown in Table 6,

complexes containing PF_6^- are much less effective in the hydrogenation of the corresponding dihydroisquinolinium salts (entries 3 and 4). This is not further astonishing since substrate and catalyst bear a positive charge. For complex [(S_P)-**9**] containing the electron-poor ligand, chloride as counter ion facilitates the reduction with higher enantioselectivity as compared to iodide (entry 1 vs. 5). The opposite is observed for the complex of the more electron-rich parent Xyliphos, for which iodide as counter ion leads to superior results (entry 2 vs. 6).

Hence, the electron-poor Xyliphos-type ligand (S_P)-**5** affords high enantioselectivity in the iridium-catalyzed hydrogenation of 1-Ph-DHIQ chloride (**12a**□HCl), while the parent ligand **7** requires using the corresponding hydroiodide salt in order to reach a comparable level of stereoselectivity. However, the addition of substoichiometric amounts of iodide salts did not improve the selectivity of hydrogenation experiments of DHIQ chlorides significantly.

Conclusion

Milestones in the hydrogenation of dihydroisoquinolines and isoquinolines were all set so far by axially chiral ligands. Ligands bearing stereogenic units were either not screened or did not lead to satisfying results. Therefore, it must be noted that the report at hand describes the first successful application of a chiral ligand bearing central and planar chirality in this type of hydrogenations. The levels of activity and enantioselectivity obtained in the hydrogenation of dihydroisoquinolinium chlorides using the *P*-trifluoromethyl Xyliphos-type ligand (S_P)-**5** are often superior to those achieved with the parent ligand and are very much similar to those previously obtained by Ružič *et al.* for P-Phos.[9] However, no additives (e.g. 1-2 eq. H_3PO_4) are necessary and the easiest activation of the substrate by simple protonation is sufficient.

Experimental

General methods and instrumentation

Ligands (S_P)-**5** and (R_P)-**5** were synthesized and isolated applying standard Schlenk techniques under an argon atmosphere. The corresponding iridium(I) precatalysts and platinum complexes were prepared and isolated under ambient atmosphere but were quickly dried after purification and stored under an argon atmosphere. Solvents were of p.a. quality and distilled from calcium hydride (DCM), sodium/benzophenone (THF), sodium/diethyl phthalate (ethanol), if necessary. Certain solvents (AcOH and ethanol) were carefully degassed by several freeze-pump-thaw cycles (Caution!). Silica gel (60 Å, 230-400 mesh) was purchased from Fluka. NMR spectra were recorded on a Bruker DPX-700, Avance III 300 or Avance III 500 spectrometer at the given frequency and room temperature. Chemical shifts (δ) are expressed in ppm relative to the following external standards: TMS (^{1}H and ^{13}C), $CFCl_3$ (^{19}F), 85% H_3PO_4 (^{31}P). The spectra were calibrated against the solvent residual peak, where applicable.[34] Signal multiplicities are specified with s for singlet, d for doublet, t for triplet, q for quartet, sept for septet, m for multiplet and assigned with a br prefix in case of obviously broadened signals. Due to extensive coupling of ^{13}C with ^{31}P and ^{19}F, for all carbon experiments additionally a ^{31}P decoupling pulse was applied apart from standard ^{1}H decoupling (noted as $^{13}C\{^{31}P,^1H\}$). $[Ir_2(cod)_2Cl_2]$ was purchased from ABCR and used as received. (*R*)-*N*,*N*-Dimethyl-1-ferrocenylethylamine[35], (R_C,S_{FC})-*N*,*N*-dimethyl-1-(2-diphenylphosphinoferrocenyl)ethyl-amine,[36] phenylbis(trifluoromethyl)phosphine[18], (S_P,R_C,S_{Fc})- and (R_P,R_C,S_{Fc})-1-[(phenyl)trifluoromethylphosphino]-2-[1-(dimethyl-amino)ethylferrocene **4**[18], (S_P,R_C,S_{Fc})- and (R_P,R_C,S_{Fc})-1-[phenyl-trifluoromethylphosphino]-2-[1-(dicyclohexylphosphino)ethyl]-ferrocene **6**[18], bis(4-cyano-phenyl) phenylphosphonite[18], (*R*)-1-[(*S*)-2-(diphenylphosphanyl)ferrocenyl]ethyldi(3,5-xylyl)phos-phane **7**[31], [Ir((R_C,S_{Fc})-Xyliphos)(cod)Cl] **10**Cl[31], [Ir((R_C,S_{Fc})-Xyliphos)(cod)I] **10**I[31], and $[Pt(cod)Cl_2]$[37] were prepared according to the cited reports.

(S_P,R_C,S_{Fc})-1-[(Phenyl)trifluoromethylphosphino]-2-{1-[di(3,5-xylyl)phosphino]ethyl}ferrocene, (S_P)-5

(S_P,R_C,S_{Fc})-1-[(Phenyl)trifluoromethylphosphino]-2-[1-(di-methylamino)ethyl]ferrocene (S_P)-**4** (1.03 g, 2.38 mmol, 1.0 eq.) was placed in a 50 mL Schlenk with a magnetic stirring bar and purged with argon. Degassed acetic acid (10 mL) was added, followed by bis(3,5-dimethylphenyl)phosphine **3** (0.6 mL, 0.61 g, 2.52 mmol, 1.1 eq.). The intense orange solution was stirred at 90 °C overnight. The next day all volatiles were removed under reduced pressure and the residue crystallized twice from boiling ethanol (30/27 mL) yielding the product as clear orange needles (1.07 g, 1.70 mmol, 71%).

^{1}H NMR (500.23 MHz, CD_2Cl_2): δ 1.37 (dd, $^3J_{HH}$ = 6.7 Hz, *J* = 6.0 Hz, 3H, CHC*H*$_3$), 2.18 (s, 6H, C*H*$_3$), 2.25 (s, 6H, C*H*$_3$), 3.62-3.68 (m, 1H, C*H*CH$_3$), 3.99 (brs, 1H, *Cp*), 4.28 (s, 5H, *Cp*'), 4.42-4.43 (m, 1H, *Cp*), 4.62 (brs, 1H, *Cp*), 6.58 (brd, *J* = 7.6 Hz, 2H, *Ph*), 6.82 (brd, *J* = 5.8 Hz, 2H, *Ph*), 6.86 (brs, 1H, *Ph*), 6.92 (brs, 1H, *Ph*), 7.30-7.34 (m, 2H, *Ph*), 7.35-7.39 (m, 1H, *Ph*), 7.52-7.56 (s, 2H, *Ph*); $^{13}C\{^1H,^{31}P\}$ NMR (125.79 MHz, CD_2Cl_2): δ 16.01 (s, CH*C*H$_3$), 21.33 (s, *C*H$_3$), 21.53 (s, *C*H$_3$), 31.10 (s, *C*HCH$_3$), 66.89 (s, *Cp*), 69.83 (s, *Cp*), 70.52 (s, *Cp*), 70.55 (s, *Cp*'), 71.66 (s, *Cp*), 99.48 (s, *Cp*), 128.40 (s, *Ph*), 129.53 (s, *Ph*), 129.68 (s, *Ph*), 130.16 (s, *Ph*), 131.07 (s, *Ph*), 132.24 (q, $^1J_{CF}$ = 321.9 Hz, *C*F$_3$), 132.68 (q, J_{CF} = 2.8 Hz, *Ph*), 133.22 (s, *Ph*), 133.92 (s, *Ph*), 134.65 (s, *Ph*), 137.41 (s, *Ph*), 137.64 (s, *Ph*), 138.10 (s, *Ph*); $^{31}P\{^1H\}$ NMR (202.50 MHz, CD_2Cl_2): δ -14.17 (qd, $^2J_{PF}$ = 67.0 Hz, $J_{PP'}$ = 54.1 Hz, *P*(CF$_3$)), 10.49 (dq, $J_{PP'}$ = 53.8 Hz, J_{PF} = 2.6 Hz, *P*Xyl$_2$); ^{19}F NMR (470.69 MHz, CD_2Cl_2): δ -54.17 (d, $^2J_{FP}$ = 67.4 Hz, C*F*$_3$); HRMS (MALDI, 3-HPA) calcd. (*m/z*) for $C_{35}H_{36}F_3FeP_2$: 631.1588 ($[M+H]^+$), Found: 631.1594 ($[M+H]^+$), 389.0366 ($[M\text{-}PXyl_2]^+$); Anal. Calc. for $C_{35}H_{35}F_3FeP_2$ (630.45): C 66.68, H 5.60, F 9.04, P 9.83, Found: C 66.73, H 5.67, F 9.02, P 9.93; [α] = -92.7 (20 °C, 589 nm, c = 0.604, $CHCl_3$).

(R_P,R_C,S_{Fc})-1-[(Phenyl)trifluoromethylphosphino]-2-{1-[di(3,5-xylyl)phosphino]ethyl}ferrocene, (R_P)-5

(R_P,R_C,S_{Fc})-1-[(Phenyl)trifluoromethylphosphino]-2-[1-(di-methylamino)ethyl]ferrocene (R_P)-**4** (330 mg, 0.76 mmol, 1.0 eq.) was placed in a 20 mL Schlenk with a magnetic stirring bar and purged with argon. Degassed acetic acid (5 mL) was added, followed by bis(3,5-dimethylphenyl)phosphine **3** (0.25 mL, 0.25 g, 1.03 mmol, 1.4 eq.). The reaction mixture was stirred at 90 °C overnight. The next day all volatiles were removed under reduced pressure and the yellow solid residue crystallized twice from boiling ethanol (8/6 mL) yielding the product as very small clear yellow needles (235 mg, 0.37 mmol, 49%).

^{1}H NMR (500.23 MHz, CD_2Cl_2): δ 1.39-1.42 (m, 3H, CHC*H*$_3$), 2.27 (s, 6H, C*H*$_3$), 2.29 (s, 6H, C*H*$_3$), 3.68 (qd, $^3J_{HH}$ = 6.6 Hz, *J* = 3.5 Hz, 1H, C*H*CH$_3$), 3.79 (s, 5H, *Cp*'), 4.02 (brs, 1H, *Cp*), 4.37-4.38 (m, 1H, *Cp*), 4.54 (brs, 1H, *Cp*), 6.92-6.93 (m, 3H, *Ph*), 6.97 (brd, *J* = 6.1 Hz, 2H,

Ph), 7.00 (brs, 1H, *Ph*), 7.54-7.60 (m, 3H, *Ph*), 8.03-8.06 (m, 2H, *Ph*); $^{13}C\{^{1}H,^{31}P\}$ NMR (125.79 MHz, CD_2Cl_2): δ 18.56 (s, CH*C*H$_3$), 21.40 (s, *C*H$_3$), 21.49 (s, *C*H$_3$), 29.34 (s, *C*HCH$_3$), 65.72 (q, J_{CF} = 4.4 Hz, *Cp*), 69.99 (s, *Cp*'), 70.52 (s, *Cp*), 70.69 (s, *Cp*), 72.23 (s, *Cp*), 101.57 (s, *Cp*), 128.94 (s, *Ph*), 129.69 (s, *Ph*), 129.82 (s, *Ph*), 130.92 (q, $^{1}J_{CF}$ = 323.3 Hz, *C*F$_3$), 131.19 (s, *Ph*), 131.54 (s, *Ph*), 131.65 (q, J_{CF} = 2.9 Hz, *Ph*), 133.33 (s, *Ph*), 135.47 (s, *Ph*), 136.24 (s, *Ph*), 137.65 (s, *Ph*), 138.09 (s, *Ph*), 138.12 (s, *Ph*); $^{31}P\{^{1}H\}$ NMR (202.50 MHz, CD_2Cl_2): δ -15.02 (qd, $^{2}J_{PF}$ = 65.9 Hz, $J_{PP'}$ = 24.2 Hz, *P*(CF$_3$)), 9.84 (dq, $J_{PP'}$ = 24.4 Hz, J_{PF} = 19.5 Hz, *P*Xyl$_2$); ^{19}F NMR (470.69 MHz, CD_2Cl_2): δ -56.24 (dd, $^{2}J_{FP}$ = 66.2 Hz, $J_{FP'}$ = 19.3 Hz, C*F*$_3$); HRMS (MALDI, 3-HPA) calcd. (*m/z*) for $C_{35}H_{36}F_3FeP_2$: 631.1588 ([M+H]$^+$), Found: 631.1588 ([M+H]$^+$), 389.0362 ([M-PXyl$_2$]$^+$); Anal. Calc. for $C_{35}H_{35}F_3FeP_2$ (630.45): C 66.68, H 5.60, F 9.04, P 9.83, Found: C 66.74, H 5.63, F 9.01, P 10.03; [α] = -320.1 (20 °C, 589 nm, c = 0.512, $CHCl_3$).

[Ir((*S*$_P$,*R*$_C$,*S*$_{Fc}$)-(Ph)(CF$_3$)-Xyliphos)(cod)Cl], [(*S*$_P$)-9]Cl

A 25 mL round bottomed flask with a magnetic stirring bar was charged with (*S*$_P$,*R*$_C$,*S*$_{Fc}$)-1-[(phenyl)trifluoromethylphosphino]-2-{1-[di(3,5-xylyl)phosphino]ethyl}ferrocene (*S*$_P$)-**5** (202 mg, 320.41 µmol, 1.0 eq.) and dissolved in DCM (5 mL). Upon the addition of $[Ir_2(cod)_2Cl_2]$ (129 mg, 192.05 µmol, 0.6 eq.), the orange solution changed to red. The reaction mixture was stirred for 30 minutes before it was filtered over silica (~20 g, starting with pure DCM, changing to pure diethyl ether after first colored species) collecting the product as second colored fraction. The solvent was removed and the yellow foam dried overnight under HV (267 mg, 274.02 µmol, 86%). The product slowly decomposes when exposed to air.

^{1}H NMR (300.13 MHz, CD_2Cl_2): δ 1.33-1.46 (m, 2H, *cod*), 1.56 (dd, *J* = 12.4 Hz, $^{3}J_{HH}$ = 7.3 Hz, 3H, CHC*H*$_3$), 1.75-1.87 (m, 2H, *cod*), 2.31 (s, 6H, C*H*$_3$), 2.18-2.36 (m, 8H, C*H*$_3$, *cod*), 2.41-2.55 (m, 2H, *cod*), 3.24 (td, *J* = 8.6 Hz, *J* = 4.5 Hz, 2H, *cod*), 3.80-3.85 (m, 2H, *cod*), 3.99 (brs, 1H, *Cp*), 4.10-4.12 (m, 1H, *Cp*), 4.29 (brs, 1H, *Cp*), 4.31 (s, 5H, *Cp*'), 5.25 (dq, *J* = 11.1 Hz, $^{3}J_{HH}$ = 6.9 Hz, 1H, C*H*CH$_3$), 6.96 (brs, 1H, *Ph*), 7.03 (brs, 1H, *Ph*), 7.15 (d, *J* = 10.2 Hz, 2H, *Ph*), 7.23 (d, *J* = 9.3 Hz, 2H, *Ph*), 7.26-7.28 (m, 2H, *Ph*), 7.34-7.38 (m, 1H, *Ph*), 7.42-7.47 (m, 2H, *Ph*); $^{13}C\{^{1}H,^{31}P\}$ NMR (125.79 MHz, CD_2Cl_2): δ 15.38 (s, CH*C*H$_3$), 21.35 (s, *C*H$_3$), 21.71 (s, *C*H$_3$), 28.67 (s, *cod*), 30.33 (s, *C*HCH$_3$), 36.94 (s, *cod*), 66.09 (s, *Cp*), 67.21 (s, *Cp*), 69.37 (s, *Cp*), 69.81 (s, *Cp*), 70.84 (s, *cod*), 71.59 (s, *Cp*'), 73.21 (s, *cod*), 76.43 (s, *Cp*), 94.39 (s, *Cp*), 126.56 (q, $^{1}J_{CF}$ = 327.7 Hz, *C*F$_3$), 127.82 (s, *Ph*), 127.95 (s, *Ph*), 129.86 (s, *Ph*), 130.04 (s, *Ph*), 131.93 (s, *Ph*), 131.98 (s, *Ph*), 132.55 (s, *Ph*), 132.76 (s, *Ph*), 133.31 (s, *Ph*), 134.03 (s, *Ph*), 137.13 (s, *Ph*), 137.56 (s, *Ph*); $^{31}P\{^{1}H\}$ NMR (121.49 MHz, $CDCl_3$): δ 6.32 (qd, $^{2}J_{PF}$ = 52.3 Hz, $J_{PP'}$ = 34.6 Hz, *P*(CF$_3$)), 25.77 (d, $J_{PP'}$ = 34.5 Hz, *P*Xyl$_2$); ^{19}F NMR (282.40 MHz, $CDCl_3$): δ -53.58 (d, $^{2}J_{FP}$ = 52.5 Hz, C*F*$_3$); HRMS (MALDI, DCTB) calcd. (*m/z*) for $C_{43}H_{47}F_3FeIrP_2$: 931.2082 ([M-Cl]$^+$), Found: 931.2079 ([M-Cl]$^+$); Anal. Calc. for $C_{43}H_{47}ClF_3FeIrP_2$ (966.31): C 53.45, H 4.90, Cl 3.67, F 5.90, P 6.41, Found: C 53.51, H 5.07, Cl 3.87, F 5.97, P 6.22; [α] = +100.9 (20 °C, 589 nm, c = 0.444, $CHCl_3$).

[Ir((*R*$_P$,*R*$_C$,*S*$_{Fc}$)-(Ph)(CF$_3$)-Xyliphos)(cod)Cl], [(*R*$_P$)-9]Cl

A 25 mL round bottomed flask with a magnetic stirring bar was charged with (*R*$_P$,*R*$_C$,*S*$_{Fc}$)-1-[(phenyl)trifluoromethylphosphino]-2-{1-[di(3,5-xylyl)phosphino]ethyl}ferrocene (*R*$_P$)-**5** (160 mg, 250.57 µmol, 1.0 eq.) and dissolved in DCM (2 mL). Upon the addition of $[Ir_2(cod)_2Cl_2]$ (136 mg, 202.47 µmol, 0.8 eq.), the orange solution turned red. The reaction mixture was stirred for 30 minutes before it was filtered over silica (~20 g, starting with pure DCM, changing to pure diethyl ether after first colored species) collecting the product as second colored fraction. The solvent was removed and the yellow foam dried overnight under HV (193 mg, 199.73 µmol, 80%). No decomposition was observed when the compound was exposed to air.

^{1}H NMR (300.13 MHz, $CDCl_3$): δ 1.37 (dd, *J* = 13.2 Hz, $^{3}J_{HH}$ = 7.3 Hz, 3H, CHC*H*$_3$), 1.43-1.55 (m, 2H, *cod*), 1.97-2.08 (m, 2H, *cod*), 2.11 (s, 6H, C*H*$_3$), 2.22-2.32 (m, 2H, *cod*), 2.37 (s, 6H, C*H*$_3$), 2.57-2.71 (m, 2H, *cod*), 3.62 (td, *J* = 8.4 Hz, *J* = 3.8 Hz, 2H, *cod*), 3.83 (s, 5H, *Cp*'), 4.01-4.06 (m, 2H, *cod*), 4.41-4.43 (m, 1H, *Cp*), 4.62 (brs, 1H, *Cp*), 4.70 (brs, 1H, *Cp*), 5.43 (dq, *J* = 14.2 Hz, $^{3}J_{HH}$ = 7.1 Hz, 1H, C*H*CH$_3$), 6.67 (d, *J* = 9.6 Hz, 2H, *Ph*), 6.90 (s, 1H, *Ph*), 7.07 (s, 1H, *Ph*), 7.48-7.60 (m, 3H, *Ph*), 7.85 (brs, 2H, *Ph*), 8.44-8.50 (m, 2H, *Ph*); $^{13}C\{^{1}H,^{31}P\}$ NMR (125.79 MHz, CD_2Cl_2): δ 15.71 (s, CH*C*H$_3$), 21.37 (s, *C*H$_3$), 21.67 (s, *C*H$_3$), 28.46 (s, *cod*), 29.11 (s, *C*HCH$_3$), 37.54 (s, *cod*), 66.42 (s, *Cp*), 70.58 (s, *Cp*), 71.25 (s, *Cp*), 71.53 (s, *Cp*'), 71.84 (s, *cod*), 74.63 (q, J_{CF} = 3.0 Hz, *Cp*), 75.85 (s, *cod*), 95.59 (s, *Cp*), 124.59 (q, $^{1}J_{PF}$ = 326.3 Hz, *C*F$_3$), 128.62 (s, *Ph*), 128.86 (s, *Ph*), 129.19 (s, *Ph*), 131.23 (s, *Ph*), 131.75 (s, *Ph*), 131.86 (s, *Ph*), 132.20 (s, *Ph*), 133.42 (s, *Ph*), 134.08 (s, *Ph*), 135.61 (s, *Ph*), 136.74 (s, *Ph*), 137.13 (s, *Ph*); $^{31}P\{^{1}H\}$ NMR (121.49 MHz, $CDCl_3$): δ 0.13 (qd, $^{2}J_{PF}$ = 64.4 Hz, $J_{PP'}$ = 31.6 Hz, *P*(CF$_3$)), 11.28 (d, $J_{PP'}$ = 31.5 Hz, *P*Xyl$_2$); ^{19}F NMR (282.40 MHz, $CDCl_3$): δ -57.18 (d, $^{2}J_{FP}$ = 64.4 Hz, C*F*$_3$); HRMS (MALDI, DCTB) calcd. (*m/z*) for $C_{43}H_{47}F_3FeIrP_2$: 931.2082 ([M-Cl]$^+$), Found: 931.2079 ([M-Cl]$^+$); [α] = +51.1 (20 °C, 589 nm, c = 0.474, $CHCl_3$).

[Ir((*S*$_P$,*R*$_C$,*S*$_{Fc}$)-(Ph)(CF$_3$)-Xyliphos)(cod)I], [(*S*$_P$)-9]I

A 50 mL round bottomed flask with a magnetic stirring bar was charged with (*S*$_P$,*R*$_C$,*S*$_{Fc}$)-1-[(phenyl)trifluoromethylphosphino]-2-{1-[di(3,5-xylyl)phosphino]ethyl}ferrocene (*S*$_P$)-**5** (100 mg, 158.62 µmol, 1.0 eq.), $[Ir_2(cod)_2Cl_2]$ (64 mg, 95.28 µmol, 0.6 eq.) and potassium iodide (79 mg, 475.90 µmol, 3.0 eq.). Acetone (10 mL) was added and the intense orange suspension stirred at rt for three hours. During the reaction time, the coarse crystalline KI slowly dissolves forming a finely crystalline KCl precipitate. Thereafter, the solvent was evaporated and the residue filtered over silica (~15 g, DCM:Et_2O 2:1). The violet first fraction was discarded, collecting the second colored compound. This was further purified by a second filtration over silica (~15 g, DCM:Et_2O 100:1) yielding the product as a glassy, dark red film in the flask (168 mg, quant.). NMR-spectra clearly indicate dynamic behavior in solution. Cooling to -40 °C leads to more than one species still indicating dynamic behavior.

^{1}H NMR (300.13 MHz, CD_2Cl_2): δ 1.62 (dd, *J* = 12.2 Hz, $^{3}J_{HH}$ = 7.3 Hz, 3H, CHC*H*$_3$), 1.77 (brs, 2H, *cod*), 1.99-2.18 (m, 10H, C*H*$_3$, *cod*), 2.27 (s, 6H, C*H*$_3$), 2.44-2.58 (m, 2H, *cod*), 3.36 (brs, 2H, *cod*), 3.87 (brs, 2H, *cod*), 3.97 (s, 1H, *Cp*), 4.18 (s, 1H, *Cp*), 4.37 (s, 5H, *Cp*'), 4.58 (s, 1H, *Cp*), 5.64 (brs, 1H, C*H*CH$_3$), 6.82-7.78 (brm, 11H, *Ph*); $^{13}C\{^{1}H,^{31}P\}$ NMR (125.79 MHz, CD_2Cl_2): δ 16.22 (brs, CH*C*H$_3$), 21.43 (s, *C*H$_3$), 21.59 (s, *C*H$_3$), 30.86 (brs, *cod*), 34.69 (brs, *cod*), 35.34 (s, *C*HCH$_3$), 69.01 (brs), 69.42 (s), 70.29 (brs), 71.89 (s, *Cp*'), 76.65 (s), 94.75 (s, *Cp*), 125.95 (q, $^{1}J_{CF}$ = 323.0 Hz, *C*F$_3$), 127.60 (s, *Ph*), 129.29 (brs, *Ph*), 130.43 (brs, *Ph*), 131.84 (brs, *Ph*), 132.09 (s, *Ph*), 132.39 (brs, *Ph*), 132.56 (s, *Ph*), 134.83 (brs, *Ph*), 137.11 (s, *Ph*), 137.69 (brs, *Ph*); $^{31}P\{^{1}H\}$ NMR (121.49 MHz, CD_2Cl_2): δ -2.32 (brm, *P*(CF$_3$)), 14.07 (brm, *P*Xyl$_2$); ^{19}F NMR (282.40 MHz, CD_2Cl_2): δ -53.29 (brd, $^{2}J_{FP}$ = 44.8 Hz, C*F*$_3$); HRMS (MALDI, DCTB) calcd. (*m/z*) for $C_{43}H_{47}F_3FeIrP_2$: 931.2082 ([M-I]$^+$), Found: 931.2074 ([M-I]$^+$); Anal. Calc. for $C_{43}H_{47}F_3FeIrP_2$ (1057.76): C 48.83, H 4.48, F 5.39, I 12.00, P 5.86, Found: C 48.69, H 4.66, F 5.37, I 12.15, P 5.73.

[Ir((*S*$_P$,*R*$_C$,*S*$_{Fc}$)-(Ph)(CF$_3$)-Xyliphos)(cod)]PF$_6$, [(*S*$_P$)-9]PF$_6$

A 25 mL round bottomed flask with a magnetic stirring bar was charged with [Ir((*S*$_P$,*R*$_C$,*S*$_{Fc}$)-(Ph)(CF$_3$)-Xyliphos)(cod)Cl] (*S*$_P$)-**9**Cl (153 mg, 158.62 µmol, 1.0 eq.) and dissolved in THF (3 mL). The clear

orange solution was added to a solution of $TlPF_6$ (56 mg, 160.30 µmol, 1.0 eq.) in THF (2 mL) under stirring. The color changed instantaneously to dark red and a precipitate (TlCl) formed. The red reaction mixture was stirred at rt for one hour before the solvent was evaporated. The residue was taken up in DCM and filtered over silica (~20 g, starting with DCM, changing stepwise to pure diethyl ether) collecting the dark red compound. The solvent was removed under reduced pressure yielding a highly viscous residue. This was sonicated several minutes in hexane (5 mL) and the bright red solid was filtered off, washed with hexane and dried under HV (149 mg, 138.50 µmol, 87%).

^{1}H NMR (300.13 MHz, CD_2Cl_2): δ 1.27 (dd, J = 13.6 Hz, $^3J_{HH}$ = 7.1 Hz, 3H, CHCH_3), 1.80-2.17 (m, 5H, *cod*), 2.27 (s, 6H, CH_3), 2.31-2.48 (m, 9H, CH_3, *cod*), 3.80-3.89 (m, 1H, CHCH$_3$), 3.95-4.04 (m, 1H, *cod*), 4.18 (s, 1H, *Cp*), 4.33 (brs, 7H, *Cp*', *Cp*, *cod*), 4.42-4.44 (m, 1H, *Cp*), 4.66-4.75 (m, 2H, *cod*), 7.11 (d, J = 10.4 Hz, 2H, *Ph*), 7.15 (s, 1H, *Ph*), 7.21 (s, 2H, *Ph*), 7.25 (s, 1H, *Ph*), 7.55-7.62 (m, 5H, *Ph*); ^{13}C{^{1}H,^{31}P} NMR (125.79 MHz, CD_2Cl_2): δ 16.26 (s, CHCH$_3$), 21.53 (s, CH$_3$), 21.77 (s, CH$_3$), 29.31 (s, *cod*), 29.87 (s, *cod*), 32.50 (s, CHCH$_3$, *cod*), 33.17 (s, *cod*), 61.52 (s, *Cp*), 71.09 (s, *Cp*), 71.81 (s, *Cp*'), 72.58 (s, *Cp*), 75.68 (s, *Cp*), 86.33 (s, *cod*), 91.08 (s, *cod*), 91.83 (s, *cod*), 91.97 (s, *Cp*), 98.06 (s, *cod*), 124.25 (s, *Ph*), 124.75 (q, $^1J_{CF}$ = 321.3 Hz, CF$_3$), 127.16 (s, *Ph*), 127.75 (s, *Ph*), 129.53 (s, *Ph*), 129.79 (s, *Ph*), 132.89 (s, *Ph*), 132.97 (s, *Ph*), 133.86 (s, *Ph*), 133.94 (s, *Ph*), 134.54 (s, *Ph*), 139.02 (s, *Ph*), 139.63 (s, *Ph*); ^{31}P{^{1}H} NMR (121.49 MHz, CD_2Cl_2): δ -144.50 (sept, $^1J_{PF}$ = 710.3 Hz, PF$_6$), 27.08 (qd, $^2J_{PF}$ = 68.0 Hz, $J_{PP'}$ = 24.1 Hz, P(CF$_3$)), 35.75 (d, $J_{PP'}$ = 24.2 Hz, PXyl$_2$); ^{19}F NMR (282.40 MHz, CD_2Cl_2): δ -73.58 (d, $^1J_{FP}$ = 710.4 Hz, PF_6), -54.93 (d, $^2J_{FP}$ = 68.5 Hz, CF_3); HRMS (MALDI, DCTB) calcd. (*m/z*) for $C_{43}H_{47}F_3FeIrP_2$: 931.2082 ([M-PF$_6$]$^+$), Found: 931.2078 ([M-PF$_6$]$^+$); Anal. Calc. for $C_{43}H_{47}F_9FeIrP_3$ (1075.82): C 48.01, H 4.40, F 15.89, P 8.64, Found: C 47.48, H 4.42, F 15.79, P 8.55.

[Ir((*R*$_C$,*S*$_{Fc}$)-Xyliphos)(cod)]PF$_6$, [10]PF$_6$

A dried 20 mL Schlenk with a magnetic stirring bar was charged with [Ir((*R*$_C$,*S*$_{Fc}$)-Xyliphos)(cod)Cl] **10**Cl (146 mg, 149.84 µmol, 1.0 eq.) and purged with argon. THF (2 mL) was added, followed by $TlPF_6$ (53 mg, 151.71 µmol, 1.0 eq.). The brown-red reaction mixture was stirred at rt for one hour before the solvent was evaporated. The residue was taken up in DCM and filtered over silica (~15 g, starting with DCM, changing stepwise to pure diethyl ether). The solvent was removed under reduced pressure yielding an intense red, glassy residue. This was scratched from the wall and sonicated in hexane to give a red-brownish solid (143 mg, 131.93 µmol, 88%).

^{1}H NMR (300.13 MHz, CD_2Cl_2): δ 1.50 (dd, J = 13.1 Hz, $^3J_{HH}$ = 7.1 Hz, 3H, CHCH_3), 1.55-1.73 (m, 3H, *cod*), 1.85-1.92 (m, 1H, *cod*), 1.99-2.13 (m, 1H, *cod*), 2.31-2.37 (m, 9H, *cod*, CH_3), 2.40 (s, 6H, CH_3), 3.25-3.35 (m, 1H, *cod*), 3.60 (qd, $^3J_{HH}$ = 7.1 Hz, J = 4.8 Hz, 1H, CHCH$_3$), 3.63-3.70 (m, 1H, *cod*), 3.74 (s, 5H, *Cp*'), 4.03-4.05 (m, 1H, *Cp*), 4.14-4.17 (m, 1H, *Cp*), 4.17-4.24 (m, 2H, *cod*), 4.33-4.35 (m, 1H, *Cp*), 7.02 (brs, 1H, *Ph*), 7.05 (brs, 1H, *Ph*), 7.20 (brs, 2H, *Ph*), 7.32-7.40 (m, 4H, *Ph*), 7.49-7.53 (m, 3H, *Ph*), 7.74-7.85 (m, 3H, *Ph*), 8.36 (ddd, J = 11.9 Hz, J = 7.6 Hz, J = 1.7 Hz, 2H, *Ph*); ^{13}C{^{1}H,^{31}P} NMR (125.79 MHz, CD_2Cl_2): δ 14.59 (s, CHCH$_3$), 21.53 (s, CH$_3$), 21.78 (s, CH$_3$), 28.14 (s, *cod*), 28.57 (s, *cod*), 33.10 (s, CHCH$_3$), 33.45 (s, *cod*), 33.75 (s, *cod*), 68.83 (s, *Cp*), 69.71 (s, *Cp*), 71.04 (s, *Cp*'), 73.34 (s, *Cp*), 75.02 (s, *Cp*), 84.81 (s, *cod*), 86.03 (s, *cod*), 89.49 (s, *cod*), 91.27 (s, *cod*), 92.34 (s, *Cp*), 127.23 (s, *Ph*), 127.45 (s, *Ph*), 128.96 (s, *Ph*), 129.10 (s, *Ph*), 129.56 (s, *Ph*), 129.62 (s, *Ph*), 131.51 (s, *Ph*), 132.92 (s, *Ph*), 133.08 (s, *Ph*), 133.46 (s, *Ph*), 134.36 (s, *Ph*), 134.44 (s, *Ph*), 135.86 (s, *Ph*), 136.90 (s, *Ph*), 138.84 (s, *Ph*), 139.53 (s, *Ph*); ^{31}P{^{1}H} NMR (121.49 MHz, CD_2Cl_2): δ -144.50 (sept, $^1J_{PF}$ = 710.5 Hz, PF$_6$), 9.36 (d, $J_{PP'}$ = 24.0 Hz, PPh$_2$), 41.05 (d, $J_{PP'}$ = 24.0 Hz, PXyl$_2$); ^{19}F NMR (282.40 MHz, CD_2Cl_2): δ -73.59 (d, $^1J_{FP}$ = 710.3 Hz, PF_6); HRMS (MALDI, DCTB) calcd. (*m/z*) for $C_{48}H_{52}FeIrP_2$: 939.2522 ([M-PF$_6$]$^+$), Found: 939.2520 ([M-PF$_6$]$^+$).

[Pt((*S*$_P$,*R*$_C$,*S*$_{Fc}$)-(Ph)(CF$_3$)-Xyliphos)Cl$_2$], [(*S*$_P$)-11]

(*S*$_P$,*R*$_C$,*S*$_{Fc}$)-1-[(Phenyl)trifluoromethylphosphino]-2-{1-[di(3,5-xylyl)phosphino]ethyl}ferrocene (*S*$_P$)-**5** (15 mg, 23.79 µmol, 1.1 eq.) was weighed into an NMR tube and dissolved in chloroform (0.6 mL). [Pt(cod)Cl$_2$] (8 mg, 21.38 µmol, 1.0 eq.) was added and the intense orange solution was agitated from time to time by inverting the tube. The product was obtained as an intense red, crystalline, chloroform solvate (suitable for X-ray diffraction experiments) by slow diffusion of pentane into the reaction solution (21 mg, quant.). CCDC 1000085.

^{1}H NMR (700.13 MHz, $CDCl_3$): δ 1.18 (dd, J = 14.4 Hz, $^3J_{HH}$ = 7.1 Hz, 3H, CHCH_3), 2.20 (s, $^1J_{HC}$ = 126.6 Hz, 6H, CH_3), 2.40 (s, 6H, $^1J_{HC}$ = 127.1 Hz, CH_3), 3.70 (dq, J = 10.8 Hz, $^3J_{HH}$ = 7.2 Hz, 1H, CHCH$_3$), 4.08 (brs, 1H, *Cp*), 4.20 (s, 5H, *Cp*'), 4.34 (brs, 1H, *Cp*), 4.37 (brs, 1H, *Cp*), 7.00 (brs, 1H, *Ph*), 7.11 (brs, 1H, *Ph*), 7.24 (brd, J = 12.0 Hz, 2H, *Ph*), 7.44-7.47 (m, 2H, *Ph*), 7.51-7.53 (m, 3H, *Ph*), 7.95 (dd, J = 12.9 Hz, J = 7.6 Hz, 2H, *Ph*); ^{13}C{^{1}H,^{31}P} NMR (125.79 MHz, CD_2Cl_2): δ 16.12 (s, CHCH$_3$), 21.47 (s, CH$_3$), 21.69 (s, CH$_3$), 33.28 (s, CHCH$_3$), 61.79 (s, *Cp*), 70.85 (s, *Cp*), 71.63 (brs, *Cp*'), 72.15 (s, *Cp*), 76.17 (brs, *Cp*), 91.92 (s, *Cp*), 121.05 (q, $^1J_{CF}$ = 320.3 Hz, CF$_3$), 124.41 (s, *Ph*), 125.24 (s, *Ph*), 127.61 (s, *Ph*), 128.88 (s, *Ph*), 131.48 (brs, *Ph*), 132.58 (s, *Ph*), 133.08 (brs, *Ph*), 133.67 (s, *Ph*), 133.96 (brs, *Ph*), 134.01 (brs, *Ph*), 138.38 (s, *Ph*), 138.64 (s, *Ph*); ^{31}P{^{1}H} NMR (283.42 MHz, $CDCl_3$): δ 14.24 (qd, $^2J_{PF}$ = 75.1 Hz, $J_{PP'}$ = 19.1 Hz, J_{PPt} = 3741.6 Hz, P(CF$_3$)), 35.04 (d, $J_{PP'}$ = 19.1 Hz, J_{PPt} = 3439.9 Hz, PXyl$_2$); ^{19}F NMR (658.78 MHz, $CDCl_3$): δ -54.49 (d, $^2J_{FP}$ = 75.1 Hz, J_{FPt} = 40.5 Hz, CF_3); HRMS (ESI) calcd. (*m/z*) for $C_{35}H_{35}ClF_3FeP_2Pt$: 860.0851 ([M-Cl]$^+$), Found: 860.0856 ([M-Cl]$^+$).

[Pt((*R*$_P$,*R*$_C$,*S*$_{Fc}$)-(Ph)(CF$_3$)-Xyliphos)Cl$_2$], [(*R*$_P$)-11]

(*R*$_P$,*R*$_C$,*S*$_{Fc}$)-1-[(Phenyl)trifluoromethylphosphino]-2-{1-[di(3,5-xylyl)phosphino]ethyl}ferrocene (*R*$_P$)-**5** (15 mg, 23.79 µmol, 1.1 eq.) was weighed into an NMR tube and dissolved in chloroform (0.6 mL). [Pt(cod)Cl$_2$] (8 mg, 21.38 µmol, 1.0 eq.) was added and the intense orange solution was agitated from time to time by inverting the tube. The product was obtained as an intense red crystalline solid (suitable for X-ray diffraction experiments) by slow diffusion of hexane into the reaction solution (17 mg, 18.96 µmol, 89%). CCDC 1000084.

^{1}H NMR (700.13 MHz, $CDCl_3$): δ 1.10 (dd, J = 14.7 Hz, $^3J_{HH}$ = 7.2 Hz, 3H, CHCH_3), 2.27 (s, $^1J_{HC}$ = 126.9 Hz, 6H, CH_3), 2.46 (s, 6H, $^1J_{HC}$ = 126.9 Hz, CH_3), 3.46-3.50 (m, 6H, *Cp*', CHCH$_3$), 4.23 (brs, 1H, *Cp*), 4.47 (brs, 1H, *Cp*), 4.53 (brs, 1H, *Cp*), 7.02 (brs, 1H, *Ph*), 7.22 (brs, 1H, *Ph*), 7.31 (brd, J = 12.5 Hz, 2H, *Ph*), 7.60-7.62 (m, 2H, *Ph*), 7.64-7.66 (m, 1H, *Ph*), 7.87 (brd, J = 11.6 Hz, 2H, *Ph*), 8.37 (dd, J = 13.1 Hz, J = 7.4 Hz, 2H, *Ph*); ^{13}C{^{1}H,^{31}P} NMR (125.79 MHz, CD_2Cl_2): δ 20.48 (brs, CHCH$_3$), 21.53 (s, CH$_3$), 21.70 (s, CH$_3$), 31.09 (s, CHCH$_3$), 59.42 (s, *Cp*), 71.31 (s, *Cp*'), 71.46 (s, *Cp*), 72.60 (s, *Cp*), 73.39 (brs, *Cp*), 94.03 (s, *Cp*), 121.07 (q, $^1J_{CF}$ = 322.1 Hz, CF$_3$), 126.06 (s, *Ph*), 126.91 (s, *Ph*), 127.02 (s, *Ph*), 128.87 (s, *Ph*), 132.74 (brs, *Ph*), 132.77 (brs, *Ph*), 133.39 (s, *Ph*), 133.56 (s, *Ph*), 134.34 (s, *Ph*), 135.48 (brs, *Ph*), 138.00 (s, *Ph*), 139.12 (s, *Ph*); ^{31}P{^{1}H} NMR (283.42 MHz, $CDCl_3$): δ 14.04 (qd, $^2J_{PF}$ = 73.6 Hz, $J_{PP'}$ = 21.0 Hz, J_{PPt} = 3739.6 Hz, P(CF$_3$)), 24.94 (d, $J_{PP'}$ = 20.9 Hz, J_{PPt} = 3416.0 Hz, PXyl$_2$); ^{19}F NMR (658.78 MHz, $CDCl_3$): δ -54.35

(d, $^{2}J_{FP}$ = 73.7 Hz, J_{FPt} = 42.5 Hz, CF_3); HRMS (ESI) calcd. (*m/z*) for $C_{35}H_{35}ClF_3FeP_2Pt$: 860.0851 ([M-Cl]$^+$), Found: 860.0853 ([M-Cl]$^+$).

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