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Zwitterionic Iridium Complexes with P,N-Ligands as Catalysts for the Asymmetric Hydrogenation of Alkenes

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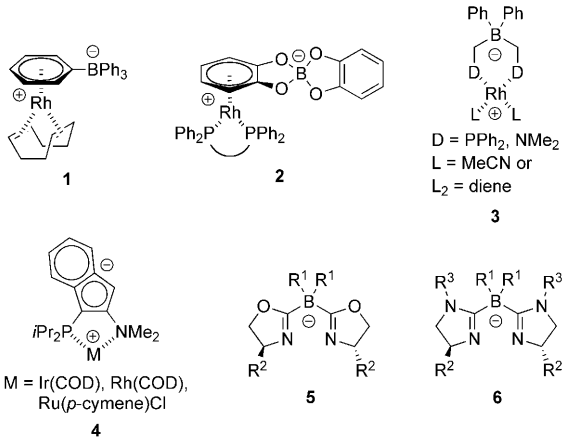
Abstract: Several zwitterionic iridium complexes based on chiral P,N-ligands with imidazoline or oxazoline donors and anionic tetraarylborate or aryltrifluoroborate substituents have been synthesized. The corresponding cationic analogues have also been prepared, to evaluate the effect of the covalent linkage between the anion and the cationic metal complex in catalytic reactions. The respective pairs of structurally analogous precatalysts have been compared for their efficacies in the asymmetric hydrogenation of unfunctionalized olefins. In most cases, the anionic derivatization has virtually no influence on the asymmetric induction of the iridium complex. This is in accordance with X-ray structural studies, which have shown that the chiral environment of the cationic metal center is not affected by the anionic substituent. Depending on the nature of the counterion employed, the zwitterionic catalysts proved to be significantly more reactive than their cationic counterparts in nonpolar solvents.

Keywords: asymmetric catalysis · borates · hydrogenation · iridium · zwitterions

Introduction

The use of zwitterionic metal complexes as catalysts for organic transformations has attracted considerable attention in the last twenty years. In particular, various well-defined systems for the polymerization of olefins with late transition metals[1] or single-site metallocene and half-sandwich catalysts[2] have been described. Furthermore, numerous anionic ligands for reactions in aqueous media have been developed,[3] although the corresponding zwitterionic metal complexes have seldom been studied in detail.

Apart from these two applications, there have only been a few examples of the use of betaines as efficient catalysts.[4] The zwitterionic rhodium species **1**, which was described by Schrock as early as 1970,[5] was applied by Alper in a multitude of transformations, such as hydroformylations and hydrogenations.[6] Complexes such as **2**, developed by Marder and Baker, were used for rhodium-catalyzed hydro- and diborations,[7] whereas Peters' borate derivatives **3** were shown to be good catalysts for several addition reactions to alkenes.[8] Stradiotto's indenide-based zwitterions **4** effect the reduction of alkenes and ketones.[9] Finally, our group recently introduced anionic N,N-ligands **5** and **6**, the copper complexes of which catalyze several asymmetric transformations, such as cyclopropanations, allylic oxidations, Henry reactions, and enantioselective acylations of secondary alcohols and diols.[10]



Compared with their cationic structural analogues, betaines are generally characterized by higher electron densities at their respective metal centers[8] as well as improved solubilities in apolar media.[9c] However, regarding the use of zwitterionic complexes as catalysts for hydrogenation reactions, the picture is less clear. Although ruthenium derivative **4** shows much higher activity than the corresponding cationic complex in the transfer hydrogenation of ketones,[9a] the related iridium betaine is significantly less efficient in the reduction of styrene or cyclohexene.[9c]

In the last decade, iridium complexes with chiral P,N-ligands have emerged as efficient catalysts for the asymmetric hydrogenation of unfunctionalized and certain function-

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alized olefins, which give unsatisfactory results with rhodium and ruthenium diphosphine catalysts.[11] These precatalysts have been successfully used in the synthesis of various natural products and useful chiral building blocks.[12] A pronounced counterion effect has been observed in these reactions, with bulky fluorinated aluminates[13] or borates such as tetrakis(pentafluorophenyl)borate[14] or tetrakis[3,5-bis-(trifluoromethyl)phenyl]borate (BAr_F)[15] proving to be the most active catalysts. Although this phenomenon has been studied in detail[16] and some experimental and theoretical investigations concerning the mechanism of the hydrogenation have been carried out,[17] the basis for this effect at the molecular level is not yet fully understood.

In light of these facts, it seemed to be of considerable interest to prepare zwitterionic derivatives of well-established cationic iridium precatalysts with a covalently attached anionic group and to study their properties in enantioselective hydrogenation reactions. If the anionic moiety could be incorporated into the backbone or at the periphery of the ligand, the formation of a tight ion pair with the cationic iridium center should be precluded. Therefore, we envisaged that the absence of a free counterion, which would otherwise interact with the cationic iridium core, could result in an increase of catalytic activity.

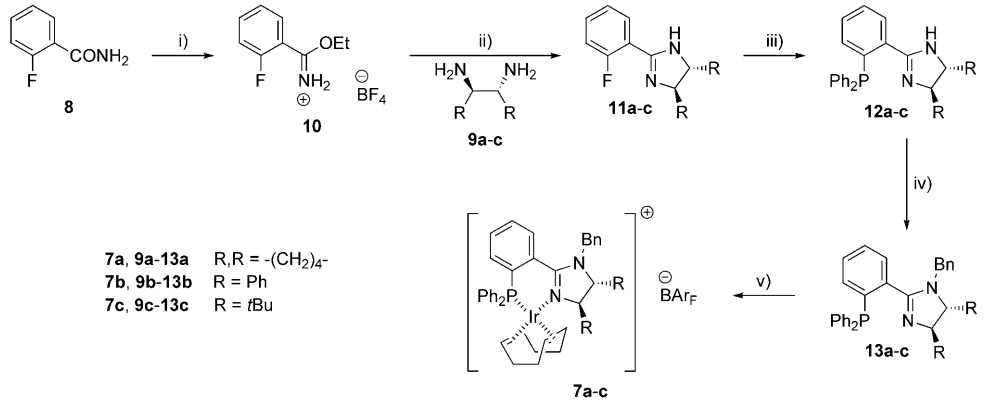
Herein, we report the development of iridium betaines based on anionic phosphinooxazoline (PHOX) or phosphinoimidazoline (PHIM or BIPI) ligands and their application in the asymmetric hydrogenation of unfunctionalized alkenes. Furthermore, structurally analogous cationic complexes are also described, and their catalytic properties compared with those of their zwitterionic counterparts.

Results and Discussion

Evaluation of cationic PHIM complexes: In contrast to the situation for the now well-established iridium PHOX derivatives,[11a,12d,16,17c–e,18] there have only been a few reports concerning the application of the corresponding imidazoline-based systems in enantioselective hydrogenation reactions.[19] Therefore, we decided to first study some cationic PHIM complexes with different steric properties, in order to identify the optimum ligand structure for the subsequent studies. Based on established literature procedures,[20] the three precatalysts **7a–c** were easily synthesized in five steps starting from *ortho*-fluorobenzamide (**8**) and the C_2-symmetric diamines **9a–c** (Scheme 1). In the course of this work, it was discovered that the nucleophilic aromatic substitution to generate phosphanes **12a–c** could be efficiently performed even at room temperature, thus avoiding the rather harsh literature conditions of refluxing THF.[20,21] Although methods are also available for the synthesis of imidazolines starting from amino alcohols,[22] the latter were not employed as chiral starting materials to avoid regioselectivity problems in the benzylation reaction. The new iridium complexes **7a–c** were subsequently evaluated in the asymmetric hydrogenation of some selected substrates (Table 1).[23]

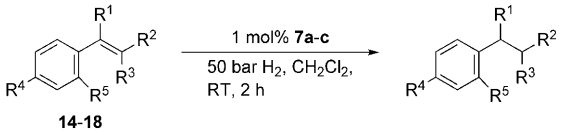
Both the phenyl-substituted derivative **7b** and the cyclohexyl-annelated representative **7a** proved to be very reactive, but their enantioselectivities were moderate at best. In contrast, the enantiomeric excesses induced by complex **7c** with *tert*-butyl moieties were promising. Especially for the methylstilbene substrate **14** and the α,β-unsaturated ester **18**, this complex clearly outperformed other structurally similar catalysts (Table 1, entries 3 and 15).[19b,24] Unfortunately, precatalyst **7c** gave only low reactivity. Even under forcing conditions (100 bar H_2, 20 h), the conversions were not improved significantly.

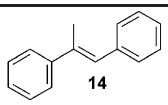
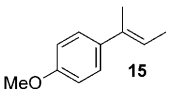
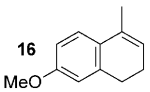
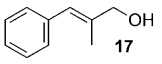
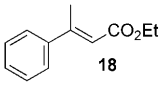
To shed light on these unexpected reactivity differences, the respective iridium complexes **7a** and **7c** were treated with dihydrogen under atmospheric pressure for 15 min in deuterodichloromethane and the resulting mixtures were analyzed by NMR spectroscopy. Although the reactive derivative **7a** had been transformed into two hydride-containing species with 73% conversion,[25] the NMR spectrum of **7c** showed only the unchanged cyclooctadiene complex. This result indicates that the low activity of **7c** might be attributed to a slow, incomplete conversion to the catalytically active species.



Scheme 1. Preparation of cationic PHIM complexes **7a–c**: i) Et_3OBF_4, CH_2Cl_2, RT, 19 h, 95%; ii) NEt_3, CH_2Cl_2, RT, 64 h, 75–85% (**11a**, **11b**) or EtOH, Δ, 91 h, 64% (**11c**); iii) $KPPh_2$, THF, Δ, 2 h, 88% (**12b**) or 0°C→RT, 2.5–4 h, 93–97% (**12a**, **12c**); iv) KH, THF (**13a**, **13b**) or THF/DMF (20:1) (**13c**), 0°C→RT, 2 h then BnBr, NBu_4I, RT, 20 h, 73–96%; v) $[Ir(COD)Cl]_2$, CH_2Cl_2, Δ, 2 h then $NaBAr_F$, H_2O, RT, 30 min, 95% to quantitative.

Table 1. Asymmetric hydrogenation reactions with cationic PHIM complexes **7a–c**.



Entry	Substrate	Precatalyst	Conversion [%][a]	*ee* [%][b]
1		**7a**	>99	64 (*S*)
2		**7b**	>99	41 (*S*)
3	**14**	**7c**	4	90 (*S*)
4		**7a**	>99	31 (*S*)
5		**7b**	>99	53 (*S*)
6	MeO **15**	**7c**	54	84 (*S*)
7		**7a**	>99	20 (*R*)
8		**7b**	>99	11 (*R*)
9	**16** MeO	**7c**	27	19 (*R*)
10		**7a**	>99	63 (+)
11		**7b**	>99	12 (−)
12	**17**	**7c**	44	85 (+)
13		**7a**	>99	50 (*S*)
14		**7b**	>99	15 (*S*)
15	**18**	**7c**	51	86 (*S*)

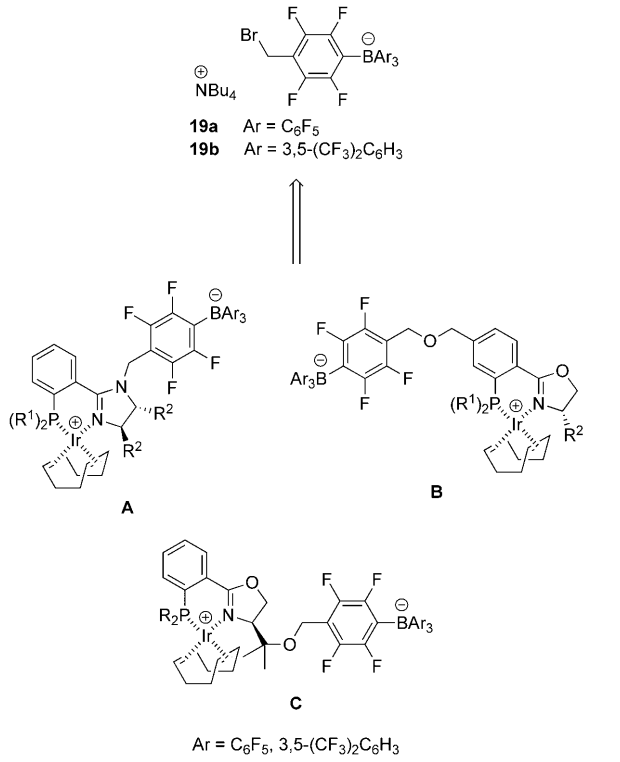
[a] Determined by GC. [b] Determined by HPLC on a chiral stationary phase.

In view of these results, further studies were focused on the highly reactive cyclohexyl-annelated imidazoline complexes and the more selective *tert*-butyl-substituted derivatives.

Synthesis of iridium betaines with P,N-ligands: Since cationic complexes with fluorinated tetraarylborates as counterions are among the most active catalysts for asymmetric hydrogenation reactions,[16] we decided to first prepare anionic P,N-ligands with borate moieties at the periphery. In this context, we have recently developed functionalized anionic building blocks **19a** and **19b** (Scheme 2).[26] They resemble structural analogues of the established tetrakis(pentafluoro)-phenylborate ($B(C_6F_5)_4$) and tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (BAr_F), and can easily be introduced in neutral precursors through nucleophilic substitution reactions.

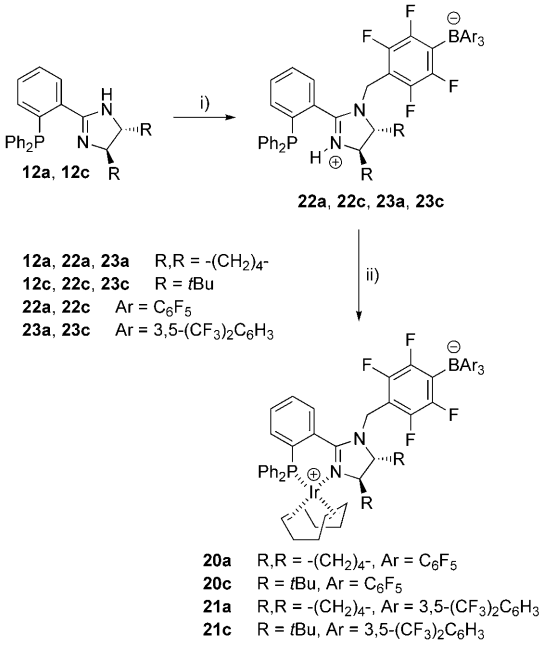
Iridium betaines **A**, **B**, and **C**, containing both imidazoline and oxazoline subunits, were chosen for these investigations (Scheme 2). In complexes **A** and **B**, the covalently linked anionic moieties are located at the rearside of the ligands, to avoid any unfavorable interaction between the opposite charges. Alternatively, the borate group can be attached to the side chain of the oxazoline ring as in derivative **C**, in which certain steric or electrostatic interactions of the anion with the cationic metal center are possible.

The preparation of precatalysts **20a–21c** as representatives of type **A**, starting from neutral precursors **12a** and **12c**, was straightforward (Scheme 3). The intermediate PHIM ligands were isolated as protonated betaines **22a–23c** after chromatography on silica gel.



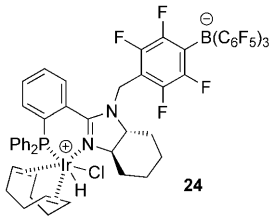
Scheme 2. Different classes of iridium zwitterions featuring P,N-ligands derived from functionalized borate building blocks **19a** and **19b**.

Metalation of ligand **22a** under the conditions described in Scheme 1 for the synthesis of cationic iridium complexes without addition of a base gave, besides the desired betaine



Scheme 3. Synthesis of PHIM-based derivatives **A**: i) KH, THF (**22a**, **23a**) or THF/DMF (20:1) (**22c**, **23c**), 0 °C→RT, 2 h then **19a** or **19b**, 0 °C→RT, 18 h then SiO_2, CH_2Cl_2, 86–97 %; ii) $[Ir(COD)Cl]_2$, $NEtiPr_2$, CH_2Cl_2, Δ, 2 h then $NaHCO_3$, H_2O, RT, 30 min, 97 % to quantitative.

20a, a second species in a ratio of 2:1. This side product was shown to be the iridium(III) compound **24** by NMR spectroscopy, the configuration at the metal center of which could not be established with certainty. Compound **24** represents the product of a formal oxidative addition of hydrogen chloride to complex **20a**. Its formation was completely suppressed by the addition of a tertiary amine base.



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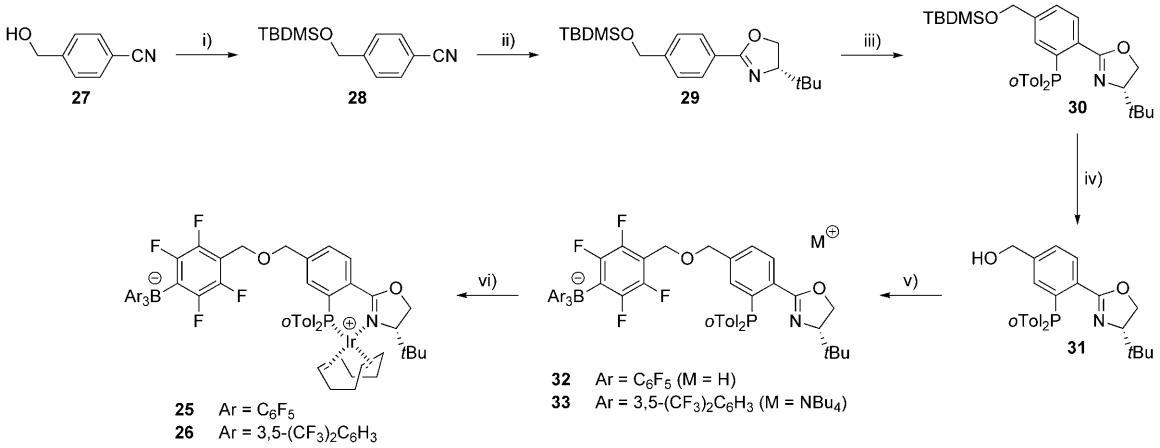
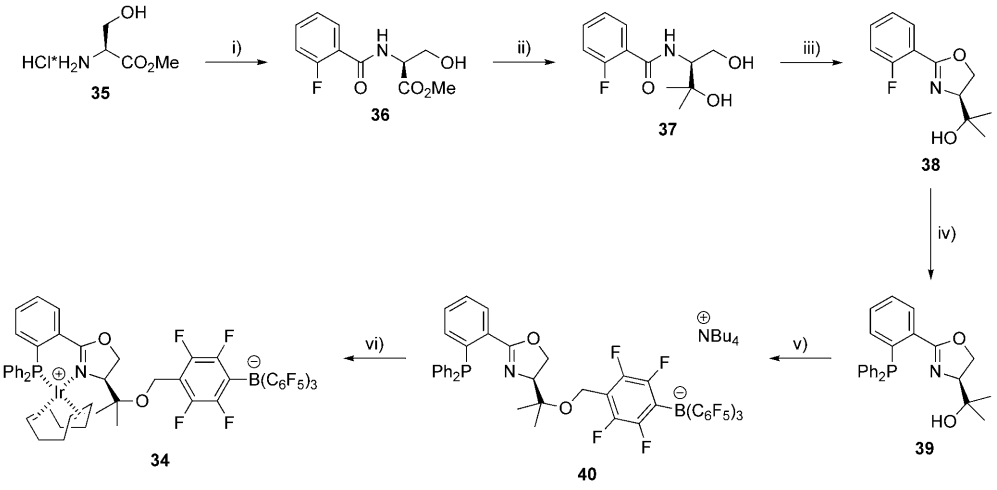
Oxazoline-based derivatives **25** and **26**, as representatives of zwitterions **B**, were easily synthesized in six steps from commercially available benzylic alcohol **27** (Scheme 4). The condensation of nitrile **28** yielding oxazoline **29** was not completed even after prolonged reaction times and 43% of starting material **28** was recovered. The PHOX ligands were partially obtained as the respective tetrabutylammonium salt (**33**) or as a mixture of the latter and the protonated betaine in a ratio of 4:5 (**32**). This reflects the lower basicity of oxazolines compared with their structurally related imidazoline counterparts.[27]

To determine the influence of the anchoring point of the anionic borate moiety on the properties of the precatalysts, iridium complex **34** was prepared as an example of class **C** complexes (Scheme 5).



27 **28** **29** **30** **31**

Scheme 4. Preparation of PHOX betaines **B**: i) TBDMSCl, imidazole, CH_2Cl_2, 0°C→RT, 2 h, 98%; ii) (*S*)-*tert*-leucinol, $ZnCl_2$ (cat.), PhCl, Δ, 71 h, 51%; iii) *s*BuLi, TMEDA, pentane, −78°C, 60 min→0°C, 15 min then *o*-Tol_2PCl, 0°C→RT, 15 h, 82%; iv) TBAF, THF, 0°C→RT, 3.5 h, 89%; v) KH, THF, 0°C→RT, 2 h then **19a** or **19b**, 0°C→RT, 19 h then SiO_2, CH_2Cl_2; vi) $[Ir(COD)Cl]_2$, NE*t*Pr_2, CH_2Cl_2, Δ, 2 h then $NaHCO_3$, H_2O, RT, 30 min, 71–92% over two steps.

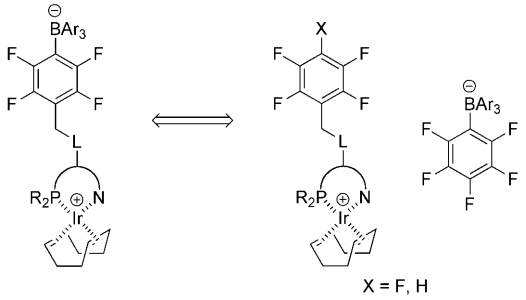


35 **36** **37** **38** **39** **40** **34**

Scheme 5. Variation of the anchoring point: i) 2-FC_6H_4COCl, NEt_3, MeOH, 0°C, 2.5 h, 91%; ii) MeMgBr, THF/Et_2O, 0°C, 60 min→RT, 17 h then NH_4Cl (aq.), 0°C, 70%; iii) TsCl, NEt_3, CH_2Cl_2, RT, 75 h, 92%; iv) $KPPh_2$, THF, 0°C, 2 h, 77%; v) KH, THF, 0°C→RT, 2 h then **19a**, 0°C→RT, 24 h, 83%; vi) $[Ir(COD)Cl]_2$, NE*t*Pr_2, CH_2Cl_2, Δ, 2 h then $NaHCO_3$, H_2O, RT, 30 min, 95%.

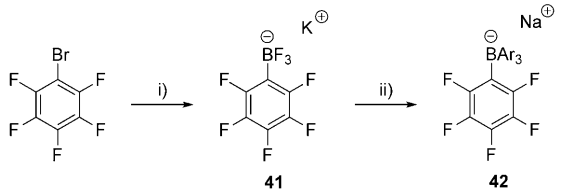
The synthesis of phosphane **39** from (*S*)-serine methyl ester hydrochloride (**35**) has been previously described by Helmchen and co-workers.[28] As a major improvement of their procedures, we found that the nucleophilic aromatic substitution to give **39** can be accomplished in the presence of the free hydroxyl group with high efficiency, avoiding protection/deprotection steps. The intermediate PHOX ligand was isolated as tetrabutylammonium salt **40** after chromatography on silica gel.

Preparation of cationic analogues: The aim of these investigations was to study the influence of the covalent linkage between the cationic iridium complexes and the respective anions on the reactivities and enantioselectivities in the hydrogenation of different olefins. Therefore, it was mandatory to also synthesize the cationic structural analogues of all of the zwitterions described above as reference systems (Scheme 6).



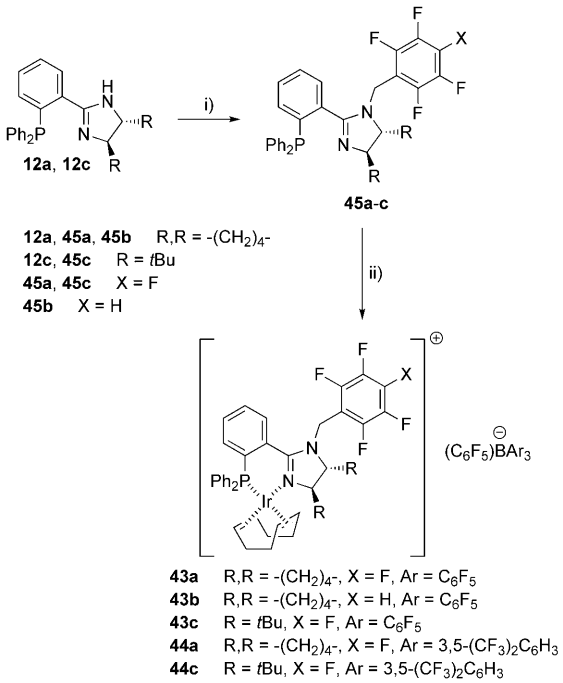
Scheme 6. The betaines and their cationic structural analogues.

Although the free anion for the representatives with Ar = C_6F_5 corresponds to the well-established tetrakis(pentafluorophenyl)borate ($B(C_6F_5)_4$), the respective counterion $(C_6F_5)BAr_3$ for the derivatives with Ar = 3,5-$(CF_3)_2C_6H_3$ is not known in the literature. However, it was easily synthesized via the reported aryltrifluoroborate **41** (Scheme 7).[29]



Scheme 7. Preparation of borate **42**: i) Mg, Et_2O, Δ, 2 h then $B(OiPr)_3$, 0 °C→RT, 20 h then KHF_2, H_2O, RT, 65 min, 55 %; ii) ArMgBr, Et_2O, 0 °C→RT, 6 h then Na_2CO_3, H_2O, RT, 60 min, 67 % (Ar = 3,5-$(CF_3)_2C_6H_3$).

With the required borates in hand, the cationic structural analogues of PHIM-based betaines **43a–44c** were easily accessible, although the yields of the intermediate P,N-ligands



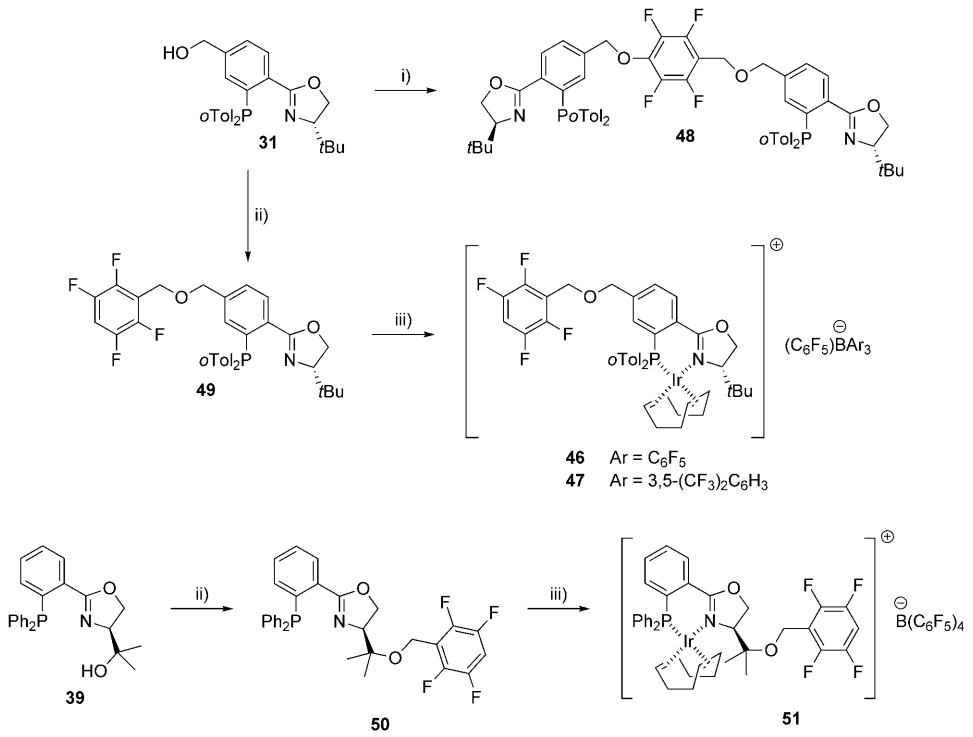
Scheme 8. Synthesis of cationic PHIM reference systems **43a–44c**: i) KH, THF (**45a**, **45b**) or THF/DMF (20:1) (**45c**), 0 °C→RT, 2 h then 4-$XC_6F_4CH_2Br$, 0 °C→RT, 17–24 h, 33–58 %; ii) $[Ir(COD)Cl]_2$, CH_2Cl_2, Δ, 2 h then $Li[B(C_6F_5)_4]$ or **42**, H_2O, RT, 30 min, 75–97 %.

45a–c were only moderate (Scheme 8). Complexes **43a** and **43b** with X = F or H were prepared to exclude an unlikely but possible influence of this substituent on the properties of the catalysts.

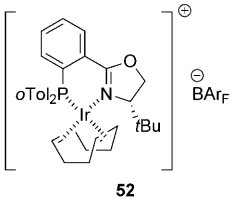
Initial attempts to prepare the cationic analogues **46** and **47** of PHOX-derived zwitterions **25** and **26** were unsuccessful. When pentafluorobenzyl bromide was used in the etherification, exclusively the dimeric P,N-ligand **48** was isolated in good yield (Scheme 9). The formation of **48** is a result of selective nucleophilic aromatic substitution of the *para*-fluoro atom by the potassium alkoxide.

However, the corresponding reaction with 2,3,5,6-tetrafluorobenzyl bromide as the electrophile gave the desired derivative **49**, which could then be easily transformed into complexes **46** and **47**. Reference compound **51** was obtained in the same manner.

Enantioselective hydrogenation reactions in dichloromethane: To investigate the properties of the new iridium betaines **20a–21c**, **25**, **26**, and **34** and their cationic counterparts **43a–44c**, **46**, **47**, and **51**, the complexes were evaluated for their efficacies in the asymmetric hydrogenation of a series of representative alkenes. As a starting point, we applied the conditions that had proven to be optimal for cationic iridium catalysts.[11,16] In particular, dichloromethane was used as solvent. To ensure maximum comparability of the results, the respective reactions with the zwitterionic complex and its cationic analogue were performed on the same day, with the same batches of substrate and solvent,



Scheme 9. Preparation of cationic PHOX precatalysts: i) KH, THF, 0 °C→RT, 2 h then $C_6F_5CH_2Br$, 0 °C→RT, 15 h, 72 %; ii) KH, THF, 0 °C→RT, 2 h then 4-$HC_6F_4CH_2Br$, 0 °C→RT, 19–23 h, 53–86 %; iii) $[Ir(COD)Cl]_2$, CH_2Cl_2, Δ, 2 h then $Li[B(C_6F_5)_4]$ or **42**, H_2O, RT, 30 min, 97 % to quantitative.



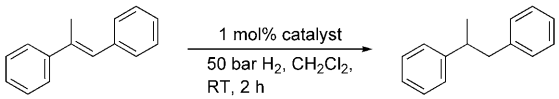
and in the same autoclave. Tables 2–6 show the results of hydrogenations of olefins **14**–**18**, respectively.[23] For comparison, the corresponding data for the standard PHOX catalyst **52** are also included.[11a,d]

In the asymmetric hydrogenation of (*E*)-1,2-diphenyl-1-propene (**14**), a test reaction that has been extensively studied in the past,[11,16a,c] both cyclohexyl-annelated PHIM complexes **20a**, **21a**, **43a**, **43b**, and **44a** and PHOX precatalysts **25**, **26**, **46**, and **47** based on *tert*-leucinol exhibited high reactivities, yielding full conversions after 2 h at 50 bar hydrogen pressure (Table 2, entries 1–5 and 10–13). Although the PHOX complexes gave highly enantioenriched products (Table 2, entries 10–13), the selectivities of the PHIM-based representatives were moderate (Table 2, entries 1–5). Most importantly, the data for the betaines and their cationic reference systems were virtually identical (Table 2, entries 10/11 and 12/13) or at least very similar (Table 2, entries 1–3 and 4/5).

In contrast, the pair of PHOX complexes **34** and **51** yielded rather different results, with cationic derivative **51** being more efficient (Table 2, entries 14 and 15). The *tert*-butyl-substituted PHIM complexes **20c**, **21c**, **43c**, and **44c** gave only trace amounts of product under the chosen reaction conditions (Table 2, entries 6–9).

Hydrogenations of other unfunctionalized acyclic or endocyclic alkenes, such as **15** and **16** (Tables 3 and 4), allylic alcohol **17** (Table 5), and α,β-unsaturated ester **18** (Table 6), gave similar results. PHIM complexes **20c**, **21c**, **43c**, and **44c** and PHOX derivatives **34** and **51** gave considerably higher conversions with these substrates, with the cationic systems being slightly more reactive than their zwitterionic analogues. Compared with their cyclohexyl-annelated counterparts **20a**, **21a**, **43a**, **43b**, and **44a**, PHIM precatalysts **20c**, **21c**, **43c**, and **44c** with *tert*-butyl subunits were clearly more selective. In general, PHOX-based representatives **25**, **26**, **34**, **46**, **47**, and **51** are considerably more efficient in terms of both reactivity and enantioselectivity, especially the latter.

Table 2. Hydrogenation of (*E*)-1,2-diphenyl-1-propene (**14**).

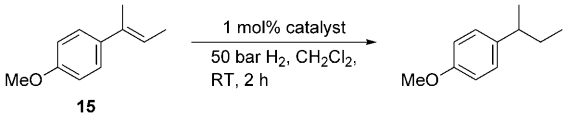


Entry	Precatalyst	Conversion [%][a]	*ee* [%][b]
1	**20a**	>99	65 (*S*)
2	**43a**	>99	73 (*S*)
3	**43b**	>99	72 (*S*)
4	**21a**	>99	68 (*S*)
5	**44a**	>99	73 (*S*)
6	**20c**	1	n.d.
7	**43c**	2	n.d.
8	**21c**	2	n.d.
9	**44c**	7	88 (*S*)
10	**25**	>99	96 (*R*)
11	**46**	>99	98 (*R*)
12	**26**	99	97 (*R*)
13	**47**	>99	97 (*R*)
14	**34**	34	82 (*S*)
15	**51**	99	93 (*S*)
16[11a]	**52**	>99	97 (*R*)

[a] Determined by GC. [b] Determined by HPLC on a chiral stationary phase. n.d. denotes "not determined".

It should be mentioned that the lower conversions of substrates **14**, **17**, and **18** with iridium betaine **34** were easily enhanced by increasing the reaction time without affecting the enantioselectivities.[23] This indicates that the diminished re-

Table 3. Hydrogenation of (*E*)-2-(4′-methoxyphenyl)-2-butene (**15**).

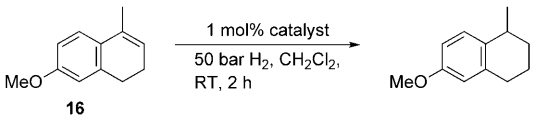


15

Entry	Precatalyst	Conversion [%][a]	*ee* [%][b]
1	**20a**	>99	22 (*S*)
2	**43a**	>99	25 (*S*)
3	**43b**	>99	22 (*S*)
4	**21a**	>99	21 (*S*)
5	**44a**	>99	24 (*S*)
6	**20c**	16	73 (*S*)
7	**43c**	60	71 (*S*)
8	**21c**	9	66 (*S*)
9	**44c**	49	65 (*S*)
10	**25**	>99	70 (*R*)
11	**46**	>99	74 (*R*)
12	**26**	>99	68 (*R*)
13	**47**	>99	71 (*R*)
14	**34**	>99	93 (*S*)
15	**51**	>99	93 (*S*)
16[11a,d]	**52**	>99	61–81 (*R*)

[a] Determined by GC. [b] Determined by HPLC on a chiral stationary phase.

Table 4. Hydrogenation of 6-methoxy-1-methyl-3,4-dihydronaphthalene (**16**).

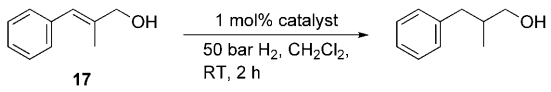


16

Entry	Precatalyst	Conversion [%][a]	*ee* [%][b]
1	**20a**	>99	17 (*R*)
2	**43a**	>99	14 (*R*)
3	**43b**	>99	15 (*R*)
4	**21a**	>99	19 (*R*)
5	**44a**	>99	15 (*R*)
6	**20c**	8	10 (*S*)
7	**43c**	26	15 (*R*)
8	**21c**	13	*rac.*
9	**44c**	49	21 (*R*)
10	**25**	>99	67 (*S*)
11	**46**	>99	73 (*S*)
12	**26**	>99	69 (*S*)
13	**47**	>99	72 (*S*)
14	**34**	97	75 (*R*)
15	**51**	98	71 (*R*)
16[11d]	**52**	>99	72 (*S*)

[a] Determined by GC. [b] Determined by HPLC on a chiral stationary phase.

Table 5. Hydrogenation of (*E*)-2-methyl-3-phenyl-2-propenol (**17**).

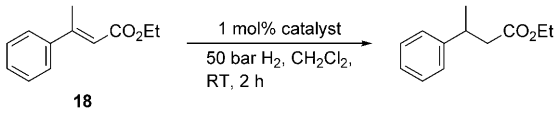


17

Entry	Precatalyst	Conversion [%][a]	*ee* [%][b]
1	**20a**	>99	54 (+)
2	**43a**	>99	58 (+)
3	**43b**	>99	57 (+)
4	**21a**	>99	58 (+)
5	**44a**	>99	57 (+)
6	**20c**	8	76 (+)
7	**43c**	28	69 (+)
8	**21c**	15	80 (+)
9	**44c**	44	71 (+)
10	**25**	>99	93 (−)
11	**46**	>99	94 (−)
12	**26**	>99	94 (−)
13	**47**	>99	94 (−)
14	**34**	73	69 (+)
15	**51**	>99	82 (+)
16[11a]	**52**	95	96 (−)

[a] Determined by GC. [b] Determined by HPLC on a chiral stationary phase.

Table 6. Hydrogenation of (*E*)-ethyl 3-phenyl-2-butenoate (**18**).



18

Entry	Precatalyst	Conversion [%][a]	*ee* [%][b]
1	**20a**	>99	46 (*S*)
2	**43a**	>99	46 (*S*)
3	**43b**	>99	46 (*S*)
4	**21a**	>99	50 (*S*)
5	**44a**	>99	47 (*S*)
6	**20c**	7	70 (*S*)
7	**43c**	23	84 (*S*)
8	**21c**	12	76 (*S*)
9	**44c**	45	86 (*S*)
10	**25**	>99	81 (*R*)
11	**46**	>99	80 (*R*)
12	**26**	>99	83 (*R*)
13	**47**	>99	81 (*R*)
14	**34**	74	26 (*S*)
15	**51**	99	40 (*S*)
16[11a]	**52**	96	84 (*R*)

[a] Determined by GC. [b] Determined by HPLC on a chiral stationary phase.

activity of **34** may be attributed to a lower turnover frequency rather than a shorter lifetime of the catalytically active species.

Based on the data presented in Tables 2–6, the following conclusions can be drawn. Covalent linkage of the negative moiety at the rearside of the ligand has, as anticipated, no pronounced influence on the chiral pocket around the catalytically active metal center. This has clearly been demonstrated by the virtually identical or at least very similar enantioselectivities afforded by PHOX-derived betaines **25** and **26** or PHIM zwitterions **20a** and **21a** and their cationic reference systems **43a**, **43b**, **44a**, **46**, and **47**. In addition, all of these derivatives show approximately the same efficiencies, yielding full conversions with 1 mol% catalyst loading. Finally, it is evident from the consistency of results with derivatives **43a** and **43b** that the *para*-substituent on the benzyl moiety in the ligands exerts no electronic influence on the properties of the respective metal complexes.

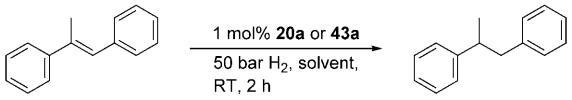
In contrast, the differences between PHOX betaine **34** and its cationic analogue **51** with respect to both reactivity

and selectivity show that the location of the anchoring point of the negatively charged subunit on the ligand backbone has a significant impact on the efficiency of the catalyst, since an interaction between the cationic metal center and the sterically demanding anionic subunit is rendered possible in complex **34**.

The generally low conversions and rather variable selectivities of PHIM complexes **20c**, **21c**, **43c**, and **44c** might be attributed to steric overcrowding of the catalytically active metal center due to the accumulation of bulky substituents on the imidazoline ring.

Variation of the reaction conditions: To further evaluate the properties of the new iridium betaines, compounds **20a** and **25** were selected for further studies of the asymmetric reduction of stilbene-type olefin **14** in various, predominantly apolar solvents. The results from these experiments are summarized and compared with the respective data for the corresponding cationic complexes **43a** and **46** in Tables 7 and 8.

Table 7. Hydrogenations with PHIM complexes **20a** and **43a** in different solvents.



14

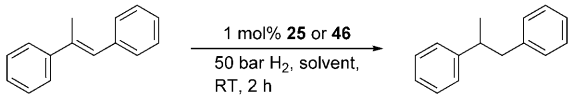
Entry	Solvent	Precatalyst	Conversion [%][a]	*ee* [%][b]
1	dichloromethane	**20a**	>99	65 (*S*)
2	dichloromethane	**43a**	>99	73 (*S*)
3	toluene	**20a**	95	22 (*R*)
4	toluene	**43a**	79	24 (*R*)
5	hexane	**20a**	>99	9 (*R*)
6	hexane	**43a**	45	14 (*R*)
7	cyclohexane	**20a**	>99	8 (*R*)
8	cyclohexane	**43a**	25	3 (*R*)
9	pentane	**20a**	>99	13 (*R*)
10	pentane	**43a**	57	14 (*R*)
11[c]	pentane	**20a**	93	8 (*R*)
12[c]	pentane	**43a**	24	13 (*R*)

[a] Determined by GC. [b] Determined by HPLC on a chiral stationary phase. [c] 0.3 mol% catalyst.

Interestingly, zwitterions **20a** and **25** maintained their high levels of activity even in pure hydrocarbons, whereas the conversions achieved with cationic complexes **43a** and **46** decreased sharply. This trend was more pronounced for the PHOX-derived precatalysts, with betaine **25** showing about tenfold higher reactivity in hexane, cyclohexane, or pentane relative to **46** (Table 8, entries 5–10). The turnover numbers for the zwitterions in pentane after reaction times of 2 h were 310 (**20a**, Table 7, entry 11) and 200 (**25**, Table 8, entry 11), respectively. The reason for the negligible activity of complex **25** in toluene (Table 8, entry 3) remains unclear, but π-complexes of the aromatic solvent with some intermediates in the catalytic cycle might play a role here.

The selectivities of all four precatalysts deteriorated with decreasing polarities of the solvents. PHOX derivatives **25** and **46** still gave high enantiomeric excesses of 77–94% in pure hydrocarbons, although the differences between the respective values of the two structural analogues were increased (Table 8, entries 5–12). In contrast, the selectivities of the PHIM systems were substantially eroded and even the direction of the asymmetric induction was inverted (Table 7, entries 5–12). In toluene and hydrocarbons, the (*R*)-product was obtained preferentially, although with very low enantiomeric excess.

Table 8. Hydrogenations with PHOX complexes **25** and **46** in different solvents.



14

Entry	Solvent	Precatalyst	Conversion [%][a]	*ee* [%][b]
1	dichloromethane	**25**	>99	96 (*R*)
2	dichloromethane	**46**	>99	98 (*R*)
3	toluene	**25**	8	93 (*R*)
4	toluene	**46**	97	97 (*R*)
5	hexane	**25**	>99	78 (*R*)
6	hexane	**46**	8	85 (*R*)
7	cyclohexane	**25**	>99	77 (*R*)
8	cyclohexane	**46**	7	94 (*R*)
9	pentane	**25**	>99	79 (*R*)
10	pentane	**46**	12	89 (*R*)
11[c]	pentane	**25**	61	78 (*R*)
12[c]	pentane	**46**	9	88 (*R*)

[a] Determined by GC. [b] Determined by HPLC on a chiral stationary phase. [c] 0.3 mol% catalyst.

The superior catalytic performances of betaines **20a** and **25** in pure hydrocarbons can most likely be attributed to the enhanced solubilities of these formally uncharged species in solvents of low polarities, although even with catalyst loadings as low as 0.3 mol% the reaction mixtures in pentane remained heterogeneous. Furthermore, the drastic variations in enantioselectivity seen in the different solvents indicate that the chiral environment of the iridium center is highly sensitive to the reaction medium. Finally, it has to be pointed out that, regardless of the solvent used, the new iridium betaines are far more reactive than the established indenide-based system **4**, which shows no conversion with trisubstituted olefins such as 1-methylcyclohexene.[9c]

Owing to their high reactivities, no pronounced differences in productivity were detected between the iridium betaines and their cationic reference compounds in dichloromethane at 1 mol% catalyst loading (Tables 3–6). Therefore, the kinetic profiles of the selected representatives **21a**, **26**, **44a**, and **47** in this solvent were investigated in more detail with only 0.02 mol% catalyst loading (Figure 1 and Table 9).[30] Every data point in Figure 1 represents an independent catalytic experiment, which was worked-up and analyzed after the time indicated. Table 9 contains approximate values for the turnover frequencies and numbers of these four iridium complexes.

The enantioselectivities of the four catalysts remained almost constant throughout the reactions and were in excel-

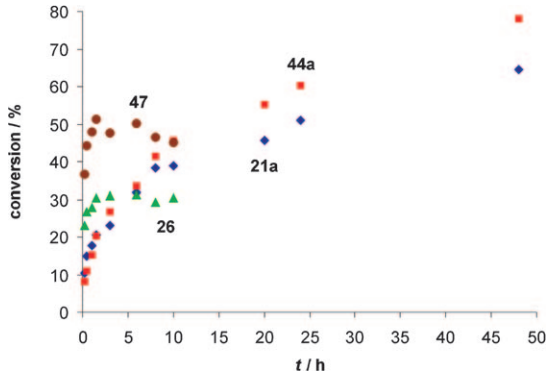


Figure 1. Kinetic profiles for **21a** (blue diamonds), **26** (green triangles), **44a** (red squares), and **47** (brown circles) for the hydrogenation of **14** in dichloromethane with 0.02 mol% catalyst loading at room temperature and 50 bar hydrogen pressure.

Table 9. Enantioselectivities, turnover frequencies (TOF), and turnover numbers (TON) for the hydrogenations of **14** shown in Figure 1.

Entry	Precatalyst	*ee* [%][a]	TOF [h^{-1}][b]	TON[c]
1	**21a**	71–68 (*S*)	2060	3230
2	**44a**	75–73 (*S*)	1640	3895
3	**26**	98–96 (*R*)	4620	1460
4	**47**	97–96 (*R*)	7340	2260

[a] Determined by HPLC on a chiral stationary phase. [b] Determined at $t=15$ min. [c] Determined at $t=10$ h (**26**, **47**) or $t=48$ h (**21a**, **44a**).

lent agreement with the values obtained in the experiments with 1 mol% catalyst loading (Table 2, entries 4, 5, 12, and 13). In both cases, the cationic complexes were somewhat more efficient than the corresponding zwitterions, resulting in about 21–55% higher turnover numbers.

However, there are striking differences between the kinetic profiles of the PHOX- and PHIM-based catalysts. Although PHOX complexes **26** and **47** exhibit very high initial rates, their lifetimes are quite short and maximum conversions are reached within the first hour. In contrast, the turnover frequencies of the PHIM complexes are lower, but they remain active even after prolonged reaction times. Most interestingly, their TOFs stay more or less constant during the final 38 h of the transformations (34 h^{-1} for **21a** and 43 h^{-1} for **44a**). This indicates that deactivation, which is a well-known problem of iridium complexes,[16,31] is much slower in the case of the PHIM-based catalysts. After an initial phase, during which the activity decreases, a steady-state concentration of catalytically active species is reached and the TOF value remains virtually constant. Thus, owing to their enhanced stabilities, the PHIM complexes are more productive catalysts than the PHOX analogues, even though their initial reactivities are markedly lower.

X-ray crystallographic studies of PHIM-derived complexes: To shed light on the molecular basis for the observed trends in reactivity and enantioselectivity of the new catalysts, crystal structures of representative PHIM-based iridium complexes were determined.[32] Since attempts to obtain suitable crystals from cationic complexes with the BAr_F anion failed, hexafluorophosphate salts **53a** and **53b** were prepared, which eventually provided single crystals suitable for X-ray analysis. Figure 2 shows the solid-state structures of precatalysts **53a**, **53b**, and **7c** with different substituents on the imidazoline moieties. Selected metric parameters of these complexes are summarized in Table 10.

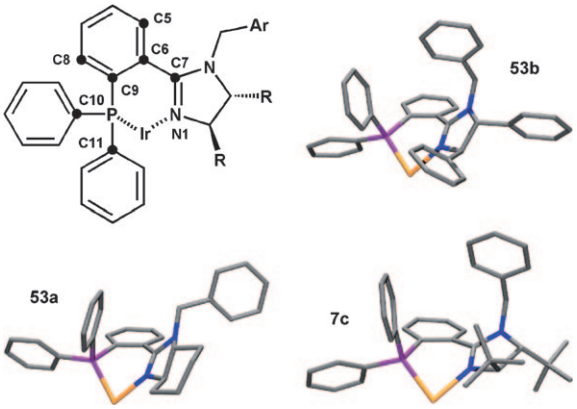


Figure 2. General atomic numbering scheme and crystal structures of cationic iridium complexes **53a**, **53b**, and **7c**. The counterions, the cyclooctadiene fragments, all hydrogen atoms, and solvent molecules eventually present have been omitted for clarity.

Table 10. Selected bond lengths [Å] and angles [°] for precatalysts **53a**, **53b**, and **7c**.[a]

Complex	**53a**	**53b**	**7c**
anion	PF_6	PF_6	BAr_F
Ir1–P1	2.285(1)	2.280(1)	2.2717(7)
Ir1–N1	2.083(3)	2.091(3)	2.091(3)
Ir1–C1 (*trans* to P)	2.201(5)	2.216(3)	2.203(3)
Ir1–C2 (*trans* to P)	2.157(3)	2.199(4)	2.177(4)
Ir1–C3 (*trans* to N)	2.165(4)	2.129(4)	2.150(4)
Ir1–C4 (*trans* to N)	2.116(4)	2.106(4)	2.110(4)
P1-Ir1-N1	81.09(9)	86.63(9)	86.08(8)
C5-C6-C7-N1[b]	48.0	47.9	40.7
C8-C9-P1-C10[b]	−117.8	−102.0	−93.2
C8-C9-P1-C11[b]	−7.2	7.7	15.9

[a] Atomic numbering according to Figure 2. [b] Determined with the help of WebLabViewerLite 3.20.

The crystal structures of the three complexes are very similar. Their six-membered chelate rings exhibit distorted boat conformations with almost identical Ir1–P1 and Ir1–N1 bond lengths, although **53a** shows a slightly smaller bite angle P1-Ir1-N1. All torsional angles C5-C6-C7-N1 between the bridging phenyl ring and the imidazoline subunit are in the range 41–48°. As expected, the Ir–C bonds *trans* to the phosphorus donor (Ir1–C1 and Ir1–C2) are somewhat longer than those *trans* to the nitrogen atom (Ir1–C3 and Ir1–C4). Finally, the torsional angles C8-C9-P1-C10 and C8-C9-P1-C11 in the series **53a**, **53b**, and **7c** change in such a way that the distances between the *P*-phenyl groups and the

progressively more bulky substituents on the imidazoline rings increase, to minimize unfavorable steric interactions.

The solid-state structure of zwitterion **20c** was also determined. Figure 3 shows one of the two almost identical molecules in the asymmetric unit, together with the crystal structure of the hexafluorophosphate salt **54**. Table 11 lists the corresponding metric parameters.

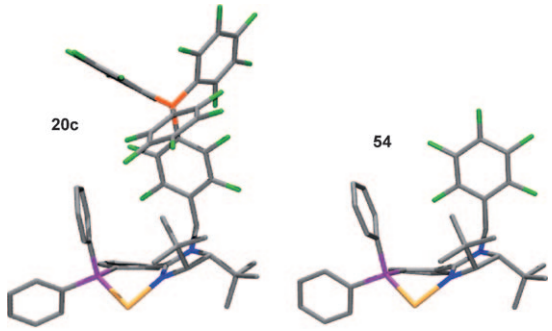


Figure 3. Crystal structures of precatalysts **20c** and **54**. The counterion of **54**, the cyclooctadiene fragments, all hydrogen atoms, and solvent molecules eventually present have been omitted for clarity.

Table 11. Selected bond lengths [Å] and angles [°] for betaine **20c** and its cationic structural analogue **54**.[a]

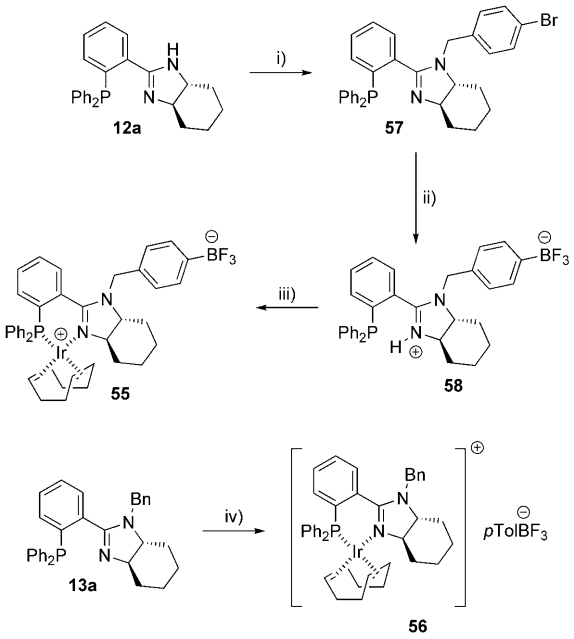
Complex	**20c**	**54**
Ir1–P1	2.285(1)/2.276(1)	2.293(1)
Ir1–N1	2.100(4)/2.113(4)	2.101(3)
Ir1–C1 (*trans* to P)	2.206(5)/2.221(4)	2.188(4)
Ir1–C2 (*trans* to P)	2.188(5)/2.212(4)	2.127(4)
Ir1–C3 (*trans* to N)	2.141(6)/2.158(5)	2.171(6)
Ir1–C4 (*trans* to N)	2.110(6)/2.124(5)	2.154(5)
P1-Ir1-N1	86.0(1)/85.1(1)	85.98(8)
C5-C6-C7-N1[b]	38.0/38.5	38.9
C8-C9-P1-C10[b]	−90.9/−92.0	−91.6
C8-C9-P1-C11[b]	19.3/15.9	14.1

[a] Atomic numbering according to Figure 2. [b] Determined with the help of WebLabViewerLite 3.20.

The coordination geometries of these two structurally analogous precatalysts are virtually identical. Furthermore, the respective parameters are very similar to those of the *tert*-butyl-substituted PHIM complex **7c** (Figure 2 and Table 10). The similarity of the coordination spheres, together with the almost identical enantioselectivities provided by the zwitterionic derivatives and their cationic analogues, indicates that the covalent linkage of the counterion at the rearside of the P,N-ligand has hardly any influence on the chiral environment of the metal center. The cyclooctadiene ligand of complex **54** is strongly twisted out of the plane of an ideally square-planar coordination geometry, such that, against all expectations, the Ir-C2 bond *trans* to the P atom is shorter than the respective distances *trans* to the N atom. This shows the limitations of assessing the characteristics of a specific donor with the help of these values.

Examination of more strongly coordinating counterions: In the comparative studies of the borate-based zwitterionic precatalysts and their cationic structural analogues, the generally very high activities turned out to be a major problem. To establish the impact of the covalent linkage of the two opposite charges, the catalyst loadings had to be lowered to such an extent that disturbing factors such as traces of water or other impurities might have obscured the effects of interest. Therefore, the corresponding complexes with more coordinating counterions, which were expected to have stronger interactions between the anion and the iridium center and thus be less active, were also investigated.

After derivatives containing sulfonate moieties had proven to be almost inactive in the hydrogenation of trisubstituted unfunctionalized olefins, we turned our attention to tetrafluoroborate and aryltrifluoroborates as the immobilizable variants of the former.[16a,33] The preparations of betaine **55** and its cationic counterpart **56**, which represent structural analogues of precatalysts **20a**, **21a**, **43a**, **43b**, and **44a** with fluorinated tetraarylborates, were straightforward (Scheme 10).



Scheme 10. Synthesis of aryltrifluoroborate-based precatalysts **55** and **56**: i) KH, THF, 0 °C→RT, 2 h then 4-Br$C_6H_4CH_2$Br, NBu_4I, RT, 19 h, 86 %; ii) *n*BuLi, THF, −78 °C, 90 min then B(O*i*Pr)$_3$, −78 °C, 60 min→RT, 90 min then KHF_2, H_2O, RT, 2 h; iii) $[Ir(COD)Cl]_2$, NEt*i*Pr$_2$, CH_2Cl_2, Δ, 2 h then $NaHCO_3$, H_2O, RT, 30 min, about 62 % over two steps; iv) $[Ir(COD)Cl]_2$, CH_2Cl_2, Δ, 2 h then K[*p*-TolBF_3], $NaHCO_3$, H_2O, RT, 30 min, 53 %.

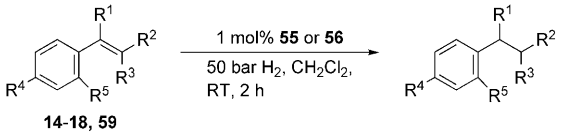
Lithiation of aryl bromide **57** and subsequent transformation into aryltrifluoroborate **58** provided, as a result of the acidity of potassium hydrogen difluoride, not the potassium salt but the protonated imidazoline **58**, as indicated by IR spectroscopy. This was used in the next step without further purification. Despite substantial experimentation, zwitterion

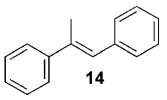
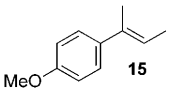
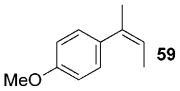
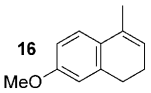
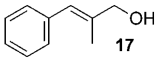
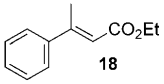
55 always contained a minor amount of a second species after recrystallization, which could not be removed. The latter was presumably a hydrolysis product with an unspecified counterion.

A slight variation of the standard procedure gave the analogous cationic complex **56** with trifluoro-*para*-tolylborate as the anion. The geometry of its cationic molecular fragment in the solid state proved to be virtually identical to the structure determined for the corresponding hexafluorophosphate derivative **53a**.[34]

Notwithstanding the impurity in all samples of complex **55**, the two precatalysts **55** and **56** were evaluated for their efficacies in the asymmetric hydrogenation of selected olefins (Table 12).[23]

Table 12. Asymmetric reductions with aryltrifluoroborate-based complexes **55** and **56**.



Entry	Substrate	Precatalyst	Conversion [%][a]	*ee* [%][b]
1		**55**	45	52 (*S*)
2		**56**	11	59 (*S*)
3[c]		**55**	91	54 (*S*)
4[c]		**56**	28	59 (*S*)
5		**55**	89	16 (*S*)
6		**56**	46	22 (*S*)
7		**55**	51	27 (*R*)
8		**56**	13	28 (*R*)
9		**55**	89	17 (*R*)
10		**56**	56	21 (*R*)
11		**55**	97	62 (+)
12		**56**	99	66 (+)
13		**55**	84	50 (*S*)
14		**56**	39	49 (*S*)

[a] Determined by GC. [b] Determined by HPLC on a chiral stationary phase. [c] 0.2 mol % catalyst loading, 24 h.

With all substrates except allylic alcohol **17**, zwitterion **55** gave substantially higher conversions than the cationic analogue **56**. In the case of methylstilbene (**14**), the maximum TONs were 455 for **55** and 140 for **56**, respectively (Table 12, entries 3 and 4). The enantioselectivities were in the same range and varied within the same limits as the values for the structurally related systems **20a**, **21a**, **43a**, **43b**, and **44a** (Tables 2–6).

Finally, the hydrogenation of olefin **14** using several batches of **55** with different amounts of the unknown impurity showed that conversion increased with decreasing proportion of the side product, which most likely contains a more strongly coordinating anion. This indicates that the values presented in Table 12 for betaine **55** actually represent a lower limit for the conversions that would be obtained with a pure catalyst.

Conclusion

Eight zwitterionic iridium complexes comprising chiral P,N-ligands with imidazoline or oxazoline nitrogen donors have been prepared in five to six steps in 76–26 % overall yield using our recently developed borate building blocks. They have been evaluated as precatalysts for the asymmetric hydrogenation of unfunctionalized olefins, and the results have been compared with respective data for the corresponding cationic structural analogues.

The catalytic experiments showed that anionic functionalization of the complexes at the rearside of the ligands, that is, pointing away from the catalytically active metal centers, has virtually no influence on their asymmetric inductions. The reactivities vary with the anionic moieties and the solvent. Although the tetraarylborate-based betaines show slightly lower turnover numbers in dichloromethane, they retain high activities in pure aliphatic hydrocarbons, in which the cationic analogues are almost inactive. In contrast, the zwitterion with an anionic aryltrifluoroborate subunit exhibits up to fourfold higher reactivity even in dichloromethane compared with its cationic counterpart.

In summary, cationic complexes with fluorinated borates as anions are superior catalysts in moderately polar solvents such as dichloromethane, whereas the new iridium betaines show promise for reactions in nonpolar media such as pure hydrocarbons.

Experimental Section

General: All reactions were performed in flame-dried glassware under argon using Schlenk techniques. Solvents, NEt_3, $NEtiPr_2$, and TMEDA were dried according to standard procedures and distilled under nitrogen or argon.[35] All other commercial reagents were used as received. Deuterated solvents for NMR spectroscopy were degassed by three freeze-pump-thaw cycles, dried over 4 Å molecular sieves, and stored under argon. Solvents for the work-up and chromatographic purification of air-sensitive compounds were purged with a stream of argon for at least 15 min prior to use. Catalytic hydrogenations were set up under a nitrogen atmosphere in an MBraun Labmaster 130 glovebox using absolute solvents purchased from Fluka. Chromatographic separations were performed on silica gel 60 (Merck, Darmstadt; 40–63 nm). Pre-coated Macherey–Nagel Polygram SIL G/UV_{254} plates were used for TLC analyses, and the compounds were visualized with the aid of UV light. $NaBAr_{F}$,[36] $Li[B(C_6F_5)_4]$,[37] and (3*R*,4*R*)-3,4-diamino-2,2,5,5-tetramethylhexane (**9c**)[38] were prepared according to modified literature procedures.

NMR experiments were performed on Bruker Avance 400, 500, or 600 spectrometers. ^1H and ^{13}C spectra were referenced relative to $SiMe_4$ using the solvent residual peaks and the solvent signals, respectively, as internal standards.[39,40] ^{31}P, ^{19}F, and ^{11}B spectra were calibrated using H_3PO_4 (85 %), $CFCl_3$, and $BF_3{\cdot}OEt_2$ as external standards. Only multiplets other than singlets are specified explicitly in the ^{13}C, ^{31}P, and ^{11}B NMR data. Mass spectra were measured on VG70–250, Finnigan MAT 95Q (EI), Finnigan MAT 312, Finnigan MAR 8400 (FAB), or Fin-

nigan MAT LCQ spectrometers (ESI). Elemental analyses were performed by the staff of the Micro Analysis Laboratory at the University of Basel. IR spectra were measured on a Perkin–Elmer 1600 FTIR spectrometer. Melting points were determined on a Büchi 535 apparatus and are uncorrected. Specific rotations were measured on a Perkin–Elmer 314 polarimeter. HPLC analyses were performed on a Shimadzu system, GC measurements on equipment from Carlo Erba Instruments. The abbreviation BAr_F refers to the tetrakis[3,5-bis(trifluoromethyl)phenyl]borate anion, whilst Ar_F denotes the 3,5-bis(trifluoromethyl)phenyl substituent in general and Ar^F any arbitrary fluorinated aryl moiety. The term dm_c refers to a doublet of centered multiplets.

General procedure for the synthesis of zwitterionic complexes

Compound 20a: Absolute NEt*i*Pr$_2$ (153 μL, 0.900 mmol) followed by ligand **22a** (318 mg, 0.300 mmol) in absolute CH_2Cl_2 (3 mL) were added dropwise to a solution of $[Ir(COD)Cl]_2$ (111 mg, 0.165 mmol) in absolute CH_2Cl_2 (5 mL) at room temperature. After the red mixture had been stirred in a closed vessel for 2 h at 50 °C, it was cooled to room temperature, whereupon saturated aqueous $NaHCO_3$ (6 mL) and H_2O (2 mL) were added. The resulting two-phase system was vigorously stirred for 30 min at room temperature, the phases were allowed to separate, and the aqueous layer was extracted with CH_2Cl_2 (3×10 mL). The combined organic phases were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Purification of the crude product by column chromatography under argon (silica gel, 4×22 cm; CH_2Cl_2) yielded precatalyst **20a** as a red, foamy solid (397 mg, 97%). R_F=0.77 (CH_2Cl_2); $[\alpha]_D^{20}$=+233 (c=0.250 in $CHCl_3$); ^{1}H NMR (500.1 MHz, $CDCl_3$, 295 K): δ=1.02 (m_c, 1H; CH(N)CH$_2$C*H*H), 1.15–1.34 (m, 3H; CH(N)C*H*HC*H*H), 1.39 (m_c, 1H; COD-C*H*H), 1.54 (m_c, 1H; COD-C*H*H), 1.71–1.89 (m, 3H; CH(N)CH*H*CH*H*), 1.90–2.04 (m, 2H; COD-CH*H*), 2.08 (t, J=12.8 Hz, 1H; Im-7a′-H), 2.22–2.50 (m, 4H; COD-CH$_2$), 2.58 (brd, J=6.8 Hz, 1H; CH(N)CH*H*), 3.07 (brs, 1H; COD-CH), 3.26 (t, J=11.8 Hz, 1H; Im-3a′-H), 3.84 (brs, 1H; COD-CH), 4.01 (d, J=15.3 Hz, 1H; Bn-C*H*H), 4.33 (d, J=15.4 Hz, 1H; Bn-CH*H*), 4.54 (m_c, 1H; COD-CH), 5.29 (brs, 1H; COD-CH), 7.11 (t, J=9.0 Hz, 2H; PPh$_2$-*o*-H), 7.40–7.73 ppm (m, 12H; Ar-H); ^{13}C{^{1}H} NMR (125.8 MHz, $CDCl_3$, 295 K): δ=24.3 (CH(N)CH$_2$*C*H$_2$), 25.3 (CH(N)CH$_2$*C*H$_2$), 25.8 (COD-CH$_2$), 28.2 (COD-CH$_2$), 29.7 (CH(N)*C*H$_2$), 34.0 (CH(N)*C*H$_2$), 34.6 (COD-CH$_2$), 37.2 (d, J=4 Hz; COD-CH$_2$), 41.4 (Bn-CH$_2$), 61.9 (COD-CH), 64.5 (COD-CH), 69.9 (Im-3a′-CH), 72.0 (Im-7a′-CH), 85.5 (d, J=16 Hz; COD-CH), 94.8 (d, J=9 Hz; COD-CH), 107.7 (t, J=16 Hz; Bn-*p*-C), 122.1 (d, J=52 Hz; PPh$_2$-*i*-C), 123.8 (br; C$_6$F$_5$-*i*-C and Bn-*i*-C), 125.0 (d, J=50 Hz; Ar-2″-C), 128.9 (d, J=53 Hz; PPh$_2$-*i*-C), 129.0 (d, J=10 Hz; Ar-CH), 129.6 (br; Ar-CH), 130.4 (br; Ar-CH), 130.9 (Ar-CH), 132.0 (Ar-CH), 132.3 (d, J=8 Hz; Ar-CH), 132.7 (d, J=13 Hz; Ar-1″-C), 132.9 (Ar-CH), 133.7 (d, J=10 Hz; PPh$_2$-*o*-CH), 136.4 (dm_c, J=249 Hz; C$_6$F$_5$-*m*-C), 138.4 (dm_c, J=250 Hz; C$_6$F$_5$-*p*-C), 143.7 (dm_c, J=248 Hz; Bn-*m*-C), 148.3 (dm_c, J=241 Hz; C$_6$F$_5$-*o*-C and Bn-*o*-C), 165.2 ppm (d, J=5 Hz; Im-2′-C); ^{19}F{^{1}H} NMR (376.5 MHz, $CDCl_3$, 300 K): δ=−167.4 (brs, 2F; C$_6$F$_5$-*m*-F), −167.2 (m_c, 2F; C$_6$F$_5$-*m*-F), −166.8 (brs, 2F; C$_6$F$_5$-*m*-F), −163.3 (t, J=21 Hz, 1F; C$_6$F$_5$-*p*-F), −163.2 (t, J=21 Hz, 2F; C$_6$F$_5$-*p*-F), −146.7 (m_c, 2F; Bn-*m*-F), −133.2 (brs, 2F; Ar^F-*o*-F), −132.8 (brs, 2F; Ar^F-*o*-F), −132.6 (brs, 2F; Ar^F-*o*-F), −131.8 (brs, 1F; Ar^F-*o*-F), −131.3 ppm (brs, 1F; Ar^F-*o*-F); ^{31}P{^{1}H} NMR (202.5 MHz, $CDCl_3$, 295 K): δ=24.1 ppm; ^{11}B{^{1}H} NMR (160.5 MHz, $CDCl_3$, 295 K): δ=−16.9 ppm; IR (KBr): $\tilde{\nu}$=3061, 2941, 2883, 1643, 1513, 1462, 1364, 1260, 1090, 978, 894, 770, 695, 664, 539, 464 cm^{-1}; elemental analysis calcd (%) for $C_{58}H_{38}BF_{19}IrN_2P$ (1357.91): C 51.30, H 2.82, N 2.06; found: C 51.41, H 2.93, N 2.21.

General procedure for the synthesis of cationic precatalysts

Compound 43a: A solution of ligand **45a** (113 mg, 0.200 mmol) in absolute CH_2Cl_2 (2 mL) was added dropwise at room temperature to a solution of $[Ir(COD)Cl]_2$ (73.9 mg, 0.110 mmol) in absolute CH_2Cl_2 (3 mL). After the resulting red solution had been stirred in a closed vessel for 2 h at 50 °C, the mixture was cooled to room temperature and Li[B(C$_6$F$_5$)$_4$] (192 mg, 0.280 mmol) was added. The slightly turbid solution was stirred for 5 min and then H_2O (5 mL) was added. After the mixture had been vigorously stirred for 30 min at room temperature, the phases were separated and the aqueous layer was extracted with CH_2Cl_2 (3×10 mL). The combined organic phases were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Purification of the crude product by column chromatography under argon (silica gel, 4×23 cm; CH_2Cl_2) gave precatalyst **43a** as a red solid (253 mg, 82%). R_F=0.65 (CH_2Cl_2, tailing); $[\alpha]_D^{20}$=+209 (c=0.230 in $CHCl_3$); ^{1}H NMR (500.1 MHz, $CDCl_3$, 295 K): δ=1.05 (m_c, 1H; CH(N)CH$_2$C*H*H), 1.17–1.47 (m, 4H; CH(N)C*H*HC*H*H and COD-C*H*H), 1.56 (m_c, 1H; COD-C*H*H), 1.70 (d, J=11.4 Hz, 1H; CH(N)CH*H*), 1.77 (d, J=13.7 Hz, 1H; CH(N)CH$_2$CH*H*), 1.87 (d, J=12.9 Hz, 1H; CH(N)CH$_2$CH*H*), 1.90–2.04 (m, 3H; COD-CH*H* and Im-7a-H), 2.21–2.48 (m, 4H; COD-CH$_2$), 2.65 (d, J=11.1 Hz, 1H; CH(N)CH*H*), 3.09 (m_c, 1H; COD-CH), 3.30 (t, J=12.6 Hz, 1H; Im-3a-H), 3.88 (d, J=15.5 Hz, 1H; Bn-C*H*H), 3.93 (brs, 1H; COD-CH), 4.46 (d, J=15.6 Hz, 1H; Bn-CH*H*), 4.52 (quint, J=7.1 Hz, 1H; COD-CH), 5.35 (brs, 1H; COD-CH), 7.13 (dd, J=10.7, 7.3 Hz, 2H; PPh$_2$-*o*-H), 7.44–7.68 (m, 11H; Ar-H), 7.70 ppm (dd, J=7.5, 3.4 Hz, 1H; Ar-6″-H); ^{13}C{^{1}H} NMR (125.8 MHz, $CDCl_3$, 295 K): δ=24.3 (CH(N)CH$_2$*C*H$_2$), 25.1 (CH(N)CH$_2$*C*H$_2$), 25.7 (COD-CH$_2$), 28.1 (COD-CH$_2$), 29.9 (CH(N)*C*H$_2$), 33.8 (CH(N)*C*H$_2$), 34.6 (COD-CH$_2$), 37.2 (d, J=5 Hz; COD-CH$_2$), 41.6 (Bn-CH$_2$), 63.0 (COD-CH), 65.7 (COD-CH), 70.2 (Im-3a-*C*H), 72.4 (Im-7a-CH), 86.0 (d, J=16 Hz; COD-CH), 95.7 (d, J=9 Hz; COD-CH), 108.4 (t, J=19 Hz; Bn-*i*-C), 121.5 (d, J=52 Hz; PPh$_2$-*i*-C), 124.1 (br; C$_6$F$_5$-*i*-C), 125.6 (d, J=49 Hz; Ar-2′-C), 129.2 (d, J=10 Hz; Ar-CH), 129.5 (d, J=52 Hz; PPh$_2$-*i*-C), 129.5 (d, J=11 Hz; Ar-CH), 130.0 (brd, J=7 Hz; Ar-6′-CH), 131.2 (Ar-CH), 132.2–132.3 (several Ar-CH and Ar-1′-C), 132.7 (d, J=7 Hz; Ar-CH), 132.8 (d, J=2 Hz; Ar-CH), 133.7 (d, J=10 Hz; PPh$_2$-*o*-CH), 136.3 (dm_c, J=244 Hz; C$_6$F$_5$-*m*-C), 137.7 (dm_c, J=253 Hz; Bn-*m*-C), 138.3 (dm_c, J=244 Hz; C$_6$F$_5$-*p*-C), 141.7 (dm_c, J=257 Hz; Bn-*p*-C), 145.3 (dm_c, J=250 Hz; Bn-*o*-C), 148.3 (dm_c, J=241 Hz; C$_6$F$_5$-*o*-C), 165.6 ppm (d, J=6 Hz; Im-2-C); ^{19}F{^{1}H} NMR (376.5 MHz, $CDCl_3$, 300 K): δ=−167.2 (brs, 8F; C$_6$F$_5$-*m*-F), −163.5 (t, J=20 Hz, 4F; C$_6$F$_5$-*p*-F), −160.0 (m_c, 2F; Bn-*m*-F), −151.4 (t, J=21 Hz, 1F; Bn-*p*-F), −141.3 (m_c, 2F; Bn-*o*-F), −132.9 ppm (brs, 8F; C$_6$F$_5$-*o*-F); ^{31}P{^{1}H} NMR (202.5 MHz, $CDCl_3$, 295 K): δ=23.8 ppm; IR (KBr): $\tilde{\nu}$=3062, 2946, 2884, 1644, 1513, 1463, 1366, 1306, 1272, 1090, 1021, 980, 774, 753, 695, 663, 606, 571, 539, 492 cm^{-1}; MS (ESI+, CH_2Cl_2): m/z (%)=865 (100) $[M-B(C_6F_5)_4]^+$; elemental analysis calcd (%) for $C_{64}H_{38}BF_{25}IrN_2P$ (1543.96): C 49.79, H 2.48, N 1.81; found: C 49.68, H 2.62, N 1.84.

General procedure for the preparation of ligands by heteroatom alkylation

Compound 45a: PHIM **12a** (577 mg, 1.50 mmol) was added to a suspension of KH (66.2 mg, 1.65 mmol) in absolute THF (15 mL) at 0 °C. After the mixture had been stirred at room temperature until no further gas evolution was detected (about 2 h), pentafluorobenzyl bromide (272 μL, 1.80 mmol) was added dropwise to the now yellow solution at 0 °C. The resulting yellow suspension was stirred for 2.5 h at 0 °C and then for 18 h at room temperature. After the addition of aqueous $Na_2S_2O_3$ (5%, 20 mL), the mixture was extracted with CH_2Cl_2 (4×20 mL). The combined organic phases were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Purification of the remaining yellow oil by column chromatography under argon (silica gel, 4×19 cm; hexanes/EtOAc (2:1) + 5 vol% NEt$_3$) yielded ligand **45a** as a colorless, foamy solid (369 mg, 44%). R_F=0.31 (hexanes/EtOAc (2:1) + 5 vol% NEt$_3$); $[\alpha]_D^{20}$=−13.2 (c=0.555 in $CHCl_3$); ^{1}H NMR (400.1 MHz, $CDCl_3$, 300 K): δ=1.13–1.39 (m, 4H; CH(N)C*H*HC*H*H), 1.65–1.86 (brm, 3H; CH(N)CH*H*CH*H*), 2.18 (brd, J=10.0 Hz, 1H; CH(N)CH*H*), 2.68 (brs, 1H; Im-7a-H), 2.88 (brs, 1H; Im-3a-H), 3.93 (brd, J=11.7 Hz, 1H; Bn-C*H*H), 4.33 (d, J=14.7 Hz, 1H; Bn-CH*H*), 7.06 (dd, J=7.1, 4.0 Hz, 1H; Ar-3′-H), 7.27–7.42 ppm (m, 13H; Ar-H); ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 300 K): δ=24.8 (CH(N)CH$_2$*C*H$_2$), 25.5 (CH(N)CH$_2$*C*H$_2$), 29.7 (CH(N)*C*H$_2$), 31.0 (CH(N)*C*H$_2$), 39.5 (br; Bn-CH$_2$), 71.9 (br; Im-CH), 112.4 (br; Bn-*i*-C), 128.6–129.0 (several Ar-CH), 129.5 (br; Ar-CH), 132.1 (br; Ar-C), 133.5 (Ar-3′-CH), 134.3 (d, J=20 Hz; PPh$_2$-*o*-CH), 136.0–138.7 (several Ar-C), 145.5 (dm_c, J=251 Hz; Bn-*o*-C), 166.6 ppm (br; Im-2-C); ^{19}F{^{1}H} NMR (376.5 MHz, $CDCl_3$, 300 K): δ=−162.4 (brs, 2F; Bn-*m*-F), −155.2 (brs, 1F; Bn-*p*-F), −141.7 ppm (brs, 2F; Bn-*o*-F); ^{31}P{^{1}H} NMR (162.0 MHz, $CDCl_3$, 300 K): δ=−10.6 ppm; IR (KBr): $\tilde{\nu}$=3056, 2935, 2860, 1962, 1891, 1825, 1654, 1607, 1578, 1505, 1436, 1330, 1303, 1250, 1122, 1015, 963, 938, 745, 696, 668, 543, 507, 418 cm^{-1}; MS (FAB, NBA): m/z (%)=565 (84) $[M+H]^+$, 487 (12) $[M-Ph]^+$, 383 (100)

$[M-C_6F_5CH_2]^+$, 278 (45), 181 (56) $[C_6F_5CH_2^+]$, 81 (30); elemental analysis calcd (%) for $C_{32}H_{26}F_5N_2P$ (564.53): C 68.08, H 4.64, N 4.96; found: C 68.35, H 5.00, N 4.52.

Compound 22a: In analogy to the synthesis of **45a**, PHIM **12a** (384 mg, 1.00 mmol) was reacted with KH (44.1 mg, 1.10 mmol) and borate **19a** (897 mg, 0.900 mmol) in absolute THF (10 mL) for 18 h at room temperature. Purification of the yellowish crude product by column chromatography under argon (silica gel, 4×19 cm; CH_2Cl_2) yielded the protonated ligand **22a** as a colorless, foamy solid (918 mg, 96%). According to ^{31}P NMR spectroscopy, **22a** is in equilibrium between two conformers in a ratio of 2:1 at 272 K when it is dissolved in [D$_6$]acetone. $R_F=0.54$ (CH_2Cl_2); $[\alpha]_D^{20}=+32.1$ ($c=1.05$ in $CHCl_3$); ^1H NMR (500.1 MHz, [D$_6$]acetone, 295 K, major conformer): $\delta=1.36$–1.62 (m, 3H; CH(N)C*H*HC*H*H), 1.71 (m$_c$, 1H; CH(N)C*H*H), 1.85–1.99 (m, 2H; CH(N)CH$_2$CH*H*), 2.20 (br d, $J=10.9$ Hz, 1H; CH(N)CH*H*), 2.38 (br d, $J=9.4$ Hz, 1H; CH(N)CH*H*), 3.94 (br s, 2H; Im-3a′-H and Im-7a′-H), 4.73 (d, $J=15.4$ Hz, 1H; Bn-C*H*H), 4.94 (d, $J=15.4$ Hz, 1H; Bn-CH*H*), 7.31 (br dd, $J=7.2$, 3.8 Hz, 1H; Ar-6″-H), 7.36–7.57 (m, 12H; PPh$_2$-H, Ar-3″-H and Ar-4″-H), 7.68 (t, $J=7.6$ Hz, 1H; Ar-5″-H), 10.02 ppm (br s, 1H; NH$^+$); ^1H NMR (500.1 MHz, [D$_6$]acetone, 295 K, characteristic signals of the minor conformer): $\delta=3.37$ (br t, $J=12.9$ Hz, 1H; Im-7a′-H), 3.67 (br t, $J=12.9$ Hz, 1H; Im-3a′-H), 4.45 (d, $J=15.7$ Hz, 1H; Bn-C*H*H), 4.60 ppm (d, $J=15.2$ Hz, 1H; Bn-CH*H*); $^{13}C\{^1H\}$ NMR (500.1 MHz, [D$_6$]acetone, 295 K, major conformer): $\delta=24.4$ (CH(N)CH$_2$*C*H$_2$), 24.5 (CH(N)CH$_2$*C*H$_2$), 28.3 (CH(N)*C*H$_2$), 29.3 (CH(N)*C*H$_2$), 39.3 (Bn-CH$_2$), 65.2 (Im-7a′-CH), 71.9 (Im-3a′-CH), 129.6–131.1 (several Ar-CH and Ar-C), 133.7 (Ar-CH), 134.3–134.7 (several Ar-CH), 135.4 (Ar-CH), 135.5 (Ar-CH), 137.1 (dm$_c$, $J=250$ Hz; C_6F_5-*m*-C), 139.0 (dm$_c$, $J=244$ Hz; C_6F_5-*p*-C), 139.1–139.2 (several Ar-C), 149.0 (dm$_c$, $J=239$ Hz; C_6F_5-*o*-C and Bn-*o*-C), 171.0 ppm (Im-2′-C) (despite prolonged data acquisition, the missing signals were not detected); $^{19}F\{^1H\}$ NMR (376.5 MHz, [D$_6$]acetone, 300 K): $\delta=-167.9$ to -167.4 (m, 6F; C_6F_5-*m*-F), -163.7 to -163.4 (m, 3F; C_6F_5-*p*-F), -146.8 to -146.2 (m, 2F; Bn-*m*-F), -132.6 to -131.5 ppm (m, 8F; C_6F_5-*o*-F and Bn-*o*-F); $^{31}P\{^1H\}$ NMR (202.5 MHz, [D$_6$]acetone, 272 K): $\delta=-11.6$ and -11.4 ppm (in a ratio of 2:1); $^{31}P\{^1H\}$ NMR (202.5 MHz, [D$_6$]acetone, 315 K): $\delta=-10.7$ ppm; $^{11}B\{^1H\}$ NMR (160.5 MHz, [D$_6$]acetone, 295 K): $\delta=-15.9$ ppm; IR (KBr): $\tilde{\nu}=3680$, 3418, 3193, 3063, 2952, 2874, 1644, 1515, 1462, 1372, 1311, 1266, 1162, 1090, 977, 759, 694, 663, 606, 574, 544, 505 cm^{-1}; MS (FAB, NBA): m/z (%) = 1059 (6) $[M+H]^+$, 891 (51) $[M-C_6F_5]^+$, 743 (30) $[M-C_6F_5-C_6F_4]^+$, 383 (53) $[M-(C_6F_5)_3B(C_6F_4CH_2)]^+$, 184 (57), 81 (100); elemental analysis calcd (%) for $C_{50}H_{27}BF_{19}N_2P$ (1058.52): C 56.73, H 2.57, N 2.65; found: C 56.50, H 2.77, N 2.57.

General procedure for enantioselective hydrogenations: The precatalyst (usually 1.0 μmol) and substrate (usually 100 μmol) were weighed in a 2 mL screw-cap glass vial equipped with a magnetic stirrer bar and the desired solvent was added (usually 0.5 mL of absolute CH_2Cl_2). Alternatively, stock solutions of the iridium complex and alkene were sometimes used. Four vessels were placed in a 60 mL autoclave (Premex), which was closed under an inert atmosphere. After pressurizing the autoclave with hydrogen (usually 50 bar), the transformation was initiated by switching on the stirrer (700 min^{-1}). After the required reaction time, the hydrogen was released and hexanes (2 mL) was added. The resulting suspension was filtered through a pad of silica gel, which was washed with Et_2O/hexanes (1:1). The eluate was concentrated under reduced pressure, the residue was redissolved in heptane (3 mL), and the conversion and enantioselectivity were directly determined by GC and HPLC analyses.[11a,41,42]

Crystal structure analyses: CCDC-798427 (**7c**), 798428 (**20c**), 798429 (**53a**), 798430 (**53b**), 798431 (**54**) and 798432 (**56**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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