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Imine hydrogenation catalyzed by iridium complexes comprising monodentate chiral phosphoramidites and N-donor ligands

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Abstract

The relatively inexpensive chiral monodentate phosphoramidite (*S*)-MONOPHOS may be used in combination with pyridines to prepare iridium complexes effective for catalysis of asymmetric imine hydrogenation with comparable enantioselectivity to some of those containing more costly chiral bidentate phosphines. [Ir(cod)((*S*)-MONOPHOS)(L)]BArF (cod = 1,5-cyclooctadiene; L = 3-methylisoquinoline, acridine, 2,6-lutidine, acetonitrile, or 2,3,3-trimethylindolenine; BArF = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate) are efficient catalysts for the asymmetric hydrogenation of 2,3,3-trimethylindolenine. An important observation is that the catalyst containing acridine is more enantioselective than the catalyst derived from 2,3,3-trimethylindolenine which suggests that the other N-donor ligands are not readily displaced by the substrate during the catalytic cycle.

Keywords: Hydrogenation; Catalysis; Imine; Asymmetric catalysis

1. Introduction

The asymmetric hydrogenation of imines is an important route to α-chiral amines [1]. Although there are many examples of highly enantioselective catalysts for olefin and ketone reduction, asymmetric imine hydrogenation is still a challenge in terms of both the turnover frequency and the lifespan of the active catalyst. This is due to the fact that C–N double bonds have certain traits, such as their preferred mode of binding and the strong donor character of the nitrogen, that are unfavorable for homogeneous catalytic hydrogenation [2,3]. Although early examples of asymmetric imine hydrogenation were achieved with poor enantioselectivity [4], some success has been achieved with rhodium [5–8] and ruthenium [9] catalysts with chiral bisphosphine ligands. Another notable system is Buchwald's *ansa*-titanocene catalyst that was particularly successful for the asymmetric hydrogenation of cyclic imines, and moderately successful for acyclic imines, but suffered from low catalyst activity [10,11].

Recently chiral bisphosphine iridium catalysts have shown greater success for asymmetric imine hydrogenation [12–18], although they often require the presence of halide ions or other additives such as amines and acids. Most of these systems are not applicable to a wide range of substrates, and require high pressures, long reaction times, and stoichiometric amounts of chiral material or additives that tend to be substrate specific. Most of the effective catalysts comprise chiral chelating bisphosphine ligands and it is to these ligands that the efficacy of the catalysts is usually ascribed. There are, however, examples that do not have ligands of this general class, such as the iridium complexes of chiral bidentate [*P*,*N*] ligands, originally reported by Pfaltz and co-workers [19–22] and the chiral tridentate [*P*,*N*,*P*] ligands reported by Sablong and Osborn [23].

Crabtree's catalyst, [Ir(cod)(py)(PCy_3)]X is particularly effective for olefin hydrogenations [24,25] and recently, [Ir(cod)(py)(PBz_3)]PF_6 was shown to be more efficient than [Ir(cod)(PBz_3)$_2$]PF_6 for the hydrogenation of an imine derived from aniline [26]. Furthermore, chiral monodentate

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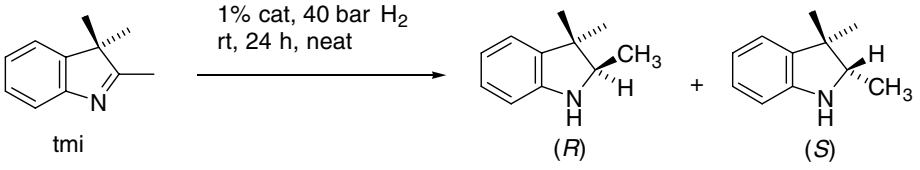
phosphoramidites have also proved to be effective ligands for enantioselective hydrogenations of olefins [27]. Based on these considerations, we set out to determine whether bidentate ligands were really required, and if a chiral catalyst analogous to Crabtree's catalyst employing a monodentate chiral phosphorus donor could act as an effective enantioselective imine hydrogenation catalyst. We chose to test these systems on 2,3,3-trimethylindolenine (tmi), an imine substrate which has been shown to be difficult to hydrogenate with good enantioselectivity in the past [8,14,23].

Although the use of a binaphthol based monodentate chiral P-donor ligand has been reported previously for imine hydrogenation, no enantioselectivity was observed [28]. We report here rare examples of an iridium catalyst containing a chiral monodentate phosphoramidite and various N-donor ligands for asymmetric imine hydrogenation. The commercially available, inexpensive chiral monodentate phosphoramidite (*S*)-MONOPHOS may be used in combination with N-donor ligands to form the complexes [Ir(cod)((*S*)-MONOPHOS)(L)]BArF (cod = 1,5-cyclooctadiene; L = 3-methylisoquinoline, acridine, 2,6-lutidine, acetonitrile, 2,3,3-trimethylindolenine; BArF = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate) which are efficient catalysts for the asymmetric hydrogenation of 2,3,3-trimethylindolenine (Scheme 1).

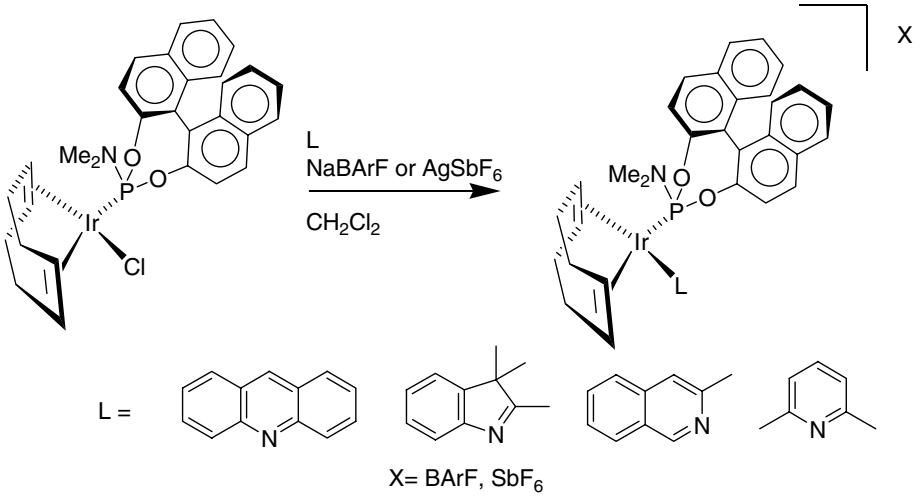
2. Results and discussion

The systems studied are related to complexes of heterobidentate ligands, particularly when the two dissimilar monodentate ligands adopt a *cis*-configuration. Complexes used were of the general formula [Ir(cod)-(P*)(L)]$^{+}$X^{-} where (P*) is a chiral monodentate phosphoramidite, (L) is a nitrogen-donor ligand and X^{-} is a non-coordinating anion, as shown in Scheme 2 for MONOPHOS.

An important consideration with complexes of this type in comparison to those involving chelates is their propensity for disproportionation. The potential for ligand displacement is also an important factor in the stability of the intermediates that are formed during the catalytic cycle. This would be expected to be a complication in imine hydrogenation wherein the imine substrate might displace some of the other ligands. Furthermore, whereas the species involved in rhodium-catalyzed hydrogenations are fairly well-understood [29–32], the case for iridium-catalyzed hydrogenations is more nebulous. In the case of rhodium catalysis, cycles involve Rh(I)/Rh(III) cycles wherein a four-coordinate Rh(I) species is converted to the Rh(III) dihydride. Recent theoretical calculations for P,N and carbene–C,N iridium systems have suggested catalytic cycles involving an Ir(III)/Ir(V) pathway with pseudo-octahedral or octahedral intermediates [33–35]. Generally one would anticipate that *cis*-dihydrides would be formed in the Ir(III) species, but the disposition of the other ligands is not clear. Our efforts here are not aimed at resolving the details of the mechanism, but to suggest that the higher oxidation state complexes of iridium should resist ligand exchange and thus provide some rationale for the notion that the phosphoramidite and the pyridine ligands initially present



Scheme 1. The hydrogenation of tmi.



Scheme 2. Preparation of [Ir(cod)((*S*)-MONOPHOS)(L)]X.

may be retained on the iridium complex during the catalytic cycle.

2.1. Properties of [Ir(cod)((S)-MONOPHOS)(L)]$^+$

[Ir(cod)((*S*)-MONOPHOS)Cl], prepared from [Ir(cod)-Cl]$_2$ and (*S*)-MONOPHOS, was used to prepare [Ir(cod)((*S*)-MONOPHOS)(L)]BArF by combination with the appropriate N-donor ligand and NaBArF. Characterization, however, was more readily carried out with SbF_6 complexes. With the C_2 symmetric acridine, 2,6-lutidine, and acetonitrile ligands only one isomer is possible. The X-ray structure of the 2,6-lutidine complex is shown in Fig. 1 and the plane of the lutidine is nearly perpendicular (93.4°) to that of P–Ir–N plane. One might note that the tilting of the pyridine plane is induced by the chirality of the MONOPHOS and represents another chiral element in the catalytic intermediates derived from these complexes that may affect enantioselectivity. With ligands such as 3-methylisoquinoline and tmi, however, diastereomers are produced since coordination to the metal center produces an axis of chirality along the M–N bond (Scheme 3). The rate of rotation about the Ir–N bond for these complexes is slow on the NMR time scale at room temperature and tmi complex exists as a mixture of diastereomers in a ~1:1 ratio in solution upon equilibration. The 3-methylisoquinoline complex, however, was found to have been formed in 64% de. Upon crystallization a single isomer of the tmi complex was isolated, as shown in Fig. 2. Dissolution of this isomer showed a gradual appearance of the other diastereomer over a period of several days. This orientation of the unsymmetrical ligands, as well as the angle of twist, can be induced by the chirality of the MONOPHOS and represents still another chiral element in catalytic intermediates derived from these complexes that can affect enantioselectivity.

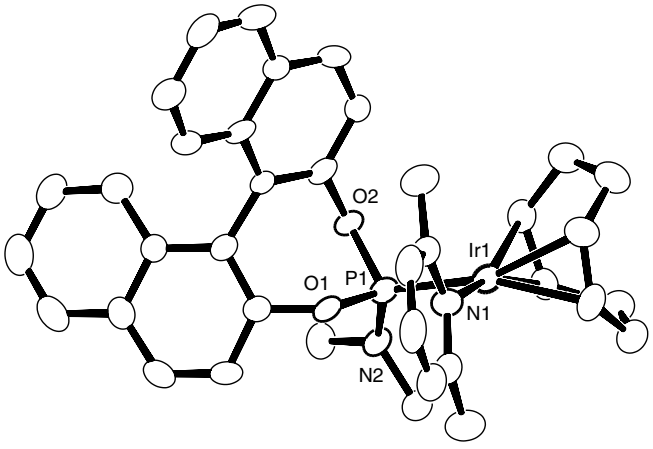
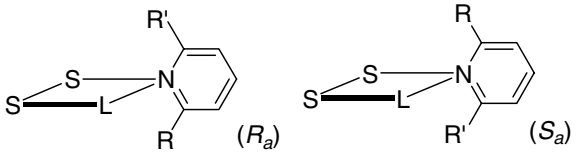


Fig. 1. ORTEP drawing of the cation in[Ir(cod)((*S*)-MONOPHOS)(2,6-lutidine)]SbF_6.



Scheme 3. The enantiomers formed due to axial chirality. ($R' > R$).

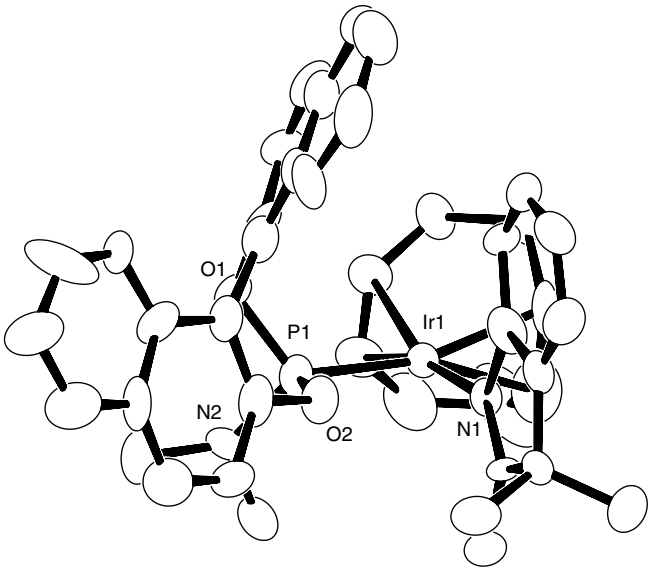


Fig. 2. ORTEP drawing of the cation in [Ir(cod)((*S*)-MONOPHOS)(tmi)] SbF_6.

The complex [Ir(cod)(3-methylisoquinoline)Cl] was prepared in order to estimate the potential variation in ligand rotational barriers in these compounds. The ^{1}H NMR spectrum at 20 °C shows four cod olefin proton resonances in C_6D_6 solution. This demonstrates that rotation of 3-methylisoquinoline is slow on the NMR timescale at 20 °C. The two olefin proton resonances at δ 5 broaden and become a single broad resonance at 60 °C and an additional broadening from exchange of the resonances of ~2 Hz was observed at 40 °C. This corresponds to a rate of ~6 s^{-1} and a rotation barrier of ~16.7 kcal mol^{-1}. Thus it is clear that in systems with greater steric interactions, barriers greater than 20 kcal mol^{-1} can be expected.

2.2. Asymmetric imine hydrogenation

Initial studies of the hydrogenation of tmi using [Ir(cod)((*S*)-MONOPHOS)(L)]X (X = SbF_6, BArF; L = 3-methylisoquinoline) showed that when using methanol solvent, the BArF salts of these catalysts were superior to the corresponding SbF_6 salts. This is in agreement with the reports of Pfaltz and co-workers [36,37] and Burgess and co-workers [38] which noted that the BArF anion increases catalyst activity in the iridium-catalyzed hydrogenation of olefins, and with reports of increased selectivity for imine hydrogenation with the BArF anion [22]. Although high ee's were obtained in methanol solution in some trials, the results were highly variable. This variability has been observed previously in enantioselective imine hydrogenation [5] and any attempts to improve

reproducibility using distilled solvents or drying agents for methanol led to poor ee's.

The problem of reproducibility was resolved by employing a solvent-less system. The catalyst slowly dissolved in the imine substrate and using a 1% catalyst loading under 40 bar H_2 for 24 h at RT, ee's of 46% ee were achieved with 3-methylisoquinoline as the ligand. These results were reproducible and unless otherwise specified, these same conditions were used throughout the hydrogenation trials.

Since the product is formed enantioselectively, over time the solvent potentially contains a product which is a chiral non-racemic ligand that could alter the selectivity. In order to examine the importance of this potential effect, the reaction was quenched at different times and the ee determined. These results are summarized in Table 1. The variability in the ee was small and did not correlate with the time of the reaction. We therefore concluded that the enantioselectivity was effectively constant throughout the reaction. There was also little effect of pressure on the enantioselectivity. The reaction was conducted at 40, 20, and 10 bar of hydrogen (Table 1) and although the conversion decreased from 65% to 40% to 20% respectively, only a small increase in ee was seen as the pressure was decreased from 40 bar to 10 bar (46–51% respectively). Furthermore, it was found that the reaction could be carried out with 0.5 mol% catalyst without loss of enantioselectivity.

The use of acridine as a ligand in place of the 3-methylisoquinoline increased the ee from 46% to 58%. Other N-donor ligands were tested for this reaction, but the observed ee's were consistently within the range of 46–58%. The acetonitrile complex was prepared, and tested for asymmetric imine hydrogenation and with this complex 47% conversion and 50% ee were achieved. Therefore, a number of experiments were performed under similar conditions to further investigate the significance of the N-donor ligand.

From examination of Table 2, it can be seen that the nature of the N-donor ligand only has a modest effect on the reaction. One possible explanation for the small effect the nature of L has on the enantioselectivity is that the ligand dissociates and scrambling of the ligands occurs to give a bis-(*S*)-MONOPHOS complex. If this complex is the active catalytic species, then one would expect a similar result with any ligand that would allow the formation of the bis-(*S*)-MONOPHOS complex under the catalytic conditions. One would also expect a previously prepared bis-(*S*)-MONOPHOS complex to give the same results.

Table 1
Effect of time and pressure (L = 3-methylisoquinoline)

Pressure (bar)	Time (h)	% Conversion	% ee
40	48	65	48 (+)
40	24	47	46 (+)
40	10	33	50 (+)
40	5	25	45 (+)
20	24	40	48 (+)
10	24	20	51 (+)

Table 2
Effect of ligand

L	% Conversion	% ee
MeCN	47	50 (+)
3-Methylisoquinoline	47	46 (+)
Acridine	56	58 (+)
2,6-Lutidine	80	50 (+)

Attempts utilizing either the BArF or SbF_6 salt of the bis-monophos complex led to variable results (Table 3), but all with low conversions and enantioselectivities (43% conversion and only 15% ee in the best trial). A second experiment was conducted with the further addition of an equivalent of (*S*)-MONOPHOS to the reaction mixture. Excess (*S*)-MONOPHOS should encourage the formation of the bis-(*S*)-MONOPHOS complex and would increase the enantioselectivity of the reaction if the bis-(*S*)-MONOPHOS complex were the active species. Although the catalytic activity (50% conversion) was unaffected by the presence of additional phosphoramidite, less than 1% ee was observed in the product amine. Conversely, when excess 3-methylisoquinoline was added to the mixture, only a small decrease in conversion (33%) and enantioselectivity (36%) was observed. It was also determined that the neutral [Ir(cod)((*S*)-MONOPHOS)Cl] compound is inactive for imine hydrogenation under these conditions.

While the above results suggest that a bis-(*S*)-MONOPHOS complex is not the species responsible for enantioselectivity, the modest, but significant effect that the N-donor ligand has on the enantioselectivity shows that a complex involving one (*S*)-MONOPHOS is likely to be principally involved in controlling the chirality of the product. Although the (*S*)-MONOPHOS may be the major determinant of enantioselectivity, the N-donor ligand must still play some role in the selectivity. The observed variations in ee show that the N-donor ligands have not been completely displaced by the imine substrate.

The complex [Ir(cod)((*S*)-MONOPHOS)(tmi)]BArF was prepared. This complex catalyzed the reduction of tmi with similar enantioselectivity (44% ee) to complexes having a pyridine type ligand but with a greater rate (75% conversion in 24 h). Only the 2,6-lutidine complex showed a similar rate with 80% conversion in 24 h. This may be because the pyridine ligands compete for binding with the substrate and therefore decrease the rate, while

Table 3
Importance of N-donor ligand

L	Anion	% Conversion	% ee
(*S*)-MONOPHOS	BArF	43	15 (+)
(*S*)-MONOPHOS	BArF	35	4 (+)
(*S*)-MONOPHOS	BArF	33	11 (+)
(*S*)-MONOPHOS	SbF_6	17	4 (−)
3-Methylisoquinoline	BArF	50	<1% (+)[a]
3-Methylisoquinoline	BArF	33	36 (+)[b]
Cl	None	<1	NA

[a] Excess (*S*)-MONOPHOS added.
[b] Excess 3-methylisoquinoline added.

2,6-lutidine may compete poorly for binding since the N is sterically hindered. An important feature is that the presence of the pyridine ligands contributes to a measurable increase in ee relative to having the tmi alone.

Acridine, which ultimately was the most successful ligand in terms of enantioselectivity, was then investigated as an additive to [Ir(cod)((*S*)-MONOPHOS)(tmi)]BArF as the catalyst (Table 4). Acridine was tested at 0.5%, 1% and 2% relative to the substrate, with the catalyst concentration held constant at 1%. Although our results varied substantially over different trials, the general trend was that any added acridine increased conversion and decreased or had little effect on enantioselectivity relative to the case where no acridine was added. *The important feature is that the results do not reflect the substantially increased enantioselectivity observed when the starting complex contains acridine as the ligand rather than tmi*. The results with the tmi complex were variable in the presence of acridine, but consistently gave lower ee's than the complex that originally contained the acridine ligand. They also consistently gave greater conversions than any system lacking added acridine. This is in contrast to the result observed with the catalyst bearing the 3-methylisoquinoline ligand, where excess 3-methylisoquinoline decreased the activity of the catalyst in terms of conversion.

2.3. Ligand displacement studies

In order to better understand the active catalyst, it was necessary to determine if the pyridine ligands remain bound to iridium in the presence of the imine substrate. The 2,6-lutidine complex was combined with an equimolar amount of the imine substrate (tmi). The ^{1}H NMR of the 0.015 M solution showed free tmi and the ^{31}P NMR showed a single resonance consistent with that of the 2,6-lutidine complex. The ^{31}P resonances of the two diastereomers of the tmi complex grew in with nearly equal intensities and although the equilibration took several days, the tmi complex was ultimately strongly favored over the 2,6-lutidine complex. This was as expected since 2,6-lutidine should be a poor competitor for binding with tmi owing to steric hindrance.

A similar experiment was undertaken for the acridine complex. The increased ee observed with the acridine complex may be due to its ability to remain bound to iridium throughout the reaction. A number of solutions with various molar ratios of [Ir(cod)((*S*)-MONOPHOS)(acridine)]SbF_6 to tmi ranging from 3:1 to 1:3 Ir:tmi, with the Ir complex concentration constant at 0.003 M, were prepared in CD_2Cl_2 and the ligand exchange was monitored by ^{1}H and ^{31}P NMR. The equilibration took several days, but resulted in effectively complete replacement of the acridine by tmi in the solutions containing an equivalent or excess of tmi (Ir:tmi, 1:3, 11 days; 1:2, 15 days; 1:1 15 days). Also, after 15 days, the two solutions with less tmi than iridium show very little free tmi in the ^{1}H NMR and were consistent with full displacement of acridine. The Ir–acridine:Ir–tmi ratio was found to be approximately 2:1 when Ir:tmi was 3:1 and 1:1 where Ir:tmi was 2:1. Acridine was then added to the 1:3 Ir:tmi solution after it had fully converted to the tmi complex. Enough acridine was added to give a concentration equal to the tmi so that Ir:tmi:acridine was 1:3:3. After four days, no evidence of the acridine complex was observed by NMR.

Since the catalytic system has a 1:100 ratio of acridine to tmi, the above data shows that the acridine will eventually be displaced by tmi. In order to determine if it could occur on the timescale of the reaction, a solution in CD_2Cl_2 of [Ir(cod)((*S*)-MONOPHOS)(acridine)]SbF_6 and tmi in a 1:10 ratio was prepared. This ratio gives a significant excess of tmi while still allowing observation of the iridium complex. The ^{1}H and ^{31}P NMR spectra of the mixture were monitored frequently. Although not strictly pseudo-first order, a half-life of $\sim$1 h is observed for a concentration of iridium complex of 0.022 M. The replacement of acridine occurred over several hours with only small amounts of the acridine complex present after 4.5 h. Our catalytic system was investigated with a 1:100 ratio of complex:tmi and this situation could in fact allow for complete displacement of the ligand by the substrate early in the reaction if similar or faster rates of displacement were involved. In fact, when a 0.03 M solution of [Ir(cod)((*S*)-MONOPHOS)(acridine)]BArF in tmi was prepared, the ^{31}P NMR showed only two resonances (δ 115.99 and 115.91) consistent with the diastereomers of the tmi complex. Therefore, one can expect tmi to displace acridine upon dissolution of the catalyst in the absence of H_2. Since the enantioselectivity does depend on the pyridine ligand, it is apparent that the ligand is not displaced to a great degree before the catalyst precursor is converted into a less labile form under the hydrogen pressure. This is consistent with a mechanism involving Ir(III), but not involving Ir(I) with lifetimes consistent with ligand displacement. It also suggests that pressurization of the reaction vessel immediately after addition of the substrate is essential to avoid degradation of the enantioselectivity of the catalyst.

Table 4
Effect of acridine as an additive to [Ir(cod)((*S*)-MONOPHOS)(tmi)]BArF

% Acridine	% Conversion	% ee
0	73	44 (+)
0.5	83	37 (+)
0.5	87	26 (+)
0.5	96	44 (+)
1	94	32 (+)
1	96	45 (+)
2	98	42 (+)

3. Conclusion

We have found that the relatively inexpensive chiral monodentate phosphoramidite (*S*)-MONOPHOS may be used in combination with pyridines for asymmetric imine hydrogenation of 2,3,3-trimethylindolenine with compara-

ble enantioselectivity to some of the more costly chiral bidentate bisphosphines. With few exceptions, such as the iridium complexes prepared from BCPM [15], Josiphos-type ligands [17], and BICP [16] which have achieved ee's of 91%, 93%, and 95.1% with the aid of specific additives, the ee's obtained with this system promise to be competitive with those containing many other more difficultly prepared ligands.

We are currently examining other systems of this type, but in preliminary experiments have found that more highly modified analogues of MONOPHOS ((*S*)-(+)-(2,6-dimethyl-3,5-dioxa-4-phospha-cyclohepta[2,1-*a*;3,4-*a*′]dinaphthalen-4-yl)dimethylamine; (*S*)-(+)-(3,5-dioxa-4-phospha-cyclohepta[2,1-*a*;3,4-*a*′]dinaphthalen-4- yl)bis[(1*S*)-1-phenylethyl]amine) did not significantly improve the enantioselectivity, although they did enhance the rate of hydrogenation. Since the [Ir(cod)((*S*)-MONOPHOS)(L)]-BArF (L = 3-methylisoquinoline, acridine, and 2,6-lutidine) complexes are more effective catalysts for the asymmetric hydrogenation of 2,3,3-trimethylindolenine than the [Ir(cod)((*S*)-MONOPHOS)(tmi)]BArF complex itself, it follows that the pyridine ligand remains coordinated in the catalytically active species. Indirectly this implies that the species involved in the catalytic cycle are dominated by the presence of higher oxidation state iridium species which would be less prone to exchange than Ir(I) intermediates. Our results are not inconsistent with the fleeting existence of an Ir(I) species, but would appear to favor the more recent mechanisms of the type which have been suggested that follow an Ir(III)/Ir(V) pathway.

4. Experimental

4.1. General methods

All synthetic manipulations were performed under a nitrogen atmosphere using standard Schlenk techniques. CH_2Cl_2 was dried by distillation over CaH_2 and 2,3,3-trimethylindolenine was distilled prior to use. $[Ir(cod)Cl]_2$ [39] and NaBArF [40] were prepared by published methods. (*S*)-MONOPHOS, $AgSbF_6$, 3-methylisoquinoline, acridine, 2,6-lutidine, acetonitrile, pentane, and diethyl ether were used as received. NMR spectra were recorded on Bruker 400 or 500 MHz instruments and the chemical shifts reported in ppm calibrated by reference to solvent resonances. Enantiomeric excesses were determined by using (*R*)-(−)-2,2,2-trifluoro-1-(9-anthryl)-ethanol as chemical shift reagent in $CDCl_3$. Complexes containing the BArF counter ion did not provide satisfactory elemental analyses. In general, compositions of these complexes were determined by comparison of NMR with the analogous hexafluoroantimonates.

4.2. Synthesis of iridium compounds

4.2.1. [Ir(cod)((S)-MONOPHOS)Cl]

This compound was prepared by analogy to [Ir(cod)((*R*)-MONOPHOS)Cl] [41]. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.07–7.92 (4H, m, aromatic-*H*); 7.50–7.29 (7H, m, aromatic-*H*); 7.20 (1H, m, aromatic-*H*); 5.42 (2H, m, cod-C*H*); 3.44 (1H, m, cod-C*H*); 2.84 (6H, d, N(CH_3)$_2$, $^3J_{PH} = 10.8$ Hz); 2.54 (1H, m, cod-C*H*); 2.29 (1H, m, cod-CH_2); 2.21 (1H, m, cod-CH_2); 2.04 (1H, m, cod-CH_2); 1.91 (2H, m, cod-CH_2); 1.39 (3H, m, cod-CH_2). ^{31}P NMR (162 MHz, $CDCl_3$) δ: 117.4. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 132.9-125.6, 124.3, 121.5 (20C, aromatic *C*); 103.7 (1C, d, cod-*C*H, $J_{PC} = 20.0$ Hz); 103.1 (1C, d, cod-*C*H, $J_{PC} = 18.5$ Hz); 55.7 (1C, cod-*C*H); 52.7 (1C, cod-*C*H); 38.6 (2C, d, N(*C*H$_3$), $^2J_{PC} = 10.0$ Hz); 34.6 (1C, d, cod-*C*H$_2$, $J_{PC} = 3.0$ Hz); 33.0 (1C, d, cod-*C*H$_2$, $J_{PC} = 3.0$ Hz); 29.4 (1C, d, cod-*C*H$_2$, $J_{PC} = 3.6$ Hz); 29.1 (1C, d, cod-*C*H$_2$, $J_{PC} = 3.6$ Hz). Anal. Calc. for $C_{30}H_{30}Cl_1Ir_1N_1O_2P_1 \cdot CH_2Cl_2$: C, 47.75; H, 4.14; N, 1.80. Found: C, 47.83; H, 4.33; N, 1.56%.

4.2.2. [Ir(cod)(3-methylisoquinoline)Cl]

$[Ir(cod)Cl]_2$ (25 mg, 0.037 mmol) was added to a flame-dried flask under N_2 and dissolved in CH_2Cl_2 (5 mL). To the orange solution was added 3-methylisoquinoline (10.7 mg, 0.074 mmol). The resulting yellow solution was stirred at RT for 30 min, then the solvent removed *in vacuo* to leave a yellow solid. Yellow crystals of the compound (91% yield) were obtained from a CH_2Cl_2 solution by vapor diffusion of ether.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.42 (1H, s, NC*H*); 7.96 (1H, d, isoq-*H*, $J = 8.4$ Hz); 7.77 (2H, m, isoq-*H*); 7.65 (2H, m, isoq-*H*); 4.56 (2H, m, cod-C*H*); 3.25 (3H, s, CH_3); 3.18 (2H, m, cod-C*H*); 2.51–2.27 (4H, m, cod-CH_2); 1.80 (1H, m, cod-CH_2); 1.62 (2H, m, cod-CH_2); 1.52 (1H, m, cod-CH_2). ^{13}C NMR (125 MHz, CD_2Cl_2) δ: 152.7, 151.3, 135.5, 132.0, 127.7, 127.5, 127.2, 125.7, 122.5 (9C, aromatic *C*); 69.8 (1C, cod-*C*H); 68.5 (1C, cod-*C*H); 60.6 (1C, cod-*C*H); 56.5 (1C, cod-*C*H); 32.7 (1C, cod-*C*H$_2$); 31.6 (1C, cod-*C*H$_2$); 31.5 (1C, cod-*C*H$_2$); 30.6 (1C, cod-*C*H$_2$); 25.2 (1C, *C*H$_3$). Anal. Calc. for $C_{18}H_{21}Cl_1Ir_1N_1$: C, 45.13; H, 4.42; N, 2.92. Found: C, 44.91; H, 4.40; N, 2.79%.

4.2.3. [Ir(cod)((S)-MONOPHOS)(3-methylisoquinoline)]BArF

[Ir(cod)((*S*)-MONOPHOS)Cl] (29 mg, 0.036 mmol) was added to a flame-dried flask under N_2. It was dissolved in CH_2Cl_2 (5 mL). NaBArF (31.9 mg, 0.036 mmol) was added to the orange solution, turning it dark orange, then 3-methylisoquinoline (5.4 mg, 0.036 mmol) was added yielding a bright red solution. The mixture was stirred at RT for 4 h and then filtered through Celite. The solvent was removed by rotary evaporation to yield a red oil which was washed with pentane and stored under vacuum until it solidified. The product was collected in 89% yield and 66% de.

Major diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.39 (1H, d, aromatic-*H*, $J = 8.8$ Hz); 8.24 (1H, d, aromatic-*H*, $J = 8.8$ Hz); 8.02 (1H, d, aromatic-*H*, $J = 8.8$ Hz); 7.75 (8H, s, BArF-*H*); 7.54 (4H, s, BArF-*H*);

7.94–7.18 (11H, complex, aromatic-*H*); 7.00 (2H, m, aromatic-*H*); 6.93 (1H, d, aromatic-*H*, $J = 8.4$ Hz); 5.79 (1H, d, aromatic-*H*, $J = 8.0$ Hz); 4.81 (1H, m, cod-C*H*); 4.60 (1H, m, cod-C*H*); 4.35 (1H, m, cod-C*H*); 3.87 (1H, m, cod-C*H*); 3.07 (3H, s, CH_3); 2.75 (6H, d, N(CH_3)$_2$, $^3J_{PH} = 11.2$ Hz); 2.59–2.15 (8H, complex, cod-CH_2). ^{31}P NMR (162 MHz, CD_2Cl_2) δ: 110.7. *Minor diastereomer*: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.41 (1H, s, aromatic-*H*); 9.25 (1H, s, aromatic-*H*); 8.97 (1H, s, aromatic-*H*); 8.17 (1H, d, aromatic-*H*, $J = 8.8$ Hz); 8.05 (1H, d, aromatic-*H*, $J = 7.6$ Hz); 7.75 (8H, s, BArF-*H*); 7.54 (4H, s, BArF-*H*); 7.94–7.18 (12 H, complex, aromatic-*H*); 6.80 (1H, d, aromatic-*H*, $J = 8.8$ Hz); 4.50 (1H, m, cod-C*H*); 3.94 (1H, m, cod-C*H*); 3.79 (2H, m, cod-C*H*); 2.72 (6H, d, N(CH_3)$_2$, $^3J_{PH} = 11.2$ Hz); 2.59–2.15 (8H, complex, cod-CH_2); 1.97 (3H, s, CH_3). ^{31}P NMR (162 MHz, CD_2Cl_2) δ: 116.9. *Diastereomeric mixture*: ^{13}C NMR (126 MHz, CD_2Cl_2) δ: 162.1 (8C, q, B*C*, $^1J_{BC} = 51.0$ Hz); 153.1–46.9, 135.4–117.8 (114C, aromatic-*C*, *C*F$_3$); 106.6 (1C, d, cod-*C*H, $J_{PC} = 16.1$ Hz, major); 105.1 (1C, d, cod-*C*H, $J_{PC} = 15.6$ Hz, minor); 99.6 (1C, d, cod-*C*H, $J_{PC} = 18.9$ Hz, minor); 98.5 (1C, d, cod-*C*H, $J_{PC} = 17.2$ Hz, major); 68.9 (1C, cod-*C*H, minor); 67.3 (1C, cod-*C*H, major); 66.6 (1C, cod-*C*H, major); 65.0 (1C, cod-*C*H, minor); 37.4 (2C, d, N(*C*H$_3$)$_2$, $^2J_{PC} = 6.4$ Hz, major); 37.2 (2C, d, N(*C*H$_3$)$_2$, $^2J_{PC} = 8.2$ Hz, minor); 34.9 (1C, d, cod-*C*H$_2$, $J_{PC} = 3.6$ Hz, minor); 33.1 (1C, d, cod-*C*H$_2$, $J_{PC} = 3.6$ Hz, major); 32.7 (1C, d, cod-*C*H$_2$, $J_{PC} = 2.9$ Hz, major); 31.8 (1C, d, cod-*C*H$_2$, $J_{PC} = 2.9$ Hz, minor); 30.6 (1C, d, cod-*C*H$_2$, $J_{PC} = 2.8$ Hz, major); 30.0 (1C, d, cod-*C*H$_2$, $J_{PC} = 3.9$ Hz, minor); 29.2 (1C, d, cod-*C*H$_2$, $J_{PC} = 2.8$ Hz, minor); 29.0 (1C, d, cod-*C*H$_2$, $J_{PC} = 2.8$ Hz, major); 25.4 (1C, *C*H$_3$, major); 23.5 (1C, *C*H$_3$, minor).

4.2.4. [Ir(cod)((S)-MONOPHOS)(3-methylisoquinoline)]SbF$_6$

[Ir(cod)((*S*)-MONOPHOS)Cl] (50 mg, 0.072 mmol) was added to a flame-dried flask under N_2 in the absence of light, and dissolved in CH_2Cl_2 (5 mL). $AgSbF_6$ (24.7 mg, 0.072 mmol) and 3-methylisoquinoline (10.3 mg, 0.072 mmol) were added. The mixture was stirred for 1 h at RT, then filtered through Celite. The solvent was removed by rotary evaporation, and the resulting orange residue was washed with pentane and dried *in vacuo*. The product was collected in 98% yield with 32% de. Red crystals were obtained from a CH_2Cl_2 solution by vapor diffusion of ether.

Major diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.54 (1H, d, aromatic-*H*, $J = 9.2$ Hz); 8.33 (1H, d, aromatic-*H*, $J = 8.0$ Hz); 8.08–7.14 (14 H, complex, aromatic-*H*); 6.89 (1H, t, aromatic-*H*, $J = 7.2$ Hz); 6.17 (1H, d, aromatic-*H*, $J = 8.8$ Hz); 4.95 (1H, m, cod-C*H*); 4.74 (1H, m, cod-C*H*); 4.36 (1H, m, cod-C*H*); 3.80 (1H, m, cod-C*H*); 3.19 (3H, s, CH_3); 2.78 (6H, d, N(CH_3)$_2$, $^3J_{PH} = 11.6$ Hz); 2.54–2.12 (8H, complex, cod-CH_2). ^{31}P NMR (162 MHz, $CDCl_3$) δ: 111.6. *Minor diastereomer*: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.70 (1H, s, aromatic-*H*); 8.45 (1H, d, aromatic-*H*, $J = 8.0$ Hz); 8.20 (1H, d, aromatic-*H*, $J = 8.8$ Hz); 8.08–7.14 (14 H, complex, aromatic-*H*); 7.04 (1H, t, aromatic-*H*, $J = 7.2$ Hz); 5.08 (1H, m, cod-C*H*); 4.58 (1H, m, cod-C*H*); 4.42 (1H, m, cod-C*H*); 3.97 (1H, m, cod-C*H*); 2.82 (6H, d, N(CH_3)$_2$, $^3J_{PH} = 11.1$ Hz); 2.54–2.12 (8H, complex, cod-CH_2); 1.95 (3H, s, CH_3). ^{31}P NMR (162 MHz, $CDCl_3$) δ: 117.9. *Diastereomeric mixture*: ^{13}C NMR (126 MHz, CD_2Cl_2) δ: 154.3–147.0, 136.2–120.0 (58C, aromatic-*C*); 106.7 (1C, d, cod-*C*H, $J_{PC} = 16.2$ Hz); 100.5 (1C, d, cod-*C*H, $J_{PC} = 14.6$ Hz); 99.4 (1C, d, cod-*C*H, $J_{PC} = 17.3$ Hz); 98.8 (1C, d, cod-*C*H, $J_{PC} = 17.3$ Hz), 68.9 (1C, cod-*C*H); 67.3 (1C, cod-*C*H); 66.4 (1C, cod-*C*H); 64.7 (1C, cod-*C*H); 37.5 (2C, d, N(*C*H$_3$)$_2$, $^2J_{PC} = 6.2$ Hz); 37.3 (2C, d, N(*C*H$_3$)$_2$, $^2J_{PC} = 7.6$); 33.4, 33.0, 32.4, 30.5, 30.1–29.7, 29.1, 25.5, 23.5 (10C, cod-*C*H$_2$, *C*H$_3$). Anal. Calc. for $C_{40}H_{39}F_6Ir_1N_2O_2P_1Sb_1 \cdot CH_2Cl_2$: C, 43.85; H, 3.68; N, 2.50. Found: C, 43.94; H, 3.77; N, 2.39%.

4.2.5. [Ir(cod)((S)-MONOPHOS)(acridine)]BArF

To a flame-dried flask under N_2 was added [Ir(cod)((*S*)-MONOPHOS)Cl] (35 mg, 0.05 mmol). The solid was dissolved in dry CH_2Cl_2 (3 mL) to give a pale orange solution. NaBArF (44.6 mg, 0.05 mmol) was added turning the solution darker orange, then acridine (9.0 mg, 0.05 mmol) was added. After an hour, precipitate had formed in the red solution. The mixture was filtered through Celite and the solvent removed by rotary evaporation. A red oil formed which was washed with pentane and yielded and orange solid under vacuum. The product was collected in 81% yield.

The complex was analyzed by mass spectrometry in a solution of methanol. Peaks at 837.79 *m*/*z*, 839.90 *m*/*z*, 840.89 *m*/*z*, and 841.95 *m*/*z* were consistent with the isotope model for [Ir(cod)((*S*)-MONOPHOS)(acridine)]$^+$. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.51 (1H, d, aromatic-*H*, $J = 8.5$ Hz); 8.87 (1H, s, aromatic-*H*); 8.35 (1H, d, aromatic-*H*, $J = 8.5$ Hz); 8.16–8.04 (3H, m, aromatic-*H*); 7.81–7.63 (7H, m, aromatic-*H*); 7.75 (8H, s, BArF-*H*); 7.54 (4H, s, BArF-*H*); 7.40 (1H, m, aromatic-*H*); 7.25 (2H, m, aromatic-*H*); 7.16 (1H, d, aromatic-*H*, $J = 8.6$ Hz); 6.84 (1H, d, aromatic-*H*, $J = 8.6$ Hz); 6.72 (1H, m, aromatic-*H*) 6.42 (1H, d, aromatic-*H*, $J = 8.6$ Hz); 6.23 (1H, m, aromatic-*H*); 4.98 (1H, m, cod-C*H*); 4.87 (1H, m, cod-C*H*); 4.62 (1H, m, cod-C*H*); 4.12 (1H, m, cod-C*H*); 2.72 (6H, d, N(CH_3)$_2$, $^3J_{PH} = 11.5$ Hz); 2.54–2.12 (4H, m, cod-CH_2); 1.34–0.99 (4H, m, cod-CH_2). ^{31}P NMR (122 MHz, CD_2Cl_2) δ: 116.1. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 162.1 (4C, q, B*C*, $^1J_{BC} = 50.2$ Hz); 148.3–117.8 (61C, aromatic *C*, *C*F$_3$); 103.6 (1C, d, cod-*C*H, $J_{PC} = 15.2$ Hz); 102.1 (1C, d, cod-*C*H, $J_{PC} = 17.6$ Hz); 66.6 (1C, cod-*C*H); 64.8 (1C, cod-*C*H); 37.6 (2C, d, N(*C*H$_3$)$_2$, $^2J_{PC} = 7.4$ Hz); 34.0 (1C, d, cod-*C*H$_2$, $J_{PC} = 3.2$ Hz); 32.3 (1C, d, cod-*C*H$_2$, $J_{PC} = 3.2$ Hz); 30.2 (1C, cod-*C*H$_2$); 28.6 (1C, cod-*C*H$_2$).

4.2.6. [Ir(cod)((S)-MONOPHOS)(acridine)]SbF_6

To a flame-dried flask under N_2 in the dark was added [Ir(cod)((*S*)-MONOPHOS)Cl] (40 mg, 0.058 mmol). It was dissolved in dry CH_2Cl_2 (3 mL). $AgSbF_6$ (20 mg, 0.058 mmol) was added to the clear yellow solution. Acridine (10.4 mg, 0.058 mmol) was then added resulting in a cloudy red solution. The reaction was stirred for 1 h at RT and filtered through Celite. The solvent was removed by rotary evaporation. The resulting red solid was washed with pentane and the excess solvent was removed under vacuum. The complex was collected in 92% yield. Crystals were obtained by vapor diffusion of ether into a CH_2Cl_2 solution of the complex.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.57 (1H, d, aromatic-*H*, $J = 8.8$ Hz); 8.99 (1H, d, aromatic-*H*, $J = 8.8$ Hz); 8.41 (2H, m, aromatic-*H*); 8.22 (3H, m, aromatic-*H*); 7.82–7.62 (6H, m, aromatic-*H*); 7.38 (1H, t, aromatic-*H*, $J = 7.2$ Hz); 7.23 (2H, m, aromatic-*H*); 7.14 (1H, m, aromatic-*H*); 6.83 (1H, d, aromatic-*H*, $J = 8.4$ Hz); 6.74 (1H, t, aromatic-*H*, $J = 7.6$ Hz); 6.49 (1H, d, aromatic-*H*, $J = 9.2$ Hz); 6.32 (1H, m, aromatic-*H*); 4.88 (2H, m, cod-C*H*); 4.59 (1H, m, cod-C*H*); 4.12 (1H, m, cod-C*H*); 2.90–2.50 (4H, m, cod-CH_2); 2.73 (6H, d, N(CH_3)$_2$ $^3J_{PH} = 10.8$ Hz); 2.38 (2H, m, cod-CH_2); 2.23 (2H, m, cod-CH_2). ^{31}P NMR (162 MHz, CD_2Cl_2) δ: 116.6. ^{13}C NMR (126 MHz, $CDCl_3$) 147.8–146.9, 140.7, 133.8–119.6 (33C, aromatic *C*); 102.9 (1C, d, cod-*C*H, $J_{PC} = 16.6$ Hz); 102.2 (1C, d, cod-*C*H, $J_{PC} = 15.6$ Hz); 66.4 (1C, cod-*C*H); 64.5 (1C, cod-*C*H); 37.3 (2C, d, N(*C*H_3)$_2$, $^2J_{PC} = 6.5$ Hz); 33.3 (1C, d, cod-*C*H_2, $J_{PC} = 3.9$ Hz); 32.3 (1C, d, cod-*C*H_2, $J_{PC} = 3.6$ Hz); 29.6 (1C, m, cod-*C*H_2); 28.5 (1C, m, cod-*C*H_2). Anal. Calc. for $C_{43}H_{39}F_6Ir_1N_2O_2P_1Sb_1$: C, 48.06; H, 3.66; N, 2.61. Found: C, 47.91; H, 3.68; N, 2.53%.

4.2.7. [Ir(cod)((S)-MONOPHOS)(2,6-lutidine)]BArF

[Ir(cod)((*S*)-MONOPHOS)Cl] (15.5 mg, 0.022 mmol) was added to a flame-dried flask under N_2 and dissolved in CH_2Cl_2 (3 mL). NaBArF (19.8 mg, 0.022 mmol) and 2,6-lutidine (2.4 mg, 0.022 mmol) were added. The mixture was stirred for 1 h at RT, then filtered through Celite. The solvent was removed by rotary evaporation, and the resulting orange residue was washed with pentane and yielded an orange solid under vacuum. The product was collected in 43% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.16 (1H, m, aromatic-*H*); 8.04 (1H, m, aromatic-*H*); 7.92 (2H, m, aromatic-*H*); 7.74 (8H, s, BArF-*H*); 7.55 (4H, s, BArF-*H*); 7.81–7.19 (8H, complex, aromatic-*H*); 7.04 (2H, m, aromatic-*H*); 6.68 (1H, m, aromatic-*H*); 4.57 (1H, m, cod-C*H*); 4.51 (1H, m, cod-C*H*); 4.40 (1H, m, cod-C*H*); 3.72 (1H, m, cod-C*H*); 3.12 (3H, s, CH_3); 2.72 (6H, d, N(CH_3)$_2$, $^3J_{PH} = 10.4$ Hz); 2.68–2.06 (8H, complex, cod-CH_2); 1.87 (3H, s, CH_3). ^{31}P NMR (162 MHz, $CDCl_3$): δ 116.3. ^{13}C NMR (125 MHz, CD_2Cl_2) δ: 161.7 (4C, q, B*C*, $^1J_{BC} = 50.0$ Hz); 158.4, 157.2, 154.9, 147.8, 147.1, 142.5, 138.7, 134.7, 132.5–123.4, 122.0, 121.3, 120.7, 119.7, 117.4 (53C, aromatic *C*, *C*F_3); 101.9 (1C, d, cod-*C*H, $J_{PC} = 16.5$ Hz); 101.4 (1C, d, cod-*C*H, $J_{PC} = 15.6$ Hz); 64.6 (1C, cod-*C*H); 64.2 (1C, cod-*C*H); 37.3 (2C, d, N(*C*H_3)$_2$, $^2J_{PC} = 7.9$ Hz); 32.7 (1C, d, cod-*C*H_2, $J_{PC} = 2.9$ Hz); 32.2 (1C, d, cod-*C*H_2, $J_{PC} = 4.0$ Hz); 28.9 (1C, d, cod-*C*H_2, $J_{PC} = 2.8$ Hz); 28.6 (1C, d, cod-*C*H_2, $J_{PC} = 2.2$ Hz); 26.1 (1C, lut-*C*H_3); 23.8 (1C, lut-*C*H_3).

4.2.8. [Ir(cod)((S)-MONOPHOS)(2,6-lutidine)]SbF_6

To a flame-dried flask under N_2 in the dark was added [Ir(cod)((*S*)-MONOPHOS)Cl] (25 mg, 0.036 mmol). It was dissolved in CH_2Cl_2 (3 mL). $AgSbF_6$ (12.4 mg, 0.036 mmol) was added to the clear yellow solution. A solution of 2,6-lutidine (38.6 mg, 0.036 mmol) in CH_2Cl_2 was then added resulting in a cloudy red solution. The reaction was stirred for 1 h at RT and filtered through Celite. The solvent was removed by rotary evaporation. The resulting red solid was washed with pentane and the excess solvent was removed under vacuum. The complex was obtained in 94% yield. It was crystallized by vapor diffusion of ether into a solution of the complex in CH_2Cl_2, and analyzed by X-ray crystallography.

^{1}H NMR (500 MHz, CD_2Cl_2) δ: 8.24 (1H, d, aromatic-*H*, $J = 9.0$ Hz); 8.10 (1H, d, aromatic-*H*, $J = 8.0$ Hz); 7.98 (2H, t, aromatic-*H*, $J = 9.0$ Hz); 7.67 (1H, d, aromatic-*H*, $J = 9.0$ Hz); 7.59 (2H, m, aromatic-*H*); 7.52 (1H, m, aromatic-*H*); 7.38–7.25 (5H, complex, aromatic-*H*); 7.15 (1H, m, aromatic-*H*); 6.79 (1H, d, aromatic-*H*, $J = 7.5$ Hz); 4.71 (1H, m, cod-C*H*); 4.61 (1H, m, cod-C*H*); 4.43 (1H, m, cod-C*H*); 3.77 (1H, m, cod-C*H*); 3.25 (3H, s, CH_3); 2.76 (6H, d, N(CH_3)$_2$, $^3J_{PH} = 11.0$ Hz); 2.78–2.21 (8H, complex, cod-CH_2); 1.90 (3H, s, CH_3). ^{31}P NMR (162 MHz, $CDCl_3$): δ 116.6. ^{13}C NMR (125 MHz, CD_2Cl_2) δ: 158.7, 157.9, 148.3, 147.6, 139.2, 132.9, 132.7–120.4 (25C, aromatic-*C*); 102.5 (1C, d, cod-*C*H, $J_{PC} = 16.2$ Hz); 102.0 (1C, d, cod-*C*H, $J_{PC} = 16.0$ Hz); 65.0 (1C, cod-*C*H); 64.6 (1C, cod-*C*H); 37.8 (2C, d, N(*C*H_3)$_2$, $^2J_{PC} = 7.7$ Hz); 33.1 (1C, d, cod-*C*H_2, $J_{PC} = 2.9$ Hz); 32.7 (1C, d, cod-*C*H_2, $J_{PC} = 3.9$ Hz); 29.4 (1C, d, cod-*C*H_2, $J_{PC} = 2.8$ Hz); 29.1 (1C, d, cod-*C*H_2, $J_{PC} = 2.9$ Hz); 26.6 (1C, lut-*C*H_3); 24.3 (1C, lut-*C*H_3). Anal. Calc. for $C_{37}H_{39}F_6Ir_1N_2O_2P_1Sb_1$: C, 44.31; H, 3.92; N, 2.79. Found: C, 44.01; H, 3.88; N, 2.67%.

4.2.9. [Ir(cod)((S)-MONOPHOS)(2,3,3-trimethylindolnine)]BArF

[Ir(cod)((*S*)-MONOPHOS)Cl] (29.4 mg, 0.042 mmol) was added to a flame-dried flask under N_2 and dissolved in CH_2Cl_2 (5 mL). NaBArF (37.1 mg, 0.042 mmol) was added to the solution which became brown and cloudy. Upon the addition of a CH_2Cl_2 solution of 2,3,3-trimethylindolenine (96.7 mg, 0.042 mmol), the solution became dark red. It was stirred at RT for 6 h, filtered through Celite, and the solvent removed by rotary evaporation. The oily residue was washed with ether and pentane and yielded an orange powder under vacuum. The product was collected in 90% yield. Two diastereomers formed in a 1:1 ratio.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.31 (1H, m, aromatic-*H*); 8.19 (1H, d, aromatic-*H*, $J = 8.8$ Hz); 8.13 (1H, d, aromatic-*H*, $J = 8.4$ Hz); 8.02 (3H, m, aromatic-*H*); 7.94 (1H, m, aromatic-*H*); 7.87 (4H, m, aromatic-*H*); 7.75 (16H, s, BArF-*H*); 7.55 (8H, s, BArF-*H*); 7.66–7.18 (14H, complex, aromatic-*H*); 6.94 (3H, m, aromatic-*H*); 6.78 (1H, d, aromatic-*H*, $J = 9.2$ Hz); 6.58 (1H, t, aromatic-*H*, $J = 7.6$ Hz); 6.40 (1H, t, aromatic-*H*, $J = 8.0$ Hz); 5.56 (1H, t, aromatic-*H*, $J = 7.6$ Hz); 4.96 (2H, m, cod-C*H*); 4.81 (1H, m, cod-C*H*); 4.74 (1H, m, cod-C*H*); 4.89 (2H, m, cod-C*H*); 3.98 (1H, m, cod-C*H*); 3.88 (1H, m, cod-C*H*); 2.74 (6H, d, N(CH_3)$_2$, $^3J_{PH} = 11.6$ Hz); 2.73 (6H, d, N(CH_3)$_2$, $^3J_{PH} = 11.6$ Hz); 2.65 (3H, s, CH_3); 2.58 (3H, s, CH_3); 2.14–2.68 (16H, m, cod-CH_2); 1.23 (3H, s, CH_3); 1.18 (3H, s, CH_3); 1.12 (3H, s, CH_3); 1.05 (3H, s, CH_3). ^{31}P NMR (162 MHz, $CDCl_3$) δ: 115.23, 115.28. ^{13}C NMR (126 MHz, CD_2Cl_2) δ: 191.7; (1C, N=*C*); 190.0 (1C, N=*C*); 161.7 (8C, q, B*C*, $^1J_{BC} = 49.9$ Hz); 149.9–142.7, 134.7–117.4 (108C, aromatic *C*, *C*F_3); 102.5 (1C, d, cod-*C*H, $J_{PC} = 15.1$ Hz); 102.4 (1C, d, cod-*C*H, $J_{PC} = 16.4$ Hz); 101.4 (1C, d, cod-*C*H, $J_{PC} = 16.4$ Hz); 101.3 (1C, d, cod-*C*H, $J_{PC} = 16.4$ Hz); 68.7 (1C, cod-*C*H); 68.5 (1C, cod-*C*H); 67.3 (1C, cod-*C*H); 67.1 (1C, cod-*C*H); 54.7 (1C, *C*(CH_3)$_2$); 54.6 (1C, *C*(CH_3)$_2$); 37.1 (2C, d, N(*C*H_3)$_2$, $^2J_{PC} = 7.5$ Hz); 37.0 (2C, d, N(*C*H_3)$_2$, $^2J_{PC} = 7.3$ Hz); 32.9 (1C, d, cod-*C*H_2, $J_{PC} = 3.6$ Hz); 32.8 (1C, d, cod-*C*H_2, $J_{PC} = 3.6$ Hz); 31.9 (2C, d, cod-*C*H_2, $J_{PC} = 3.7$ Hz); 31.8 (2C, d, cod-*C*H_2, $J_{PC} = 3.4$ Hz); 29.7 (1C, d, cod-*C*H_2, $J_{PC} = 2.6$ Hz); 29.6 (1C, cod-*C*H_2); 28.8 (1C, cod-*C*H_2); 28.7 (1C, d, cod-*C*H_2, $J_{PC} = 2.6$ Hz); 22.7 (1C, C(*C*H_3)$_2$); 22.4 (1C, C(*C*H_3)$_2$); 22.2 (1C, C(*C*H_3)$_2$); 22.0 (1C, C(*C*H_3)$_2$); 17.5 (1C, *C*H_3); 15.1 (1C, *C*H_3).

4.2.10. [Ir(cod)((S)-MONOPHOS)(2,3,3-trimethylindolenine)]SbF_6

[Ir(cod)((*S*)-MONOPHOS)Cl] (50 mg, 0.072 mmol) was added to a flame-dried flask under N_2 in the dark and dissolved in CH_2Cl_2 (10 mL). $AgSbF_6$ (24.7 mg, 0.072 mmol) was added to the solution which turned brown and cloudy. Upon the addition of a CH_2Cl_2 solution of 2,3,3-trimethylindolenine (11.5 mg, 0.072 mmol), the solution became dark red. It was stirred at RT for 1 h, filtered through Celite, and the solvent removed by rotary evaporation. The resulting red solid was washed with ether and dried *in vacuo*. The compound was collected in 97% yield. The complex formed in a 1:1 mixture of diastereomers. Crystals of a single diastereomer were obtained by vapor diffusion of ether into a CH_2Cl_2 solution of the complex. This diastereomer is shown in Fig. 2. Obtaining the NMR of freshly dissolved crystals initially showed a set of resonances predominantly of one diastereomer and allowed the assignment of the ^{1}H resonances to a given diastereomer.

Diastereomer from solid: ^{1}H NMR (400 MHz, CD_2Cl_2) δ: 8.37 (1H, d, aromatic-*H*, $J = 8.9$ Hz); 8.19 (1H, d, aromatic-*H*, $J = 8.4$ Hz); 7.93 (2H, t, aromatic-*H*, $J = 8.4$ Hz); 7.81 (1H, d, aromatic-*H*, $J = 8.9$ Hz); 7.64 (1H, t, aromatic-*H*, $J = 7.2$ Hz); 7.48 (1H, t, aromatic-*H*, $J = 6.7$ Hz); 7.26 (3H, m, aromatic-*H*); 7.10 (1H, d, aromatic-*H*, $J = 8.9$ Hz); 7.02 (1H, d, aromatic-*H*, $J = 7.6$ Hz); 6.90 (1H, d, aromatic-*H*, $J = 8.9$ Hz); 6.62 (1H, t, aromatic-*H*, $J = 7.6$ Hz); 6.47 (1H, d, aromatic-*H*, $J = 7.6$ Hz); 5.62 (1H, m, aromatic-*H*); 5.03 (1H, m, cod-C*H*); 4.86 (1H, m, cod-C*H*); 4.55 (1H, m, cod-C*H*); 3.95 (1H, m, cod-C*H*); 2.80 (6H, d, N(CH_3)$_2$, $^3J_{PH} = 11.6$ Hz); 2.78 (3H, s, CH_3); 2.74–2.23 (8H, complex, cod-CH_2); 1.34 (3H, s, CH_3); 1.27 (3H, s, CH_3). ^{31}P NMR (162 MHz, CD_2Cl_2) δ: 115.5. *Second diastereomer*: ^{1}H NMR(400 MHz, CD_2Cl_2) δ: 8.28 (1H, m, aromatic-*H*, $J = 8.9$ Hz); 8.12 (2H, m, aromatic-*H*); 8.04 (1H, m, aromatic-*H*); 7.93 (2H, m, aromatic-*H*); 7.73 (1H, d, aromatic-*H*, $J = 8.9$ Hz); 7.17–7.67 (8H, m, aromatic-*H*); 6.84 (1H, d, aromatic-*H*, $J = 8.9$ Hz); 5.05 (1H, m, cod-C*H*); 4.89 (1H, m, cod-C*H*); 4.54 (1H, m, cod-C*H*); 4.04 (1H, m, cod-C*H*); 2.79 (3H, s, CH_3); 2.77 (6H, d, N(CH_3)$_2$, $^3J_{PH} = 11.6$ Hz); 2.74–2.29 (8H, complex, cod-CH_2); 1.19 (3H, s, CH_3) 1.13 (3H, s, CH_3). ^{31}P NMR (162 MHz, CD_2Cl_2) δ: 115.8. *Diastereomeric mixture*. ^{13}C NMR (100 MHz, CD_2Cl_2) δ: 191.8; (1C, N=*C*); 190.7 (1C, N=*C*); 150.0–146.9, 143.8, 142.9, 133.0–131.0, 128.6–125.6, 124.0–117.7 (52C, aromatic *C*); 102.8 (1C, d, cod-*C*H, $J_{PC} = 16.3$ Hz, minor); 102.6 (1C, d, cod-*C*H, $J_{PC} = 16.3$ Hz, major); 101.6 (1C, d, cod-*C*H, $J_{PC} = 16.7$ Hz, major); 101.5 (1C, d, cod-*C*H, $J_{PC} = 15.9$ Hz, minor); 68.8 (1C, cod-*C*H, minor); 68.7 (1C, cod-*C*H, major); 67.2 (1C, cod-*C*H, minor); 67.0 (1C, cod-*C*H, major); 54.7 (1C, *C*(CH_3)$_2$, major); 54.6 (1C, *C*(CH_3)$_2$, minor); 37.2 (2C, d, N(*C*H_3)$_2$, $^2J_{PC} = 8.1$ Hz, major); 37.1 (2C, d, N(*C*H_3)$_2$, $^2J_{PC} = 7.3$ Hz, minor); 33.2 (1C, d, cod-*C*H_2, $J_{PC} = 3.2$ Hz); 32.9 (1C, d, cod-*C*H_2, $J_{PC} = 3.6$ Hz); 32.0 (1C, d, cod-*C*H_2, $J_{PC} = 3.9$ Hz); 31.7 (1C, d, cod-*C*H_2, $J_{PC} = 2.9$ Hz); 29.9 (1C, d, cod-*C*H_2, $J_{PC} = 3.7$ Hz); 29.7 (1C, d, cod-*C*H_2, $J_{PC} = 3.2$ Hz); 28.9 (1C, d, cod-*C*H_2, $J_{PC} = 2.0$ Hz); 28.8 (1C, d, cod-*C*H_2, $J_{PC} = 2.0$ Hz); 22.9 (1C, C(*C*H_3)$_2$); 22.5 (1C, C(*C*H_3)$_2$); 22.3 (1C, C(*C*H_3)$_2$); 22.0 (1C, C(*C*H_3)$_2$); 17.8 (1C, *C*H_3); 15.2 (1C, *C*H_3). Anal. Calc. for $C_{41}H_{43}F_6Ir_1N_2O_2P_1Sb_1$: C, 46.69; H, 4.11; N, 2.66. Found: C, 46.33; H, 4.19; N, 2.70%.

4.2.11. [Ir(cod)((S)-MONOPHOS)(MeCN)]BArF

To a flame-dried flask under N_2 was added [Ir(cod)((*S*)-MONOPHOS)Cl] (40 mg, 0.058 mmol). It was dissolved in dry CH_2Cl_2 (5 mL). NaBArF (51.0 mg, 0.058 mmol) was added to the clear yellow solution. A solution of acetonitrile (2.4 mg, 0.058 mmol) in CH_2Cl_2 was then added resulting in a cloudy red solution. The reaction was stirred for 1 h at RT and filtered through Celite. The compound was recrystallized from a CH_2Cl_2 solution layered with pentane and the resulting red powder was dried *in vacuo* resulting in 30% yield. The low yield is a result of the difficulty in crystallizing BArF complexes.

^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.06–7.87, 7.54, 7.25, 7.38 (12H, aromatic-*H*); 7.68 (8H, s, BArF-*H*); 7.51 (4H, s, BArF-*H*); 5.15 (1H, m, cod-C*H*); 5.09 (1H, m, cod-C*H*); 4.21 (1H, m, cod-C*H*); 3.27 (1H, m, cod-C*H*); 2.68

(6H, d, N(CH_3)$_2$, $^3J_{PH}$ = 11.5 Hz); 2.30 (3H, s, CH_3); 2.26–1.98, 1.78–1.62 (8H, m, cod-CH_2). ^{31}P NMR (202 MHz, $CDCl_3$) δ: 111.5. ^{13}C NMR (101 MHz, $CDCl_3$) δ: 162.7 (4C, q, B*C*, $^1J_{BC}$ = 49.8 Hz); 134.8–117.5 (49C, aromatic *C*, *C*N, *C*F$_3$); 101.9 (1C, cod-*C*H); 100.1 (1C, cod-*C*H); 70.1 (1C, cod-*C*H); 67.6 (1C, cod-*C*H); 37.4 (2C, d, N(*C*H$_3$)$_2$, $^2J_{PC}$ = 8.7 Hz); 32.9 (1C, d, cod-*C*H$_2$, J_{PC} = 3.4 Hz); 32.2 (1C, d, cod-*C*H$_2$, J_{PC} = 3.4 Hz); 29.2 (1C, d, cod-*C*H$_2$, J_{PC} = 3.4 Hz); 29.0 (1C, d, cod-*C*H$_2$, J_{PC} = 3.4 Hz); 0.76 (1C, *C*H$_3$).

4.3. X-ray structure determination and refinement

Crystals of [Ir(cod)((*S*)-MONOPHOS)(lutidine)]SbF_6 and [Ir(cod)((*S*)-MONOPHOS)(tmi)]SbF_6 were obtained by vapor diffusion of ether into methylene chloride solutions of the complexes. Important data are presented in Table 5 and the ORTEP diagrams are shown in Figs. 1 and 2. Data were collected on a Nonius KappaCCD (Mo Kα radiation) diffractometer and were not specifically corrected for absorption other than the inherent corrections provided by Scalepack [42]. The structures were solved by direct methods (SIR92) [43] and refined on *F* for all reflections [44]. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included at calculated positions.

In the case of the tmi complex a disordered diethyl ether molecule was found. The data for this structure were adjusted using program SQUEEZE in PLATON [45,46] to remove the scattering from this moiety. Absolute configurations were determined by reference to the known configuration of the monophos and by inverting the coordinates which gave large increases in *R* factors. Detailed information is provided in the supporting information.

4.4. Imine hydrogenation

A representative procedure for the hydrogenation of 2,3,3-trimethylindolenine is given. Freshly distilled 2,3,3-trimethylindolenine (200 mg, 1.26 mmol) was transferred to an oven-dried glass liner, and [Ir(cod)((*S*)-MONOPHOS)(acridine)]BArF (21.4 mg, 0.0126 mmol) was added. The glass liner was placed in the pressure vessel, which was purged with H_2. The H_2 pressure was then brought to 40 bar and the pressure vessel sealed. The reaction was run for 24 h. The glass liner was then removed from the pressure vessel and the reaction quenched immediately with pentane. The pentane solution was then filtered through Celite and the pentane removed *in vacuo* to leave the imine/amine mixture. The conversion and the ee were determined by ^{1}H NMR using the chiral shift agent (*R*)-(−)-2,2,2-trifluoro-1-(9-anthryl)-ethanol.

Appendix A. Supplementary data

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 609789 and 609790 for the lutidine and tmi complex respectively compound. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ UK; fax: (int code) +44 (1223) 336 033; or email: deposit@

Table 5
Crystallographic data

	[Ir(cod)((*S*)-MONOPHOS)(lut)]SbF_6	[Ir(cod)((*S*)-MONOPHOS)(tmi)]SbF_6
Color, shape	Orange, block	Red, block
Empirical formula	$C_{37}H_{39}IrN_2O_2P$, SbF_6	$C_{41}H_{43}IrN_2O_2P$, $C_4H_{10}O$, SbF_6
Formula weight	1002.66	1128.86
Radiation/Å	Mo Kα (monochromatic) 0.71073	Mo Kα (monochromatic) 0.71073
T/K	173	123
Crystal system	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$ (no. 19)	$P2_1$ (no. 4)
Unit cell dimensions		
a/Å	11.394(2)	13.4736(7)
b/Å	14.8727(4)	11.8511(4)
c/Å	21.5025(5)	13.8736(6)
β/°	90	92.553(3)
V/Å^3	3643.7(6)	2213.1(2)
Z	4	2
D_{calc}/g cm^{-3}	1.828	1.694
μ/cm^{-1} (Mo Kα)	45.09	37.24
Crystal size/mm	0.10 × 0.10 × 0.12	0.08 × 0.08 × 0.20
Total no. of reflections, unique reflections	8297, 4648	9756, 5677
R_{int}	0.073	0.048
No. of observed data ($I > 3\sigma(I)$)	5742	4384
Parameters, constraints	451, 0	485, 0
R^a, $R_w{}^b$, GOF	0.035, 0.028, 1.25	0.036, 0.035, 2.39
Resolved density/e Å^{-3}	−1.01 < 0.78	−1.80 < 2.86

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$, for all $I > 3\sigma(I)$.
[b] $R_w = [\sum[w(|F_o| - |F_c|)^2]/\sum[w(F_o)^2]]^{1/2}$.

ccdc.cam.ac.uk or www:http://www.ccdc.cam.ac.uk. The metrical parameters are also available in the supporting information. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.08.032.

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