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Chiral poisoning of *rac*-diop iridium complexes in the catalytic enantioselective hydrogenation of imines

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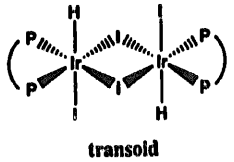
Abstract

Dimeric Ir(III) complexes $[Ir(P-P)HI_2]_2$ (P–P = enantiopure bisphosphine) have previously been shown to be efficient catalysts for the enantioselective hydrogenation of imines. In the present study we have prepared the analogues using *rac*-diop. Among the possible dimers, there was only a slight preference for the μ-I_2 heterodimer {[Ir(*R,R*)-diopHI_2][Ir(*S,S*)-diopHI_2]}. Although this mixture of dimers was a moderately good catalyst for the hydrogenation of imines, it showed no enantioselectivity, as expected. Addition of the readily available aminophosphinephosphinite ligand, (+)-(*S*)-pronop, to this dimer mixture in a ratio of [(*S*)-pronop]:$[Ir]_{tot}$ = 1:1 produced a poor catalyst which effected only a few turnovers in 100 h. However, addition of (+)-(*S*)-pronop to this dimer mixture in a ratio of [(*S*)-pronop]:$[Ir]_{tot}$ = 1:2 produced an effective catalyst for the enantioselective hydrogenation of imines. Significant chiral amplification was not observed in catalysis with dimers prepared from nonracemic diop.

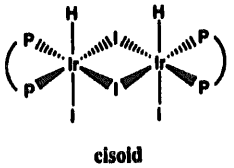
Keywords: Iridium; Hydrogenation; Chiral poisoning; Enantioselective catalysis

1. Introduction

In contrast to the hydrogenation of carbonyl compounds, the reduction of imines is rather difficult [1]. The dimeric Ir(III) complexes $[Ir(P-P)HI_2]_2$ (P–P = chiral bisphosphine) are active catalysts for enantioselective hydrogenation of imines. The compounds exist as two isomers, a transoid and a cisoid form [1], the proportions depending on the bisphosphine.

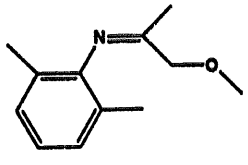


transoid

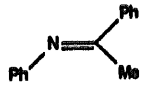


cisoid

Some previous catalytic results with imine substrates **1** and **2** are summarized in Table 1 [1].



1



2

A reasonable catalytic cycle would involve dissociation of a dimer to yield an unsaturated monohydride complex $Ir(P-P)HI_2$ as the active species, as shown in Scheme 1 (note that only one diastereomer of the unsaturated species is shown).

We have also observed that the dimers could react with chelating ligands (L–L) such as bipyridines [2], pyridinimines [2] or bisphosphines [2] to give the

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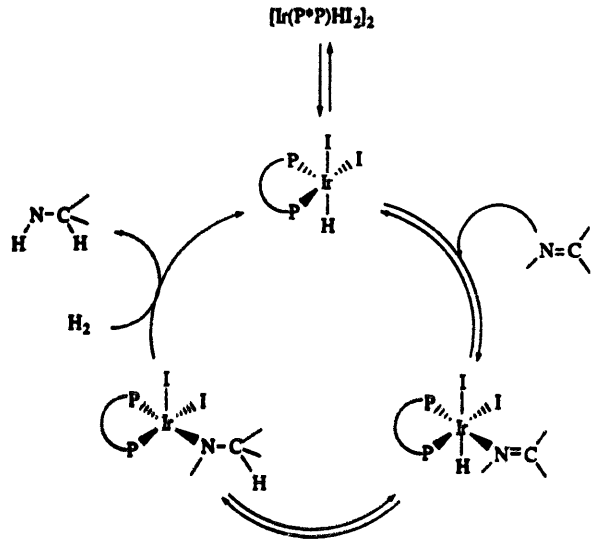
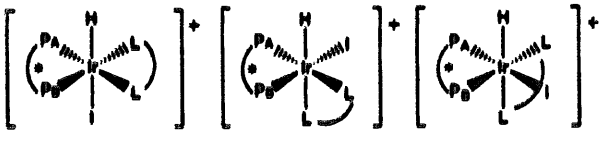


Scheme 1. A proposed catalytic cycle for imine hydrogenation.

monomeric species [Ir(P–P)(L–L)HI]I (as a mixture of three diastereomers), which have low or zero catalytic activity in the hydrogenation of imines.



This suggested that if one used the racemic analogues of the phosphines in Table 1, one enantiomeric form of the racemic active species might be selectively deactivated using an enantiomerically pure chelate. Thus, as an analogy to the [Rh(*rac*-chiraphos)]$_2^{2+}$ / methophos system [3], we have studied the effect of an enantiopure chiral ligand on a catalyst prepared from a racemic bisphosphine in order to evaluate the potential of chiral poisoning in this system.

Table 1
Enantioselective hydrogenation of imines (S) catalyzed by [Ir(P-P)HI$_2$]$_2$[a]

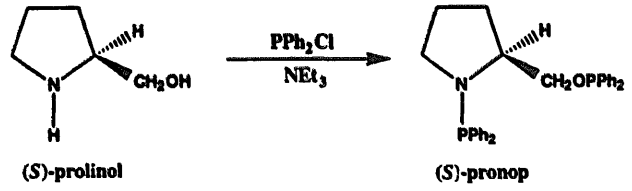
P–P	S	Time (h)	*ee* (%)
(*S,S*)-diop	1	8	54 (*S*)
(*S,S*)-bdpp	1	6.5	34 (*R*)
(*R*)-binap	1	145	22 (*S*)
(*S,S*)-bdpp	2	2	40 (*S*)
(*S,S*)-diop[b]	2	5	11 (*S*)

[a] Conditions: [Ir$_2$] = 7.83×10^{-3} mmol; [S]/[Ir$_2$] = 1000; pH_2 = 40 bar; T = 30°C; solvent, THF–CH_2Cl_2 (v/v = 3/1) = 10 ml; bdpp = 2,4-bis(diphenylphosphino)pentane; diop = 2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane; binap = 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl. [b] pH_2 = 28 bar.

2. Results

2.1. Catalyst preparation and characterization

We have focused on the diop dimer owing to its high activity and relatively high enantioselectivity in hydrogenation of imine **1** (see Table 1). We have also investigated Petit and coworkers' aminophosphinephosphinite (+)-(*S*)-pronop [4] as a poison, as it can be synthesized in one step starting from the corresponding aminoalcohol (prolinol: (*S*)-(+)-2-pyrrolidinemethanol).



(1)

The dimeric catalyst with *rac*-diop was obtained following the previously described procedure for (*S,S*)-diop [1].

$$2[Ir(cod)(diop)]BF_4 \xrightarrow[\text{excessLiI}]{\text{acetone, }\Delta} [Ir(diop)HI_2]_2 \quad (2)$$

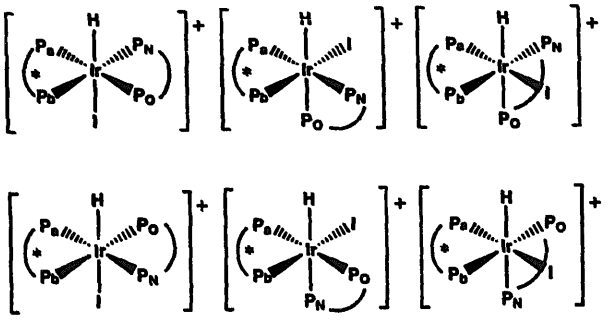
The (*S*)-pronop ligand reacts with the dimer [Ir(diop)HI$_2$]$_2$ to give a monomeric species as shown in the following equation:

$$[Ir(diop)HI_2]_2 + 2(S)\text{-pronop} \xrightarrow[12h]{CH_2Cl_2} 2[Ir(diop)(S)\text{-pronopHI}]I \quad (3)$$

The ^{1}H NMR (300 MHz, $CDCl_3$; hydride region) showed that the reaction in Eq. (3) gave a complex mixture of isomers. Eighteen hydride multiplets of moderate intensity were observed between δ −15 and −21. The most intense was an apparent triplet of triplets at δ −17.1, indicative of all cis phosphorus donors relative to the hydride. In view of the numerous isomers formed, a number must include isomers with the hydride trans to a phosphorus atom. The larger trans coupling should give rise to two multiplets with smaller couplings for each isomer. The ^{31}P{^{1}H} spectra showed complex regions between δ −5 and −45 (diop); δ 20 and 40, and δ 55 and 92 (pronop).

The elemental analysis corresponded to the proposed formula and the MS-FAB$^+$ spectrum revealed fragments previously observed for [Ir(P–P)(L–L)HI]I complexes [2] (e.g. [Ir(P–P)(L–L)HI], [Ir(P–P)(L–L)], [Ir(P–P)HI], [Ir(L–L)HI], [Ir(P–P)–2H] and [Ir(L–L)–2H]). Significantly, there was an absence of fragments corresponding to dimeric species. Thus, we propose that

the bischelate monomer exists as a mixture which includes the following isomers:



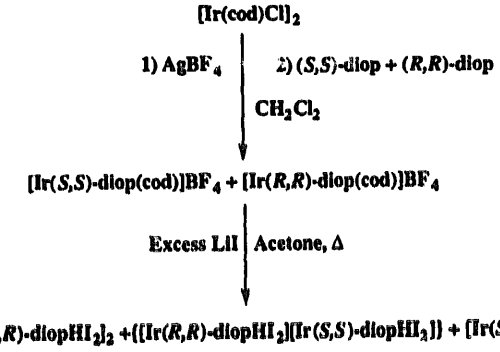
in addition to others formed by permuting the diop phosphorus donors to the position trans to the hydride.

The product mixture prepared from racemic diop has a low catalytic activity in hydrogenation of **1**. Nevertheless, a difference between [Ir(*S,S*)-diop(*S*)-pronopHI]I, **A** (prepared from [Ir(*S,S*)-diopHI$_2$]$_2$ and (*S*)-pronop) and [Ir(*R,R*)-diop(*S*)-pronopHI]I (**B**) was observed under our standard conditions [1]; there was virtually no hydrogenation with **A** (2% after 110h, *ee* low (*S*)), unlike that with **B** (90h, 20%, *ee*: 31% (*R*), 8% after 14h).

Although the bischelate monomer with (*R,R*)-diop exhibits fair enantioselectivity, it has low activity. It appears that precursors other than dimers may be largely responsible for producing the principal active catalyst when bis chelate complexes are present in high concentration. This suggested that (*S*)-pronop acted as an effective poison for [Ir(diop)HI$_2$]$_2$ in certain relative concentration ranges. Equilibration between various isomers and compositions of monomers can be quite slow (vide infra). In order to examine potential chiral poisoning effects with (*S*)-pronop, we have studied two systems which differ in the mode of preparation of the dimers in order to reduce possible complications from time-dependent compositions.

Method I: addition of (*S*)-pronop to the dimer synthesized from equal amounts of (*S,S*) and (*R,R*)-diop:

[1] Standard conditions: $[Ir]_{tot} = 1.57 \times 10^{-2}$ mmol; $[S]/[Ir]_{tot} = 250$; $H_2 = 40$ bar; $T = 30$°C; solvent, THF–CH_2Cl_2 (v/v = 3/1) = 10 ml.



(4)

Method II: poisoning of the catalyst formed by adding equal amounts of [Ir(*S,S*)-diopHI$_2$]$_2$ and [Ir(*R,R*)-diopHI$_2$]$_2$

3. Discussion

3.1. Dimer mixture composition

With Method I, ^{1}H and particularly ^{31}P{^{1}H} NMR spectral evidence suggests that the product consists of approximately equal amounts of heterodimeric and homodimeric species given in Eq. (4). In the ^{1}H NMR a triplet (11 Hz) is expected at $\delta -16.2$ for the major isomer of the homodimer [1]. This triplet is observed at $\delta -16.2$ but it is superimposed on another more complex feature revealing the presence of at least one other complex. (Note that the hydrides are not equivalent in the cisoid heterodimer.)

The ^{31}P {^{1}H} spectrum provides a more clear-cut determination of the species that are formed. The homodimers, [Ir(*S,S*)-diopHI$_2$]$_2$ and [Ir(*R,R*)-diopHI$_2$]$_2$ are characterized by a major isomer with ^{31}P resonances at $\delta -12.5$ and -18.7 (apparent triplets) and a minor isomer at $\delta -11.4$ and -21.5 (complex multiplets with intense outer lines) in $CDCl_3$. These resonances are reduced to 40% of the total intensity in the product from Method I. New multiplets appear at $\delta -12.6$ (20%), $\delta -15.0$ (10%) complex, and $\delta -19.1$ (20%) superimposed on a complex feature at $\delta -19.0$ (10%), presumably representing the heterocisoid and heterotransoid structures. (Note that one expects an ABXY spectrum for the heterotransoid dimer.)

One should note that in the absence of substrate or other donors, equilibration of the dimers can be quite slow. A mixed dimer study with diop and a modified diop dimer had a half-life of 11 h for equilibration [1]. For Method II, it is interesting to observe that after mixing the two preformed homodimers, heterodimer

Table 2
Hydrogenation of 1 catalyzed by [Ir(*R,R*)-diopHI$_2$]$_2$ + [Ir(*S,S*)-diopHI$_2$]$_2$ + {[Ir(*S,S*)-diop)HI$_2$][Ir(*R,R*)-diopHI$_2$]} + (*S*)-pronop[a]

Bis chelate monomer (% in Ir)	Time (h)	Yield (%)	*ee* (%)
0	3	100	0
35	2.75	63	12 (R)
50	12	90	17 (R)
60	17	91	23 (R)
75	20	89	16 (R)
85	32	78	10 (R)
100	200	5	-(R)

[a] Standard conditions: $[Ir]_{tot} = 1.57 \times 10^{-2}$ mmol; $[S]/[Ir]_{tot} = 250$; $H_2 = 40$ bar; $T = 30$ °C; solvent, THF–CH_2Cl_2 (v/v = 3/1) = 10 ml.

was formed very slowly (the distribution found in Method I is not reached even after 24 hours). In the ^{1}H NMR an 11 Hz triplet at $\delta -16.2$ for the major isomer of the homodimer was cleanly observed initially and the multiplets of the heterodimer gradually gained intensity with time. The minor homodimer was not readily observed in these spectra shortly after preparation, which might indicate that it reacted more quickly.

3.2. Enantioselective catalysis

The catalyst was prepared by mixing the dimer and the (*S*)-pronop ligand for about 12 h. Dimer:monomer ratios were determined by ^{1}H (integration in the hydride region) and ^{31}P{^{1}H} NMR. The catalyst was used without any further purification (dissolved in 7.5 ml of THF and 2.5 ml of CH_2Cl_2 with 1.5 ml of 1 (250 eq/Ir), transferred to a stainless steel autoclave and then pressurized at 40 bar). The results from these catalysis studies are summarized in Tables 2 and 3.

The A and B systems discussed earlier and the 0% and 100% entries in the tables provide the controls for considering the poisoning phenomena. Although the *rac*-diop catalyst was efficient (100% conversion in 3 h), it produced 0% *ee* (entry 0% pronop). In contrast, the catalyst which was totally converted to bischelate monomers was inefficient, but also had low enantioselectivity (entry 100% pronop). Intermediate ratios of (*S*)-pronop to dimer can produce catalysts which are reasonably effective and have nearly half the enantioselectivity of the catalyst prepared from pure (*R,R*)-diop. In both cases (Tables 1 and 2), we observed an increase of *ee* upon increasing the monomer fraction, the maximum being obtained for a percentage (in Ir) of the monomer between 50 and 75%. For case II, an idealized interpretation might suggest that the (*S*)-pronop ligand would react preferentially with the (*S,S*)(*S,S*) dimer, increasing the (*R,R*)/(*S,S*) ratio of homo dimers which in turn would allow the (*R,R*) dimer to yield a greater proportion of the (*R*) amine as shown in the reaction of Eq. (5).

$$[\text{Ir}(R,R)\text{-diopHI}_2]_2 + [\text{Ir}(S,S)\text{-diopHI}_2]_2 + (S)\text{-pronop} \rightarrow 1/2[\text{Ir}(R,R)\text{-diopHI}_2]_2 + [\text{Ir}(S,S)\text{-diop}(S)\text{-pronopHI}]\text{I (ideal case)} \quad (5)$$

Moreover, the *ee* appears to be slightly higher for system I (mixture of homo and hetero dimers). This could indicate that, in parallel to the reaction of E$_i$ (5), a preference for (*S*)-pronop to react with the (*S,S*) dimer. Furthermore, when the ligand reacts with the heterodimer, the favored bischelate monomer would be [Ir(*S,S*)-diop(*S*)-pronopHI]I as above, and the remaining unsaturated Ir(*R,R*)-diopHI$_2$ moiety would form the (*R,R*) dimer:

$$\{[\text{Ir}(R,R)\text{-diopHI}_2][\text{Ir}(S,S)\text{-diopHI}_2]\} + (S)\text{-pronop} \rightarrow 1/2[\text{Ir}(R,R)\text{-diopHI}_2]_2 + [\text{Ir}(S,S)\text{-diop}(S)\text{-pronopHI}]\text{I} \quad (6)$$

The observation that the *ee* was slightly higher in case I might imply a kinetic selectivity with (*S*)-pronop which favors reaction with the heterodimer over the homodimer.

It is important to recognize that earlier kinetic studies [1] showed that conversions between dimers in the absence of imine or hydrogen were first-order in dimer with a $t_{1/2} \sim 11$ h. Furthermore, incomplete scrambling of dimers occurred over the course of the catalytic reaction. This is consistent with a small amount of dissociation of dimer to yield an active monomer which turns over many catalytic cycles before reassociating to a monomer (see Scheme 1). Thus, potential kinetic selectivities in dimer breaking by (*S*)-pronop could influence the enantioselectivity.

Regardless, an alternative simple rationale is that whatever dimers are present when equal amounts of (*S,S*)-diop and (*R,R*)-diop are in the mixture, dissociation occurs to give equal amounts of the unsaturated monomers: [(*S,S*)-diopIrHI$_2$] and [(*R,R*)-diopIrHI$_2$].

Table 3
Hydrogenation of 1 catalyzed by [Ir((*S,S*)-diopHI$_2$]$_2$ + [Ir(*R,R*)-diopHI$_2$]$_2$ + (*S*)-pronop[a]

Bis chelate monomer (% in Ir)	Time (h)	Yield (%)	*ee* (%)
0	3	100	0
15	3	81	11 (R)
25	5.5	84	13 (R)
50	8	89	16 (R)
80	20	77	19 (R)
95	48	54	14 (R)
100	300	8	-(R)

[a] Standard conditions: $[Ir]_{tot} = 1.57 \times 10^{-2}$ mmol; $[S]/[Ir]_{tot} = 250$; $H_2 = 40$ bar; $T = 30$ °C; solvent, THF–CH_2Cl_2 (v/v = 3/1) = 10 ml.

The poisoning phenomena then can then be attributed to the selectivity of the deactivation associated with the (*S*)-pronop for binding preferentially to [(*S,S*)-diopIrHI$_2$], which leaves the excess of [(*R,R*)-diopIrHI$_2$] to carry out the cycle of Scheme 1.

$$\begin{aligned} &\text{Ir}(R,R)\text{-diopHI}_2 \\ &\qquad + (S)\text{-pronop} \\ &\text{Ir}(S,S)\text{-diopHI}_2 \\ &\rightarrow 1/2[\text{Ir}(R,R)\text{-diopHI}_2]_2 \\ &\quad + [\text{Ir}(S,S)\text{-diop}(S)\text{-pronopHI}]\text{I} \end{aligned} \qquad (7)$$

This oversimplification does not account for the observed lowering of *ee* at high bischelate monomer:dimer ratios. This result is not expected, because when [dimer] tends to zero, the *ee* should be near 31% (*R*) (obtained with (*R,R*) bischelate monomer catalyst **B**; **A** giving nearly no hydrogenation). Furthermore, the bischelate monomer, considering its weak catalytic activity, should have only a minor influence on the catalytic systems, even if it represents 85% of [Ir]$_{tot}$. A further possibility exists in the *rac*-diop system that does not exist in **A** or **B**, that is disproportionation could occur to yield some bischelate monomer [(*S,S*)-diop(*R,R*)-diopIrHI]I. This could provide a competent catalyst for providing racemic **1**, which would compete and dilute the enantioselective efficiency of **B**.

3.3. Tests for chiral amplification

When there is selective formation of heterodimeric catalysts, the phenomenon of chiral amplification if often observed [5,6]. This is generally the result of lowering the concentration of the minor enantiomeric monomer via deactivation in the formation of a stable heterodimer. Since there is not an especially great preference for heterodimer vs. homodimer formation, a large chiral amplification would not be expected in this diop-Ir system.

There appears to be no significant chiral amplification effect (or perhaps a weak one) in this system. Indeed, the hydrogenation of **1** catalyzed by 1/3[Ir(*R,R*)-diopHI$_2$]$_2$ + 2/3[Ir(*S,S*)-diopHI$_2$]$_2$ gave an *ee* of 19% (*S*). When the catalyst used was synthesized with 1/3(*R,R*)-diop and 2/3(*S,S*)-diop (see Method I above), an *ee* of 15% (*S*) was obtained. If there were no chiral amplification effect, the *ee* should be 18% (*S*)-**1**. When the nonracemic dimer was prepared starting with one equivalent of (*S,S*)-diop and two equivalents of (*R,R*)-diop, the NMR integrations also remained very similar to the statistical distribution, i.e. 55% homodimer and 45% heterodimer (expected: $(R,R)_2$, 44.5%; $(S,S)_2$, 11%; (*R,R*)(*S,S*), 44.5%).

4. Conclusion

The (*S*)-pronop ligand acts as a chiral poison on the systems I and II, especially when the total (*S*)-pronop concentration is approximately half of that of the total iridium concentration. The *rac*-diop system was studied here owing to its ready availability and cost, even though the maximum observable *ee* which could be obtained was 54%. One might anticipate that more exotic and more expensive enantiopure bisphosphines might yield higher *ee*s. An analogous chiral poisoning technique, properly tuned, might allow the use of the less expensive racemic bisphosphine and an inexpensive chiral poison.

5. Experimental section

5.1. The preparation of [Ir(rac-diop)HI$_2$]$_2$

This preparation followed to procedure for the (*S,S*) analogue which was previously reported [1]. Spectral data are discussed in the results section.

5.2. The preparation of [Ir(rac-diop)HI$_2$]$_2$ / (S)-pronop mixtures

The catalyst was prepared by mixing the dimer and the (*S*)-pronop ligand for about 12 h in CH_2Cl_2 at room temperature. The solvent was evaporated and the complex washed with pentane. Dimer/monomer ratios were determined by ^{1}H (integration in the hydride region) and ^{31}P{^{1}H} NMR and the catalyst was used without any further purification (dissolved in 7.5 ml of THF and 2.5 ml of CH_2Cl_2 with 1.5 ml of **1** (250 eq/Ir). (N.B.: as the corresponding peaks of the formed hydrides are complex multiplets the determination of dimer:monomer ratio is approximate).

5.3. The preparation of [Ir(rac-diop)(S)-pronopHI]I

The compound was prepared as a mixture of isomers by mixing the dimer and an equivalent of (*S*)-pronop ligand for about 12 h in $CDCl_3$. The ^{1}H NMR (300 MHz, $CDCl_3$; hydride region) showed that reaction of Eq. (3) gave a complex mixture of isomers. Eighteen hydride multiplets of moderate intensity were observed between δ −15 and −21. The most intense was an apparent triplet of triplets at δ −17.1, indicative of all cis phosphorus donors relative to the hydride. In view of the numerous isomers formed, a number must include isomers with the hydride trans to a phosphorus atom. The ^{31}P{^{1}H} spectra showed complex regions between δ −5 and −45 (diop), δ 20 and 40 (pronop, NP), and δ 55 and 92 (pronop OP).

The MS-FAB$^+$ spectrum reveals fragments previously observed for [Ir(P–P)(L–L)HI]I complexes [2] (e.g. [Ir(P–P)(L–L)HI], [Ir(P–P)(L–L)], [Ir(P–P)HI], [Ir(L–L)HI], [Ir(P–P)–2H] and [Ir(L–L)–2H]). Significantly, there was an absence of fragments corresponding to dimeric species.

5.4. Preparation of [Ir(S,)-diop(S)-pronopHI]I

The compound was prepared as a mixture of isomers by mixing the dimer and an equivalent of (*S*)-pronop ligand for about 12 h in CH_2Cl_2 at room temperature. The solvent was evaporated and the complex washed with pentane. Anal. Found: C, 49.78; H, 4.50; N, 1.03. $C_{60}H_{62}I_2IrNO_3P_4 \cdot 2H_2O$. Calc.: C, 49.66; H, 4.58; N, 0.97%. MS-FAB$^+$ (*m/z* species, intensity): 1304.2 ([M + O]$^+$; 18%); 1288.2 ([M]$^+$; 12%); 1104.1 ([M − PPh_2 + H]$^+$; 73%); 1075.1 ([M − CH_2OPPh_2]$^+$; 22%); 945.2 ([Ir(diop)I_2]$^+$; 10%); 818.8 ([M − pronop]$^+$; 31%); 789.9 ([M − diop]$^+$; 100%). FT-IR (KBr, cm^{-1}): 2243 (w; ν_{Ir-H}).

5.5. Catalysis studies

These results are summarized in Tables 1 and 2. Yields were determined by GC. Enantiomeric purities were determined by polarimetry $[\alpha]_D = +23.3$ for (*S*)-**1** (20 °C, $c = 3$, hexane) [7,8].

In a typical reaction [Ir(*rac*-diop)HI_2]$_2$ (30 mg; 1.57×10^{-2} mmol) was dissolved in 10 ml THF–CH_2Cl_2 (v/v = 3/1). DMA, **1**, (0.4 g, 2 mmol), as well as an appropriate amount of (*S*)-pronop (see Tables 2 and 3), was then added to the solution and the homogeneous mixture transferred to an autoclave thermostated at 30 °C. The void volume was degassed three times with hydrogen (25 bar) and then the pressure was raised to 40 bar. At the end of the reaction the pressure was released and the solution transferred into a Schlenk vessel and the solvent evaporated. The amine was recovered quantitatively via vacuum distillation. A portion of the amine was further purified by liquid chromatography (alumina, hexane–EtOAc 6:1)

Acknowledgements

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