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Application of Monodentate Secondary Phosphine Oxides, a New Class of Chiral Ligands, in Ir(I)-Catalyzed Asymmetric Imine Hydrogenation

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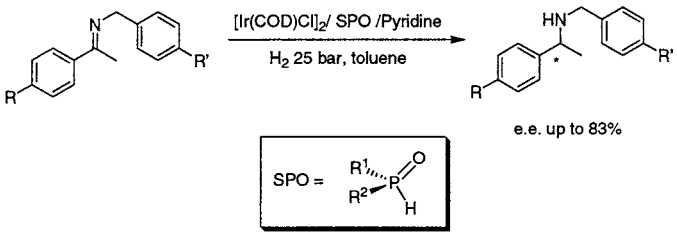
ABSTRACT



Secondary phosphine oxides were prepared from R^1PCl_2 and R^2MgBr, followed by hydrolysis. They were obtained in an enantiopure form by preparative chiral HPLC. These new monodentate ligands were tested in the iridium-catalyzed hydrogenation of imines at 25 bar. Enantioselectivities up to 76% were obtained at L/Ir = 2. Addition of pyridine (Pyr/Ir = 1:2) raised the ee to 83%. Using pyridine as an additive allowed reduction of the L/Ir ratio to 1 without reduction of ee.

Asymmetric catalysis is in principle the most desirable method for producing enantiopure chemicals.[1] This is due to the high atom economy as compared to methods based on the resolution of racemates. Asymmetric hydrogenation, based on the use of enantiopure transition metal complexes as catalysts, has been particularly prevalent in the past 30 years, and many successful examples are known.[2] However, recent analyses show that the application of asymmetric hydrogenation for the production of fine chemicals is limited.[3,4] Two major factors that hamper its use are the cost and the availability of the catalysts, in particular of the ligand that is often prepared in a tedious multistep synthesis. For this reason, we have embarked on a program aimed at the development of enantiopure ligands that are easily prepared

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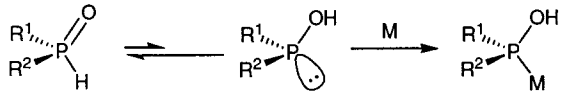
in 1−3 synthetic steps.[5] A recent breakthrough has been the development of monodentate phosphoramidites for the highly enantioselective hydrogenation of α- and β-dehydroamino acids[6] and enamides.[7] Other groups have developed monodentate phosphonites,[8] phosphites,[9] and phosphines[10] that also perform well in asymmetric hydrogenation.

An area that remains underdeveloped is the asymmetric hydrogenation of imines.[11] Although catalysts are known that give rise to high enantioselectivities in the hydrogenation of acetophenone-based imines such as rhodium/monosulfonated bdpp[12] and of cyclic imines using *ansa*-titanocene,[13] the rate of these is still too low for industrial use. A very fast iridium catalyst was developed by Blaser et al. for the asymmetric hydrogenation of an intermediate for the herbicide (*S*)-Metolachlor.[14] However, the enantioselectivity did not exceed 80%. Nevertheless, this process is used industrially. Enantioselective transfer hydrogenation of imines has been developed recently and seems to have great potential.[15]

In this paper, we report our results on the application of secondary phosphine oxides,[16,17] an entirely new class of enantiopure monodentate ligands, in the iridium-catalyzed asymmetric hydrogenation of acetophenone-based imines.

Secondary Phosphine Oxides (SPOs). In solution, SPOs exist in equilibrium between pentavalent (phosphine oxide form) and trivalent (phosphinite form) tautomeric structures (Scheme 1).[17] Although at room temperature the phosphine oxide form is the more stable one,[18] it is the phosphinite form that coordinates to the transition metal.[19]

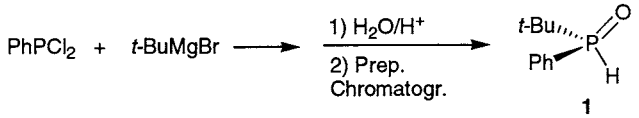
Scheme 1. Tautomeric Forms of SPOs

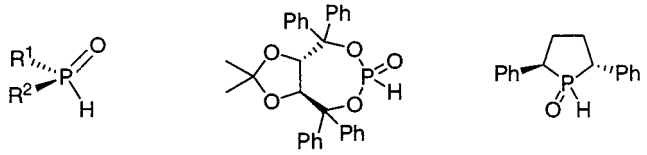


SPOs are easily prepared in a two-step one-pot procedure from readily available starting materials[16−20] and are thus highly suited to a modular or a combinatorial approach. They are air and moisture stable. Nonchiral or racemic SPOs have been used as ligands in Pt-catalyzed hydroformylation,[21] in Pt-catalyzed hydrolysis[22] and amination[23] of nitriles, and in Pd-catalyzed aromatic substitution reactions.[24] Enantiopure SPOs have been obtained by classical resolution using (*S*)-mandelic acid[18,25] or a three-step resolution procedure developed by Chan.[26a] They do not racemize easily.[17] It is thus very surprising that they have been used only as intermediates in the preparation of chiral phosphines and bisphosphines.[26] We have not been able to find any reports on their application in asymmetric catalysis.

We have prepared a range of monodentate SPOs (**1**−**7**) by reaction of R^2MgBr with R^1PCl_2 (reversed addition) followed by hydrolysis (Scheme 2). Ligand **8** was prepared from Taddol by treatment with PCl_3 followed by hydrolysis. Ligand **9** was prepared following the procedure of Fiaud et al. (Figure 1).[10a]

Scheme 2. Synthesis of *tert*-Butyl-phenylphosphine Oxide





1 R^1= *t*-Bu, R^2=Ph
2 R^1= *i*-Pr, R^2=Ph
3 R^1= *t*-Bu, R^2=2-Naphthyl
4 R^1= *t*-Bu, R^2=2-MeOPhenyl
5 R^1= *t*-Bu, R^2=3,5-di-MePhenyl
6 R^1= *t*-Bu, R^2=2,4,6-tri-MePhenyl
7 R^1= Ph, R^2=2-Naphthyl

8 **9**

Figure 1. Secondary phosphine oxides.

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SPO **1** was conveniently resolved using preparative chiral HPLC. As the separation between the two peaks was very large (4.3 min), 100 mg could be separated per run. SPOs **2**−**7** and **9** were all separated in the same manner, although none of these ligands afforded the same spectacular separation achieved with **1**.

Iridium/SPO-Catalyzed Imine Hydrogenation. It is conceivable that the acidic proton of SPOs has an accelerating effect upon the transition metal-catalyzed hydrogenation of imines.[27] We thus tested the hydrogenation of a range of acetophenone-based imines and *N*-diphenylphosphinyl-imine **15**[28] (Figure 2) at 25 bar at room temperature in CH_2Cl_2.

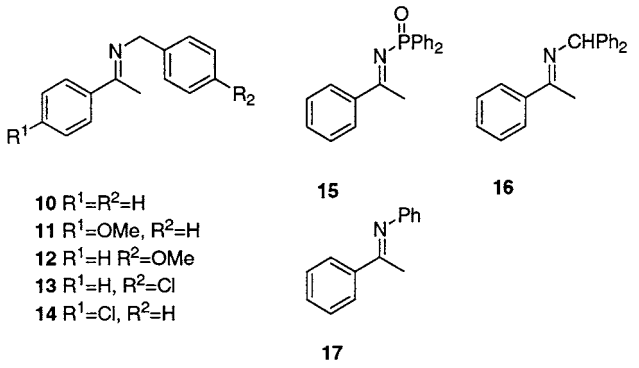
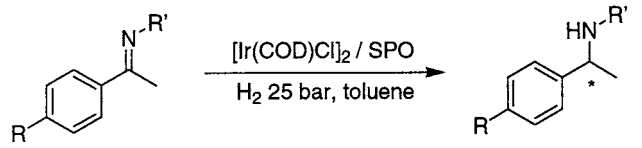


Figure 2. Imines.

Initial tests with $[Ir(COD)Cl]_2$, $[Rh(COD)Cl]_2$, $[Ir(COD)_2]BF_4$, and $[Rh(COD)_2]BF_4$ showed that use of the neutral chloride-containing iridium catalyst precursor gave both the highest rates and the highest enantioselectivity. High rates were obtained with SPO/Ir ratios of 1, but the enantioselectivity in the hydrogenation of **10** was only 10% (Table 1, entry 1). The enantioselectivity could be increased by raising the SPO/Ir ratio to 2, though this reduced the rate of the reaction markedly. Next, a range of solvents (Et_2O, EtOAc, THF, MeOH, *i*PrOH, benzene, α,α,α-trifluorotoluene, CH_3CN, and *c*-hexane) were tested using $[Ir(COD)Cl]_2$/**1** in the hydrogenation of **10**. From these tests, toluene and α,α,α-trifluorotoluene emerged as the best solvents (entries 3 and 5). Changes in the ligand structure did not lead to any improvement in enantioselectivity (entries 6−9). Of the other imines tested (entries 9−11), only the phosphinylated imine **15** could be hydrogenated with reasonable enantioselectivity. The *N*-phenyl imine **17** always gave racemic product under a variety of conditions. A rather surprising feature of these catalysts is their ability to hydrogenate imines at 1 bar H_2, although at this pressure the rate becomes very low (entry 12).

Not satisfied with these results, we decided to test the effects of additives such as I_2,[29] *n*-Bu_4NI,[30] K_2CO_3, *t*-BuOK, Na_2CO_3, primary amines,[31] phthalimide,[32] $AgCOOCF_3$,[33] and

Table 1. Iridium/SPO-Catalyzed Hydrogenation of Imines[a]



entry	imine	ligand	*t* (h)	conversion (%)[b]	ee (%)[c]
1[d]	**10**	**1** (*R*)	0.8	100	10 (*S*)
2[e]	**10**	**1** (*R*)	24	75	45 (*S*)
3	**10**	**1** (*R*)	51	>95	69 (*S*)
4[f]	**10**	**1** (*R*)	72	100	4 (*S*)
5[g]	**10**	**1** (*R*)	114	89	70 (*S*)
6	**10**	**6**	24	100	7
7	**10**	**7**	24	100	2
8	**10**	**8**	48	>95	9
9	**11**	**9**	24	>95	51
10[h]	**15**	**1** (*R*)	24	100	70
11	**17**	**1** (*R*)	24	100	0
12[i]	**10**	**1** (*R*)	168	100	76 (*S*)

[a] General conditions: $[Ir(COD)Cl]_2$/SPO/imine = 2.5:10:100, 25 bar H_2, toluene, room temperature. [b] Conversion was determined by ^1H NMR ($CDCl_3$). [c] Ee was determined by HPLC (chiralpak AD or OD, heptane/2-propanol = 95/5 or 90/10) on the *N*-acetyl derivatives. Configuration is unknown when none is shown. [d] CH_2Cl_2 as solvent, Ir/**1** =1:1. [e] CH_2Cl_2 as solvent. [f] $[Ir(COD)_2]BF_4$ as a precursor. [g] $CF_3C_6H_5$ as a solvent. [h] Temperature = 40 °C. [i] H_2 (1 bar; balloon).

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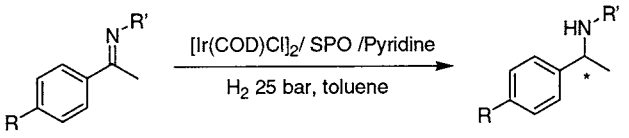
Table 2. Ir/SPO/Pyridine-Catalyzed Hydrogenation of Imines[a]



entry	imine	ligand	*t* (h)	conversion (%)[b]	ee (%)[c]
1	**10**	**1** (*R*)	24	100	78 (*S*)
2[d]	**10**	**1** (*R*)	24	>98	78 (*S*)
3	**11**	**1** (*R*)	24	100	**80**
4[e]	**10**	**1** (*R*)	120	75	**82** (*S*)
5[e]	**11**	**1** (*R*)	120	80	**83**
6	**12**	**1** (*R*)	24	85	76
7	**13**	**1** (*R*)	24	75	77
8	**14**	**3**	17	76	62
9	**15**	**1** (*R*)	139	85	12
10[f]	**16**	**1** (*R*)	48	50	57
11[f]	**10**	**1** (*R*)	48	100	73 (*S*)
12[g]	**10**	**1** (*R*)	24	30	68 (*S*)
13[h]	**11**	**1** (*R*)	72	100	76
14[i]	**11**	**1** (*R*)	10	100	73
15	**11**	**2**	17	>95	33
16	**11**	**3**	17	>95	68
17	**11**	**4**	17	60	70
18	**10**	**5**	17	>95	66 (*S*)
19	**10**	**6**	24	100	7 (*S*)
20	**10**	**7**	24	100	4 (*S*)
21[j]	**10**	**8**	48	100	1 (*S*)
22	**10**	**9**	24	>95	23 (*S*)

[a] General conditions:: $[Ir(COD)Cl]_2$/SPO/pyridine/imine = 2.5:10:10:100, 25 bar H_2, toluene, room temperature. [b] Conversion was determined by ^1H NMR ($CDCl_3$). [c] Ee determination: see Table 1. [d] Ir/SPO = 1:1. [e] Temperature = 0 °C. [f] H_2 (70 bar). [g] Cyclohexane as a solvent. [h] Benzene as a solvent. [i] Temperature 40 °C. [j] $[Ir(COD)_2]BF_4$ as a precusor.

$AgBF_4$. All of these were found to have a negative effect on the Ir/SPO-catalyzed imine hydrogenations, however. When I_2 was used, acetophenone was found as the only decomposition product.

Inspired by Crabtree's catalyst, $[Ir(COD)(PCy_3)Py]PF_6$, which shows high activity in alkene hydrogenation,[34] we decided to test the effectiveness of pyridine as an additive. Using 2 equiv of pyridine with respect to iridium, the hydrogenation becomes faster and the ee increases to 78% with full conversion after 24 h (Table 2, entry 1). Surprisingly, when 1 equiv of ligand was used in combination with 2 equiv of pyridine, the reaction worked equally well (entry 2). This seems to imply that pyridine exerts its effect as a ligand. When larger amounts of pyridine (5 or 10 equiv) were used, the hydrogenation proceeded slower with a small drop in ee. Other pyridine derivatives performed somewhat more poorly. A slight improvement in ee could be obtained by lowering the temperature to 0 °C, though at the expense of rate (entries 4, 5). Substituted *N*-benzyl acetophenone imines could all be hydrogenated with medium-high enantioselectivity (entries 3, 5−8). However, addition of pyridine did not improve the hydrogenation of the phosphinylated imine **15** (entry 9) but led to the opposite enantiomer instead. The more hindered *N*-benzhydryl imine **16** could only be hydrogenated at higher pressure (entry 10). The use of higher pressure did not have an appreciable influence on the rate of hydrogenation of **10**, although the ee was somewhat lower (entry 11). Use of ligands other than **1** did not lead to any improvements (entries 15−22).

In conclusion, we have developed a new class of monodentate ligands, enantiopure secondary phosphine oxides that show good performance in the iridium-catalyzed asymmetric hydrogenation of imines. The enantioselectivities obtained are comparable to the best results obtained so far in iridium-catalyzed hydrogenation of similar imines.[35]

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Supporting Information Available: Experimental details and spectroscopic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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