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Phosphines versus phosphinites as ligands in the rhodium catalyzed asymmetric hydrogenation of imines: a systematic study

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Abstract

The asymmetric hydrogenation of *N*-(1-phenylethylidene)benzylamine with a range of rhodium(I)-diphosphine and diphosphinite catalysts is studied. The reaction is strongly sensitive to the size of the metal chelate. Complexes based on five- and six-membered chelates or electron-rich alkylphosphines gave poor or moderate conversions. The reactivity of diphosphine catalysts could be increased by the addition of *p*-toluenesulfonic acid. Unexpectedly, Rh-complexes based on chiral diphosphinites and a diphosphite also rapidly converted the substrate to the desired amine. Highest efficiency was observed with a rhodium(I) complex with (*R*,*R*)-1,2-cyclohexanol-bisdiphenylphosphinite [(*R*,*R*)-bdpch] as chiral ligand. Without any additive complete hydrogenation of the imine was achieved within 5 h. The product was produced in an enantioselectivity of 71%.

1. Introduction

In contrast to the high enantioselectivities reported in the hydrogenation of olefins and ketones, only limited success has been achieved in the catalytic asymmetric hydrogenation of prochiral imines[1] although the reaction is of considerable industrial interest.[2] Up to now a range of Rh-, Ir- and Ru-complexes have been investigated in detail.[3,4] As ligands chiral diphosphines were utilized preferentially. Interestingly, most of those phosphines which are reputed to induce high enantioselectivity in the Rh(I) or Ru(II) catalyzed hydrogenation of other prochiral substrates failed or gave poor results in this particular reaction. In some instances Ir-catalysts were found to be superior.[3,5] Unfortunately, the

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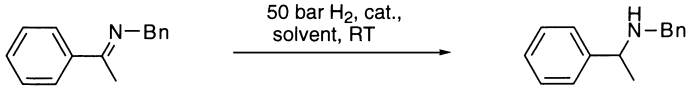
presence of additives like amines,[6] imides[7] or iodide[5d] in the solution is frequently required to avoid deactivation of the catalyst and to achieve satisfactory yields and/or elevated degrees of enantioselectivity. As an alternative the reduction of *N*-acylhydrazones was suggested.[8] However, this approach requires additional reaction steps and therefore a straightfoward method is highly desired.

It is interesting to note that besides diphosphines other chelating *P*-ligands were rarely employed. Only recently has the application of a tridentate diphosphinite been reported.[9] Amidophosphine–phosphinites were suggested as ligands for the hydrogenation of cyclic iminium salts.[10]

Herein, we report on a systematic study on the asymmetric hydrogenation of imines based on Rh-diphosphine, diphosphinite and diphosphite catalysts under varying conditions. As a test substrate *N*-(1-phenylethylidene)benzylamine was chosen (Scheme 1).



Scheme 1.

2. Results and discussion

2.1. Nonasymmetric hydrogenation

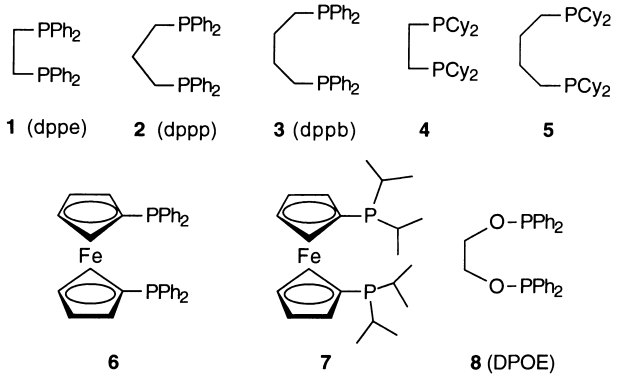
In order to identify main requisites and conditions for the achievement of high conversion in the hydrogenation of the imine, first achiral precatalysts with chelating diphosphines and diphosphinites, respectively, were tested. The reaction was carried out at an initial hydrogen pressure of ca. 50 bar in methanol at room temperature. As ligands 1,2-bis(diphenylphosphino)ethane (**1**=dppe), 1,3-bis(diphenylphosphino)propane (**2**=dppp), 1,4-bis(diphenylphosphino)butane (**3**=dppb), the corresponding cyclohexyl-substituted diphosphines **4** and **5**, the 1,1′-ferrocenyldiphosphines $(Ph_2PCp)_2Fe$ **6** and $(i\text{-}Pr_2PCp)_2Fe$ **7**,[11] respectively, and 1,2-ethandiol-bis-diphenylphosphinite (**8**=DPOE) were applied. The results are summarized in Table 1.

As clearly illustrated five- and six-membered Rh(I)-chelates afforded the desired amine in poor or modest yield (runs 1, 3). In contrast the more flexible seven-membered Rh(I)-chelate based on dppb as ligand converted the imine within 2 h into the desired product (run 4). Surprisingly, catalysts based on dialkylphosphines had inferior performance compared to those with diarylphosphines as ligands (runs 5, 10). It is remarkable that the addition of TsOH increased the rate of the reaction (runs 2, 7). Obviously, the hydrogenation of imines is not subject to the same effects as the reduction of ketones, where electron-rich phosphine ligands have been shown to be advantageous.[12] This conclusion is supported by the result obtained with the Rh(I)-complex of an electron-deficient ligand, such as the diphosphinite DPOE (run 11). This catalyst hydrogenated the imine rather effectively.

2.2. Asymmetric hydrogenation

Inspired by the results listed in Table 1, we next turned our attention to the asymmetric hydrogenation of *N*-(1-phenylethylidene)benzylamine with 7-membered Rh(I)-chelates of chiral bis-diphenylphosphines such as (*S*,*S*)-bppm[13] and (*R*,*R*)-DIOP[14] (Table 2, runs 1, 3).[15] Both catalysts afforded the amine in only moderate yields.[16] The enantiomeric excess observed was low. Interestingly the application of the neutral precatalysts significantly increased the efficiency (runs 2, 4).

Table 1
Hydrogenation of *N*-(1-phenylethylidene)benzylamine with achiral rhodium catalysts[a]



Run	Precatalyst	Additive	Time	Conversion (%)
1	[Rh(**1**)NBD]BF_4/[Rh(**1**)$_2$]BF_4[b]	-	20	16
2	[Rh(**1**)NBD]BF_4/[Rh(**1**)$_2$]BF_4[b]	TsOH·H_2O[c]	20	84
3	[Rh(**2**)COD]BF_4	-	20	86
4	[Rh(**3**)COD]BF_4	-	2	98
5	[Rh(**4**)COD]BF_4 (*in situ*)	-	20	4
6	[Rh(**5**)COD]BF_4	-	20	18
7	[Rh(**5**)COD]BF_4	TsOH·H_2O[c]	20	45
8	[Rh(**6**)COD]BF_4 (*in situ*)	-	7	32
9	[Rh(**6**)COD]BF_4 (*in situ*)	-	20	35
10	[Rh(**7**)COD]BF_4 (*in situ*)	-	20	3
11	[Rh(**8**)COD]BF_4	-	20	91

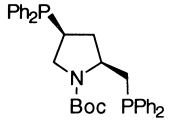
[a] Conditions of the hydrogenation: 5 mmol of substrate, 0.01 mmol of catalyst, 10 ml of MeOH, initial pressure of H_2: 50±2 bar, room temperature. [b] 1/1 mixture; [c] molar ratio TsOH·H_2O : Rh = 100:1.

By modifications of the structure of DIOP the catalytic properties of the parent catalyst were significantly changed. Thus, the introduction of a remote HO-group in the backbone of the DIOP-moiety (ligands **11** and **12**)[17] decreased the ee (runs 5, 6). It is noteworthy that the HO-groups in the catalyst with ligand **13** did not seriously diminish the yield (run 7) as observed in the hydrogenation of bidentate olefins.[18] A superior reaction rate was observed when the benzoate group in ligand **14** (run 8) was replaced by the sulfonatobenzoate moiety (ligand **15**, run 9).[19] This result corresponds well to observations made in the aqueous two phase hydrogenation of imines with Rh(I)(mono-sulfonated bdpp) catalysts[20] and to results observed in the asymmetric hydrogenation of prochiral olefins with catalysts bearing chiral phosphines with low degrees of sulfonation.[19b]

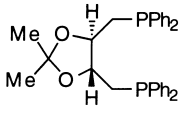
As seen in Table 2 'active' functional groups, e.g. the sulfonate group in the backbone of the catalyst, can significantly improve the performance of the catalyst. Therefore, we investigated the influence of different additives on the reaction. In Table 3 the effects of acids and bases upon the imine hydrogenation with (*R*,*R*)-DIOP-complexes are summarized.

In comparison to the blank experiment (run 1) by addition of increasing amounts of *p*-toluenesulfonic acid the degree of the conversion was improved (runs 2–5). Simultaneously, the formation of the (*S*)-product was favored. This effect is likely to be due to the coordination of the tosylate anion (formed by reaction of TsOH with the imine) on the rhodium center. Proof for this hypothesis came from run 6, where a decrease of the ee was observed after replacement of the weakly coordinated BF_4^- by TsO^- in

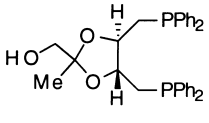
Table 2
Hydrogenation with Rh(I) catalysts based on chiral diphosphines as ligands[a]



9 [(*S*,*S*)-bppm]



10 [(*R*,*R*)-DIOP]



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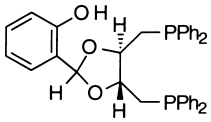

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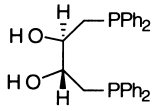

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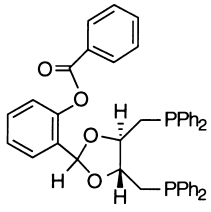

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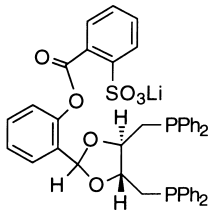

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Run	Precatalyst	Conversion[b] (%)	ee (%)
1	[Rh(**9**)COD]BF_4[c]	36	22 (*R*)
2	[Rh(**9**)Cl]$_2$ (*in situ*)[d]	60	27 (*R*)
3	[Rh(**10**)COD]BF_4[c]	68	19 (*R*)
4	[Rh(**10**)Cl]$_2$ (*in situ*)[d]	90	20 (*R*)
5	[Rh(**11**)COD]BF_4	68	8 (*R*)
6	[Rh(**12**)COD]BF_4	84	6 (*R*)
7	[Rh(**13**)COD]BF_4	52	15 (*R*)
8	[Rh(**14**)COD]BF_4	73	2 (*S*)
9	[Rh(**15**)COD]BF_4	>99	2 (*S*)

[a] Conditions of hydrogenation see Table 1; [b] conversion measured after 20 h; [c] when the precatalyst was prepared in situ significant loss of enantioselectivity resulted; [d] molar ratio substrate:metal = 250:1.

Table 3
Influence of additives on the efficiency of different catalysts with **10** [(*R*,*R*)-DIOP] as ligand[a]

Run	Precatalyst	Additive (Ad/Rh)[b]	Conversion (%)	ee (%)
1	[Rh(**10**)COD]BF_4	-	68	19 (*R*)
2	[Rh(**10**)COD]BF_4	TsOH·H_2O (5:1)	91	2 (*R*)
3	[Rh(**10**)COD]BF_4	TsOH·H_2O (11:1)	91	0
4	[Rh(**10**)COD]BF_4	TsOH·H_2O (20:1)	98	2 (*S*)
5	[Rh(**10**)COD]BF_4	TsOH·H_2O (99:1)	94	18 (*S*)
6	[Rh(**10**)COD]TsO	-	66	9 (*R*)
7	[Rh(**10**)COD]TsO	TsOH·H_2O (20:1)	79	7 (*S*)
8	[Rh(**10**)COD]BF_4	Bu_4NI (1.1:1)	39	2 (*R*)
9	[Rh(**10**)Cl]$_2$ (*in situ*)[d]	Bu_4NI (0.96:1)	46	0
10	[Rh(**10**)COD]BF_4	*t*-BuOK (12:1)	37	41 (*R*)
11	[Rh(**10**)COD]BF_4	*t*-BuOK (100:1)	42	19 (*R*)

[a] Conditions of hydrogenation see Table 1; [b] molar ratio.

the precatalyst. The addition of TsOH increased the tendency for the formation of the (*S*)-product (run 7). It is noteworthy that the presence of iodide or *t*-BuOK diminished the rate of the hydrogenation (runs 8–11). In the presence of a 12-fold amount of the alcoholate 41% ee of the (*R*)-product was obtained (run 10).

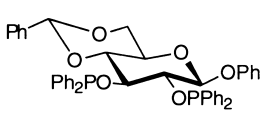
As described above, *P*-ligands like diphosphinites with diminished *p*-accepting properties can advantageously support the hydrogenation of our test imine. Thus, as listed in Table 4, by application of Rh(I)-complexes of phosphinites like Ph-β-glup[21] **16**, K_{β^+}−OH[22] **17** or Propraphos **18**[23] full conversion of the substrate was achieved, although the enantioselectivities obtained were disappointingly low (runs 1–3). Noteworthy is the high conversion observed with the catalyst based on the diphosphite **19**[24] (run 4). The best result afforded the cationic BF_4^- complex with (*R*,*R*)-bdpch[25] **20** as ligand (run 5). The desired amine was obtained in 71% ee. Inferior results were observed with the corresponding Rh(acac) complex (run 6) and by application of the neutral chloro-precatalyst (run 7). As illustrated in Table 3, additives in the reaction mixture may have a beneficial effect on the asymmetric hydrogenation of *N*-(1-phenylethylidene)benzylamine with Rh-diphosphine catalyst. In contrast to these observations the Rh-bdpch catalyst showed a different behavior. Thus, the addition of an excess of TsOH diminished the rate of the hydrogenation (runs 8–10). However, the ee was not affected significantly. It is noteworthy that the reaction is quite insensitive to an excess of benzyl amine (run 11). On the contrary, the addition of *t*-BuOK or Bu_4NI diminished the overall efficiency of the catalyst (runs 12, 13). The decelerating effect was more pronounced with the cationic than with the neutral complex (run 14). In nonpolar solvents like toluene or methylene chloride the reaction was also less efficient (runs 15–17).

It is known that ees obtained in the asymmetric hydrogenation of *N*-(1-phenylethylidene)benzylamine are sometimes poorly reproducible.[26] We have faced the same problem with two freshly prepared batches of the substrate. Thus, with [Rh(**20**)COD]BF_4 as the precatalyst instead of 71% ee only 50 and 63% ees were observed. Redistillation of the solvent MeOH, repeated recrystallizations of the substrate and addition of water or acetophenone (fivefold molar excess to the precatalyst) did not improve the ee. With these two batches the presence of $BnNH_2$ gave 64 and 72% ee, respectively. Finally, we found that distillation of the substrate in vacuo was important to reproduce the enantioselectivity of 71% given in Table 4. It is noteworthy that in the hydrogenation of the pretreated substrate the addition of $BnNH_2$ had no effect on the enantioselectivity. The ee value of the product in the range of 70–73% was reproducible and did not depend on the pressure (50 bar and 100 bar), the temperature (15 and 25°C) and the concentration of the catalyst (1.0 and 2.5 mmol/L) as well as on the concentration of the substrate (0.5 and 0.1 mol/L). It was also found that at a molar substrate:[Rh(bdpch)COD]BF_4 ratio of 500:1 more than 98% of the substrate was converted into the product within 5 h at room temperature. The [Rh(**20**)NBD]BF_4 complex was as efficient as the [Rh(**20**)COD]BF_4 precatalyst.

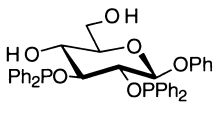
3. Conclusion

Several achiral and chiral diphosphine and diphosphinite Rh(I) complexes have been tested in the hydrogenation of *N*-(1-phenylethylidene)benzylamine. The reaction with diphosphines as ligand was strongly sensitive to the size of the chelate ring formed with the metal and the substituents on the phosphorus. In the presence of additives like TsOH the rate of the reaction could be increased. Surprisingly, rhodium complexes of chiral diphosphinites showed an excellent reactivity. This is in contrast to results obtained with the achiral ligands, where a 1,4-diphosphine catalyst was revealed to be more active than its 1,2-diphosphinite counterpart. With a cationic Rh(I)–(*R*,*R*)-bdpch complex up to 71% ee was achieved. It is noteworthy that this result was obtained without any additive und under rather smooth conditions. Our

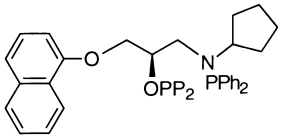
Table 4
Hydrogenation with chiral Rh(I) catalysts based on electron poor *P*-ligands **16**–**20**:[a]



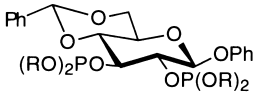
16 (Ph-ß-glup)



17 (K_{β}^{+}-OH)



18 (Propraphos)



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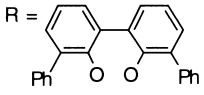

20 [(*R*,*R*)-bdpch]

Run	Precatalyst	Additive (Additiv:Rh)[b]	Conversion (%)	ee (%)
1	[Rh(**16**)COD]BF_4	-	97	28 (*S*)
2	[Rh(**17**)COD]BF_4	-	98	28 (*S*)
3	[Rh(**18**)COD]BF_4	-	99	57 (*S*)
4	[Rh(**19**)COD]BF_4 (*in situ*)	-	97	1 (*S*)
5	[Rh(**20**)COD]BF_4	-	> 99	71 (*R*)
6	[Rh(**20**)(acac)] (*in situ*)	-	15	22 (*R*)
7	[Rh(**20**)Cl]$_2$ (*in situ*)	-	> 99	57 (*R*)
8	[Rh(**20**)COD]BF_4	TsOH· H_2O (5.1:1)	> 99	70 (*R*)
9	[Rh(**20**)COD]BF_4	TsOH· H_2O (10.2:1)	99	67 (*R*)
10	[Rh(**20**)COD]BF_4	TsOH· H_2O (104:1)	60	71 (*R*)
11	[Rh(**20**)COD]BF_4	$BnNH_2$ (5:1)	> 99	72 (*R*)
12	[Rh(**20**)COD]BF_4	*t*-BuOK (10:1)	49	6 (*R*)
13	[Rh(**20**)COD]BF_4	Bu_4NI (1.3:1)	11	45 (*R*)
14	[Rh(**20**)Cl]$_2$ (*in situ*)	Bu_4NI (1.1:1)	54	4 (*S*)
15	[Rh(**20**)COD]BF_4	solvent: MePh	> 99	42 (*R*)
16	[Rh(**20**)COD]BF_4	solvent: MePh/MeOH (1/1)	98	65 (*R*)
17	[Rh(**20**)COD]BF_4	solvent: CH_2Cl_2	15	50 (*R*)

[a] Conditions of hydrogenation see Table 1; [b] molar ratio.

preliminary results make diphosphinite Rh(I)-complexes[27] attractive catalysts for further investigations with the potiential for additional synthetic power. Currently, work is in progress to test other imines in this reaction.

Acknowledgements

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27. Corresponding cationic Ir(I)-complexes with DIOP or bdpch as a ligand gave inferior results. [Ir(DIOP)COD]BF_4: 3% conversion, % ee not analyzed; $[Ir(DIOP)Cl]_2$ (in situ): 63% conversion, 3% ee (S); [Ir(bdpch)COD]BF_4: 4% conversion, % ee not analyzed; $[Ir(bdpch)Cl]_2$ (in situ): 57% conversion, 4% ee (S).