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Enantioselective Rhodium Catalyzed Hydroboration of Olefins Using Chiral Bis(aminophosphine) Ligands

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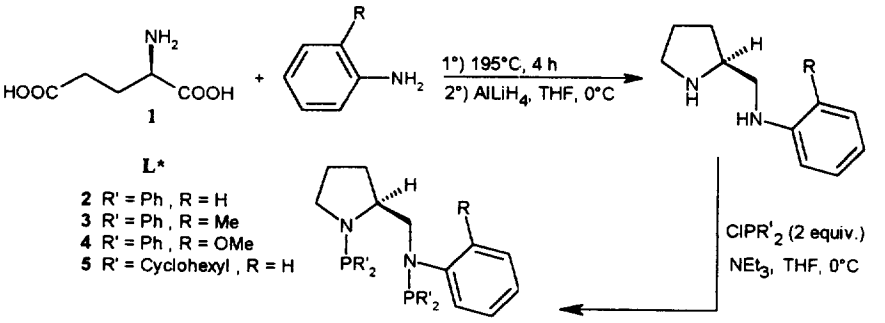
Abstract : The synthesis of new chiral bis(aminophosphine) ligands **1-5** was achieved and assessed in the enantioselective rhodium catalyzed hydroboration of various olefins with catecholborane. Enantioselectivities up to 77% were obtained.

In the last thirty years, the enantioselective hydroboration of olefins has appeared as an important challenge[1]. Indeed, since 1961, Brown *et al.* have extensively developped this reaction using a stoichiometric amount of diisopinocampheylborane as hydroboration reagent[2]. Enantiomeric excesses (ee) up to 98% have been observed in the case of symmetrical olefins[3]. Nevertheless, in the case of di- or trisubstituted olefins, a decrease of enantioselectivity has been noticed. In 1985, a catalytic hydroboration reaction of olefins by catecholborane has been described by Mannig *et al.* using Wilkinson's catalyst[4]. The catalytic enantioselective hydroboration of olefins using a chiral rhodium complex as catalyst has been nearly simultaneously introduced by Evans[5] and Burgess[6] in 1988. Thus, enantioselectivities varying from 16 to 96% were obtained using (*R*)-BINAP ligand. In this paper, we report the synthesis of new chiral bis(aminophosphines) ligands and their successful use in asymmetric rhodium catalyzed hydroboration of olefins by catecholborane.

The synthesis of chiral bis(aminophosphine) ligands **1-4** was achieved from L-glutamic acid following the general procedure outlined in Scheme 1[7].



Scheme 1

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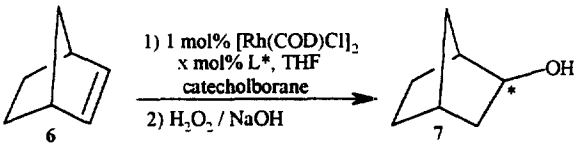
PII: S0040-4039(99)00538-9

Compounds **2-5** were obtained in 31-73% yield as solids, stable to air and moisture. Catalyst precursors were prepared *in situ* by reaction of $[Rh(COD)Cl]_2$ with these ligands, giving the corresponding complexes which have been successfully used in the asymmetric rhodium catalyzed hydroboration of norbornene **6** by catecholborane. The results are summarized in Table 1.



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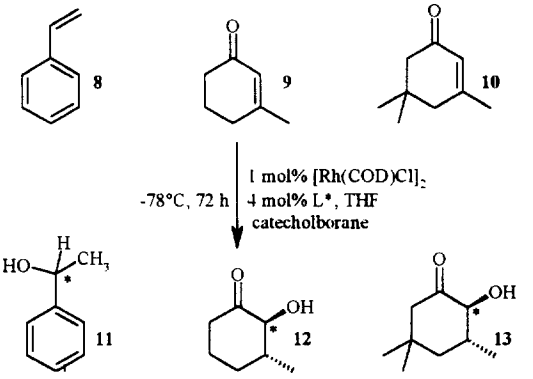
Entry[a]	L*	T (°C)	Reaction time(h)	Yield (%)[b]	Ee (%)[c]
1[d]	**2**	25	24	58	12
2[d]	**2**	-78	72	61	63
3[e]	**2**	-78	72	60	37
4[f]	**2**	-78	72	64	72
5[f]	**3**	-78	72	62	65
6[f]	**4**	-78	72	57	60
7[f]	**5**	25	24	60	31
8[f]	**5**	-78	72	86	77

[a] Experiment performed on a 0.16 mmole scale. [b] Isolated yield. [c] Ee measured on a GC INTERSMAT 110 apparatus using a XE-S-60-(*S*)-Valine-(*S*)-α-phenylethylamide. [d] Reaction performed with 2 mol% of L*. [e] Reaction performed with 1 mol% of L*. [f] Reaction performed with 4 mol% of L*.

Table 1

Using compound **2** as a test ligand, it clearly appears that the enantioselectivity of the reaction dependson the temperature of the reaction. Thus, a decrease of temperature from 25 to –78°C led to an important increase of ee from 12 to 63% (entries 1 and 2). Furthermore, an increase of the amount of ligand **1** used has a beneficial effect on the outcome of the reaction in terms of enantioselectivity (respectively 37% with 1 mol% (entry 3) and 72% ee with 4 mol% of **1** (entry 4)). Moreover, an increase of the steric hindrance on the phenyl group did not lead to an improvement of the enantiomeric excess (entries 5-8). In all cases, *exo*-norborneol is obtained as the major product (ratio *exo*-norborneol / *endo*-norborneol : 95/5 determined by GC). On the other hand, it is noteworthy that the replacement of a phenyl group at the phosphorus atom by a cyclohexyl moiety led to an improvement of the chemical yield (86% yield, entry 8) and at the same time to an increase of the enantioselectivity (77% ee). Under various experimental conditions, we have studied the catalytic enantioselective hydroboration reaction by catecholborane of different olefins[8] (Table 2).



Entry[a]	L*	Substrate	Product	Yield (%)[b]	Ee (%)[c]
1	**2**	**8**	**11**	58	30 (*S*)
2	**5**	**8**	**11**	61	42 (*S*)
3	**2**	**9**	**12**	64	10 (*S,R*)
4	**5**	**9**	**12**	60	15 (*S,R*)
5	**2**	**10**	**13**	62	8 (*S,R*)
6	**5**	**10**	**13**	57	10 (*S,R*)

[a] Experiment performed on a 0.16 mmole scale during 72 hours at –78°C. [b] Isolated yield. [c] Ee measured on a GC INTERSMAT 110 apparatus using a XE-S-60-(*S*)-Valine-(*S*)-α-phenylethylamide. [d] *Trans* conformation determined by comparison by GC analysis with pure *trans* and *cis* samples of **12** and **13**.

Table 2

Styrene has been converted into chiral 1-phenyl ethanol **11** in moderate chemical yield and enantiomeric excesses up to 42% (entry 2). On the other hand, hydroboration of methyl cyclohexene **9** and isophorone **10** into the corresponding alcohols has been successfully achieved in moderate chemical yields (respectively 64 and 62%, entries 3 and 5). Nevertheless, in these two cases no significant enantiomeric excess (around 10% ee) has been encountered probably due to the fact that norbornene and styrene are more reactive olefins in hydroboration reaction than cyclic olefins.

In conclusion, we have shown that readily accessible bis(aminophosphine) compounds are efficient ligands for asymmetric rhodium catalyzed hydroboration of olefins. Further studies including modification of ligands design and mechanistic aspects to understand the regio-and stereoselectivity of this reaction are in progress.

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(8) *General procedure for asymmetric catalyzed hydroboration of styrene* : A mixture of $[RhCODCl]_2$ (8 mg, 1.63 10^{-5} mol) and **2** (17.7 mg, 6.52 10^{-5} mol) in 3 mL of THF was stirred under nitrogen at room temperature for 1.5 h and styrene (170 mg, 1.63 mmol) was added at –78°C. Catecholborane (1.7 mL, 1M in THF) was added at –78°C. The mixture was stirred at –78°C for 18 hours and then quenched with 3 mL of MeOH, 3.5 mL of 3M NaOH solution and 0.5 mL of 30% H_2O_2. Stirring was maintained for 3 hours. Extraction with Et_2O followed by chromatography on a silica gel column with pentane/Et_2O (v/v, 1 :1) as eluent led to phenyl ethanol in 58% yield and 30% ee.