ELSEVIER

Journal of Organometallic Chemistry 624 (2001) 333–343

Journal of Organometallic Chemistry

www.elsevier.nl/locate/jorganchem

Direct use of chiral or achiral organophosphorus boranes as pro-ligands for transition metal catalyzed reactions

Christophe Darcel [a], El Bachir Kaloun [a], Rachid Merdès [b,1], Dominique Moulin [a], Nadège Riegel [a], Serge Thorimbert [b,2], Jean Pierre Genêt [b], Sylvain Jugé [a,*]

[a] *Unité Mixte Université de Cergy-Pontoise/ESCOM, 'Synthèse Organique Sélective et Chimie Organométallique', FRE CNRS 2126, 5 mail Gay Lussac, 95031 Cergy-Pontoise, Cedex, France*

[b] *Laboratoire de Synthèse Organique Sélective et Produits Naturels, UMR 7573, ENSCP, 11 rue Pierre et Marie Curie, 75005 Paris, France*

Received 16 November 2000; accepted 4 January 2001

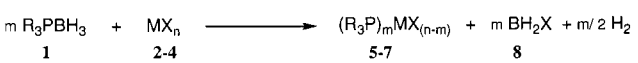
Abstract

Chiral or achiral organophosphorus borane complexes were used without isolation of the free tricoordinate P(III) ligand; thus, the borane adducts could be used either directly with metal salts to perform the catalysis, or they could be decomplexed by DABCO, or cyclooctadiene, and used in situ to generate the catalytic species. Chiral copper, palladium and rhodium complexes prepared using this method, were tested in asymmetric organometallic catalyzed 1,4-addition to 2-cyclohexenone, allylation of Schiff base and hydrogenation of α-acetamidocinnamic acid derivatives, respectively. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Phosphine boranes; Rhodium catalysts; Copper catalysts; Palladium catalysts; Asymmetric synthesis; Catalysis; Addition reaction; Hydrogenation; Allylation

1. Introduction

Since the first examples of asymmetric cyclopropanation [1] and hydrogenation [2], transition metal catalysis has become an important methodology for the preparation of enantiomerically enriched products from prochiral substrates [3]. In this area, the usefulness of chiral P(III)-organophosphorus derivatives (diphosphines [4], diphosphinites [5], aminophosphine phosphinites [6], chelating monophosphines or P(III) derivatives) [7], has been widely demonstrated.



Scheme 1.

Although the chirality of the ligands was generally borne on the carbon backbone, significant strides have been achieved in the asymmetric synthesis of P-chirogenic phosphine ligands, owing to the use of borane protecting groups [8–12]. Recently, P-chirogenic trivalent phosphines have received a renewed interest [13], because the chirality is closer to the metal center. Thus, new kinds of bulky [14], hybrid or chelating monophosphine ligands [15,16] were studied in order to perfect highly stereoselective catalytic species. Moreover, the design of ligands with both chirogenic carbon and phosphorus groups [9g,17], allowed to increase the number of available catalysts.

In connection with our continued work on the asymmetric synthesis of organophosphorus compounds, we have investigated the direct use of borane complexes in order to avoid the use of P(III) labile ligands. The reductive properties of the borane protecting group are of particular interest for the preparations of Pd(0) or Rh(I) phosphine complexes, from Pd(II) or Rh(III) salts; Taking into account that such preparations were currently achieved with partial oxidation of the phosphine into the oxide derivative [18].

* Corresponding author. Tel.: +33-1-34257066; fax: +33-1-34257067.

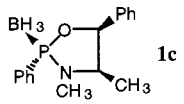
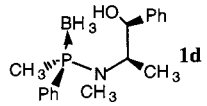
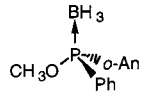
E-mail address: sylvain.juge@chim.u-cergy.fr (S. Jugé).

[1] Present addresses: Medjez, SFA, W. Guelma, Algeria.

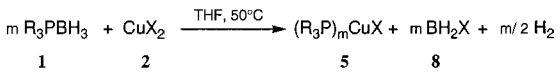
[2] Present address: Laboratoire de Chimie Organique de Synthèse, Université Pierre et Marie Curie, 4 place Jussieu, BP 229, 75231 Paris Cedex 05, France.

PII: S0022-328X(01)00666-0

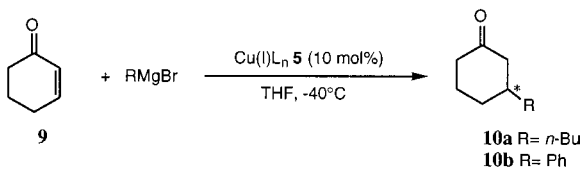
Table 1
Conjugate addition to 2-cyclohexenone (**9**) catalyzed by chiral or achiral copper(I) complexes **5**

Entry	Ligand	RMgBr	3-subtituted cyclohexanone		
				Yield (%)[a]	e.e. (%)[b]
1	$(CH_3Ph_2P)BH_3$ **1a**	*n*-Bu	**10a**	70	–
2	 **1c**	*n*-Bu	**10a**	99	5
3	" **1c**	Ph	**10b**	84	18
4	 **1d**	*n*-Bu	**10a**	99	< 4
5	 **1e**	*n*-Bu	**10a**	61	3

[a]Isolated yield. [b]Determinated by ^{13}C NMR using the (*R*,*R*)-1,2-diphenyl ethylenediamine.[25]



Scheme 2.



Scheme 3.

To the best of our knowledge, few examples of direct reaction of organophosphorus boranes with transition metal complexes have been reported until now: We can underline the preparation of tungsten pentacarbonyl complexes [19], or palladium–rhodium catalysts grafted on a polypyrrole matrix [20], and some examples in asymmetric catalysis [21,22].

We report herein the preparation of new copper, palladium and rhodium complexes **5**–**7**, from chiral and achiral organophosphorus boranes **1** and the corresponding transition metal salts **2**–**4** (Scheme 1). Then, the catalytic properties of the complexes **5**–**7** were investigated in asymmetric 1,4-addition, allylation and hydrogenation reactions.

2. Results and discussion

2.1. Preparation of phosphine copper(I) complexes

The Cu(I) complexes were usually prepared by mixing ligands and halide salts in appropriate stoichiometric ratios. Nevertheless, it may be pointed out that pure compounds were often difficult to obtain, because the reaction leads to different stoichiometric mixtures, whose attempted purification entailed disproportions. Furthermore, complexes often retained the solvents of crystallization, rather difficult to remove even at high temperature and under vacuum [23].

Before the recent development of the asymmetric conjugate additions catalyzed by chiral phosphine or phosphinite copper complexes [24], we have investigated their preparation from organophosphorus borane derivatives. When phosphine boranes **1** were heated at 50°C in THF with Cu(I) salts, no reaction occurred, but with CuX_2 **2**, the corresponding organophosphorus copper(I) complexes **5** were obtained (Scheme 2).

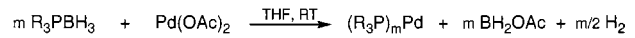
Thus, heating the methyldiphenylphosphine borane **1a** with one equivalent of copper dichloride, in THF at 50°C for 48 h, led to the copper complex **5a**, isolated by chromatography in 78% yield. ^{1}H-NMR and elemental analysis indicated the presence of solvent and a phosphorus–copper ratio of 3 which were in good agreement with the structure $(MePh_2P)_3CuCl$ for **5a**. Comparatively, direct complexation of CuCl with the free phosphine gave a similar complex with a copper–ligand ratio of 3. When the reaction was carried out with $dppe(BH_3)_2$ **1b** or various copper (II) salts **2** (nitrate, sulfate, acetate, halide), complexes **5** were obtained in low to good yields. Nevertheless, the isolated complexes were unstable and their NMR analyses revealed very often different stoichiometries and the presence of solvent.

2.2. Copper-catalyzed conjugate addition of organometallic reagents to 2-cyclohexenone

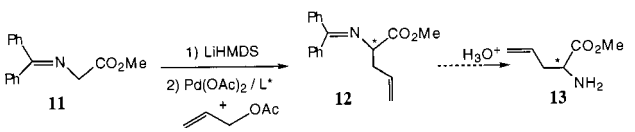
In the presence of the complex **5a** (10% mol), previously prepared in situ on heating $CuCl_2$ with $MePh_2PBH_3$ **1a**, addition of *n*-butylmagnesium bromide to 2-cyclohexenone (**9**) at −40°C for 1 h, gave the 3-butylcyclohexanone **10a** in 70% yield (Scheme 3; Table 1, entry 1).

Following the same methodology, several chiral copper complexes **5** prepared from P-chirogenic organophosphorus boranes **1c–e**, were used to promote the conjugate addition. The results are summarized in Table 1.

When oxazaphospholidine, aminophosphine or phosphinite boranes **1c–e** were used to generate the copper catalysts from $CuCl_2$, the reaction of **9** with *n*-butylmagnesium bromide, provides the 1,4-addition products **10a** in 61–99% yields (entries 2, 4, 5). Unfortunately,



Scheme 4.



Scheme 5.

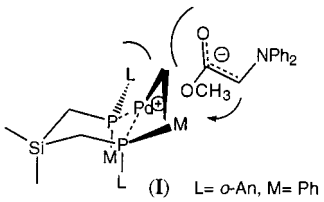


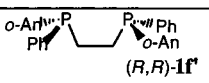
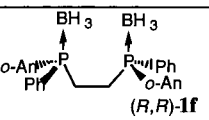
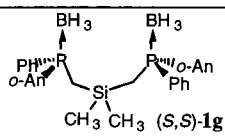
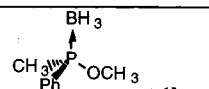
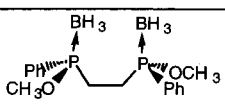
Fig. 1.

the enantiomeric excesses of **10a** determined from ^{13}C-NMR data of the aminal derivative [25], were very low (e.e. < 5%). Nevertheless, in the case of the addition of phenylmagnesium bromide, the oxazaphospholidine borane **1c** led to the 3-phenylcyclohexanone **10b** with 18% e.e. (entry 3).

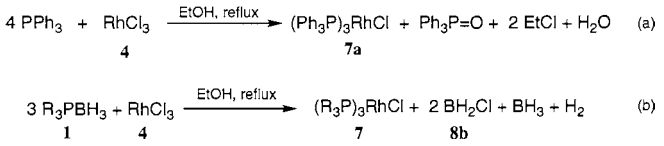
2.3. Asymmetric allylation catalyzed by chiral organophosphorus palladium(0) complexes

We have described previously the direct use of phosphine boranes grafted on polypyrrole, in order to generate supported palladium catalysts applied to allylic alkylation and Heck coupling reactions [20]. Effectively, a simple addition of $Pd(OAc)_2$ to a solution of triphenylphosphine borane in THF, led to the formation of Pd(0) catalyst. Although the mechanism of the formation of the Pd(0) complex **6** was unknown, it could be explained by the reduction of Pd(II) into Pd(0) by the borane, and simultaneously deprotection of the phosphine ligand (Scheme 4).

Table 2
Pd(0) catalyzed asymmetric allylation of the Schiff base **11**

Entry	Ligand or borane derivative	Ligand/ Pd ratio	Conditions T °C	Conditions time (h)	Allylated product **12** yield (%)(a)	Allylated product **12** e.e. (%)(b)
1	 (*R*,*R*)-**1f'**	2	-35	1.5	70	10 (*R*)
2	 (*R*,*R*)-**1f**	2	-35	1.5	66	13 (*R*)
3	 (*S*,*S*)-**1g**	2	-55	2.5	42	43 (*S*)
4	 (*S*)-**1h**	4	-30	16	80	2
5	 (*S*,*S*)-**1i**	2	-55	1	60	5

(a) Isolated yield. (b) Determined by HPLC using a chiral Pirkle I column.



Scheme 6.

New P-chirogenic organophosphorus borane compounds were investigated as proligands for the in situ preparation of chiral Pd(0) catalysts, and used in the asymmetric allylation of the prochiral Schiff base **11** (Scheme 5) [26]. The synthesis of allylglycine **13**, was achieved using the carbanion of **11** generated by the action of LiHMDS, and a catalyst with a phosphorus–Pd(0) ratio of 4. The results are summarized in Table 2.

When DIPAMP (*R*,*R*)-**1f′** was used as ligand, the allylic alkylation afforded the expected product (*R*)-**12** in 70% yield, after 1.5 h at −35°C (Table 2, entry 1). A very low enantiomeric excess (10% e.e.) was obtained in this case. When the DIPAMP diborane complex (*R*,*R*)-**1f** was used to generate the palladium catalyst, the compound **12** was obtained in similar yield and enantioselectivity, 66% and 13% e.e. respectively (entry 2). More interestingly, the modified (*S*,*S*)-DIPAMP pro-ligand **1g**, having a three atom bridge between the two phosphorus, gave the allylated product **12** with a (*S*)-configuration and 43% e.e. (entry 3). This result can be explained by the conformation of the six membered chelated palladium ring (**I**), which must give a better spatial interaction at the π-allyl end with the prochiral nucleophile, than the corresponding DIPAMP **1f′** adduct (Fig. 1). It may be pointed out that this effect is in good agreement with the 'pocket model' proposed by Trost [27].

Finally, the mono and diphosphinite boranes **1h** and **1i** also exhibited their efficiency in promoting the palladium catalysis, entailing allylic alkylation of the Schiff base **11** in yields up to 80% (entry 4,5); But in this case also, very low enantioselectivities were observed.

2.4. Preparation of rhodium(I) complexes

The Wilkinson catalyst $Rh(PPh_3)_3Cl$ **7a**, certainly the most representative of the transition metal complexes used for homogeneous catalysis, is usually prepared with an excess of triphenylphosphine (4 equiv. or more), in order to reduce the Rh(III) chloride into Rh(I) species (Scheme 6a) [18a]. In fact, a part of the phosphine was transformed into the oxide derivative, involving the decomposition of a dichlorotriphenyl phosphorane intermediate, in ethanol.

The preparation of rhodium complexes **7** was also investigated, by reacting directly the rhodium(III) trichloride **4** with phosphine boranes **1** (Scheme 6b). Thus, the heating $RhCl_3$ in refluxing ethanol with 3 equiv. of methyldiphenylphosphine borane **1a**, provided two complexes which were characterized by ^{31}P-NMR spectroscopy. The $^{31}P\{^1H\}$-NMR spectrum of the crude mixture after 10 min of reaction, displayed two groups of signals (Fig. 2a). The signals at −1.86 ppm (td, $^1J_{PRh} = 113$, $^2J_{PP} = 24.5$ Hz) and −4.27 ppm (dd, $^1J_{PRh} = 85$, $^2J_{PP} = 24.5$ Hz), were assigned to the phosphorus (ii) and (i) respectively in the Rh(III) hexacoordinated intermediate **14**, while the tetracoordinated Rh(I) complex **7b** gave rise to the signals at +33.15 ppm (td, $^1J_{PRh} = 138$, $^2J_{PP} = 27$ Hz), and +20.45 ppm (dd, $^1J_{PRh} = 98$, $^2J_{PP} = 27$ Hz), corresponding to phosphorus (ii) and (i), respectively. No signal was observed in the 30 ppm region, indicating that methyl diphenyl phosphine oxide was not produced under these conditions. After longer heating, the signals at higher field decreased in favour of the ^{31}P-NMR pattern at +20 and +33 ppm. Indeed, this spectrum was in very good agreement with the formation of the Rh(III) hexacoordinated intermediate **14**, which then led to the Rh(I) complex **7b** (Fig. 2a).

On the other hand, reaction of $RhCl_3$ with the diborane complex (*S*,*S*)-**1i** was carried out according to a second method, using cyclooctadiene as borane trapping reagent. It is noteworthy that **1i**, prepared by oxidative coupling of methylphosphinite borane (*S*)-**1h** (Scheme 7) [9e], provided a rare example of a C_2-symmetric P-chirogenic bidendate ligand, bearing phosphorus heteroatom bonds.

Heating the diphosphinite borane **1i** with one equivalent of $RhCl_3$ and cyclooctadiene (4 equiv.), in refluxing THF for 19 h, produced a yellow solid after evaporation of the solvent. The ^{31}P-NMR spectrum of the solid obtained after cristallization in ethanol, displayed a signal at 153.6 ppm (d, $^1J_{PRh} = 129$ Hz) caracteristic of a rhodium(I) complex, having certainly the dimeric structure **7c** (Fig. 2b).

2.5. Asymmetric hydrogenation catalyzed by organophosphorus rhodium(I) complexes

The asymmetric hydrogenation induced by the rhodium(I) catalysts **7**, prepared from various P-chirogenic organophosphorus boranes **1**, was tested with the α-acetamidocinnamic acid derivatives **15** (Scheme 8). After 24 h under 10 atm of H_2, the *N*-acetylphenylalanine derivatives **16a**, **b** were obtained quantitatively (Table 3).

The hydrogenation of **15a** in MeOH under 10 atm of H_2, in presence of the catalyst prepared from DIPAMP (*S*,*S*)-**1f′** and $[Rh(COD)Cl]_2$, led to the phenylalanine derivative (*R*)-**16a** after 18 h, with 87%

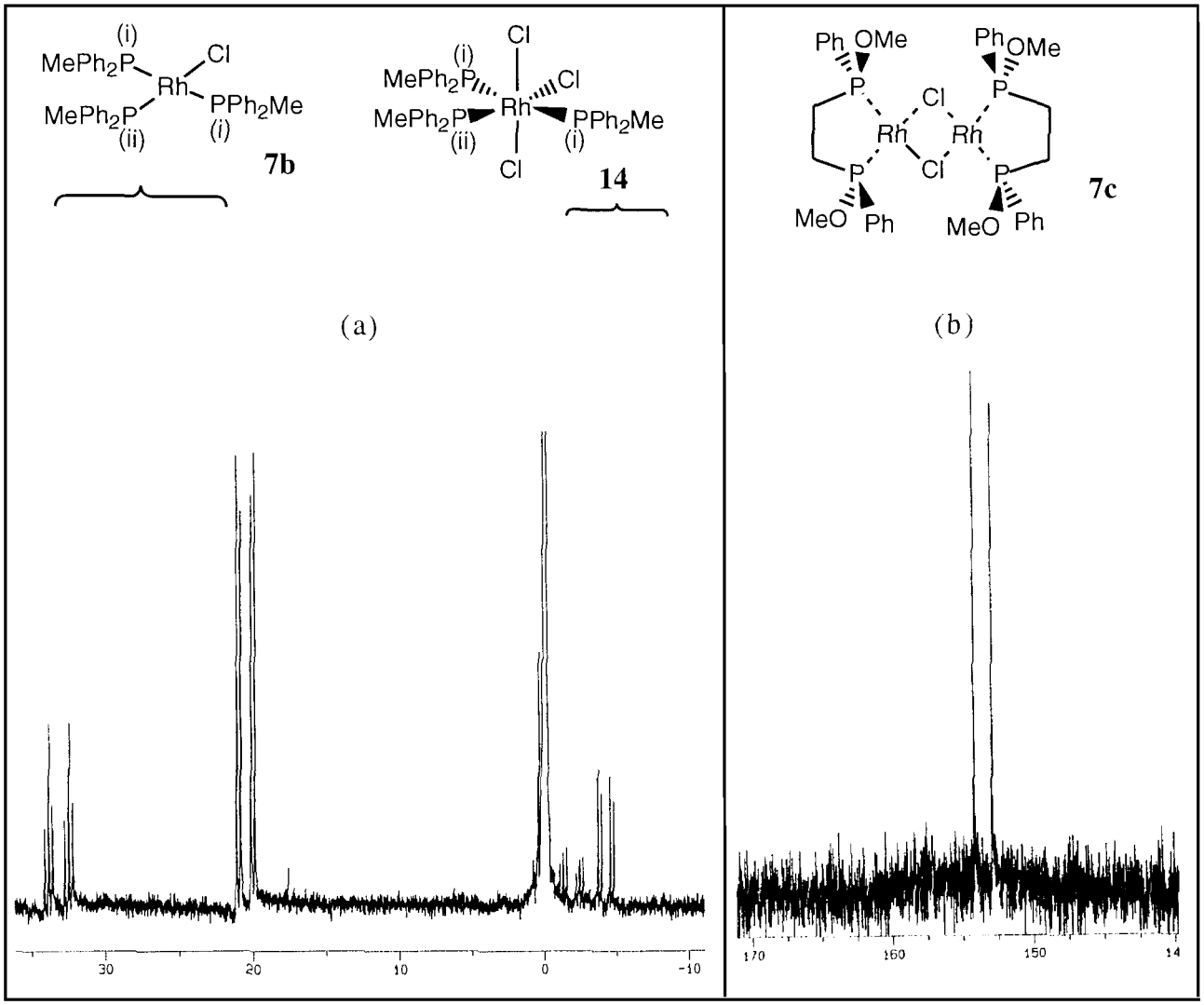
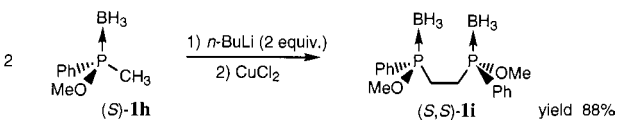
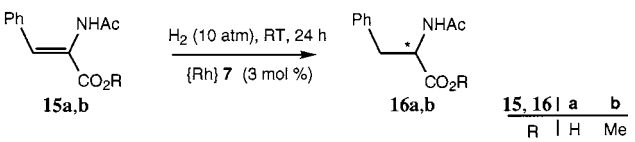


Fig. 2. ^{31}P-NMR spectra of the $RhCl_3$ mixture, heated after: (a) 10 min in EtOH at 78°C with $MePh_2PBH_3$ (**1a**). (b) 19 h in refluxing THF with diborane **1i**.



Scheme 7.

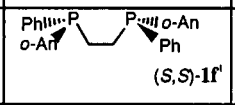
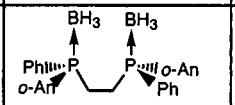
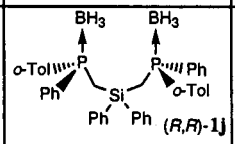
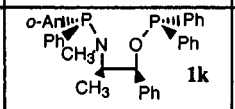
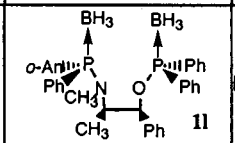
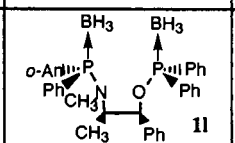


Scheme 8.

e.e. (Table 3, entry 1; see Ref. [2d]: 94% e.e., with run in MeOH). (*R*)-**16a** was obtained with a similar result (90% e.e., entry 2), when the DIPAMP diborane (*S*,*S*)-**1f** was used to form the catalyst by reaction with $RhCl_3$. Using the diphosphine borane (*R*,*R*)-**1j**, prepared by grafting two (*R*)-methyl phenyl *o*-tolyl phosphine boranes **1n** with dichloro diphenylsilane [9e], the resulting catalyst with $RhCl_3$, gave the phenyl alanine derivative (*S*)-**16a** with 52% e.e.(entry 3).

We had reported the high stereoselectivity of the catalyzed hydrogenation of **15b** with the aminophosphine-phosphinite (AMPP) **1k**, as rhodium ligand (99% e.e., entry 4) [9g]. Unfortunately, when the corresponding AMPP diborane **1l** was heated with $RhCl_3$ in refluxing ethanol, a degradation of the ligand occurred as observed by ^{31}P-NMR analysis, and the catalyzed hydrogenation of **15a** gave unreproducible results. Likewise, when the decomplexation of AMPP diborane

Table 3
Rh(I) catalyzed asymmetric hydrogenation of substrate **15a,b**

entry	Ligand or borane derivative	Catalyst preparation	Solvent	Product **16**	e.e[a](%)	abs.conf.
1	 (*S,S*)-**1f'**	[Rh(COD)Cl]$_2$ (1%)/ **1f'** (2%)/ EtOH/ RT	MeOH	**16a**	87	(*R*)
2	 (*S,S*)-**1f**	$RhCl_3$ (1%)/ **1h** (1.5%)/ EtOH reflux	MeOH	**16a**	90	(*R*)
3	 (*R,R*)-**1j**	$RhCl_3$ (1%)/ **1j** (1.5%)/ EtOH reflux	MeOH	**16a**	52	(*S*)
4	 **1k**	$Rh(COD)_2BF_4$ (3%)/ **1k** (6%)/CH_2Cl_2/RT	C_6H_6	**16b**	99	(*S*)
5	 **1l**	**1l** (6%)/DABCO(4 equiv)/ [Rh(COD)Cl]$_2$(3%)/$AgBF_4$ Toluene/50°C	C_6H_6	**16b**	8	(*R*)
6	 **1l**	**1l** (6%)/DABCO(4 equiv)/ Toluene/50°C; after 12 h: [Rh(COD)Cl]$_2$ (3%)/$AgBF_4$ then precipitated in ether	C_6H_6	**16b**	96	(*S*)

[a] Determined by HPLC on chiral colum for **16b**, and from optical purity for **16a**

1l was carried out in situ with DABCO, in the presence of the precatalyst [Rh(COD)Cl]$_2$ and $AgBF_4$, the catalyzed hydrogenation led to a poor result (8% e.e., entry 5). But, when the catalyst was prepared in a one pot procedure, with three consecutive steps: decomplexation of **1l** by DABCO, addition of [Rh(COD)Cl]$_2$ and $AgBF_4$, and then addition of ether to precipitate the rhodium complex, the hydrogenated product (*S*)-**16b** was obtained with 96% e.e. (entry 6).

3. Conclusions

A new versatile method for generating transition metal catalysts from organophosphorus borane adducts has been investigated. The preparation of copper (I) complexes was described for the first time, by direct reaction of copper (II) salts with phosphine boranes. Chiral copper complexes, prepared from P-chirogenic phosphine boranes, have been tested in the asymmetric conjugate addition of organomagnesium reagents to 2-cyclohexenone, entailing enantioselectivities lower than 18%.

On the other hand, palladium complexes were simply generated by mixing $Pd(OAc)_2$ with organophosphorus boranes; Their catalytic properties were studied in the asymmetric allylation of the Schiff base **11**. Although, DIPAMP **1f'** or its borane adduct **1f**, entailed low e.e., however promising asymmetric induction has been obtained with the modified DIPAMP diborane **1g**, since the allylated Schiff base **12** was obtained with 43% e.e.

Finally, rhodium(I) complexes were prepared either on heating organophosphorus boranes with $RhCl_3$ in refluxing ethanol, or in the presence of cyclooctadiene; Better results were obtained by carrying out the borane decomplexation in situ. Several chiral rhodium catalysts, prepared from P-chirogenic phosphorus borane complexes, have been investigated for the asymmetric hydrogenation of α-acetamido cinnamic acid derivatives **15b**, to yield the phenylalanine derivatives **16b** with 96% e.e.

Consequently, this transition metal complex synthesis, involving easily handled and stable organophosphorus boranes, as pro-ligands, provides a suitable methodology towards asymmetric catalysis. New P-chirogenic phosphorus ligands, synthesized via their borane complexes, which are very difficult to isolate in

tricoordinate form, could now be tested in asymmetric catalysis. Therefore, very promising developments of such transition metal catalysts can be expected.

4. Experimental

4.1. General

All reactions were carried out under argon or nitrogen atmosphere in dried glassware. Solvents were dried and freshly distilled under nitrogen atmosphere over sodium–benzophenone for THF, toluene and benzene, P_2O_5 for CH_2Cl_2 and sodium ethylate for EtOH. Hexane, ethanol and isopropanol for HPLC were of chromatographic grade and used without further purification. Methyllithium, *s*-butyllithium, $CuCl_2$, $CuBr_2$, $Pd(OAc)_2$, $RhCl_3$, $BH_3.S(CH_3)_2$ in toluene, diphenylmethylphosphine and 1,2-bis(diphenylphosphino)ethane (dppe), DABCO, α-acetamidocinnamic acid **15a**, were purchased from Aldrich, Acros and Avocado. The $[Rh(COD)Cl]_2$ complex was prepared according to the previously described procedure [28], and used without further purification. Methyl α-acetamido cinnamate **15b** was obtained by reaction of **15a** with methyl iodide, in the presence of K_2CO_3 [29]. Commercially available bromobutane, and bromobenzene, were distilled before use. Flash chromatography was performed on silica gel (60ACC, 35–70 μm; SDS) or neutral aluminium oxide (Carlo Erba; ref. 417241). HPLC analyses were performed on a Gilson 305/306 chromatograph equipped with an UV 116 detector. All NMR spectra data were recorded on Bruker DPX 250 spectrometer using TMS as internal reference for ^1H (250 MHz) and ^{13}C-NMR (62.9 MHz) and 85% phosphoric acid as external reference for ^{31}P-NMR (101.3 MHz). The δ ^{31}P-NMR chemical shifts are countered negatively at higher field than phosphoric acid. IR spectra were recorded on a Perkin–Elmer 1600 FT and a Bruker Equinox 55. Melting points were determined on a Büchi melting point apparatus and are uncorrected. Optical rotations were measured at 20°C with a Perkin–Elmer 241 polarimeter. Mass spectra analyses and exact mass were performed on a JEOL MS 700 at the Mass Spectroscopy Laboratories of ENS, Paris. The major peak m/z is mentioned with the intensity as a percentage of the base peak in brackets. Elemental analyses were determined with a precision superior to 0.4% at the Microanalysis Laboratories of Pierre and Marie Curie University, Paris.

4.2. Preparation of the organophosphorus boranes *1*

The diphenylmethylphosphine borane **1a** and 1,2-bis(diphenylphosphino)ethane diborane **1b** were prepared as described [20b], from the corresponding phosphine and borane dimethylsulfide in THF, then recrystallized in cyclohexane or toluene respectively (**1a**: m.p. = 55°C; **1b**: m.p. = 166–168°C). The complexes (2*S*,4*R*,5*S*)-(−)-3,4-dimethyl-2,5-diphenyl-1,3,2-oxaza phospholidine borane **1c**, (*S*p)-(+)-*N*-methyl-*N*-[(1*S*,2*R*)-(1-hydroxy-2-methyl-1-phenyl-2-propyl)]-aminomethylphenyl phosphine borane **1d**, (*S*)-(+)-[(*O*-methyl)-*o*-anisylphenylphosphinite] borane (**1e**), (*R*,*R*)-(+)-1,2-bis(*o*-anisylphenylphosphino borane) ethane **1f** and (*R*,*R*)-(−)-1,2-bis(*o*-anisylphenylphosphino)ethane **1f′**, were prepared from the (+)-ephedrine according to the published procedure [9b,9f]. Likewise, (*S*)-(−)-[(*O*-methyl)-methylphenylphosphinite]borane **1h**, (*S*,*S*)-(−)-1,2-bis(*o*-anisyl phenylphosphinoborane)ethane **1f**, and (*S*,*S*)-(+)-1,2-bis(*o*-anisylphenylphosphino)ethane **1f′**, were obtained starting from the (−)-ephedrine. (*R*p)-*N*-Methyl-*N*-{(1*R*,2*S*)-[2-(diphenylphosphinito)-1-methyl-2-phenyl]ethyl}amino-*o*-anisylphenylphosphine **1k** and its diborane complex **1l**, were prepared as previously described [9g].

4.2.1. (*S*,*S*)-(−)-Bis[(*o*-anisylphenylphosphinoborane) methylene]dimethylsilane ***1g***

In a 50 ml two-necked flask equipped with a magnetic stirrer and an argon inlet, 1 mmol of (*S*)-(+)-*o*-anisylmethylphenylphosphine borane **1m** [9b] was dissolved in 1 ml of dry THF at −78°C. Then, 1 mmol of *s*-butyllithium was slowly added under stirring. The temperature of the mixture was kept at −78°C for 15 min, then allowed to warm at −30°C. After 1 h in these conditions, the dimethyldichlorosilane (0.5 mmol) was added and the mixture was hydrolyzed at 0°C. After removal of the THF, the aqueous layer was extracted with CH_2Cl_2. The solvent was removed and the residue was purified by chromatography on silica gel with a mixture toluene–hexane (3:1) as eluent (85% yield).

White solid: m.p. 139–140°C (hexane); $[\alpha]_D^{20} = -69.1$ ($c = 0.7$, $CHCl_3$); IR (KBr, $\bar{\nu}$ cm^{-1}): 3052, 2972, 2403 (s, B–H), 2365 (s, B–H), 1589, 1478, 1431, 1276, 1249; ^1H-NMR ($CDCl_3$): δ 8.13 (2H, ddd, $J = 1$, $J = 7$, $J = 14$ Hz, *H* arom), 7.80–7.72 (4H, m, *H* arom), 7.64 (2H, t, $J = 8$ Hz, *H* arom), 7.54 (6H, sl, *H* arom), 7.22 (2H, t, $J = 7.5$ Hz, *H* arom), 6.99 (2H, dd, $J = 8$, $J = 3$ Hz, *H* arom), 3.79 (6H, s, CH_3O), 2.38 (2H, dd, $^2J_{PH} = 18$, $^1J_{HH} = 14$ Hz, PC*H*HSi), 1.80 (2H, t, $^2J_{PH} = {}^1J_{HH} = 13.5$ Hz PCH*H*Si), 1.9–0.4 (6H, ql, $^1J_{HH} = 49$ Hz, BH_3), 0.0 (6H, s, $(CH_3)_2Si$); ^{13}C-NMR ($CDCl_3$): δ 161.33 (*C* arom), 135.89 (d, $J_{PC} = 15$ Hz, *C* arom), 133.61 (*C* arom), 132.7 (*C* arom), 130.88–127.96 (*C* arom), 120.93 (d, $J_{PC} = 12$ Hz, *C* arom), 118.13 (d, $J_{PC} = 53$ Hz), 110.99 (*C* arom), 55.20 (CH_3O), 11.13 (d, $^1J_{PC} = 23$ Hz, PCH_2Si), 0.13 (CH_3Si); ^{31}P-NMR ($CDCl_3$): δ +12.9 (d, $^1J_{PB} = 58$ Hz); HRMS Calc. for $C_{30}H_{40}B_2O_2P_2Si$ [M^+]: 544.2459; Found: 544.2435; Anal. Calc. for $C_{30}H_{40}B_2O_2P_2Si$: C, 66.20; H, 7.41; Found: C, 66.06; H, 7.42%.

*4.2.2. (S,S)-(−)-1,2-Bis(methoxyphenylphosphinoborane) ethane **1i***

The diphosphinite diborane **1i** was prepared by coupling the anion derived from the (*S*)-(−)-[(*O*-methyl) methylphenylphosphinite) borane **1h**, according to the procedure described for the DIPAMP diborane **1f** [9b].

In a 50 ml two-necked flask equipped with a magnetic stirrer and an argon inlet, 1 mmol of **1h** was dissolved in 2 ml of dry THF at −78°C. Then, 1 mmol of *s*-butyl lithium was slowly added under stirring. The temperature of the mixture was kept at −78°C for 15 min, then allowed to warm at −30°C. After 1 hour in these conditions, dry $CuCl_2$ (1.1 mmol) was added and the temperature was brought to 0°C and allowed under air. After 12 hours, the mixture was hydrolyzed by HCl 10%, and extracted with CH_2Cl_2. The solvent was removed and the residue purified by chromatography on silica gel with a mixture of hexane–CH_2Cl_2 (6:4) as eluent (88% yield).

White solid: m.p. 114–115°C (hexane); $R_f = 0.48$ (hexane–CH_2Cl_2 55:45); $[\alpha]_D^{20} = -115.1$ ($c = 1.3$, $CHCl_3$); IR (KBr, $\bar{\nu}$ cm^{-1}): 3058, 2941, 2844, 2370 (B–H), 1438, 1114, 1069, 1034; ^{1}H-NMR ($CDCl_3$): δ 7.73–7.59 (4H, m, *H* arom), 7.59–7.45 (6H, m, *H* arom), 3.52 (6H, distorted d, $^3J_{PH} = 12$ Hz, POCH_3), 2.17–2.01 (2H, m, PC*H*H), 1.98–1.85 (2H, m, PCH*H*), 1.4–0.0 (6H, q, $^1J_{BH} = 94$ Hz, BH_3); ^{13}C-NMR ($CDCl_3$): δ 132.82 (d, $J_{PC} = 2$ Hz, *C* arom), 132.44 (*C* arom), 132.12 (d, $J_{PC} = 2$ Hz, *C* arom), 131.34 (d, $J_{PC} = 11$ Hz, *C* arom), 130.93 (distorted d, $J_{PC} = 11$ Hz, *C* arom), 130.62 (d, $J_{PC} = 11$ Hz, *C* arom), 129.72 (d, $J_{PC} = 55$ Hz, *C* arom), 128.95–128.63 (*C* arom), 54.06 (s, OCH_3), 23.14 (d, $^1J_{PC} = 44$ Hz); ^{31}P-NMR ($CDCl_3$): δ +118.4 (d, $^1J_{PB} = 58$ Hz); MS (DCI, CH_4) *m*/*z* (relative intensity): 302 (1), 270 (10), 229 (4), 192 (100), 180 (100), 148 (20), 123 (100), 77 (45), 58 (100); Anal. Calc. for $C_{16}H_{26}B_2O_2P_2$ (333.95): C, 57.55; H, 7.85; Found: C, 57.23; H, 7.78%.

*4.2.3. (R,R)-(−)-Bis[(o-tolylphenylphosphino borane)methylene] diphenylsilane **1j***

The diphosphine diborane **1j** was prepared by coupling the anion derived from the (*R*)-(−)-methylphenyl-*o*-tolyl phosphine borane **1n**, with dichlorodiphenylsilane (0.5 equiv.), according to the same procedure described above for **1g** (yield 80%).

*4.2.4. Synthesis of (R)-(−)-methylphenyl-o-tolyl phosphine borane (**1n**)*

The (*R*)-(−)-methylphenyl-*o*-tolylphosphine borane **1n** was prepared from the starting complex **1c** [9b], by opening the oxazaphospholidine ring with *o*-tolyl lithium reagent, then acid methanolysis of the aminophosphine intermediate, and finally substitution by methyllithium (overall yield >70%). Oil; $R_f = 0.60$ (toluene –hexane 8:2); $[\alpha]_D^{20} = -31.1$ ($c = 0.8$, $CHCl_3$); IR (KBr, $\bar{\nu}$ cm^{-1}): 3058, 2367 (B–H), 2339 (B–H), 1592, 1454, 1437; ^{1}H-NMR ($CDCl_3$): δ 7.95–7.67 (2H, m, *H* arom), 7.63–7.43 (6H, m, *H* arom), 7.41–7.24 (1H, m, *H* arom), 2.23 (3H, s, CH_3Ph), 1.87 (3H, d, $^2J_{PH} = 10$ Hz, CH_3P), 1.4–0.3 (3H, m, BH_3); ^{13}C-NMR ($CDCl_3$): δ 132.39–125.84 (*C* arom), 12.48 (d, $^1J_{PC} = 42$ Hz, PCH_3); ^{31}P-NMR ($CDCl_3$): δ +10.5 (d, $^1J_{PB} = 71$ Hz); MS (DCI, CH_4) *m*/*z* (relative intensity): 214 (100), 199 (90), 165 (90), 121 (100), 103 (80), 91 (100), 77 (80); Anal. Calc. for $C_{14}H_{18}BP$ 228.08: C, 73.73; H, 7.95; Found: C, 73.89; H, 7.94%.

*4.2.5. Diphosphine diborane **1j***

White solid: m.p. 197°C (toluene–hexane 7:3); $R_f = 0.14$ (toluene–hexane 3:1); $[\alpha]_D^{20} = -3.9$ ($c = 0.8$, $CHCl_3$); IR (KBr, $\bar{\nu}$ cm^{-1}): 3053, 2368 (B–H), 2343 (s, B–H), 1428, 1108, 1062, 697; ^{1}H-NMR ($CDCl_3$): δ 7.63 (2H, dd, $J = 3$, $J = 2$ Hz, *H* arom), 7.44–7.18 (20H, m, *H* arom), 7.04–6.98 (6H, m, *H* arom), 2.77–2.45 (4H, m, PCH_2Si), 1.99 (6H, s, CH_3Ph), 1.8–0.4 (6H, m, BH_3); ^{13}C-NMR ($CDCl_3$): δ 141.6 (*C* arom), 135.3–125.6 (*C* arom), 21.7 (*C*H$_3$Ph), 9.12 (PCH_2Si); ^{31}P-NMR ($CDCl_3$): δ +15.5 (d, $^1J_{PB} = 36$ Hz); MS (EI) *m*/*z* (relative intensity): 622 (5), 609 (35), 531 (37), 517 (100), 409 (15), 304 (18), 259 (30), 197 (15), 91 (60); HRMS (DCI, CH_4) Calc. for $C_{40}H_{41}BP_2Si$ [$M^+ - BH_3$]: 622.2546; Found: 622.2537; Anal. Calc. for $C_{40}H_{44}B_2P_2Si$ (636.4): C, 75.49; H, 6.97; Found: C, 75.10; H, 6.97%.

*4.3. Preparation and applications of organophosphorus copper(I) complexes **5***

*4.3.1. Preparation of copper(I) complexes **5** from phosphine boranes **1***

4.3.1.1. Typical procedure. In a 50 ml two-necked flask equipped with a magnetic stirrer and an argon inlet, 1 mmol of phosphine borane **1** was dissolved in 3 ml of dry THF. Then, 1 mmol of CuX_2 (2 mmol for the dppe diborane **1b**) was added under stirring, and the mixture was heated at 50°C for 48 h. After cooling and filtration, the organic solvent was removed and the residue was purified by chromatography on silica gel using a mixture of toluene–EtOH as eluent.

*4.3.1.2. $(CH_3PPh_2)_3CuCl$ complex **5a***. Colorless solid (78% yield); $R_f = 0.5$ (toluene–^{i}PrOH 96:4); ^{1}H-NMR ($CDCl_3$): δ 7.4 (30H, m, *H* arom), 3.6 (8H, m, solvent), 1.9 (9H, d, $^2J_{PH} = 16$ Hz, PCH_3), 1.8 (12H, m, solvent); Anal. Calc. for $(CH_3PPh_2)_3CuCl$, 4 EtOH (881): C, 64.0; H, 6.8; O, 7.2; Cl, 4.0; P, 10.5; Found: C, 63.6; H, 6.3; O, 8.6; Cl, 4.7; P, 11.4%.

When methyl diphenylphosphine **1a** (4 equiv.) was complexed in EtOH by CuCl, colorless crystals was obtained after cooling (yield 79%); Anal. Calc. for

$(CH_3PPh_2)_3CuCl$ (699.7) [23a]: C, 66.95; H, 5.62; Cl, 5.07; P, 13.28; Found: C, 67.17; H, 5.65; Cl, 5.38; P, 13.12%.

*4.3.2. Catalyzed conjugate addition of organomagnesium reagent with 2-cyclohexenone **9**, by copper(I) complexes **5** prepared from phosphine boranes **1***

In a 10 ml flask equipped with a magnetic stirrer and an argon inlet, 0.4 mmol of monophosphine borane **1a**,**c**–**e** was dissolved in 1 ml of dry THF. Then, 0.2 mmol of $CuCl_2$ was added under stirring, and the mixture was heated at 50°C for 12 h. After cooling, the copper complex was poured in a 100 ml two-necked flask with 40 ml of toluene.The solution was cooled at −40°C and the 2-cyclohexenone (2 mmol) was added. Then, two equivalents of *n*-butyl (or phenyl) magnesium reagent was slowly added under stirring. After 1 h in these conditions, the reaction was allowed to warm at room temperature (r.t.) and hydrolyzed with 20 ml of HCl 5 M. The mixture was extracted with 2 × 50 ml of ether, and the combined organic extracts were washed with H_2O and dried with $MgSO_4$. After filtration, the organic solvent was removed and the residue was purified by chromatography on silica gel using a mixture of pentane–ether 8:2 as eluent, to give the 3-butyl (or 3-phenyl) cyclohexanone **10a** (or **10b**) in 61–84% yields. The enantiomeric excesses were determinated by ^{13}C-NMR of the aminal derived with (*R*,*R*)-1,2-diphenylethylene diamine [25].

*4.3.2.1. 3-n-butylcyclohexan-1-one **10a**.* ^{1}H-NMR ($CDCl_3$): δ 2.45–0.72 (m); ^{13}C-NMR ($CDCl_3$): δ 212.22 (*C*O), 48.27, 41.56, 39.09, 36.32, 31.35, 28.87, 25.34, 22.74, 14.04.

*4.3.2.2. 3-phenylcyclohexan-1-one **10b**.* ^{1}H-NMR ($CDCl_3$): δ 7.20–6.80 (5H, m, *H* arom), 2.35–0.90 (9H, m, C*H*, CH_2); ^{13}C-NMR ($CDCl_3$): δ 211 (*C*O), 144 (*C* arom), 128.7 (*C* arom), 126.7 (*C* arom), 126.6 (*C* arom), 48.9 (CO*C*H_2CHPh), 44.7 (*C*HPh), 41.2 (CH_2*C*H_2CO), 32.7 (CH_2*C*H_2CHPh), 25.5 (*C*H_2CH_2CHPh).

*4.4. Allylation of Shiff base **11** catalyzed by a palladium(0) complex generated from $Pd(OAc)_2$ and phosphine boranes **1***

4.4.1. Typical procedure

A suspension of phosphine borane **1** (6 mol%) and $Pd(OAc)_2$ (3 mol%) in anhydrous THF (1 ml), was stirred at r.t. for 30 min. Then, allylacetate (108 μl, 1.0 mmol) was added, and the mixture was stirred at r.t. for 30 min. In another flask under argon atmosphere, 1.1 mmol of LiHMDS was added to a solution of Schiff base **11** ([26], 1.0 mmol) in anhydrous THF (2 ml), and the mixture was stirred at 0°C for 30 min. The resulting anion was cooled at −50°C and slowly added dropwise to the catalyst solution, cooled at the same temperature. The new mixture was stirred at −40°C and the reaction was monitored by TLC. After 3 h, the reaction was hydrolyzed by 2 ml of saturated NH_4Cl solution and allowed to warm at r.t.. The mixture was extracted with 2 × 10 ml of ether. The combined organic extracts were dried with $MgSO_4$, and after filtration, the organic solvent was removed under vacuum. The residue was purified by chromatography on silica gel using a mixture of hexane–AcOEt 4:1 as eluent, to yield the allylated Schiff base **12** as a colorless oil.

^{1}H-NMR ($CDCl_3$): δ 7.8–7.2 (10H, m, *H* arom), 6.0–5.5 (1H, m, CH_2=C*H*), 5.3–4.9 (2H, m, CH_2=CH), 4.2 (1H, t, C*H*CO_2CH_3), 3.75 (3H, s, CO_2CH_3), 2.65 (2H, m, CH_2=CHCH_2).

The enantiomeric excess of **12** was determined by HPLC on a Pirkle I column, with hexane–THF 95:5 as eluent (flow rate 1 ml min^{-1}; UV detection: $\lambda = 254$ nm; (*R*) enantiomer $t_R = 9.3$ min, (*S*) enantiomer $t_R = 9.7$ min).

*4.5. Preparation and applications of organophosphorus rhodium (I) complexes from phosphine boranes **1***

4.5.1. Typical procedure

In a 10 ml flask equipped with a stirrer, a condenser and an argon inlet, 0.03 mmol (6 mg) of $RhCl_3$ and 0.045 mmol (1.5 equiv., 22 mg) of DIPAMP$(BH_3)_2$ **1f** were dissolved in 1 ml of dry ethanol. The mixture was then heated at reflux for 1 h. After cooling, the solvent was removed under vacuum. The precatalyst was used without further purification.

4.5.2. Alternative procedure using COD as borane trapping reagent

In a 10 ml flask equipped with a stirrer, a condenser and an argon inlet, 10 mg (0.04 mol) of $RhCl_3 \cdot nH_2O$, 12.7 mg (1 equiv., 0.04 mmol) of the ligand **1i** and 20 μl (4 equiv., 0.16 mmol) of COD were dissolved in 1.5 ml of dry and degassed THF. The mixture was then heated at reflux for 15 h. After cooling, the solvent was removed under vacuum and the residue was then precipitated in dry ethanol (1 ml). The yellow solid was used without further purification (yield > 80%).

^{31}P-NMR ($CDCl_3$): δ 120 (d, $J_{PRh} = 172$ Hz), 92 (dl).

4.5.3. Alternative procedure: three steps in a one pot procedure

In a 10 ml flask equipped with a magnetic stirrer, a condenser and an argon inlet, 0.020 mmol of diphosphorus borane ligand **1**, 0.120 mmol of DABCO (6 equiv., 13.2 mg) were dissolved in 2 ml of dry and degassed toluene. The mixture was then warmed at 50°C for 12 h. After cooling, the solution was added to a mixture of 0.012 mmol of $[Rh(COD)Cl]_2$, 0.048 mmol (4 equiv.) of $AgBF_4$ and 0.015 ml of COD. The mixture

was stirred at r.t. in the absence of light for 5 h. The black suspension was then filtered through celite, which was washed with 2×3 ml of dry CH_2Cl_2. The solvent was removed under vacuum, and the yellow oil was then precipated in ether. The yellow precipitate was used without further purification.

^{31}P-NMR ($CDCl_3$): δ 153 (d, $J_{PRh} = 129$ Hz).

*4.5.4. Hydrogenation of methyl α-acetamidocinnamic acid derivatives **17** using rhodium catalysts **7***

4.5.4.1. Typical procedure. Into a 100 ml autoclave, under argon atmosphere, were introduced 0.6 mmol of *Z*-α-acetamidocinnamic acid derivative **15**, 3% mol (0.02 mmol) of catalyst (prepared according to the above mentioned procedure) and 8 ml of degassed dry solvent. The reactor was then connected with a hydrogen cylinder, and subjected to six vacuum/H_2 cycles, before pressurizing to initial pressure of 15 bar of H_2. The reaction mixture was allowed to stir for 3–24 h at r.t.. When the reaction was finished, the solvent was removed under reduced pressure. The residue was purified by flash chromatography on silica gel using toluene–AcOEt 3:1 as eluent for **16b**, and by extraction under acid-base conditions for **16a**.

*4.5.4.2. N-Acetyl phenylalanine **16a***. The optical purity was measured by comparison with the standard optical rotation of **16a** ($[\alpha]_D^{20} = +40.7°$, *c* 1 MeOH) [2d].

^{1}H-NMR (DMSO-d_6): δ 7.30 (5H, s, *H* arom), 4.45 (1H, m, C*H*), 3.08 (1H, dd, $^2J_{HH} = 14$, $^3J_{HH} = 4$ Hz, PhCH(*H*)), 2.86 (1H, dd, $^2J_{HH} = 14$, $^3J_{HH} = 12$ Hz), 2.50 (1H, sl, N*H*), 1.78 (3H, s, CH_3CO).

*4.5.4.3. Methyl α-N-acetyl-phenylalaninate **16b***. The enantiomeric excesses and the absolute configuration of compound **16b** were determined on a Chiralcel OD column (Daicel), with a hexane–^{i}PrOH 95:5 mixture as eluent, flow rate 1 ml min^{-1} and UV detection $\lambda = 254$ nm: (*S*)-enantiomer; $t_R = 21.9$ min, (*R*)-enantiomer; $t_R = 26.3$ min.

^{1}H-NMR ($CDCl_3$): δ 1.90 (3H, s, $COCH_3$), 3.04 (2H, m, CH_2Ph), 3.64 (3H, s, CO_2CH_3), 4.81 (1H, m, $CHCO_2CH_3$), 5.90 (1H, br, $NHCOCH_3$), 6.90–7.3 (5H, m, *H* arom); ^{13}C-NMR ($CDCl_3$): δ 22.9 ($COCH_3$), 37.7 (CH_2Ph), 52.1 ($CHCO_2CH_3$), 53.1 (CO_2CH_3), 127 (*C* arom), 128.4 (*C* arom), 129.1 (*C* arom), 135.8 (*C* arom), 169.6 ($COCH_3$), 172.0 (CO_2CH_3).

Acknowledgements

We thank Drs J. Salaün and M. Stéphan for helpful discussions on this work and the Ministry of Research and the CNRS for financial support to our team. We also thank the students S. Lamy, S. Faraüs for their technical help during their undergraduate studies.

References

[1] H. Nozaki, S. Moriuti, H. Takaya, R. Noyori, Tetrahedron Lett. 43 (1966) 5239.

[2] (a) L. Horner, H. Büthe, H. Siegel, Tetrahedron Lett. 37 (1968) 4023. (b) L. Horner, H. Siegel, H. Büthe Angew. Chem. Int. Ed. Engl. 7 (12) (1968) 942. (c) W.S. Knowles, M.J. Sabacky, J. Chem. Soc. Chem. Commun. (1968) 1445. (d) B.D. Vineyard, W.S. Knowles, M.J. Sabacky, G.L. Bachman, D.J. Weinhauff, J. Am. Chem. Soc. 99 (1977) 5946.

[3] (a) R. Noyori, Chem. Soc. Rev. 18 (1989) 187. (b) H. Brunner, W. Zettlmeier, Handbook of Enantioselective Catalysis with Transition Metal Compounds; Products and Catalysis, vols. 1 and 2, VCH, Basel, (1993). (c) I. Ojima, Catalytic Asymmetric Synthesis, VCH, New York, (1993). (d) R. Noyori, Asymmetric Catalysis in Organic Synthesis, Wiley, New York, (1994). (e) M.J. Palmer, M. Wills, Tetrahedron: Asymmetry 10 (1999) 2045. (f) A.Tenaglia, A. Heumann, Angew. Chem. Int. Ed. 38 (1999) 2180.

[4] For recent selected examples of enantioselective catalysis using diphosphine ligands, see: (a) B.M. Trost, F.D. Toste, J. Am. Chem. Soc. 121 (1999) 4545. (b) M.J. Burk, F. Bienewald, S. Challenger, A. Derrick, J.A. Ramsden, J. Org. Chem. 64 (1999) 3290. (c) T. Ireland, G. Grossheimann, C. Wieser-Jeunesse, P. Knochel, Angew. Chem. Int. Ed. 38 (1999) 3212. (d) A. Marinetti, J.P. Genêt, S. Jus, D. Blanc, V. Ratovelomanana-Vidal, Chem. Eur. J. 40 (1999) 1160. (e) H.U. Blaser, H.P. Buser, H.P. Jalett, B. Pugin, F. Spindler, Synlett (1999) 867. (f) Z. Zhang, G. Zhu, Q. Jiang, D. Xiao, X. Zhang, J. Org. Chem. 64 (1999) 1774. (g) M.J. Fehr, G. Consiglio, M. Scalone, R. Schmidt, J. Org. Chem. 64 (1999) 5768. (h) R. Kuwano, Y. Ito, J. Org. Chem. 64 (1999) 1232.

[5] For recent selected enantioselective catalysis using phosphinite or phosphite ligands, see: (a) T.V. Rajanbabu, B. Radetich, K.K. You, T.A. Ayers, A.L. Casalnuovo, J.C. Calabrese, J. Org. Chem. 64 (1999) 3429. (b) K. Yonehara, T. Hashizume, K. Mori, K. Ohe, S. Uemura, J. Org. Chem. 64 (1999) 9374. (c) D.S. Clyne, Y.C. Mermet-Bouvier, N. Nomura, T.V. Rajanbabu, J. Org. Chem. 64 (1999) 7601. (d) W. Hu, M. Yan, C.P. Lau, S.M. Yang, A.S.C. Chan, Y. Jiang, A. Mi, Tetrahedron Lett. 40 (1999) 973. (e) M.T. Reetz, T. Neugebauer, Angew. Chem. Int. Ed. 38 (1999) 179. (f) Y. Chen, X. Li, S.K. Tong, M.C.K. Choi, A.S.C. Chan, Tetrahedron Lett. 40 (1999) 957. (g) E.P. Kündig, C.M. Saudan, G. Bernardinelli, Angew. Chem. Int. Ed. 38 (1999) 1220.

[6] (a) F. Agbossou, J.F. Carpentier, F. Hapiot, I. Suisse, A. Mortreux, Coord. Chem. Rev. 178/180 (1998) 1615. (b) M. Devocelle, A. Mortreux, F. Agbossou, J.R. Dormoy, Tetrahedron Lett. 40 (1999) 4551.

[7] For recent selected enantioselective catalysis using chelating monophosphines or derivative ligands, see: (a) R. Imbos, M.H.G. Brilman, M. Pineschi, B.L. Feringa, Org. Lett. 1 (1999) 623. (b) H. Doucet, E. Fernandez, T.P. Layzell, J.M. Brown, Chem. Eur. J. 5 (1999) 1320. (c) M. Kanai, Y. Nakagawa, K. Tomioka, Tetrahedron 55 (1999) 3843. (d) E.P. Kündig, P. Meier, Helv. Chim. Acta 82 (1999) 1360. (e) K. Ito, R. Kashiwagi, K. Iwasaki, T. Katsuki, Synlett 10 (1999) 1563. (f) S. Kainz, A. Brinkmann, W. Leitner, A. Pfaltz, J. Am. Chem. Soc. 121 (1999) 6421. (g) T. Hayashi, J. Organomet. Chem. 576 (1999) 195. (h) A. Alexakis, C. Benhaïm, X. Fournioux, A. van den Heuvel, J.M. Levêque, S. March, S. Rosset, Synlett (1999) 1811. (i) J.M. Brunel, T. Constantieux, G. Buono, J. Org. Chem.

64 (1999) 8940. (j) E.J. Bergner, G. Helmchen, Eur. J. Org. Chem. (2000) 419. (k) J.A. Blacker, M.L. Clarke, M.S. Loft, M.F. Mahon, M.E. Humphies, J.M.J. Williams, Chem. Eur. J. 6 (2000) 353. (l) F. Lagasse, H.B. Kagan, Chem. Pharm. Bull. 48 (2000) 315.

[8] (a) M. Ohff, J. Holz, M. Quirmbach, A. Börner, Synthesis (1998) 1391. (b) J.M.Brunel, B. Faure, M. Maffei, Coord. Chem. Rev. 178/180 (1998) 665. (c) B. Carboni, L. Monnier, Tetrahedron 55 (1999) 1197.

[9] (a) US Patent 5 043 465 (1989). (b) S. Jugé, M. Stephan, S. Achi, J.P. Genêt, Phosphorus Sulfur 49/50 (1990) 267. (c) S. Jugé, M. Stephan, J.A. Laffitte, J.P. Genêt, Tetrahedron Lett. 31 (1990) 6357. (d) S. Jugé, M. Stephan, R. Merdès, J.P. Genêt, S. Halut-Desportes, J. Chem. Soc. Chem. Commun. (1993) 531. (e) S. Jugé, R. Merdès, S. Stéphan, J.P. Genêt, Phosphorus, Sulfur, Silicon Relat. Elem. 77 (1993) 199. (f) E.B. Kaloun, R. Merdès, J.P. Genêt, J. Uziel, S. Jugé, J. Organomet. Chem. 529 (1997) 455. (g) D. Moulin, C. Darcel, S. Jugé, Tetrahedron: Asymmetry 10 (1999) 4729. (h) D. Moulin, S. Bago, C. Bauduin, C. Darcel, S. Jugé, Tetrahedron: Asymmetry 11 (2000) 3939.

[10] (a) T. Imamoto, T. Oshiki, T. Onozawa, T. Kusumoto, K. Sato, J. Am. Chem. Soc. 112 (1990) 5244. (b) T. Oshiki, T. Hikosaka, T. Imamoto, Tetrahedron Lett. 32 (1991) 3371. (c) T. Imamoto, T. Oshiki, T. Onozawa, M. Matsuo, T. Hikosaka, M. Yanagawa, Heteroatom. Chem. 3 (1992) 563. (d) T. Imamoto, Pure Appl. Chem. 65 (1993) 655. (e) T. Imamoto, M. Matsuo, T. Nonomura, K. Kishikawa, M. Yanagawa, Heteroatom Chem. 4 (1993) 475. (f) T. Imamoto, H. Tsuruta, Y. Wada, H. Masuda, K. Yamaguchi, Tetrahedron Lett. 36 (1995) 8271. (g) T. Miura, H. Yamada, S.I. Kikuchi, T. Imamoto, J. Org. Chem. 65 (2000) 1877.

[11] A.R. Muci, K.R. Campos, D.A. Evans, J. Am. Chem. Soc. 117 (1995) 9075.

[12] B. Wolfe, T. Livinghouse, J. Am. Chem. Soc. 120 (1998) 5116.

[13] (a) U. Nagel, T. Krink, Chem. Ber. 126 (1993) 1091. (b) G. Zhu, M. Terry, X. Zhang, J. Organomet. Chem. 547 (1997) 97. (c) T. Imamoto, J. Watanabe, Y. Wada, H. Masuda, H. Yamada, H. Tsuruta, S. Matsukawa, K. Yamaguchi, J. Am. Chem. Soc. 120 (1998) 1635. (d) R.M. Stoop, A. Mezzetti, F. Spindler, Organometallics 17 (1998) 668. (e) D. Carmichael, H. Doucet, J.M. Brown, J. Chem. Soc. Chem. Commun. (1999) 262. (f) U. Nettekoven, P.C.J. Kamer, P.W.N. van Leeuven, M. Widham, A.L. Spek, M. Lutz, J. Org. Chem. 64 (1999) 3996. (g) F. Maienza, M. Wörle, P. Steffanut, A. Mezzetti, F.Spindler, Organometallics 18 (1999) 1041. (h) H. Tsuruta, T. Imamoto, Tetrahedron: Asymmetry 10 (1999) 877. (i) T. Miura, T. Imamoto, Tetrahedron Lett. 40 (1999) 4833. (j)Y. Yamanoi, T. Imamoto, J. Org. Chem. 64 (1999) 2988. (k) I.D. Gridnev, N. Higashi, K. Asakura, T. Imamoto, J. Am. Chem. Soc. 122 (2000) 7183.

[14] For pioneering works concerning P-chiral bulky phosphines, see: J.M. Brown, J.C.P. Laing, J. Organomet. Chem. 529 (1997) 435.

[15] For pertinent works concerning P-chirogenic monophosphines with a nitrogen chelating group, see: (a) G. Brenchley, E. Merifield, M. Wills, M. Fedouloff, Tetrahedron Lett. 35 (1994) 2791. (b) M. Peer, J.C. de Jong, M. Kiefer, T. Langer, H. Rieck, H. Schell, P. Sennhenn, J. Sprinz, H. Steinhagen, B. Wiese, G. Helmchen, Tetrahedron 52 (1996) 7547. (c) H. Yang, N. Lugan, R. Mathieu, Organometallics 16 (1997) 2089. (d) S. Kudis, G. Helmchen, Angew. Chem. Int. Ed. 37 (1998) 3047.

[16] For P-chirogenic monophosphines with an hydroxy chelating group, see reference 9h.

[17] R. Ewalds, E.B. Eggeling, A.C. Hewat, P.C.J. Kamer, P.W.N. van Leeuwen, D. Vogt, Chem. Eur. J. 6 (2000) 1496.

[18] (a) J.A. Osborn, F.H. Jardine, J.F. Young, G. Wilkinson, J. Chem. Soc. A (1966) 1711. (b) F. Ozawa, A. Kubo, T. Hayashi, Chem. Lett. (1992) 2177. (c) C. Amatore, A. Jutand, M.A. M'Barki, Organometallics 11 (1992) 3009. (d) C. Amatore, A. Jutand, J. Organomet. Chem. 576 (1999) 254. (e) C. Amatore, A. Jutand, Acc. Chem. Res. 33 (2000) 314.

[19] N. Brodie, S. Jugé, Inorg. Chem. 37 (1998) 2438.

[20] (a) O. Stéphan, N. Riegel, S. Jugé, J. Electroanal. Chem. 421 (1997) 5. (b) N. Riegel, C. Darcel, O. Stéphan, S. Jugé, J. Organomet. Chem. 567 (1998) 219.

[21] (a) S. Thorimbert, Ph.D. Thesis, University of Paris VI, 1993. (b) Y. Hamada, F. Matsuura, M. Oku, K. Hatano, T. Shioiri, Tetrahedron Lett. 52 (1997) 8961.

[22] For an in situ decomplexation of the ligand with DABCO, see: H. Brisset, Y. Gourdel, P. Pellon, M. LeCorre, Tetrahedron Lett. 34 (1993) 4523.

[23] (a) S.J. Lippard, J.J. Mayerle, Inorg. Chem. 11 (1972) 753. (b) H. Marsich, A. Camus, E. Cebulec, J. Inorg. Nucl. Chem. 34 (1972) 933. (c) J.T. Gill, J.J. Mayerle, P.S. Welcker, D.F. Lewis, D.A. Ucko, D.J. Barton, D. Stowens, S.J. Lippard, Inorg. Chem. 15 (1976) 1155. (d) M.R. Churchill, F.J. Rotella, Inorg. Chem. 18 (1979) 166.

[24] (a) A. Alexakis, J. Vastra, J. Burton, C. Benhaim, P. Mangeney, Tetrahedron Lett. 39 (1998) 7869. (b) X. Hu, H. Chen, X. Zhang, Angew. Chem. Int. Ed. 38 (1999) 3518. (c) S.M.W. Bennett, S.M. Brown, A. Cunningham, M.R. Dennis, J.P. Muxworthy, M.A. Oakley, S. Woodward, Tetrahedron 56 (2000) 2847. (d) Y. Nakagawa, K. Matsumoto, K. Tomioka, Tetrahedron 56 (2000) 2857. (e) L.A. Arnold, R. Imbos, A. Mandoli, A.H.M. de Vries, R. Naasz, B.L. Feringa, Tetrahedron 56 (2000) 2865. For a recent review on enantioselective conjugate additions, see: M.P. Sibi, S. Manyem, Tetrahedron 56 (2000) 8033.

[25] A. Alexakis, J.C. Frutos, P. Mangeney, Tetrahedron: Asymmetry 4 (1993) 2431.

[26] (a) J.P. Genêt, S. Jugé, S. Achi, S. Mallart, J. Ruiz-Montès, G. Levif, Tetrahedron 44 (1988) 5263. (b) J.P. Genêt, S. Jugé, I. Besnier, J. Uziel, D. Ferroud, N. Kardos, S. Achi, J. Ruiz-Montès, S. Thorimbert, Bull. Soc. Chim. Fr. 127 (1990) 781.

[27] B.M. Trost, Acc. Chem. Res. 29 (1996) 355.

[28] J. Chatt, L.M. Venanzi, J. Chem. Soc. A (1957) 4735.

[29] The methyl ester **15b** was prepared from **15a**, according to a procedure described by: S. Gladiali, L. Pinna, Tetrahedron: Asymmetry 2 (1991) 623.