Dicle Üniversitesi Fen Bilimleri Enstitüsü Dergisi

Dicle University Journal of Institute of Natural and Applied Science

https://dergipark.org.tr/tr/pub/dufed

Araştırma Makalesi / Research Article

Catalytic activity of two Ru(II) complexes in transfer hydrogenation reaction of simple ketones

İki Ru(II) kompleksinin basit ketonların transfer hidrojenasyon reaksiyonundaki katalitik aktivitesi

Nevin ARSLAN[1*]

[1]*Şırnak University, Faculty of Agriculture, Department of Field Crops, Şırnak 73000, Turkey*

ARTICLE INFO

Article History

Received:04.04.2020
Revised:02.05.2020
Accepted:09.05.2020
Available Online:08.06.2020

Keywords

Transfer hydrogenation, Ruthenium, Catalysis, Ketone.

ABSTRACT

Hydrogen transfer reduction reactions have been attracted significant attention in organic synthesis due to their operational easiness. For this purpose, two Ru(II) complexes of P-N-P ligand were prepared starting from $[Ru(\eta^6\text{-}p\text{-cymene})\ (\mu\text{-}Cl)Cl]_2$. Then, their catalytic activity was investigated in the transfer hydrogenation of different simple alkyl and aryl alkyl ketones to respective alcohols in the existence of isopropanol as the hydrogen source. Notably, **2** exhibits a good catalytic activity and affords the respective alcohols with good conversions up to 98 % (TOF: 392 h^{-1}).

MAKALE BİLGİSİ

Makale Tarihi

Alınış: 04.04.2020
Revize: 02.05.2020
Kabul: 09.05.2020
Online Yayınlama:08.06.2020

Anahtar Kelimeler

Transfer hidrojenasyon, Rutenyum, Kataliz, Keton

ÖZ

İşlem yapmanın nispeten kolay olmasından dolayı hidrojen transfer indirgenme reaksiyonları organik sentezde oldukça dikkat çekmektedir. Bu amaçla, $[Ru(\eta^6\text{-p-simen})(\mu\text{-}Cl)Cl]_2$'den yola çıkılarak P-N-P ligandının iki Ru(II) kompleksi hazırlandı. Daha sonra ise, hidrojen kaynağı olarak izopropanol varlığında bu komplekslerin değişik basit alkil ve aril alkil ketonların sekonder alkollere transfer hidrojenasyonundaki katalitik etkinlikleri araştırıldı. **2** nolu kompleksin iyi bir katalizör gibi davranarak % 98'e varan yüksek dönüşümlerle (TOF: 392 h^{-1}) alkolleri vermesi dikkate değerdir.

Corresponding Author

E-mail address: narslan@sirnak.edu.tr (Nevin Arslan)

1. INTRODUCTION

One of the most important conversions in organic synthesis is catalytic hydrogenation using molecular hydrogen, which can be efficiently translated to fundamental industrial processes [1]. The direct hydrogenation by using this gaseous reactant entails special processes or equipment, and its physico-chemical features and reactivity require huge storage and transport expenses. Alternatively, the use of alcohols as a liquid hydrogen carrier is an exciting choice, in which hydrogen may be stored in an organic molecule, followed by employing in transfer hydrogenation [2].

In transfer hydrogenation (TH) reaction catalyzed by transition metal complexes, H^- ion is exchanged between hydride donors and acceptors mediated by a metal. This reaction is widely used in biology as well as chemistry. TH reaction is broadly applied in organic synthesis to reduce ketones, imines, and carbonyls [3]. Numerous alcohols such as isopropanol, glycerol, 2-butanol, ethanol or other hydrogen donors such as aqueous sodium formate, formic acid, formic acid/triethylamine mixture have been employed as a hydrogen donor in TH. Among them, isopropanol and formic acid are commonly used as a hydrogen donor [4].

Bis(phosphino)amine ligands contain P-N-P skeletons and are an efficient arrangement for the production of chelated complexes carrying phosphorus atom. P-N-P fragments have also been demonstrated as adaptable ligands and making a change in the substituents on both the P and N atoms leads to the alterations in the angles of P-N-P moiety [5-6]. These P-N-P based ligands possess the advantages in that they are rather modular and relatively stable toward air or moisture, their synthesis is straightforward, they can easily be optimized and they enable to chelate many transition metals such as rhodium, ruthenium, nickel, platinum, palladium or copper [7].

In this paper, a bis(phosphino)amine ligand [$(Ph_2P)_2NCH_2$–C_4H_3S] and its respective ruthenium(II) complexes, [Ru($(PPh_2)_2NCH_2$-C_4H_3S)(η^6-p-cymene)Cl]Cl, **2** and trans-[Ru($(PPh_2)_2NCH_2$–$C_4H_3S)_2Cl_2$], **3** were synthesized as reported before [8]. In the previous study, the ruthenium complexes were used as a catalyst in transfer hydrogenation of acetophenone and its derivatives. Since a good catalytic activity was observed in these reactions, now, we extend our investigation to cover transfer hydrogenation of substituted alkyl/phenyl and simple alkyl/alkyl ketones by using these complexes as a catalyst.

2. MATERIAL AND METHOD

2.1 General Considerations

All manipulations were performed under inert atmosphere, solvents were dried and distilled under argon before use. Deuterated solvents, PPh_2Cl and thiophene-2-methylamine were supplied from Fluka and used without further manipulation. [Ru(η^6-*p*-cymene)(μ-Cl)Cl]$_2$ [9] was synthesized as

reported before. The IR spectra were measured on a Mattson 1000 ATI UNICAM FT-IR instrument. ^{1}H (400.1 MHz), ^{13}C NMR (100.6 MHz) and ^{31}P-{^{1}H} NMR spectra (162.0 MHz) were obtained on a Bruker AV400 device. Microanalysis was conducted on a Fisons EA 1108 CHNS-O apparatus. Melting points were obtained by a Gallenkamp Model device and are uncorrected.

2.2 GC analyses

GC -analyses -were carried out on a -Shimadzu -GC 2010 -Plus Chromatograp -equipped with capillary column (5% biphenyl, 95% dimethylsiloxane) (30m x -0.32mm x -0.25μm). The -GC -parameters - for -transfer hydrogenation -of -ketones were as reported before [8].

2.3 Synthesis and Characterization of compounds

Thiophene-2-(N,N-bis(diphenylphosphino))methylamine, $[(Ph_2P)_2NCH_2\text{-}C_4H_3S]$, (**1**), $[Ru((PPh_2)_2NCH_2\text{-}C_4H_3S)(\eta^6\text{-p-cymene})Cl]Cl$, (**2**) and trans-$[Ru((PPh_2)_2NCH_2\text{-}C_4H_3S)_2Cl_2]$, (**3**) were synthesized and characterized according to the literature [8].

3. RESULT AND DISCUSSION

3.1 Synthesis of the compounds 1-3

As can be seen in Scheme 1, synthesis of thiophene-2-(N,N-bis(diphenylphosphino)) methylamine, $[(Ph_2P)_2NCH_2\text{-}C_4H_3S]$ **1** was carried out from one equivalent thiophene-2-methylamine and two equivalents of PPh_2Cl in the existence of triethylamine [10-11] in tetrahydrofuran at 0 ^{o}C according to the literature procedure [8]. The ^{31}P NMR spectrum of **1** depicts a singlet signal at 59.83 ppm, which is similar to those found for closely related ligands [12].

In the next step, coordination ability of **1** was investigated with $[Ru(\eta^6\text{-}p\text{-cymene})\ (\mu\text{-}Cl)Cl]_2$ precursor to obtain **2** and **3** [5]. When $(PPh_2)_2NCH_2\text{–}C_4H_3S$, **1** was reacted with one equivalent of $[Ru(\eta^6\text{-}p\text{-cymene})(\mu\text{-}Cl)Cl]_2$, only its respective mono(chelate) complex, $[Ru((PPh_2)_2NCH_2\text{–}C_4H_3S)(\eta^6\text{-}p\text{-cymene})Cl)Cl]$ **2**, was obtained in high yield. There exists a singlet signal at δ 88.2 ppm in the ^{31}P NMR spectrum of **2**, which is in accord with the proposed structure of the complex as well as the literature [13, 14].

When $(PPh_2)_2NCH_2\text{–}C_4H_3S$, **1** was treated with $[Ru(\eta^6\text{-}p\text{-cymene})\ (\mu\text{-}Cl)Cl]_2$ in tetrahydrofuran solution with a molar ratio of 1:1/4 at RT for 1 h, trans-$[Ru((PPh_2)_2NCH_2\text{–}C_4H_3S)_2Cl_2]$, **3** was obtained as crystalline orange powders.

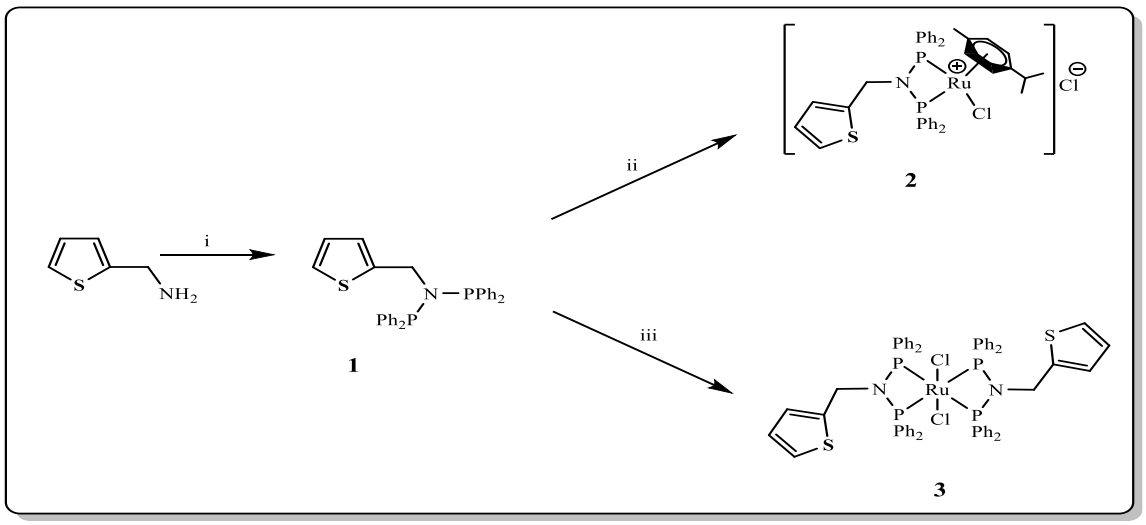


Figure 1. Synthesis of the [Ru((PPh$_2$)$_2$NCH$_2$–C$_4$H$_3$S)(η^6-*p*-cymene)Cl)Cl] **2** and trans-[Ru((PPh$_2$)$_2$NCH$_2$–C$_4$H$_3$S)$_2$Cl$_2$] **3** complexes. (i) 2 equivalent Ph$_2$PCl, 2 equivalent Et$_3$N, thf; (ii) 1 equivalent [Ru(η^6-*p*-cymene))(μ-Cl)Cl]$_2$, thf; (iii) ¼ equivalent [Ru(η^6-*p*-cymene))(μ-Cl)Cl]$_2$, thf.

3.2 Catalytic transfer hydrogenation of ketones

It is well-known that catalysts containing ruthenium metal are often used for the hydrogenation of various ketones [15, 16]. In a recent study, it was shown that the half-sandwich ruthenium complexes of the P-N-P based ligands are active catalysts for the reduction of simple ketones [17]. These ligands are attracting considerable interest and their ruthenium complexes were extensively employed for hydrogenation reactions as catalysts [18, 19]. Ru(II) complexes **2** and **3** were used for catalytic transfer hydrogenation of acetophenone in isopropanol solution (**Scheme 2**). Then, experiments were carried out to obtain optimal conditions as follows: (100:1:5) substrate-catalyst-base molar ratio, isopropanol as a solvent and NaOH as a base at 82 °C. Under these optimum conditions, acetophenone was converted to 1-phenylethanol in 10 min and 1 h, when **2** and **3** were employed, respectively, as the catalysts [5,8]. Now, in this study, it was aimed to reduce various alkyl/phenyl and alkyl/alkyl ketones to their respective alcohols. Thus, as a first step, optimum conditions were investigated for transfer hydrogenation using selected phenyl/alkyl and alkyl/alkyl ketones as a substrate. As a result of these experiments, it was found that these ketones were reduced under similar conditions. Namely, the best molar ratio of substrate-catalyst-base was found to be (100:1:5), isopropanol was a good solvent as well as an alcohol that undergoes oxidation. There was insignificant difference in conversions by using KOH as a base instead of NaOH. So we preferred NaOH as a base. The reactions progressed quicker at 82 °C, which is reflux temperature of isopropanol. Hence, in the next experiments, these optimum conditions were used for the hydrogenation of the ketones (Tables **1** and **2**).

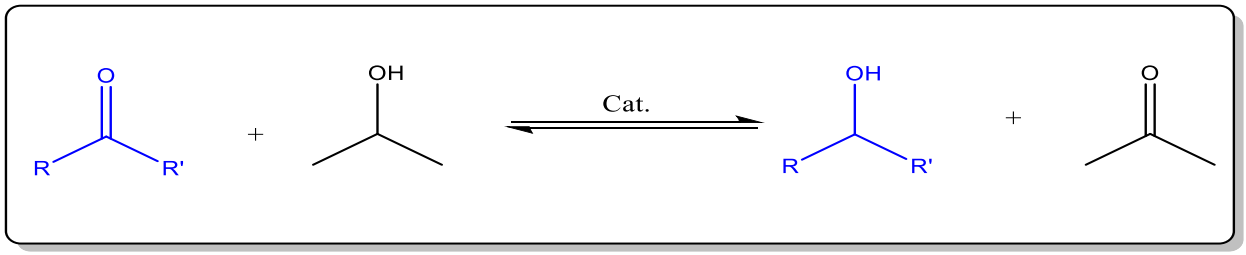
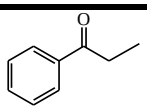
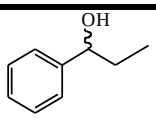
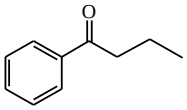
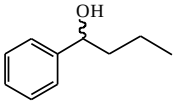
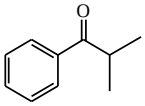
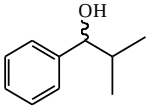
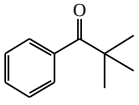
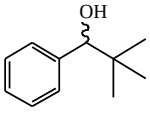


Figure 2 Transfer hydrogenation from isopropanol to acetophenone

Several examples of the hydrogenations carried out employing **2** and **3** as catalysts are shown in Table 1. As can be seen in the Table, the reaction of alkyl/phenyl ketones gave the respective alcohols in high conversions. Then, experiments were performed to explore the effect of steric hindrance of the alkyl moieties on the conversion rate (Table 1, entries 1-8). For this purpose, various simple phenyl/alkyl ketones were converted to the respective alcohols, and it was realized that the activity of the catalysts depends on the steric hindrance of the alkyl moiety, as expected. Conversion rate of phenyl/alkyl ketones having a bulky alkyl substituent was highly low. When the bulkiness of the alkyl moiety increases from ethyl to *tert*-butyl, the transformation rate is reduced gradually. Indeed, the lowest activity was obtained for the reduction of phenyl/*tert*-butyl ketone (Entries 7-8, TOF: 50-11 h^{-1}).

Table 1 Transfer hydrogenation of the substituted alkyl phenyl ketones by using [Ru((PPh$_2$)$_2$NCH$_2$-C$_4$H$_3$S)(η^6-p-cymene)Cl]Cl, (**2**) and trans-[Ru((PPh$_2$)$_2$NCH$_2$-C$_4$H$_3$S)$_2$Cl$_2$] (**3**) [a]

Entry	*Cat.*	*Time*	*Substrate*	*Product*	*Conv. (%)[b]*	*TOF(h^{-1})[c]*
1	**2**	**15 min**			**98**	**392**
2	**3**	**2 h**			**98**	**49**
3	**2**	**30 min**			**97**	**194**
4	**3**	**3 h**			**99**	**33**
5	**2**	**1 h**			**98**	**98**
6	**3**	**5 h**			**97**	**19**
7	**2**	**2 h**			**99**	**50**
8	**3**	**9 h**			**97**	**11**

Reaction conditions:

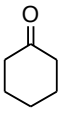
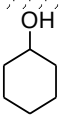
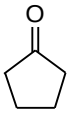
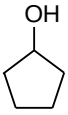
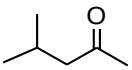
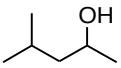
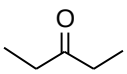
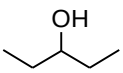
[a] Catalyst (0.005 mmol), substrate (0.5 mmol), isopropanol (5 mL), NaOH (0.025 mmol %), 82 °C, the concentration of alkyl phenyl ketones was 0.1 M;

[b] Purity of the products was checked by ^{1}H NMR and GC (three independent catalytic experiments), conversions were based on methyl aryl ketone;

[c] TOF = (mol product/mol Cat.) x h^{-1}.

Since a rather good catalytic activity was obtained in the previous experiments, then reduction of different simple ketones was studied. Therefore, catalytic activity of complexes **2** and **3** was investigated for simple ketones and the results obviously indicated that they are effective catalysts, which give nearly quantitative conversion of the ketones as can be seen in Table 2 (entries 1–8). It was found that reactivities of two complexes were not the same and activity of **2** is higher (Table 2). For example, under identical conditions, cyclohexanone and cyclopentanone can be reduced with 98 % conversion within 15 min and 2h by complex **2** and **3**, respectively (Table 2 entry1-4). On the other hand, methyl isobutyl ketone hydrogenated with TOF values of 198 and 32 h^{-1}, while diethyl ketone was reduced with TOF values of 97 and 25 h^{-1}, respectively. Thus, it can easily be concluded that **2** is more active than **3,** which has a similar structure except binding manner of ruthenium to the ligand. This indicates importance of binding way on catalytic activity.

Table 2. Transfer hydrogenation of different simple ketones in isopropanol catalyzed by **2** and **3.**[a]

Entry	*Cat.*	*Substrate*	*Product*	*Time*	*Conv. (%)[b]*	*TOF(h^{-1})[c]*
1	**2**			**15 min**	**98**	**392**
2	**3**			**2 h**	**99**	**49**
3	**2**			**15 min**	**98**	**392**
4	**3**			**2 h**	**99**	**50**
5	**2**			**30 min**	**99**	**198**
6	**3**			**3 h**	**97**	**32**
7	**2**			**1 h**	**97**	**97**
8	**3**			**4 h**	**98**	**25**

Reaction conditions:

[a] Refluxing in isopropanol; acetophenone/Cat./NaOH, 100:1:5;

[b] Determined by GC (three independent catalytic experiments), purity of the products was checked by ^{1}H NMR and GC (three independent catalytic experiments), conversions were based on methyl aryl ketone;

[c] TOF = (mol product/mol Cat.) x h^{-1}.

4. CONCLUSION

Two Ru(II) complexes of a P-N-P based ligand were synthesized and then employed in transfer hydrogenation of phenyl/alkyl and simple alkyl/alkyl ketones. The results of catalytic investigations showed clearly that the complexes are effective homogeneous catalysts and give rise to the respective alcohols with good conversions. [Ru((PPh$_2$)$_2$NCH$_2$-C$_4$H$_3$S)(η^6-*p*-cymene)Cl]Cl, **2** is a better catalyst than trans-[Ru((PPh$_2$)$_2$NCH$_2$–C$_4$H$_3$S)$_2$Cl$_2$], **3**. It was also found that the protocol is rather simple and effective towards a variety of ketones and does not necessitate an induction period.

CONFLICTS OF INTEREST

No conflict of interest was declared by the author.

REFERENCES

[1] J. G. de Vries., C, J. Elsevier, The Handbook of Homogeneous Hydrogenation, Wiley-VCH, 2006.

[2] W. Niklas, K. Jürgen, Transfer Hydrogenation of Carbon Dioxide to Methanol Using a Molecular Ruthenium-Phosphine Catalyst, Chem. Cat. Chem, 11 (2019) 1-6.

[3] N. H. Anh, H. Loi, Structure–activity relationship study of halfsandwich metal complexes in aqueous transfer hydrogenation catalysis, Inorg. Chem. Front. 7 (2020) 583-591.

[4] F. A. Georgy, van P. Robbert, J. M. H Emiel, P.A. Evgeny, Catalytic (de)hydrogenation promoted by non-precious metals – Co, Fe and Mn: recent advances in an emerging field, Chem. Soc. Rev. 47 (2018) 1459-1483.

[5] M. Aydemir, A. Baysal, S. Özkar, L. Tatar, trans- and cis-Ru(II) aminophosphine complexes: Syntheses, X-ray structures and catalytic activity in transfer hydrogenation of acetophenone derivatives, Inorg. Chem. Acta. 367 (2011) 166-172.

[6] M. Aydemir, A. Baysal, N. Gurbuz, İ. Ozdemir, B. Gumgum, S. Ozkar, L.T. Yıldırım, Appl. Organomet. Chem. 24 (2010) 17-24.

[7] M-M. Felicite, P. Lo¨nnecke, EV. Novikova, GP. Belov, H-H. Evamarie, Oligodentate P,N ligands: N,N,N′,N′-tetrakis(diphenylphosphanyl)-1,3-diaminobenzene complexes of rhodium, nickel and palladium, Dalton Trans. (2005) 3326–3330.

[8] M. Aydemir, A. Baysal, S. Özkar, L. Tatar, Ruthenium complexes of aminophosphine ligands and their use as pre-catalysts in the transfer hydrogenation of aromatic ketones: X-ray crystal structure of thiophene-2-(N-diphenylthiophosphino)methylamine, Polyhedron 30(5) (2011) 796-804.

[9] M.A. Bennet, A.K. Smith, Arene ruthenium (II) complexes formed by dehydrogenation of

cyclohexadienes with ruthenium (III) trichloride, Chem. Soc. Dalton. Trans. (1974) 233-241.

[10] A. Baysal, M. Aydemir, F. Durap, B. Gümgüm, S. Özkar, L.T. Yıldırım, Synthesis and characterizations of 3,3'-Bis(diphenylphosphinoamine)-2,2'-bipyridine and 3,3'-Bis(diphenylphosphinite)-2,2'-bipyridine and their chalcogenides, Polyhedron, 26 (2007) 3373-3378.

[11] M. Aydemir, A. Baysal, F. Durap, B. Gümgüm, S. Özkar, L.T. Yıldırım, Synthesis and characterization of new transition metal complexes of thiophene-2-methylamine: X-ray crystal structure of palladium (II), platinum (II) complexes and use of palladium(II) complexes as pre-catalyst in Heck and Suzuki cross-coupling reaction, Appl. Organomet. Chem, 23 (2009) 467-475.

[12] A.D. Burrows, M.F. Mahona, M. T. Palmera, Ether functionalised aminophosphines: synthesis and coordination chemistry of palladium(II) and platinum(II) complexes, J. Chem. Soc. Dalton Trans. (2000) 1669-1677.

[13] M.S. Balakrishna, R. Panda, D.C. Smith Jr, A. Klaman, S.P. Nolan, Ruthenium(II) Chemistry of Phosphorus Based Ligands. Ph2PN(R)PPh2 (R=Me or Ph) and Ph2PN(Ph)P(E)Ph2 (E = S or Se). Solution Thermochemical study of Ligand Substitution Reactions in the Cp'RuCl(COD) (Cp' = Cp, Cp*; COD = cyclooctadiene) System, J. Organometal.Chem, 599 (2000) 159-165.

[14] M.S. Balakrishna, K. Ramaswarmy, R.M. Abhyankar, Transition Metal Chemistry of Phosphorus based ligands. Ruthenium (II) Chemistry of Bis(diphosphino)amines, $X_2PN(R)PX_2$ (R=H or Ph, X=Ph; R=Ph, X2=O2C6H4), J. Organometal Chem. 560 (1998) 131-136.

[15] J. W. Faller, A. R. Lavoie, Catalysts for the Asymmetric Transfer Hydrogenation of Ketones Derived from l-Prolinamide and $(p\text{-CymeneRuCl}_2)_2$ or $(Cp^*RhCl_2)_2$, Organometallics 20 (2001) 5245-5247.

[16] J.-X. Gao, X.-D. Yi, P.-P. Xu, C. -L. Tang, H.-L. Wan, T. Ikariya, New chiral cationic rhodium–aminophosphine complexes for asymmetric transfer hydrogenation of aromatic ketones, J. Organometal. Chem. 592 (1999) 290-295.

[17] M. Aydemir, A. Baysal, Ruthenium-catalyzed transfer hydrogenation of aromatic ketones with aminophosphine or bis(phosphino)amine ligands derived from isopropyl substituted anilines, Polyhedron 29 (2010) 1219-1224.

[18] Y. Chen, S. Yekta, A.K. Yudin, Modified BINOL Ligands in Asymmetric Catalysis, Chem. Rev. 103 (2003) 3155-3212.

[19] T. Jerphagnon, J.L. Renaud, C. Bruneau, Chiral monodentate phosphorus ligands for rhodium-catalyzed asymmetric hydrogenation, Tetrahedron: Asymmetry, 15 (2004) 2101-2111.