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Journal of Organometallic Chemistry 691 (2006) 741–747
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

New chiral oxazoline based-rhodium(I) catalysts: Synthesis, characterisation, heterogeneisation and applications

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Received 4 August 2005; received in revised form 3 October 2005; accepted 6 October 2005
Available online 18 November 2005

Abstract

New chiral oxazoline-based rhodium(I) homogeneous and heterogeneous catalysts have been prepared and fully characterised through ^{1}H and ^{13}C NMR, CP-MAS NMR and XPS. The method used for anchoring the catalyst onto silica was found particularly suitable, since the organometallic complexes remained unchanged over the procedure. The catalysts exhibited a moderate activity and enantioselectivity in hydrogenation of C=O and C=C double bond.

Keywords: Bis(oxazoline); Pyridino-oxazolines; Chiral rhodium(I)-complexes; Tethered catalysts; Hydrogenation

1. Introduction

Enantioselective catalysis became one of the most efficient methodologies for asymmetric organic synthesis of biologically relevant natural or synthetic molecules in fine chemistry and related disciplines.

Based on the pioneering Pfaltz works related to the synthesis of the C_2-symmetric semicorrins, the chemistry of C_2-symmetric chiral bis(oxazoline) ligands and of their corresponding transition-metal complexes, have received during the last decades a great attention through their successful applications in asymmetric catalysis of numerous reactions [1]. Since the early 1990s, chiral bis(oxazoline) complexes have been successfully applied to carbon–carbon coupling reactions such as the Diels–Alder reactions [2,3] or the cyclopropanation reactions [4], to aziridination reactions [5], hydrosilylations [6], oxidations [7] or reductions [8,9]. Usually, high conversions and enantioselectivities were observed. Recently, new chiral pyridino-oxazoline ligands have been developed giving more stable catalysts, however few applications were reported [10–14].

While successful, the use of chiral nitrogen based catalysts remains limited in the fine chemical industry mainly due to the tedious separation and recycling of these homogeneous complexes. These difficulties can be overcome by the development of heterogeneous catalysts based on the oxazoline ligands. Several methods have been applied to immobilise the bis(oxazoline) ligands onto organic polymers or inorganic supports.

The first example was reported by Mayoral et al. in 1997 [15]. The authors used electrostatic interactions between an anionic support, i.e. a clay, and a cationic copper (II) bis(oxazoline) complex for cyclopropanation reactions [16,17]. Latter, the same authors reported the copolymerisation of allyl- or styryl-modified bis(oxazoline) ligands as an interesting alternative method [18,19]. Following these pioneering works, several authors reported the grafting of chiral bis(oxazoline) ligands on organic polymers (ArgoGel [20], PEG [21,22]), or on metal oxides [23–27]. On the contrary, very few reports concern, the heterogeneisation of chiral pyridine-oxazoline based complexes [28–30].

These supported bis(oxazoline)-based catalysts were tested successfully in cyclopropanations, Diels–Alder reactions, aziridination or hydrosilylation reaction but no

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doi:10.1016/j.jorganchem.2005.10.016

successful example of reduction have been reported in the literature.

We previously reported the reduction of phenyl-alkyl ketones by transfer hydrogenation catalysed by chiral bis(oxazoline) transition metal complexes [31]. Encouraged by these results, we investigated further the development of heterogeneous catalysts for enantioselective reduction based on the C_2-symmetric bis(oxazoline) ligands.

In the present contribution, we describe the preparation of the different homogeneous and heterogeneous complexes and the characterisation of new homogeneous and silica supported chiral bis(oxazoline)- and pyridino-oxazoline-rhodium(I) complexes. The first results achieved with the different catalysts for the hydrogenation of prochiral carbonyl and olefinic compounds are reported.

2. Results and discussion

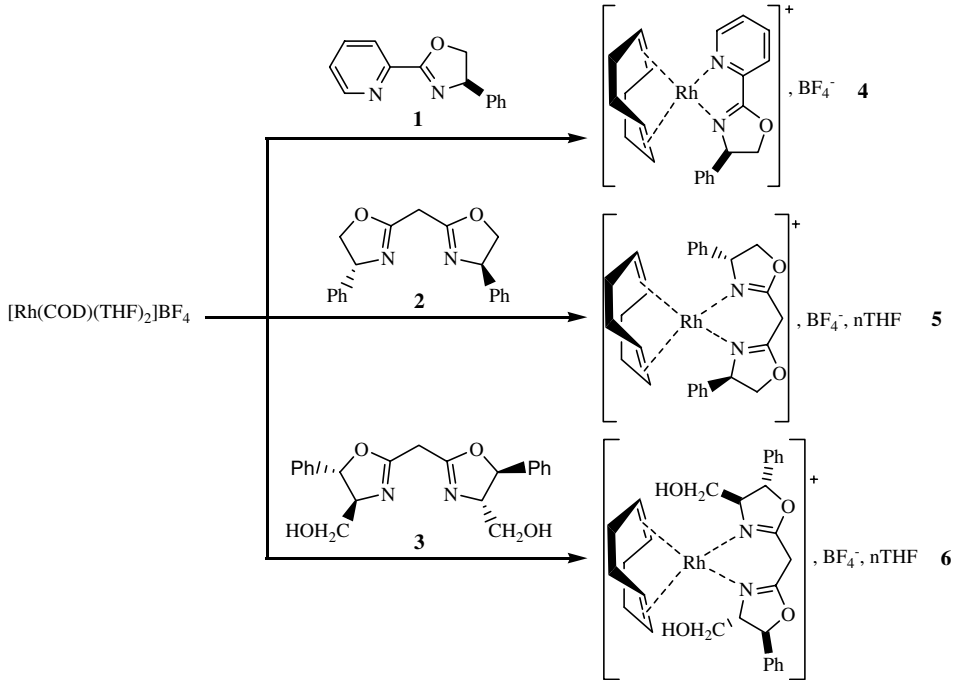
The chiral pyridine-oxazoline ligand (PyOx) **1** was prepared from the commercial picolinic acid and (*S*)-phenylglycinol following the 4 steps procedure reported by Meyers et al. [32] in 36% overall yield. The chiral bis(oxazoline) ligand **2** (BoxPh) and **3** (BoxOH) were synthesised from the diethylmalonimidate dihydrochloride and the commercial (*S*)-phenylglycinol or (1*S*, 2*S*)-2-amino-1-phenylpropane-1,3-diol, respectively, in CH_2Cl_2 according to a procedure reported by Aggarwal et al. [33] in good yields.

The corresponding rhodium(I) complexes [Rh(I)-PyOx-COD]$^+$[BF_4]$^-$ (**4**), [Rh(I)-BoxPh-COD]$^+$[BF_4]$^-$ (**5**) and [Rh(I)-BoxOH-COD]$^+$[BF_4]$^-$ (**6**) were prepared from the cationic precursor [Rh(I)(COD)$(THF)_2$]$^+$[BF_4]$^-$ in dry THF in excellent isolated yields (>89%) (Scheme 1) [34].

The homogeneous complexes [Rh(I)-PyOx-COD]$^+$[BF_4]$^-$ (**4**), [Rh(I)-BoxPh-COD]$^+$[BF_4]$^-$ (**5**), and [Rh(I)-BoxOH-COD]$^+$[BF_4]$^-$ (**6**) were fully characterised through NMR spectra, IR, $[\alpha]_D$ and elemental analysis. IR spectra (film) show the characteristic $\nu_{C=N}$ band at 1643–1653 cm^{-1}, in good agreement with values reported in the literature for structurally close bis(oxazoline) complexes [35,36]. ^{13}C NMR spectra of the complexes **4–6** gave a signal at 168–172 ppm corresponding to the C=N of the oxazoline ring. The presence of THF was observed by NMR (^{1}H: 1.78 and 3.67 ppm; ^{13}C: 25.6 and 67.9 ppm), for the complexes prepared from the bis-oxazoline ligands. Considering the ^{1}H integration, one molecule of THF was probably enclosed into the crystal net of the complex **5** during the removal of the solvent. Such phenomenon was not observed with the PyOx corresponding complex **4**, but was already reported in the literature for rhodium complexes [37].

All other signals of the ^{1}H and ^{13}C NMR spectra were attributed to the cyclooctadienyl and bis(oxazoline) ligands coordinated to the rhodium(I) centre. More specifically, the ^{1}H NMR spectra of rhodium(I) complexes show signal corresponding to the bridging CH_2 group of the BOX moiety as a singlet at 4.05 ppm for **5** and 3.99 ppm for **6**, suggesting a C_2-symmetry in these complexes [38].

In order to achieve the heterogeneisation of **5** onto silica (SiO_2), the chiral bis(oxazoline) ligand **2** was functionalised at the bridging CH_2 carbon by introduction of a tris(ethoxy)silyl-alkyl chain (Scheme 2). ^{1}H and ^{13}C NMR spectra of the resulting ligand (C_3BoxPh) **7** indicate that the C_2-symmetry of the bis(oxazoline) moiety is not disordered by such modification. The corresponding rhodium(I) complex [Rh(I)-C_3BoxPh-COD]$^+$[BF_4]$^-$ (**8**) was obtained



Scheme 1. Synthesis of the chiral rhodium(I) complexes **4–6**.

following the procedure described above starting from the crude substrate **7** and was used in further steps without purification.

Anchoring of **8** was performed by treatment of a suspension of activated silica in dichloromethane to give the heterogeneous catalysts {[Rh(I)-C_3BoxPh-COD]$^+$[BF_4]$^-$}@SiO_2 (**9**). At this stage, a new chiral centre was created but according to previous report, modification at this carbon did not affect the enantiocontrol of the reaction [39]. The success of the covalent anchoring was assessed by analytical and spectroscopic characterisations (NMR and XPS) of the resulting solids. According to the chemical analyses (C, H, N and Rh), 0.12–0.14 $mmol_{complex}$ g^{-1} were grafted on the silica support, in good agreement with results usually reported in the literature for such preparations [24,26,27]. ^{13}C CP-MAS NMR spectra of the supported homogeneous catalyst {[Rh(I)-C_3BoxPh-COD]$^+$[BF_4]$^-$}@SiO_2 (**9**) was in good agreement with the expected structure containing the oxazoline ring bearing a C3-pendant chain and the cyclooctadienyl ligand. The signals observed at 19 and 51 ppm were attributed to residual CH_3CH_2O group linked to the bridging silicon atom at the silica surface. According to Corma et al., [26] this observation would attest that the {[Rh(I)-C_3BoxPh-COD]$^+$[BF_4]$^-$} complex **8** is grafted onto the support by two Si–O–Si links (see Fig. 1).

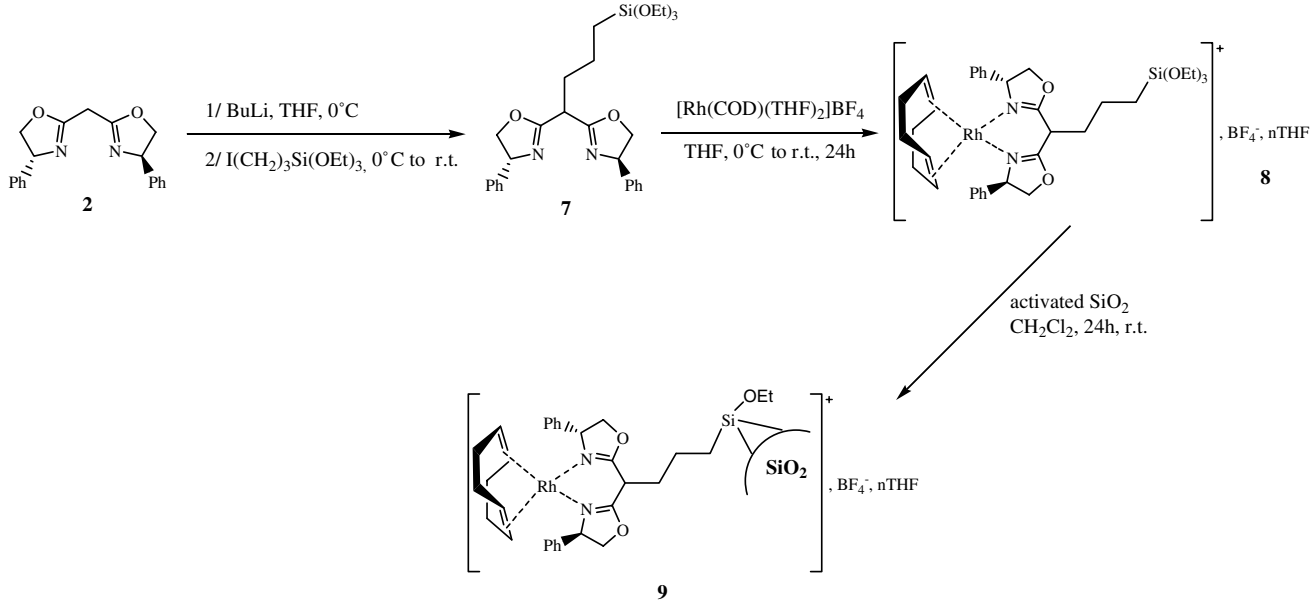
X-ray photoelectron spectroscopy (XPS) has been used for qualitative and quantitative characterisation of the homogeneous and heterogeneous catalysts **5** and **9**. The binding energies for the [Rh]-$3d_{5/2}$ as well as the atomic ratio of N/Rh are summarized in Table 1. A binding energy of 285 eV of the C1s level was used as internal standard. The position of the $Rh3d_{5/2}$ peaks of the homogeneous **5** and grafted **9** complexes were observed at 308.85 and 308.80 eV, respectively, with a slightly larger width in the case of the latter one (Fig. 2).

Typically, such binding energies can be assigned to $Rh^{(I)}$ species [40,41]. The close values observed for both homogeneous and grafted complexes would indicate that the sphere coordination around the metallic center is the same in the two rhodium catalysts **5** and **9**. Since NMR characterisation of **5** confirmed the expected structure for the {[Rh(I)-BoxPh-COD]$^+$[BF_4]$^-$} complex, we assume that both complexes have the same coordination properties (ligand field) and that the rhodium centre is in the same oxidation state 1+. These results, together those issued from the characterisation by ^{13}C CP-MAS NMR of the catalyst **9**, indicate that the rhodium complex {[Rh(I)-C_3BoxPh-COD]$^+$[BF_4]$^-$} (**8**) was not altered during the grafting procedure.

In most cases the semi-quantitative XPS analysis of the catalysts gave results in good agreement with the expected structure, generally close to those obtained from elemental analyses (Table 1). The N/Rh atomic ratios calculated from these analyses were used to confirm both the structures and the purities of the rhodium catalysts. If for the homogeneous catalyst **5**, both the XPS and the elemental analyses gave values in agreement with the expected structure (respectively, 1.7 and 2.0; expected 2.0), those obtained for the heterogeneous catalysts **9** show higher N/Rh ratio (respectively, 4.5 and 3.6) indicating that some free bis(oxazoline) ligand is present at the silica surface probably due to partial decomplexation during the grafting procedure. Extensive washing of the heterogeneous catalyst **9** assured the absence of free complex.

We reported previously the use of bisoxazoline-Rh complex **6** in the transfer hydrogenation of acetophenone. Low conversion (22%) and ee (16%) were achieved [31].

Alternatively, the homogeneous Rh(I)-catalysts **4**–**6** were evaluated for the enantioselective hydrogenation of C=O and C=C bonds. These catalysts exhibited very low activity towards the hydrogenation of α-acetamido cinnamic acid



Scheme 2. Preparation of the heterogeneous catalyst **9**.

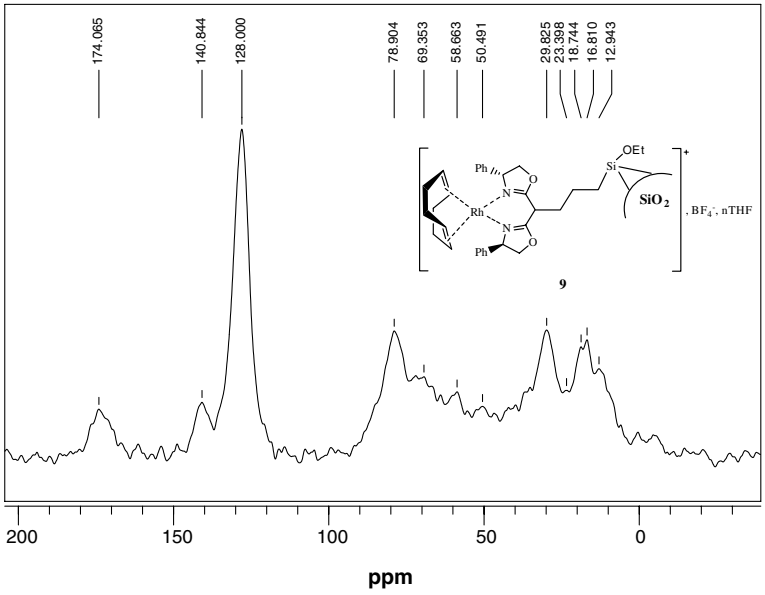


Fig. 1. CP MAS ^{13}C NMR of the heterogeneous catalyst **9**.

Table 1
XPS analysis of homogeneous complex **5** and heterogeneous catalyst **9**

Complex	Binding energy (eV) Rh $3d_{5/2}$	Atomic ratio N/Rh[a]
5	308.85	1.7 (2)
9	308.8	3.5 (4.6)
9 after H_2	307.5	
9 after HTR	309.2	

[a] Calculated from XPS analysis (calculated from elemental analysis).

even under hydrogen pressure. At atmospheric pressure, the methyl tiglate was slowly hydrogenated. Increasing the pressure yielded total conversion but gave only racemic product mixture (Table 2). Low to moderate conversions were observed for the hydrogenation of acetophenone or methyl acetoacetate corresponding to modest TON (<50 mol/mol_{Rh}). Except for phenyl ethanol, for which low ee's were observed (<10%), racemic products were analyzed.

The heterogeneous {[Rh-C_3BoxPh-COD]$^+$[BF_4]$^-$}@SiO_2 catalyst **9** was evaluated for the hydrogenation of the methyl acetoacetate. Using only 0.06 mol% Rh, a reasonable conversion of 24% within 6 h was obtained, corresponding to the unexpected TON of 800 mol/mol_{Rh}, giving again the racemic product.

The XPS binding energies observed for the used heterogeneous rhodium catalyst **9** at 307.3 eV accounting for the formation of metallic Rh(0) species [42], indicating that the rhodium(I) complex **8** was reduced during the hydrogenation reaction. The rhodium(0) species precipitated, most probably, onto the silica support during the reaction. Reduction of nitrogen-containing rhodium complex under

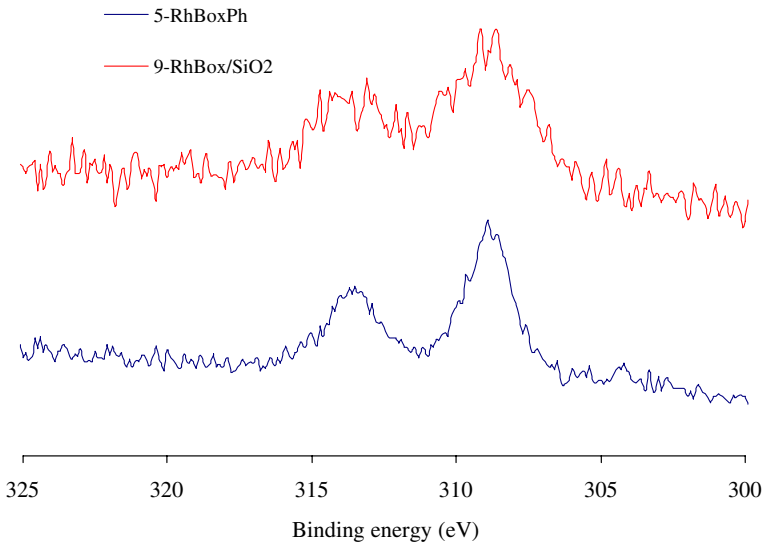
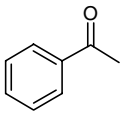
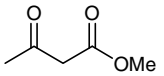
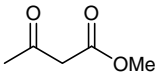


Fig. 2. XPS analysis of the homogeneous catalyst **5** and heterogeneous catalyst **9**.

Table 2
Hydrogenation in the presence of homogeneous Rh(I)-catalysts **4**–**6**

Catalyst			
	Conversion (%)[a] (ee) (%)	Conversion (%)[b]	Conversion (%)
4	13 (10)	50	100 (20 bar, 30 °C) 31 (1 bar, r.t.)
6	76 (7)	30	100 (20 bar, 30 °C) 10 (1 bar, r.t.)
5	63 (6)	41	96 (20 bar, 30 °C)

[a] 200 mg of acetophenone, 1 mol% Rh/S, 10 mL MeOH, 10 bar H_2, r.t.
[b] 200 mg of methyl acetoacetate, 1 mol % Rh/S, 10 mL MeOH, 20 bar H_2, 30 °C.

nitrogen pressure was previously reported in the literature in the presence of diamine ligand [43]. Excess of ligand may prevent this decomplexation.

Such reduction of the rhodium has not been observed when the catalyst **9** was used in transfer hydrogenation (iPrOH, tBuOK) [44]. Under those conditions, $Rh3d_{5/2}$ peak at 309.2 eV was detected for the used catalyst **9** accounting for the remaining presence of $Rh^{(I)}$-species on the silica support.

The absence of enantioselectivity can be clearly correlated to the lack stability of the different rhodium complexes under hydrogenation reaction conditions. These results are coherent with the formation of metallic rhodium during the reaction as observed by the apparition of black colour after hydrogenation. The higher activity observed for the supported complex **8** can be attributed to a good dispersion of the precipitated metallic rhodium particles during the reaction onto the silica support, rather than rhodium agglomeration in the reaction media as probably observed for the homogeneous catalysts **4**–**6**.

3. Conclusion

New homogeneous and heterogeneous chiral rhodium-catalysts based onto chiral bis(oxazoline) and pyridino-oxazoline ligands have been prepared and fully characterised. After anchoring onto inorganic support (SiO_2) the structure of the organometallic {[Rh(I)-C_3Box-Ph-COD]$^+$[BF_4]$^-$} complex **8** remained intact as outlined by the ^{13}C CP-MAS NMR and XPS analyses.

The activity and selectivity of the homogeneous catalysts were evaluated for the enantioselective hydrogenation of prochiral C=O and C=C bonds. While the catalysts gave generally a moderate activity, no significant enantioselectivities were observed.

This was reasonably attributed to the instability of the catalysts under the reaction conditions. As shown by XPS analysis of the used catalyst **9**, the rhodium(I) species are converted to rhodium(0) particles that were probably precipitated onto the support surface, those being not enantioselective for the hydrogenation reaction. These nitrogen-based complexes are preferably used in transfer hydrogenation involving reaction conditions more favourable to their stability.

4. Experimental

All preparations, manipulations and reactions were carried out under argon (Schlenk techniques), including the transfer of the catalysts to the reaction vessel. All glassware was base- and acid-washed and oven dried.

THF was distilled under argon before use over sodium from purple benzophenone ketyl and CH_2Cl_2 and $CHCl_3$ were distilled over CaH_2. Silica Aerosil 200 was agglomerated prior to use by treatment with water. After evaporation and drying at 120 °C for 3 days the resulting material was crushed and sieved to give a selected fraction with a particle size of 40–60 mesh. BET of a silica sample dehydroxylated at 500 °C under 10^{-5} mmHg for 6 h gave the following characteristics: specific surface = 204 ± 4 m^2/g. The organometallic precursor [Rh(I)(COD)-$(THF)_2$]$^+$[BF_4]$^-$ was prepared according to the literature [34].

Solution NMR spectra were recorded with a Bruker AM 250 spectrometer (^{1}H NMR were referenced to the residual protio-solvent: $CDCl_3$, $\delta = 7.25$ ppm; ^{13}C NMR were referenced to the C-signal of the deutero solvent: $CDCl_3$, $\delta = 77$ ppm). Solid-state ^{13}C-CP-MAS NMR spectra were recorded on a Bruker DSX 300 or DSX 500 spectrometer. ^{13}C NMR were arbitrarily referenced to the internal aromatic signal of the phenyl-ring substituent on the oxazoline ring at 128 ppm. The absolute rhodium content of the catalysts was determined by ICP-AES from a solution obtained by treatment with a mixture of H_2SO_4 and HNO_3 and HCl in a Teflon reactor at 250–300 °C. XPS measurements were recorded on an ESCALAB 250 spectrometer equipped with a Al–K source (1486.6 eV). The measurements of the binding energies were referred to the characteristic C1s peak of the carbon fixed at the generally accepted value of 285.0 eV.

Gas chromatography was performed on a Shimadzu 14A chromatograph equipped with a FID detector and a Lipodex A column for the methyl acetoacetate and the Chirasil Dex CB for the acetophenone. Flash chromatography was performed at a pressure slightly greater than atmospheric pressure using silica (Merck Silica Gel 60, 230–400 mesh). Thin layer chromatography was performed on Fluka Silica Gel 60 F_{254}.

*4.1. Synthesis of the 2-(4R-phenyl-4,5-dihydrooxazoli-2-yl)-pyridine (**1**)*

A solution of picolinic acid (2.07 g, 16.8 mmoles) in freshly distilled thionyl chloride (20 mL) was refluxed for 20 h. After cooling, the excess of thionyl chloride was removed under vacuum to give the corresponding acid

chloride as a dark red solid. A solution of (*R*)-phenylglycinol (2.47 g, 18.0 mmoles) and triethylamine (6.8 mL) in dry chloroform (40 mL) was added dropwise at 0 °C to a solution of acid chloride in dry chloroform (20 mL). The mixture is stirred for 20 h at room temperature then thionyl chloride (12 mL) was added and the solution was refluxed for 4 h. After cooling, the solution was slowly poured in ice water (100 mL). After 10 min, the organic layer was collected and washed with brine (40 mL), an aqueous solution of K_2CO_3 0.1 M (2×50 mL) and brine (40 mL). The organic layer was dried over Na_2SO_4 and the solvent was removed under vacuum. The residue was purified by flash chromatography eluting with Et_2O/heptane (50/50) to give the ligand as orange viscous oil in 36% yield.

^{1}H RMN ($CDCl_3$, 250 MHz): 8.68 (dq, $J = 4.8$ Hz, 0.8 Hz, 1H, C*H*$_{(C_5H_4)}$); 8.10 (pseudo dt, $J = 7.9$ Hz, 1H, C*H*$_{(C_5H_4)}$); 7.74 (td, $J = 7.8$ Hz, 1.8 Hz, 1H, C*H*$_{(C_5H_4)}$); 7.36 (ddd, $J = 7.6$ Hz, 4.9 Hz, 1.1 Hz, 1H, C*H*$_{(C_5H_4)}$); 7.28 (m, 5H, C*H*$_{(C_6H_5)}$); 5.40 (dd, $J = 10.2$ Hz, 8.6 Hz, 1H, C*H*$_2$O); 4.84 (dd, $J = 10.3$ Hz, 8.5 Hz, 1H, C*H*$_2$O); 4.33 (pseudo t, $J = 8.5$ Hz, 1H, CH_2CHN). ^{13}C RMN ($CDCl_3$, 62.9 MHz): 163.86 (O*C*N); 149.75 (*o*-*C*H$_{(C_5H_4N)}$); 146.65 (*Cq*$_{(C_5H_4N)}$); 141.77 (*Cq*$_{(C_6H_5)}$); 136.68 (*C*H); 128.78 (*m*-*C*H$_{(C_6H_5)}$); 127.73 (*C*H); 126.79 (*o*-*C*H$_{(C_6H_5)}$); 125.75 (*C*H); 124.24 (*C*H); 75.30 (CH_2CHN); 70.33 (*C*H$_2$). IR : ν(CN) = 1644 cm^{-1}.

4.2. Synthesis of the bis(oxazoline) 2 and 3 [33]

A solution of aminoalcohol (11.9 mmol) and diethyl malonimidate hydrochloride (5.9 mmol) in dry dichloromethane (20 mL) was refluxed for 18 h under argon. At completion of the reaction (TLC), water (40 mL) was added and the mixture was extracted by CH_2Cl_2 (3×20 mL). The combined organic layers were dried over $MgSO_4$ and the solvent was removed under vacuum to give a brown oil. The residue was purified by flash chromatography eluting with CH_2Cl_2/MeOH (90:10) to give bis(oxazoline).

bis[(4*R*)-*Phenyl*-2-*oxazoline*]*methylene* (**2**) was obtained as orange viscous oil in 57% yield. IR: ν(CN) = 1663 cm^{-1}. ^{1}H and ^{13}C NMR data are consistent with those reported [4].

bis[(4S,5S) (4-*Hydroxymethyl*-5-*phenyl*-2-*oxazoline*)]*methylene* (**3**) was obtained as a white solid in 62% yield. IR: ν(CN) = 1673 cm^{-1}. ^{1}H and ^{13}C NMR data are consistent with those reported [33].

4.3. Preparation of homogeneous catalyst 4–6

The pyridine-oxazoline ligand or, the bis(oxazoline) ligands (0.34 mmol) was added at 0 °C to a solution of $[Rh(COD)(THF)_2]^+[BF_4]^-$ (150.2 mg, 0.34 mmol) in dry THF (10 mL). The solution was stirred for 20 h at room temperature and the solvent was removed under vacuum to give the expected complex.

{[Rh(I)-PyOx-COD]$^+$[BF$_4$]$^-$} (***4***): orange solid, 95% yield, m.p. = 222–228 °C (decomposition). ^{1}H NMR (CD_2Cl_2, 250 MHz): 8.16 (td, $J = 7.6$ Hz, 1.7 Hz, 1H, *m*-C_5H_4N); 7.93 (m, 1H, *o*-C_5H_4N); 7.83 (m, 1H, *m*-C_5H_4N); 7.78 (m, 1H, *p*-C_5H_4N); 7.30 (m, 5H, (C*H*$_{(C_6H_5)}$)); 5.24 (dd, $J = 4$ Hz, 2 Hz, 1H, C*H*$_2$O); 5.22 (t, $J = 4$ Hz, 1H, C*H*$_2$O); 4.59 (dd, $J = 4$ Hz, 2 Hz, 1H, NC*H*); 4.45 (m, 2H, CH$_{(COD)}$); 4.31 (m, 2H, CH$_{(COD)}$); 2.38 (m, 4H, C*H*$_{2(COD)}$); 1.90 (m, 4H, C*H*$_{2(COD)}$). ^{13}C NMR (CD_2Cl_2, 62.9 MHz): 172.2 (O*C*N); 149.9 (Cq$_{(C_5H_4N)}$); 145.0 (*o*-C_5H_4N); 141.8 (*m*-C_5H_4N); 138.4 (Cq$_{(C_6H_5)}$); 131.1 (*m*-C_5H_4N); 129.9 (*m*-C_6H_5); 129.8 (*p*-C_5H_4N); 127.5 (*o*-C_6H_5); 126.6 (*p*-C_6H_5); 83.4 (*C*H$_{(COD)}$); 80.1 (*C*H$_{(COD)}$); 67.4 (*C*H$_{2(COD)}$); 29.9 (*C*H$_{2(COD)}$). Anal. for $C_{22}H_{24}N_2O_4RhBF_4$ [Found (Calc.)]: C, 49.7 (50.6); H, 4.7 (4.6); N, 5.3 (5.4); Rh, 19.7 (19.7). $[\alpha]_D = -33.6°$ (*c* 0.22, $CHCl_3$). IR: ν(CN) = 1643 cm^{-1}

{[Rh(I)-BoxPh-COD]$^+$[BF$_4$]$^-$} (***5***): yellow solid, 89% yield, m.p. = 130–135 °C (decomposition) ^{1}H NMR ($CDCl_3$, 250 MHz): 7.25 (m, 10H, (CH$_{(C_6H_5)}$); 5.01 (dd, $J = 10.0$ Hz, 4.4 Hz, 2H, C*H*C$_6$H$_5$); 4.96 (dd, $J = 9.0$ Hz, 9.0 Hz, 2H, C*H*$_2$OCN); 4.21 (dd, 2H, $J = 9$ Hz, 4.5 Hz, C*H*$_2$OCN); 4.18 (m, 2H, C*H*$_{(COD)}$); 4.05 (s, 2H, CC*H*$_2$C); 3.67 (m, 4H, C*H*$_2$O$_{(THF)}$); 3.48 (m, 2H, C*H*$_{2(COD)}$); 2.25 (m, 2H, C*H*$_{2(COD)}$); 1.78 (m, 4H, C*H*$_2$CH$_2$O$_{(THF)}$); 1.62 (m, 2H, C*H*$_{2(COD)}$); 1.31 (m, 2H, C*H*$_{2(COD)}$). ^{13}C NMR ($CDCl_3$, 62.9 MHz): 168.7 (O*C*N); 139.6 (*Cq*$_{(C_6H_5)}$); 129.4 (*m*-C_6H_5); 128.9 (*p*-C_6H_5); 126.0 (*o*-C_6H_5); 83.1 (*C*H$_{(COD)}$, *J*(*Rh–C*) = 12.4 Hz); 80.4 (*C*H$_{(COD)}$, *J*(*Rh–C*) = 12.4 Hz); 77.8 (O*C*H$_2$); 67.9 (O*C*H$_{2(THF)}$, *C*H–C$_6$H$_5$); 30.7 (*C*H$_{2(COD)}$); 29.3 (*C*H$_{2(COD)}$); 27.9 (C*C*H$_2$C); 25.6 (*C*H$_2$CH$_2$O$_{(THF)}$). Anal. for $C_{35}H_{46}N_2O_4RhBF_4$ [Found (Calc.)]: C, 56.17 (56.11); H, 6.19; (6.14); N, 3.74 (3.74); Rh, 13.75 (13.75). $[\alpha]_D = -143°$ (*c* 0.2, $CHCl_3$). IR: ν(CN) = 1647 cm^{-1}.

{[Rh(I)-BoxOH-COD]$^+$[BF$_4$]$^-$} (***6***): yellow solid, 90% yield, m.p. = 130–135 °C (decomposition). ^{1}H NMR ($CDCl_3$, 250 MHz): 7.41 (m, 10H, (C*H*$_{(C_6H_5)}$); 5.76 (d, J = 4.1 Hz, 2H, C*H*O); 4.35 (m, 2H, C*H*N); 4.06 (m, 2H, C*H*$_2$OH); 3.99 (s, 2H, CC*H*$_2$C); 3.88 (m, 2H, C*H*$_2$OH); 3.75 (m, 10H, C*H*$_2$O (THF), C*H*$_{(COD)}$); 2.58 (m, 4H, C*H*$_{(COD)}$); 1.85 (m, 8H, C*H*$_2$CH$_2$O$_{(THF)}$); 1.70 (m, 4H, C*H*$_{(COD)}$).^{13}C NMR ($CDCl_3$, 62.9 MHz): 168.1 (O*C*N); 137.5 (*Cq*$_{(C_6H_5)}$); 129.6 (*m*-C_6H_5); 129.4 (*p*-C_6H_5); 125.6 (*o*-C_6H_5); 85.8 (*C*H–C$_6$H$_5$); 83.1 (*C*H$_{(COD)}$, *J*(*Rh–C*) = 12.4 Hz); 80.5 (*C*H$_{(COD)}$, *J*(*Rh–C*) = 12.4 Hz); 73.7 (*C*HN); 67.9 (O*C*H$_{2(THF)}$); 65.8 (*C*H$_2$OH); 30.9 (*C*H$_{2(COD)}$); 29.5 (*C*H$_{2(COD)}$); 28.1 (C*C*H$_2$C); 25.6 (*C*H$_2$CH$_2$O$_{(THF)}$). Anal. for $C_{37}H_{50}N_2O_6RhBF_4$ [Found (Calc.)]: C, 56.2 (56.9); H, 6.2 (6.4); N, 3.6 (3.6); Rh, 13.5 (13.2). $[\alpha]_D = -87.8°$ (*c* 0.2, $CHCl_3$). IR: ν(CN) = 1653 cm^{-1}.

4.4. Preparation of the modified ligand bis[4-phenyl-2-oxazoline]methylene propyltriethoxysilane (7)

n-BuLi (1.9 mL of a solution 2.1 M in *n*-hexane, 4.1 mmol) was added dropwise at 0 °C to a solution of **2** (1.26 g, 4.1 mmol) in dry THF (60 mL). The solution was allowed to warm to room temperature and stirred for 3 h. Then, the 3-iodopropylethoxysilan (1.36 g, 4.1 mmol) was added drop wise at 0 °C. The mixture was allowed to warm

to room temperature and stirred for 21 h. The solvent was removed under vacuum. The residue was dissolved in CH_2Cl_2 (20 mL) and washed with an aqueous saturated NH_4Cl solution (1 × 20 mL). The organic layer was dried over Na_2SO_4 and the solvent evaporated under vacuum to give the ligand **7** as orange viscous oil in 98% yield.

^{1}H NMR ($CDCl_3$, 250 MHz): 7.26 (m, 10H, ($CH_{(C_6H_5)}$)); 5.23 (m, 2H, NC*H*); 4.64 (m, 2H, OCH_2CH); 4.14 (m, 2H, OCH_2CH); 3.79 (m, 7H, OCH_2CH$_3$ and NCC*H*CN); 2.11 (m, 2H, CHCH_2CH$_2$); 1.77 (m, 2H, CH$_2$CH_2CH$_2$); 1.19 (m, 9H, OCH$_2$CH_3); 0.69 (m, 2H, CH_2Si). ^{13}C NMR ($CDCl_3$, 62.9 MHz): 168.57 (*C*=N); 141.99 ($Cq_{(C_6H_5)}$); 128.30 ($CH_{(C_6H_5)}$); 127.14 (*p*-$CH_{(C_6H_5)}$); 126.41 ($CH_{(C_6H_5)}$); 74.64 (*C*H$_2$O); 69.23 (N*C*H); 57.96 (*C*H$_2$OSi); 36.93 (NC*C*HCN); 34.57 (CH$_2$*C*H$_2$CH$_2$); 17.97 (*C*H$_3$CH$_2$); 17.41 (CH$_2$*C*H$_2$CH); 10.52 (*C*H$_2$Si).

4.4.1. General procedure for anchoring the {[Rh(I)-C$_3$BOX-COD]$^+$[BF$_4$]$^-$} complex **8**

The complex **8** was added to a suspension of SiO_2 in dry CH_2Cl_2 (15 mL/0.1 mmol of **8**). The mixture was stirred for 24 h at room temperature. The heterogeneous catalyst **9** was filtered under argon, washed twice with 10 mL of dry CH_2Cl_2 and dried under vacuum.

^{13}C CP-MAS NMR (75.5 MHz): 174 (*C*N); 140 ($Cq_{(C_6H_5)}$); 128 ($Cq_{(C_6H_5)}$); 78 (*C*H (COD)); 59 (*C*H$_2$O); 50 (CH$_3$*C*H$_2$O); 41 (CH$_2$*C*H$_2$CH$_2$); 35 (NC*C*HCN); 30 (*C*H$_2$ (COD)); 19 (*C*H$_3$CH$_2$O); 17 (CH$_2$*C*H$_2$CH); 13 (*C*H$_2$Si). Found Anal.: Rh, 1.38; C, 7.91; H, 1.04; N, 0.87.

4.4.2. General procedure for hydrogenation reactions

All hydrogenation reactions were performed in stainless steel autoclaves equipped with a glass inlet. The substrate (200 mg) and the catalyst (1 mol %) were dissolved in 10 mL MeOH. The glass inlet was introduced in the autoclave that was then purge by series of pressurisation/depressurisation under hydrogen before the pressure was set to the desire value. The reaction was performed at 30 °C for 24 h.

Acknowledgements

The authors thank Pierre Delichère for XPS analysis and discussions and Frédéric Lefèbvre for ^{13}C-CP-MAS NMR. N.D. thanks the Ministry of Education for a grant.

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