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Asymmetric reduction of ketones with ruthenium-oxazoline based catalysts

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ABSTRACT

New chiral oxazoline-based ruthenium(II) complexes have been synthetized and fully characterised. The corresponding grafted catalysts were prepared by anchoring the complexes onto SiO_2 or Pd/SiO_2 supports. ^{13}C CP-MAS NMR and XPS spectroscopies showed that the organometallic complexes remained unchanged when they were deposited on the support. High activity and enantioselectivity in the reduction of acetophenone were achieved with some homogeneous complexes.

1. Introduction

The synthesis of optically pure compounds is still challenging. Asymmetric catalytic reduction of ketones has been extensively studied over last three decades. However few practical industrial applications have been developed mainly due to the problem of recycling the costly catalytic system (i.e. sensitive chiral ligand and transition metals). In order to circumvent these constraints, preparations of heterogeneous catalytic systems were reported according to two main approaches: either grafting of organometallic systems to solid support, or development of heterogeneous catalysts based on supported metals modified by chiral inductors (modifiers) [1]. Although these extensive works allowed high enantioselectivities, these systems remained very specific to the substrates or needed hard reaction conditions. More recently, an alternative approach was reported by Gao and Angelici in which they combined two catalytic systems: a covalently grafted homogeneous complex (i.e. molecular catalyst) associated to supported metallic nanoparticles (i.e. heterogeneous catalyst) on a single support [2]. These so-called TCSM (Tethered Complexes on a Supported Metal), exhibited higher activities than that of the corresponding tethered complex on the support or the supported metal particles separately. These combined catalysts proved to be very efficient not only for the reduction of arene to the corresponding saturated cyclic compounds [3], but also for the hydrogenation of cyclohexanone to cyclohexanol [4], the hydrodehalogenation of fluorobenzene [5] and the hydroformylation of terminal olefins [6]. The enantioselective hydrogenation of methyl-α-acetamidocinnamate with such catalysts (rhodium-chiral phosphine complexes tethered to palladium on silica) was also reported [7]. In ref. [3], the organometallic complex was immobilized over silica through sulfonato groups that formed strong H-bonds to silanols. Such a "hybrid system" (i.e. $Rh(I)–Pd(0)/SiO_2$) is four times more active than the heterogeneous $Pd(0)/SiO_2$ for the hydrogenation of arenes. Blum and co-workers reported the preparation of entrapped rhodium complex and palladium nanoparticle in a sol–gel material that exhibited high activities towards aromatic hydrogenation [8]. It has been proposed that the catalytic efficiency of the TCSM is a consequence of a hydrogen-spillover process enhancing thus the hydrogenation activity of the grafted molecular catalyst. However, this mechanism remains a subject of discussions. More recently, Bianchini et al. proposed that the enhanced activity of a $Rh(I)–Pd(0)/SiO_2$ was due to a simultaneous activation of the substrate through isolated rhodium-grafted complex (i.e. single sites catalytic activation) and the palladium nanoparticles [9]. This explanation was supported by EXAFS, DRIFT measurements and batch catalytic experiments [10].

TCSM, when involving chiral complexes, could bring advantages to the development of enantioselective catalysts. Considering the previous literature reports, it can be expected that milder conditions should be necessary to achieve similar activities for a combined catalyst and the "parent" single species. As a

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consequence, one can expect enhanced optical purity using such systems. To our knowledge, a single report is dealing with the use of combined catalysts in asymmetric hydrogenation [7]. The authors grafted a [(2*S*,4*S*)-4-(diphenylphosphino)-2-(diphenylphosphinomethyl)pyrrolidine-rhodium-(COD)] complex on silica (SiO_2) and supported-palladium on silica (Pd-SiO_2) after modification of the diphosphine ligand. These catalysts were evaluated for the enantioselective hydrogenation of methyl-α-acetamidocinnamate, both giving high conversions and enantioselectivities (>90%); however, one should mention that the original rhodium complex used in this study was known to be highly active and selective for this reaction (ee >94%).

Previously, we reported the synthesis of new heterogeneous chiral bis(oxazoline)-ruthenium complexes efficient for asymmetric transfer hydrogenation of ketones [11]. The corresponding rhodium-based complexes were less efficient in terms of optical purity but they could be grafted on silica without affecting their structures [12].

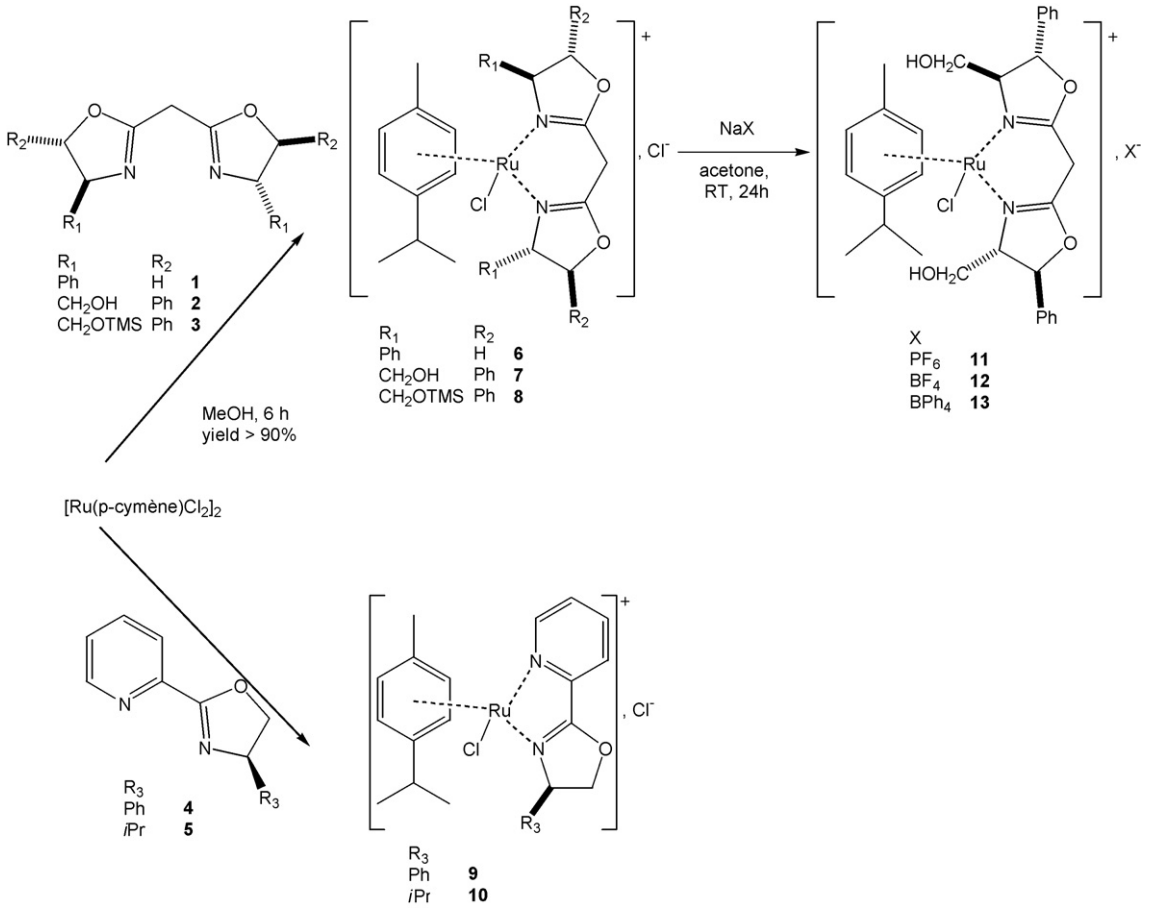
In this paper, we report the synthesis of homogeneous oxazoline-based ruthenium catalysts, as well as the corresponding grafted ([Ru]/SiO_2) and combined ([Ru]/Pd@SiO_2) catalysts. These catalysts were characterized by liquid- and solid-state NMR and XPS measurements and their catalytic properties were evaluated in the asymmetric reduction of acetophenone.

2. Results and discussion

2.1. Preparation of the homogeneous catalysts

The chiral bis(oxazoline) ligand **1** (BoxPh) and **2** (BoxOH) were synthesized in good yields (50–62%) from the commercially available diethylmalonimidate dihydrochloride and (*S*)-phenylglycinol or (1*S*, 2*S*)-2-amino-1-phenylpropanediol, respectively. Subsequently, the OH-protected ligand **3** (BoxOTMS) was obtained in high yield (94%) by treatment of **2** with TMSCl in THF/NEt_3 [11,12]. The chiral pyridine-oxazoline ligands **4** (PyOxPh) and **5** (PyOxPr) were synthesized from commercially available picolinic acid and (*S*)-phenylglycinol or (*S*)-valinol, respectively, in reasonable yields (30%).

Neutral chiral diphosphine ruthenium(2-Methylallyl)$_2$ complexes are known to be very efficient in enantioselective hydrogenation of C=C bonds or as precursors to active complexes for asymmetric hydrogenation of C=O bonds [13]. These complexes are synthesized by reaction of the corresponding diphosphine with the [Ru(COD)(Metallyl)$_2$] precursor complex. As to our knowledge, the corresponding pyridine-oxazoline or bis(oxazoline) complexes (named after along this paper "*dinitrogen*" complexes for convenience) were not described, we studied the reaction of [Ru(COD)(Metallyl)$_2$] with the above ligands and more precisely BoxPh **1**. Unfortunately, whatever the reaction conditions, the NMR analysis of the solid isolated after the reaction showed that the cyclooctadiene ligand was still chelated to the metallic centre. This was probably due to the fact that the *dinitrogen* BoxPh was not a ligand as good as the commonly used diphosphine [13] and was not able to shift the cyclooctadiene moiety from the ruthenium. Alternatively, cationic ruthenium complexes were then studied. The synthesis of the *dinitrogen*-chelated cationic ruthenium complexes from commercial [Ru(*p*-Cymene)Cl_2]$_2$ dimer was previously described [14]. These complexes exhibited efficient activity in Diels-Alder reaction or Claisen rearrangement. The Ru(II)-catalysts



Scheme 1. Synthesis of *dinitrogen* ruthenium complexes.

6–10 were then synthesized in high yields (90–99%) in degassed methanol at room temperature for 6 h by using a procedure very similar to that described by Dixneuf and co-workers [14] (Scheme 1).

All complexes were fully characterized through their NMR and IR spectra, $[\alpha]_D$ and elemental analysis. As a typical example, the ^1H and ^{13}C NMR spectra of complex **7** are given in Fig. 1. All signals corresponding to the BoxOH ligand in the complex **7**

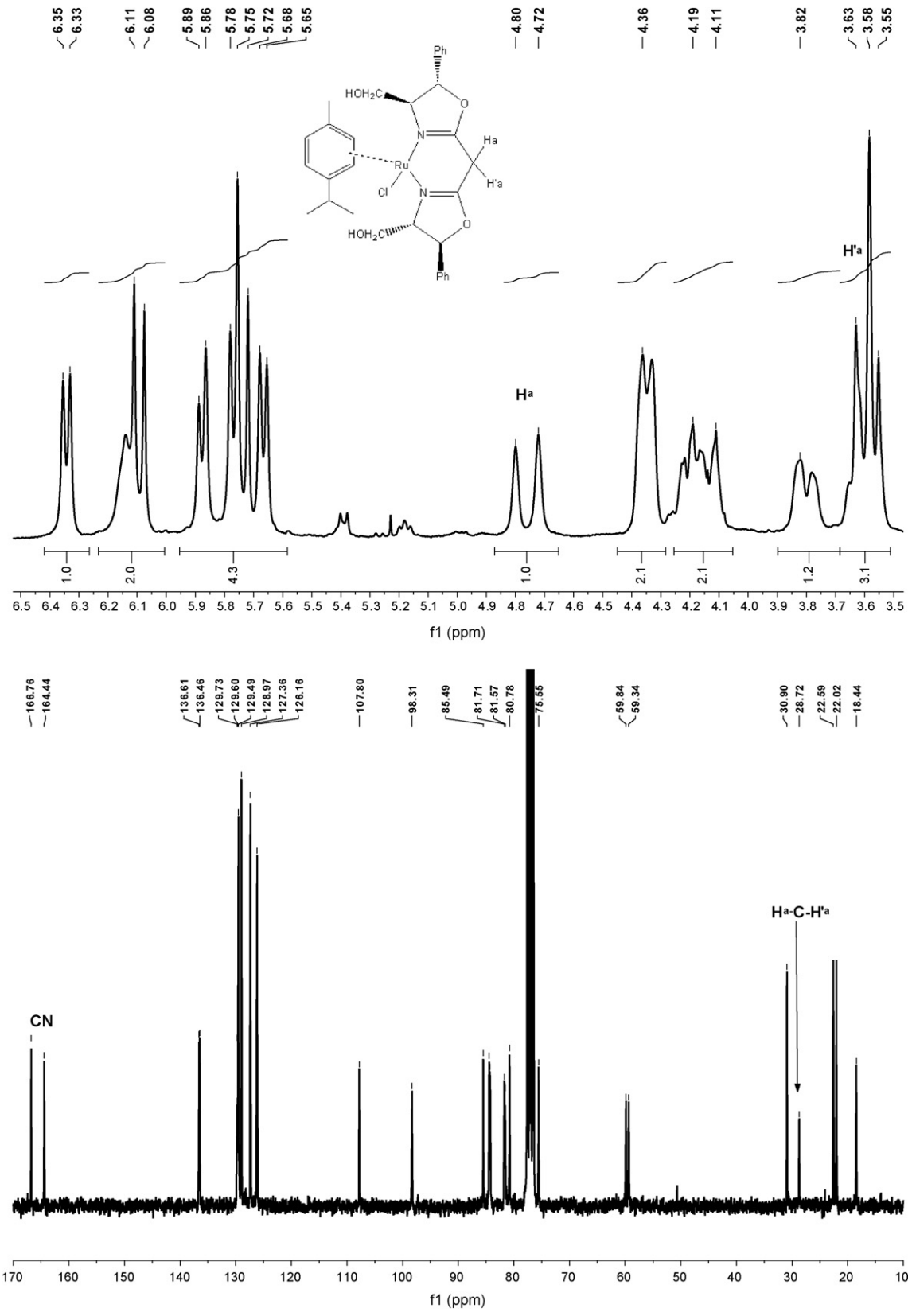


Fig. 1. ^{13}C and ^1H enlargement NMR spectra of [(BoxOH)RuCl(*p*-Cym)]Cl complex **7**.

were split compared to the naked ligand **2** meaning that the C_2 symmetry of the ligand was not retained in the complex. The extensive attribution of the peaks was established with HMQC and COSY45 analyses. A clear difference (more than 2 ppm: 164.5 and 166.8 ppm) was observed for the two C=N moieties. Moreover, both protons borne by the central carbon of the bisoxazoline ligand were significantly separated by more than 1 ppm (3.64 and 4.71 ppm).

As the counter-ion could affect significantly the activity and/or selectivity of the catalyst, the hexafluorophosphate **11**, tetrafluoroborate **12** and tetraphenylborate **13** complexes analogous of **7** were prepared by metathesis. Typically, complex **7** was treated with one equivalent of the corresponding sodium salt in acetone (Scheme 1) to give the expected cationic complexes isolated by filtration and evaporation of the solvent. ^{1}H NMR spectra similar to that of **7** were observed for complexes **11–13**.

Whatever the counter ion, no single crystal could be isolated. Molecular modelling of complex **7** was made using MM2 parameters extended to transition metals. The structure corresponding to the thermodynamic energy minimum was further investigated using DFT calculations with the B3LYP functional and the LanL2DZ pseudopotential. At completion, it was checked that the optimized structure corresponds to a minimum by calculation of the infrared spectrum. Absence of imaginary frequencies confirms the energy minimization. As shown on Fig. 2, a piano-stool arrangement is observed for the sandwich complex in which the ruthenium centre is coordinated to the *p*-cymene ring on one face, and to the two nitrogen atoms of the BoxOH ligand and the chloride ion on the second face, in good agreement with previous reports for similar complexes [15,16]. The main feature of the calculated structure is the presence of one hydrogen bond between one of the hydroxymethyl substituent of the Box ligand and the chlorine atom on ruthenium (d(H—Cl) = 2.19 Å), accounting for the loss of C2-symmetry in the complex **7** as observed from NMR experiments.

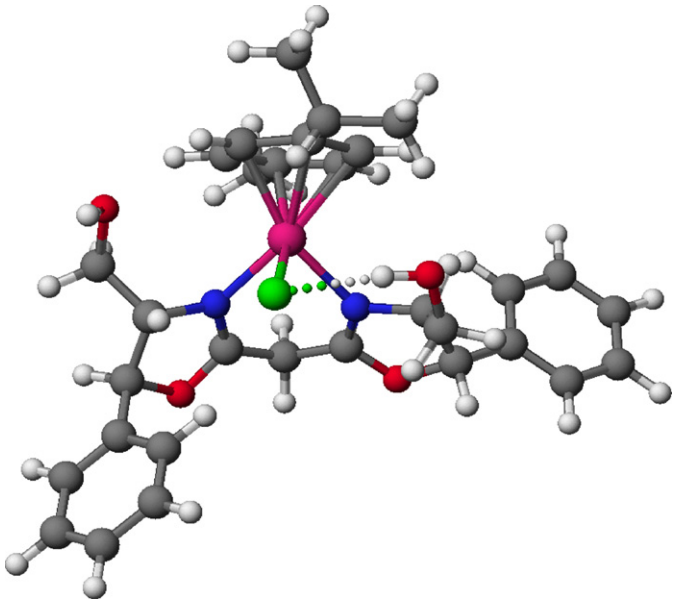
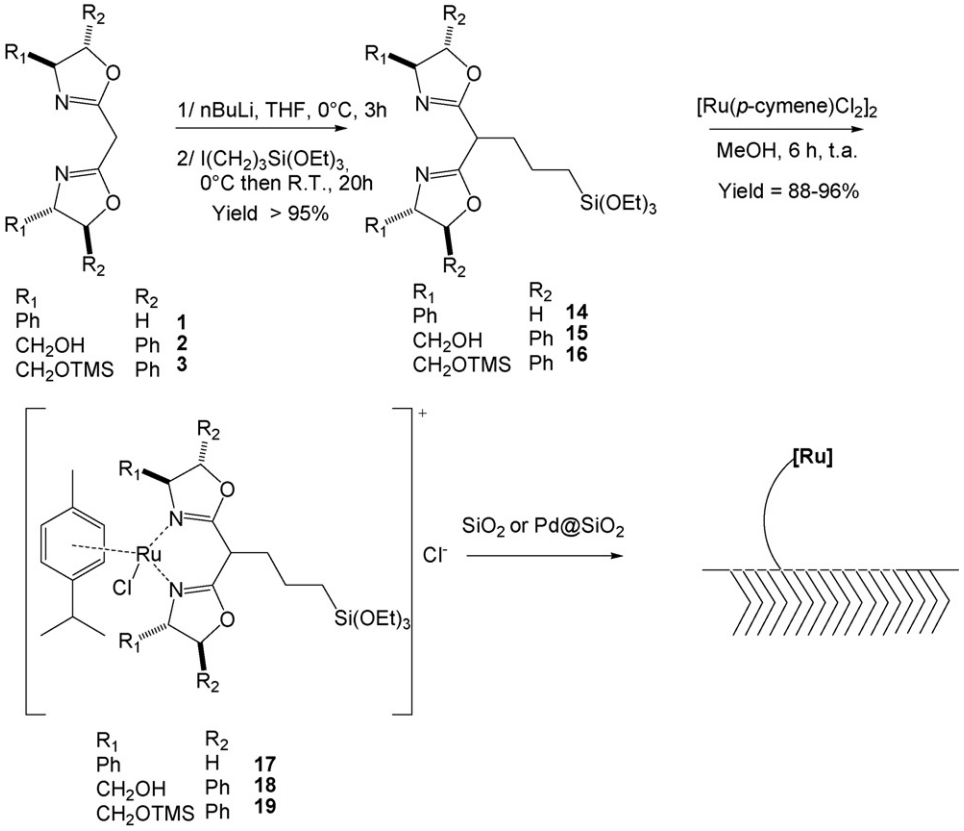


Fig. 2. Calculated structure of [(BoxOH)RuCl(*p*-Cym)]Cl complex **7**.

2.2. Preparation of the grafted and combined catalysts

In order to achieve the heterogeneisation of complexes **6–8** onto silica, a tris(ethoxy)silyl-alkyl chain was introduced at the bridging CH_2 of the bis(oxazoline) ligands **1–3** following reaction conditions described by Clarke and Shannon [17]. Treating **1–3**



Scheme 2. Heterogeneization of ruthenium complexes.

Table 1
Chemical composition of heterogeneous catalysts

Entry	Catalyst	%Ru[a]	%Pd[a]	%Complex	$mmol_{complex}/g$
1	**17**/SiO_2	1.62		10.5	0.16
2	**18**/SiO_2	1.73		12.7	0.17
3	**19**/SiO_2	2.01		17.4	0.20
4	**17**/Pd@SiO_2	1.62	0.43	10.5	0.16
5	**18**/Pd@SiO_2	1.72	0.55	12.5	0.17
6	**19**/Pd@SiO_2	1.93	0.50	16.7	0.19

[a] weight percentage determined by elemental analysis.

Table 2
XPS analysis of ruthenium complexes[a]

Entry	Catalyst	N/Ru	Ru/Pd	Ru $3d_{5/2}$
1	**8**	2.0		281.8
2	**19**/SiO_2	1.7		281.6
3	**19**/Pd@SiO_2	2.0	6.2 (4.1)[b]	281.5

[a] A1 source (1486.6 eV), analysis energy 50 eV, internal reference C1s = 285,0 eV.
[b] Calculated from elemental analysis.

with nBuLi and $I(CH_2)Si(OEt)_3$ in THF gave the new ligands **14–16** in high yield (>95%). These ligands were further used without any purification. The corresponding cationic ruthenium complexes **17–19** were obtained in excellent yields (88–96%) following the procedure described above.

NMR analyses of the new complexes **17–19** were similar to that observed for the related complexes **6–8**. The grafted catalysts ([Ru]/SiO_2) and the combined one ([Ru]/Pd@SiO_2) were prepared by treating a suspension of activated silica (SiO_2) or silica supported-palladium (Pd@SiO_2) with the corresponding ruthenium complexes **17–19**, respectively (Scheme 2). After filtration, extensive washing to remove the soluble non-grafted complexes and drying, the catalysts were analyzed to determine the grafting level. The corresponding data are collected in Table 1.

According to the elemental analysis, the presence of palladium on the silica did not affect the amount of grafted complex on the support. Whatever the initial complex, 0.16–0.20 $mmol_{complex}\ g^{-1}$ were grafted on the support, in good agreement with literature data [18,19]. The successful grafting of the three complexes was supported by ^{13}C CP-MAS NMR analysis of the different catalysts. Whatever the support used, identical NMR spectra were obtained for BoxOH-based complexes grafted on SiO_2 (**18**/SiO_2) or Pd@SiO_2 (**18**/Pd@SiO_2) meaning that in both cases the complex was grafted on the silicium oxide via silicate bridges and was not adsorbed on the metallic surface, as predictable, in the case of [Ru]/Pd@SiO_2 (Fig. 3).

X-ray photoelectron spectroscopy (XPS) analysis was used for qualitative and quantitative characterizations of the homogeneous **8**, grafted **19**/SiO_2 and combined **19**/Pd@SiO_2 catalysts. The binding energy for the Ru $3d_{5/2}$ as well as the N/Ru and Ru/Pd atomic ratios is reported in Table 2. A binding energy of 285 eV corresponding to the C1s level was used as internal standard.

The Ru $3d_{5/2}$ binding energies were in the range 281.5–281.8 eV whatever the catalyst. Such values are in accordance with the presence of ruthenium in the +2 oxidation state as reported in the literature ($[Ru(bpy)_3]Cl_2 \cdot xH_2O$; Ru $3d_{5/2}$ 281.6 eV) [20]. The close values observed for the three catalysts indicate that no modifications in the coordination sphere around the ruthenium centre, even in the presence of metallic palladium, occurred during the grafting procedure.

The nitrogen/ruthenium atomic ratio calculated for the molecular catalyst **8** (2.0) was in good agreement with the expected value (2.0). Moreover, similar N/Ru ratios were obtained for the heterogeneous catalysts: the complex was then stable upon grafting without decomposition unlike the behaviour of the

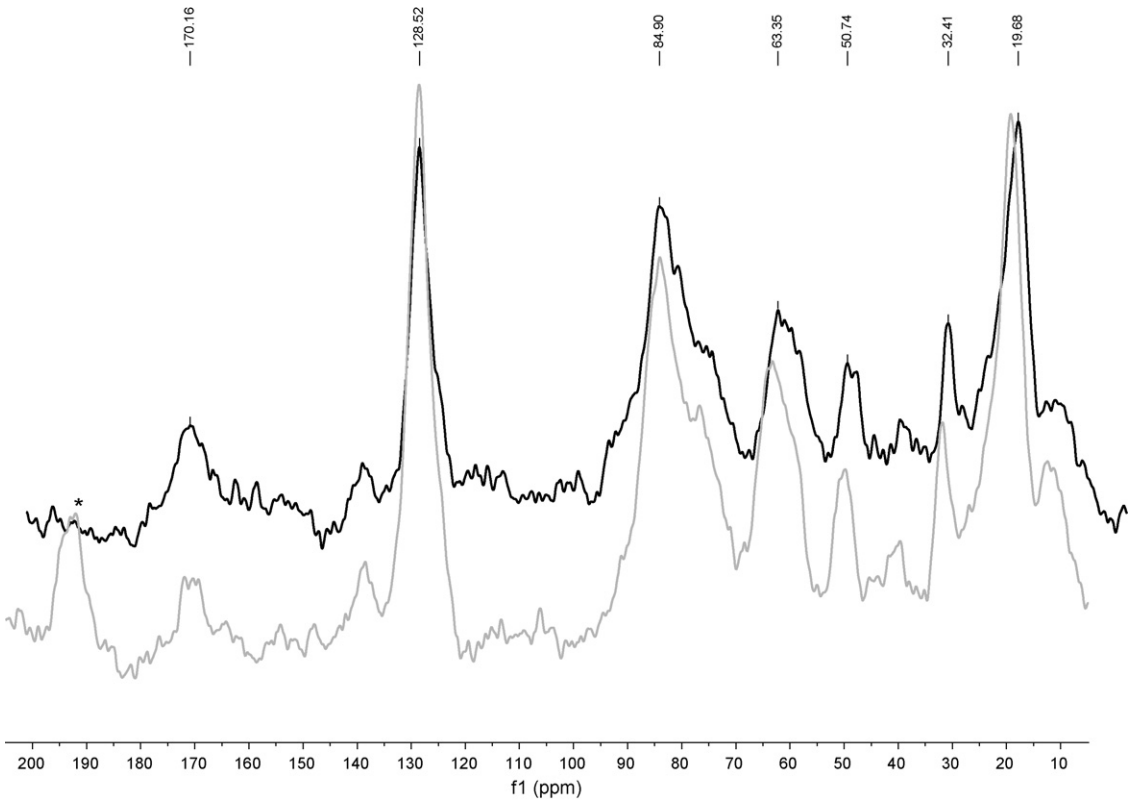


Fig. 3. ^{13}C CP-MAS NMR spectra of **18**/SiO_2 (grey) and **18**/Pd@SiO_2 (black). (* denotes spinning sideband).

Table 3
Enantioselective reduction of acetophenone with homogeneous complexes[a]

Entry	Complex	iPrOH/tBuOK		H_2O-iPrOH/HCOONa	
		Conversion (%)	ee (%)	Conversion (%)	ee (%)
1	**6**	32	10 (*R*)	3	n.d.
2	**7**([b]	95	90 (*S*)	51[e]	90[e]
3	**7**([b]			90	90
4	**7**([c]	95	88 (*S*)		
5	**7**([d]	68 (3 days)	68 (*S*)		
6	**8**	20	30 (*S*)		

[a] Reaction conditions: 1 mol% catalysts, 50 °C, 24 h.
[b] The catalyst was prepared *in-situ*.
[c] The catalyst was isolated.
[d] One hundred microlitre of H_2O was added in the reaction.
[e] H_2O was used as solvent.

corresponding rhodium complexes. As expected from the XPS technique, the ruthenium/palladium ratio of the combined catalyst is higher than the corresponding ratio calculated from elemental analysis (6.2 and 4.1, respectively).

2.3. Reduction of acetophenone with ruthenium-based catalysts.

Asymmetric reduction of acetophenone in the presence of the *dinitrogen* chelated ruthenium complexes **6–13** and the heterogeneous catalysts [Ru]/SiO_2 or [Ru]/Pd@SiO_2 was studied. Both iPrOH/tBuOK and HCOONa/H_2O conditions were evaluated and the main results are reported in Table 3.

Using the reductive system iPrOH/tBuOK, all homogeneous ruthenium-based complexes **6–13** were evaluated. The pyridine-based complexes **9** and **10** showed no activity.

On the other hand, the bisoxazoline based complexes **6–8** were efficient for this transformation. It was checked that the enantioselectivities kept constant all over the conversion. The highest enantioselectivity was achieved with complex **7** (90%, entry 2) bearing nitrogen functions as well as free hydroxyl groups [11]. The groups of Andersson and Wills reported the large enantiodifferentiation in transfer hydrogenation of ketones with stereochemically rigid β-amino alcohols [21,22].

The preparation of the catalyst did not influence its catalytic behaviour since similar conversions and enantioselectivities were achieved with the isolated complex **7** or the *in-situ* prepared catalyst (entry 2 *versus* 4). As the nature of the counter anions was known to modify the activity of some complexes in hydrogenation reactions [23], we examined their influence in the hydride transfer reduction of acetophenone. Surprisingly, none of the weaker coordinating anions led to an active catalyst (not shown).

At this stage, we focussed on the most active complex **7**. Careful attention to perform iPrOH/tBuOK reduction under strictly anhydrous conditions must be followed since the presence of water induced lower yield and enantioselectivity (entry 5). Xiao and coworkers reported recently very elegant asymmetric reduction of ketones using HCOONa as reducing agent in water [24,25]. We studied these reduction conditions in the presence of bisoxazoline-based ruthenium complexes **6** and **7**. For this study, only *in-situ* prepared catalytic systems were evaluated. Negligible conversion was observed with complex **6** (entry 1). On the other hand, in the presence of complex **7**, in pure water, a high enantiomeric excess was achieved but with a moderate yield (entry 2). This was easily overcome by addition of iPrOH in the reaction medium. Thanks to the presence of the cosolvent, all species were completely dissolved yielding very high conversion and optical yield (90% ee, 90% conversion; entry 3). Such reduction conditions are very useful as they do not need anhydrous conditions neither high pressure.

Table 4
Enantioselective reduction of acetophenone with heterogeneous catalysts[a]

Entry	Catalyst	%Ru	%Pd	Conversion (%)	ee (%)	r_0 (mmol h^{-1} g_{Ru}^{-1})
1	Pd-SiO_2		1	0		
2	**18**/SiO_2	3.6		14	20	0.8
3	**18**/Pd@SiO_2	3.8	1.1	15	<1	0.4
4	**19**/SiO_2	3.4		15	7	0.25
5	**19**/Pd@SiO_2	3.3	0.8	43	16	1

[a] Reaction conditions: 3.5% [Ru] or/and, if apply, 1% [Pd], 50 °C, 24 h.

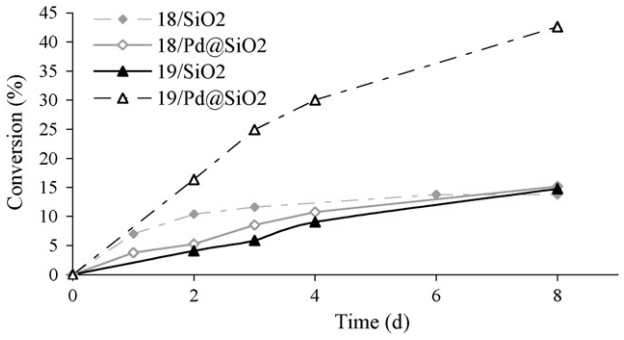


Fig. 4. Conversion of acetophenone as a function of time. Reaction conditions: iPrOH, tBuOK (15%), catalyst see Table 4, 50 °C.

The grafted [Ru]/SiO_2 and combined [Ru]/Pd@SiO_2 catalysts were evaluated in the same reaction. The reactions were performed in the presence of 3.3–3.8% Ru complexes and 1% Pd when mentioned (Table 4). No significant conversion was achieved with BoxPh-based catalysts (**17**/SiO_2 and **17**/Pd@SiO_2). Fig. 4 gives the conversion of acetophenone as a function of time with the BoxOH and BoxOTMS-based catalysts (i.e. **18** and **19**/SiO_2; **18** and **19**/Pd@SiO_2).

Significant lower reaction rates were achieved with the grafted complexes whatever the ligand and the support. The highest conversion was achieved in the presence of **19**/Pd@SiO_2 yielding 43% conversion after 8 days while almost complete conversion was observed with the homogeneous catalyst after 24 h.

The calculated initial reaction rates and the observed conversions and ees after 8 days are summarized in Table 4.

As expected, silica supported palladium was not active for the reduction of acetophenone (entry 1). Using the BoxOH-based catalysts **18**/SiO_2 or **18**/Pd@SiO_2, similar activities were observed whatever the support (entry 2 *versus* 3) showing no influence of the presence of palladium particles. Surprisingly, the behaviour of the BoxOTMS-based catalyst **19**/SiO_2 or **19**/Pd@SiO_2 was affected by the presence of palladium on the support (entry 4 *versus* 5). The role of the palladium particles is not clear. It can be suggested that some dehydrogenation of iPrOH occurs on the surface improving thus the catalytic activity, while we do not have evidences for such a hypothesis. Unfortunately, very low enantiomeric excesses were achieved with these catalysts.

3. Conclusion

Homogeneous and heterogeneous chiral ruthenium-catalysts based on bis(oxazoline) and pyridino-oxazoline ligands have been prepared and fully characterized. These catalysts were then immobilised by grafting onto silica or silica supporting palladium particles. After anchoring, the structure of the organometallic complexes remained intact even in the presence of palladium on the support as outlined by the ^{13}C CP-MAS NMR and XPS analyses.

The activity and selectivity of the homogeneous catalysts were evaluated for the asymmetric transfer hydrogenation of acetophenone using iPrOH/tBuOK or H_2O-iPrOH/HCOONa systems as hydrogen donors, the last conditions being particularly of interest for applications (cheap, no need of anhydrous conditions). While the heterogeneous [Ru]/SiO_2 and combined [Ru]/Pd@SiO_2 catalysts exhibited low activity (<20%) and enantioselectivity (<20), up to high conversions and enantioselectivities were achieved using homogeneous systems. The best results were achieved in the presence of {[RuCl(BoxOH)(*p*-cymene)][Cl]}catalyst (90% conversion and 90% ee).

Further studies aim at developing more active heterogeneous mixed catalysts [M]/Pd@SiO_2 (M: Rh, Ru, Ir. . .) by controlling carefully the distance between the two partners of such catalytic system to improve their cooperation during the reaction.

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 over sodium from purple benzophenone under argon before use while CH_2Cl_2 and $CHCl_3$ were distilled over CaH_2. Ligands **1**–**6** were prepared according literature [11,12]. Flash chromatography was performed using silica (Merck Silica Gel 60, 230–400 mesh). Thin layer chromatography was performed on Fluka Silica Gel 60 F_{254}.

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. All catalyst supports were dried before use at 120 °C for 48 h under 5.10^{-2} mmHg.

Solution NMR spectra were recorded with a Bruker AM 250 spectrometer (^{1}H NMR were referenced to the residual proton of the solvent: $CDCl_3$, δ = 7.25 ppm; ^{13}C NMR were referenced to the C-signal of the deuterated solvent: $CDCl_3$, δ = 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.

XPS measurements were recorded on an ESCALAB 250 spectrometer equipped with an 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.

The absolute ruthenium 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 HF in a Teflon reactor at 150 °C then with HCl at room temperature. The absolute palladium content of the catalyst was determined by ICP-AES from a solution obtained by treatment with a mixture of HF, HNO_3 and HCl in a Teflon reactor at 180 °C.

Gas chromatography was performed on a Shimadzu 14A chromatograph equipped with a FID detector and a Chirasil Dex CB column.

4.1. Synthesis of homogeneous complexes

The ligand (2 eq.) and the ruthenium dimer [Ru(*p*-cymene)Cl_2]$_2$ (1 eq.) were dissolved in degazed methanol (0.5 mmole per 10 mL of MeOH) and stirred 6 h at room temperature. The solvent was then evaporated and the obtained solid was dried under vacuum.

{[*RuCl*(*BoxOH*)(*p-cymene*)][*Cl*]} **7**: orange solid, 95% yield, m.p. = 118–126 °C (decomposition), $[\alpha]_D^{25} = -111.1$ (c = 0.2, $CHCl_3$), IR: ν(CN) = 1667 cm^{-1}, ^{1}H NMR ($CDCl_3$, 250 MHz): 7.30 (m, 10H, $CH_{(C6H5)}$); 6.33 (d, $^3J(H,H)$ = 8.7 Hz, 1H, $CH_{(C6H4)}$); 6.10 (d, $^3J(H,H)$ = 8.7 Hz, 1H, CHO); 5.93 (d, $^3J(H,H)$ = 8.7 Hz, 1H, $CH_{(C6H4)}$); 5.83 (d, $^3J(H,H)$ = 8.7 Hz, 1H, $CH_{(C6H4)}$); 5.78 (d, $^3J(H,H)$ = 8.7 Hz, 1H, CHO); 5.71 (d, $^3J(H,H)$ = 8.7 Hz, 1H, $CH_{(C6H4)}$); 4.71 (d, $^2J(H,H)$ = 19.5 Hz, 1H, NCCH_2CN); 4.44 (d, $^3J(H,H)$ = 8.7 Hz, 1H, CHN); 4.38 (d, $^3J(H,H)$ = 8.7 Hz, 1H, CHN); 4.19 (m, 2H, CH_2OH); 3.83 (m, 1H, CH_2OH); 3.66 (m, 1H, CH_2OH); 3.64 (d, ^{2}J(H,H) = 19.5 Hz, 1H, NCCH_2CN); 2.92 (sept, $^3J(H,H)$ = 6.8 Hz, 1H, $CH_{(iPr)}$); 2.32 (s, 3H, CH_3); 1.23 (d, $^3J(H,H)$ = 7.0 Hz, 6H, $CH_{3(iPr)}$); ^{13}C NMR ($CDCl_3$, 62.9 MHz): 166.8 (CN); 164.5 (CN); 136.6 ($Cq_{(C6H5)}$); 136.5 ($Cq_{(C6H5)}$); 126.1 to 129.6 ($CH_{(C6H5)}$); 107.8 ($Cq_{(C6H4)}$); 98.3 ($Cq_{(C6H4)}$); 85.5 (CHO); 84.4 (CHO); 84.3 ($CH_{(C6H4)}$); 84.2 ($CH_{(C6H4)}$); 81.7 ($CH_{(C6H4)}$); 81.6 ($CH_{(C6H4)}$); 80.8 (CHN); 75.6 (CHN); 59.9 (CH_2OH); 59.4 (CH_2OH); 30.9 ($CH_{(iPr)}$); 28.7 (NCCH_2CN); 22.6 ($CH_{3(iPr)}$); 22.0 ($CH_{3(iPr)}$); 18.4 (CH_3). $C_{31}H_{36}Cl_2N_2O_4Ru$: calcd: C 55.34, H 5.36, N 4.17, Cl 10.41, Ru 15.04, found C 54.01, H 5.76, N 4.23, Cl 9.11, Ru 13.49.

{[*RuCl*(*BoxOH*)(*p-cymene*)][PF_6]} **11**: orange solid, 99% yield, m.p. = 105–110 °C (decomposition), $[\alpha]_D^{25} = -105.3$ (c = 0.2, $CHCl_3$), IR: ν(CN) = 1668 cm^{-1}, ^{1}H NMR ($CDCl_3$, 250 MHz): 7.25 (m, 10H, $CH_{(C6H5)}$); 5.87 (m, 1H, CHO); 5.86 (m, 1H, $CH_{(C6H4)}$); 5.78 (m, 1H, CHO); 5.77 (m, 1H, $CH_{(C6H4)}$); 5.64 (d, $^3J(H,H)$ = 6.0 Hz, 1H, $CH_{(C6H4)}$); 5.60 (d, $^3J(H,H)$ = 5.9 Hz, 1H, $CH_{(C6H4)}$); 4.38 (d, $^3J(H,H)$ = 9.2 Hz, 1H, CHN); 4.29 (m, 1H, CHN); 4.25 (m, 1H, CH_2OH); 4.15 (d, $^3J(H,H)$ = 10.5 Hz, 1H, CH_2OH); 4.07 (d, $^2J(H,H)$ = 19.6 Hz, 1H, NCCH_2CN); 3.78 (d, $^3J(H,H)$ = 11.5 Hz, 1H, CH_2OH); 3.41 (d, $^3J(H,H)$ = 7.0 Hz, 1H, CH_2OH); 3.64 (d, $^2J(H,H)$ = 19.6 Hz, 1H, NCCH_2CN); 2.87 (sept, $^3J(H,H)$ = 6.8 Hz, 1H, $CH_{(iPr)}$); 2.20 (s, 3H, CH_3); 1.25 (d, $^3J(H,H)$ = 7.6 Hz, 6H, $CH_{3(iPr)}$). ^{13}C NMR ($CDCl_3$, 62.9 MHz): 166.3 (CN); 164.3 (CN); 136.0 ($Cq_{(C6H5)}$); 135.9 ($Cq_{(C6H5)}$); 126.0 to 130.0 ($CH_{(C6H5)}$); 107.6 ($Cq_{(C6H4)}$); 99.7 ($Cq_{(C6H4)}$); 85.6 (CHO or $CH_{(C6H4)}$); 84.6 (CHO or $CH_{(C6H4)}$); 83.2 ($CH_{(C6H4)}$); 82.3 ($CH_{(C6H4)}$); 81.5 (CHO or $CH_{(C6H4)}$); 80.3 (CHN); 74.8 (CHN); 59.7 (CH_2OH); 59.5 (CH_2OH); 31.0 (CH (iPr)); 27.5 (NCCH_2CN); 22.2 (CH_3 (iPr)); 22.2 (CH_3 (iPr)); 18,3 (CH_3). $C_{31}H_{36}ClN_2O_4PF_6Ru$: calcd C 47.56, H 4.60, N 3.58, Cl 4.54, Ru 12.92; found C 45.75, H 4.55, N 3.42, Cl 5.85, Ru 11.94.

{[*RuCl*(*BoxOH*)(*p-cymene*)][BF_4]} **12**: dark orange solid, 99% yield, m.p. = 112–120 °C (decomposition), $[\alpha]_D^{25} = -106.5$ (c = 0.2, $CHCl_3$), IR: ν(CN) = 1636 cm^{-1}, ^{1}H NMR ($CDCl_3$, 250 MHz): 7.4 (m, 10H, $CH_{(C6H5)}$); 5.95 (d, $^3J(H,H)$ = 5.1 Hz, 1H, $CH_{(C6H4)}$); 5.85 (d, $^3J(H,H)$ = 9.3 Hz, 1H, CHO); 5.72 (m, 1H, CHO and 2 $CH_{(C6H4)}$); 5.64 (d, $^3J(H,H)$ = 5.2 Hz, 1H, $CH_{(C6H4)}$); 4.36 (m, 2H, CHN); 4.32 (m, 1H, CH_2OH); 4.11 (m, 1H, CH_2OH); 4.17 (d, $^2J(H,H)$ = 18.0 Hz, 1H, NCCH_2CN); 3.77 (d, $^3J(H,H)$ = 11.4 Hz, 1H, CH_2OH); 3.57 (d, $^2J(H,H)$ = 19.7 Hz, 1H, NCCH_2CN); 3.52 (m, 1H, CH_2OH); 3.27 (m, 1H, OH); 2.85 (sept, $^3J(H,H)$ = 6.6 Hz, 1H, CH(iPr)); 2.19 (s, 3H, CH_3); 1.20 (d, $^3J(H,H)$ = 6.6 Hz, 3H, $CH_{3(iPr)}$); 1.19 (d, $^3J(H,H)$ = 6.6 Hz, 3H, $CH_{3(iPr)}$). ^{13}C NMR ($CDCl_3$, 62.9 MHz): 166.4 (CN); 166.3 (CN); 136.1 ($Cq_{(C6H5)}$); 129.8 ($CH_{(C6H5)}$); 129.5 ($CH_{(C6H5)}$); 129.1 ($CH_{(C6H5)}$); 127.2 ($CH_{(C6H5)}$); 126.4 ($CH_{(C6H5)}$); 108.0 ($Cq_{(C6H4)}$); 99.0 ($Cq_{(C6H4)}$); 85.6 (CHO or $CH_{(C6H4)}$); 84.5 (CHO); 83.8 ($CH_{(C6H4)}$); 83.6 (CHO or $CH_{(C6H4)}$); 82.1 ($CH_{(C6H4)}$); 81.2 (CHO or $CH_{(C6H4)}$); 80.2 (CHN); 74.9 (CHN); 59.5 (CH_2OH); 31.0 ($CH_{(iPr)}$); 27.7 (NCCH_2CN); 22.4 ($CH_{3(iPr)}$); 22.2 ($CH_{3(iPr)}$); 18.3 (CH_3). $C_{31}H_{36}ClN_2O_4BF_4Ru$: calcd C 51.37, H 4.97, N 3.87, Cl 4.90, Ru 13.96; found C 52.24, H 5.31, N 3.47, Cl 6.99, Ru 13.40.

{[*RuCl*(*BoxTMS*)(*p-cymene*)][*Cl*]} **8**: dark orange solid, 90% yield, m.p. = 117–121 °C (decomposition), $[\alpha]_D^{25} = -19.1$ (c = 0.1, $CHCl_3$), IR: ν(CN) = 1648 cm^{-1}, ^{1}H NMR ($CDCl_3$, 250 MHz): 7.54 (m, 2H, $CH_{(C6H5)}$); 7.33 (m, 8H, $CH_{(C6H5)}$); 6.26 (d, $^3J(H,H)$ = 5.9 Hz, 1H, $CH_{(C6H4)}$); 6.04 (d, $^3J(H,H)$ = 8.7 Hz, 1H, CHO);

5.97 (d, $^3J(H,H)$ = 5.9 Hz, 1H, $CH_{(C6H4)}$); 5.83 (d, $^3J(H,H)$ = 5.9 Hz, 1H, $CH_{(C6H4)}$); 5.78 (d, $^3J(H,H)$ = 8.7 Hz, 1H, CHO); 5.71 (d, $^3J(H,H)$ = 5.9 Hz, 1H, $CH_{(C6H4)}$); 4.58 (d, $^2J(H,H)$ = 19.8 Hz, 1H, $NCCH_2CN$); 4.54 (d broad, $^3J(H,H)$ = 8.7 Hz, 1H, CHN); 4.32 (d, $^3J(H,H)$ = 8.7 Hz, 1H, CHN); 4.10 (m, 2H, CH_2OH); 3.76 (m, 2H, CH_2OH); 3.56 (d, $^2J(H,H)$ = 19.8 Hz, 1H, $NCCH_2CN$); 2.92 (sept, $^3J(H,H)$ = 6.8 Hz, 1H, $CH_{(iPr)}$); 2.25 (s, 3H, CH_3); 1.17 (d, $^3J(H,H)$ = 6.6 Hz, 6H, $CH_{3(iPr)}$). ^{13}C NMR ($CDCl_3$, 62.9 MHz): 166.3 (CN); 164.3 (CN); 136.6 ($Cq_{(C6H5)}$); 136.5 ($Cq_{(C6H5)}$); 126.3 to 129.5 ($CH_{(C6H5)}$); 107.3 ($Cq_{(C6H4)}$); 98.9 ($Cq_{(C6H4)}$); 85.6 (CHO); 84.4 ($CH_{(C6H4)}$); 83.8 ($CH_{(C6H4)}$); 82.3 ($CH_{(C6H4)}$); 81.8 ($CH_{(C6H4)}$); 80.3 (CHN); 75.7 (CHN); 60.1 (CH_2OH); 59.0 (CH_2OH); 30.8 ($CH_{(iPr)}$); 28.5 ($NCCH_2CN$); 22.4 ($CH_{3(iPr)}$); 22.1 ($CH_{3(iPr)}$); 18.4 (CH_3). $C_{37}H_{52}Cl_2N_2O_4Si_2Ru$; calcd: C 54.40, H 6.37, N 3.43, Ru 12.38; found C 54.01, H 5.76, N 3.23, Ru 12.49

{[*RuCl*(*BoxPh*)(*p-cymene*)][*Cl*]} **6**: orange solid, 99% yield, m.p. = 111–115 °C (decomposition), $[\alpha]_D^{25} = -155.7$ (c = 0.1, $CHCl_3$), IR: ν(CN) = 1665 cm^{-1}, ^{1}H NMR ($CDCl_3$, 250 MHz): 7.44 (m, 10H, $CH_{(C6H5)}$); 6.26 (m, 1H, CHN); 5.96 (d, $^3J(H,H)$ = 5.1 Hz, 1H, $CH_{(C6H4)}$); 5.63 (m, 1H, CHN); 5.38 (m, 1H, $CH_{(C6H4)}$); 5.11 (d, $^3J(H,H)$ = 5.8 Hz, 1H, $CH_{(C6H4)}$); 4.86 (pseudo t, $^3J(H,H)$ = 9.8 Hz, 1H, CH_2O); 4.58 (m, 2H, CH_2O); 4.20 (m, 3H, CH_2O, $CH_{(C6H4)}$ and $NCCH_2CN$); 3.79 (d, $^2J(H,H)$ = 20.3 Hz, 1H, $NCCH_2CN$); 2.42 (sept, $^3J(H,H)$ = 6.8 Hz, 1H, $CH_{(iPr)}$); 1.95 (s, 3H, CH_3); 1.08 (d, $^3J(H,H)$ = 6.8 Hz, 3H, $CH_{3(iPr)}$); 0.82 (d, $^3J(H,H)$ = 6.8 Hz, 3H, $CH_{3(iPr)}$). ^{13}C NMR ($CDCl_3$, 62.9 MHz): 167.4 (CN); 166.6 (CN); 139.1 ($Cq_{(C6H5)}$); 138.2 ($Cq_{(C6H5)}$); 129.5 ($CH_{(C6H5)}$); 128.3 ($CH_{(C6H5)}$); 128.1 ($CH_{(C6H5)}$); 127.5 ($CH_{(C6H5)}$); 109.7 ($Cq_{(C6H4)}$); 96.1 ($Cq_{(C6H4)}$); 85.1 ($CH_{(C6H4)}$); 83.8 ($CH_{(C6H4)}$); 78.3 ($CH_{(C6H4)}$); 77.8 ($CH_{(C6H4)}$); 77.4 (CH_2O); 76.5 (CH_2O); 74.6 (CHN); 72.5 (CHN); 30.3 ($CH_{(iPr)}$); 27.8 ($NCCH_2CN$); 22.3 ($CH_{3(iPr)}$); 21.0 ($CH_{3(iPr)}$); 18.1 (CH_3). $C_{29}H_{32}Cl_2N_2O_2Ru$: calcd C 56.85, H 5.23, N 4.57, Cl 11.44, Ru 16.51; found C 52.32, H 5.34, N 4.45, Cl 11.08, Ru 16.13.

{[*RuCl*(*PyOxPh*)(*p-cymene*)][*Cl*]} **9**: dark brown solid, 92% yield, m.p. = 128–132 °C (decomposition), $[\alpha]_D^{25} = -9.8$ (c = 0.2, $CHCl_3$), IR: ν(CN) = 1645 cm^{-1}, ^{1}H NMR ($CDCl_3$, 250 MHz): 10.34 (d, $^3J(H,H)$ = 4.6 Hz, 1H, $CH_{(NC5H4)}$); 8.07 (m, 1H, $CH_{(NC5H4)}$); 7.92 (m, 2H, $CH_{(NC5H4)}$); 7.57 (s, 5H, $CH_{(C6H5)}$); 6.00 (d, $^3J(H,H)$ = 5.9 Hz, 1H, $CH_{(C6H4)}$); 5.63 (d, $^3J(H,H)$ = 5.7 Hz, 1H, $CH_{(C6H4)}$); 5.36 (d, $^3J(H,H)$ = 6.5 Hz, 1H, $CH_{(C6H4)}$); 5.27 (m, 2H, CH_2 and $CHCH_2$); 4.91 (m, 2H, CH_2 and $CH_{(C6H4)}$); 2.60 (m, 1H, $CH_{(iPr)}$); 2.06 (s, 3H, CH_3); 0.98 (d, $^3J(H,H)$ = 6.8 Hz, 3H, CH-CH_3); 0.88 (d, $^3J(H,H)$ = 6.8 Hz, 3H, $CH_{3(iPr)}$). ^{13}C NMR ($CDCl_3$, 62.9 MHz): 167.7 (CN); 159.4 ($CH_{(NC5H4)}$); 143.0 ($Cq_{(C5H4N)}$); 139.4 ($CH_{(NC5H4)}$); 137.6 ($Cq_{(C6H5)}$); 130.8 ($CH_{(NC5H4)}$); 130.7 ($CH_{(C6H5)}$); 129.7 ($CH_{(C6H5)}$); 128.8 ($CH_{(C6H5)}$); 126.4 ($CH_{(NC5H4)}$); 105.6 ($Cq_{(C6H4)}$); 101.8 ($Cq_{(C6H4)}$); 84.2 ($CH_{(C6H4)}$); 83.4 ($CH_{(C6H4)}$); 83.2 ($CH_{(C6H4)}$); 82.1 ($CH_{(C6H4)}$); 79.4 (CH_2O); 70.5 (CHN); 30.8 ($CH_{(iPr)}$); 22.4 ($CH_{3(iPr)}$); 22.0 ($CH_{3(iPr)}$); 18.9 (CH_3). $C_{25}H29Cl_2N_2Oru$; calcd C 55.00, H 5.32, N 5.13, Cl 12.83, Ru 18.53; found C 50.09, H 5.31, N 5.14, Cl 11.90, Ru 17.39.

{[*RuCl*(*PyOxiPr*)(*p-cymene*)][*Cl*]} **10**: dark yellow solid, 91% yield, m.p. = 124–129 °C (decomposition), $[\alpha]_D^{25} = 183.4$ (c = 0.2, $CHCl_3$), IR: ν(CN) = 1648 cm^{-1}, ^{1}H NMR ($CDCl_3$, 250 MHz): 10.57 (d, $^3J(H,H)$ = 4.9 Hz, 1H, $CH_{(NC5H4)}$); 7.98 (m, 1H, $CH_{(NC5H4)}$); 7.77 (m, 2H, $CH_{(NC5H4)}$); 6.73 (d, $^3J(H,H)$ = 6.2 Hz, 1H, $CH_{(C6H4)}$); 6.27 (d, $^3J(H,H)$ = 5.9 Hz, 1H, $CH_{(C6H4)}$); 5.83 (d, $^3J(H,H)$ = 6.2 Hz, 1H, $CH_{(C6H4)}$); 5.77 (d, $^3J(H,H)$ = 6.0 Hz, 1H, $CH_{(C6H4)}$); 4.72 (m, 2H, OCH_2); 4.35 (m, 2H, OCH_2); 2.86 (sept, $^3J(H,H)$ = 6.9 Hz, 1H, CH (iPr) $_{(C6H4)}$); 2.54 (septd, $^3J(H,H)$ = 3.3 Hz, $^3J(H,H)$ = 6.9 Hz, 1H, CH (iPr) $_{(PyOx)}$); 2.20 (s, 3H, CH_3); 1.05 (m, 12H, $CH_{3(iPr)}$). ^{13}C NMR ($CDCl_3$, 62.9 MHz): 167.9 (CN); 159.9 ($CH_{(NC5H4)}$); 143.0 ($Cq_{(C5H4N)}$); 139.3 ($CH_{(NC5H4)}$); 130.7 ($CH_{(NC5H4)}$); 125.8 ($CH_{(NC5H4)}$); 106.3 ($Cq_{(C6H4)}$); 102.1 ($Cq_{(C6H4)}$); 85.1 ($CH_{(C6H4)}$); 83.4 ($CH_{(C6H4)}$); 83.1 ($CH_{(C6H4)}$); 82.4 ($CH_{(C6H4)}$); 72.2 (CH_2O); 71.4 (CHN); 31.1 (CH (iPr) $_{(C6H4)}$); 29.4 (CH(iPr) $_{(PyOx)}$); 22.4 (CH_3(iPr)); 22.1 (CH_3(iPr)); 19.3 (CH_3).

4.2. Preparation of support Pd-SiO_2

A solution of $Pd(acac)_2$ in toluene (made from 143.1 mg of $Pd(acac)_2$ in 15 ml of toluene) was added to 1 g of agglomerated silica. The mixture was then stirred for 1 h at room temperature (r.t.) under argon. Then toluene was removed by evaporation leading a slightly yellow material. This solid was calcined under air flow (100 mL/min) at 300 °C for 2 h and then reduced under H_2 flow (80 mL/min) in a U-reactor at 300 °C for 2 h to give the desired $Pd(0)/SiO_2$ catalyst as a black material. AAS determination gave 0.84 ± 0.05%wt Pd.

4.3. Preparation of tethered complexes on silica or on Pd-SiO_2. Typical procedure

The desired complex (1 eq./surface OH) was added to a suspension of SiO_2 or Pd-SiO_2 in dry CH_2Cl_2 (15 mL/0,1 mmol). The mixture was stirred for 24 h at room temperature. The heterogeneous catalyst was filtered under argon, washed twice with 10 mL of dry CH_2Cl_2 and dried under vacuum.

{[*RuCl*(*BoxOH*)(*p-cymene*)][*Cl*]}/SiO_2 ***18***/SiO_2: NMR ^{13}C (125.4 MHz): 170 (CN); 139 ($Cq_{(C6H5)}$); 128 ($CH_{(C6H5)}$); 84 (OCH; $CH_{(C6H4)}$; $Cq_{(C6H4)}$); 77 (NCH); 63 (CH_2OH); 50 ($CH_2CH_2CH_2$); 32 (NCCHCN; CH (p-cy)); 19 (CH_2CH_2CH; CH_3 (p-cy)); 11 (CH_2Si). Anal. [Found]: Ru 1.73, C 8.81, H 1.17, N 0.65, Cl 1.52 corresponding to 0.17 $mmol_{Ru}$/g.

{[*RuCl*(*BoxOH*)(*p-cymene*)][*Cl*]}/*Pd@SiO*$_2$ ***18***/*Pd@SiO*$_2$: Anal. [Found]: Pd 0.55, Ru 1.73, C 8.79, H 1.18, N 0.69, Cl 1.61 corresponding to 0.17 $mmol_{Ru}$/g.

{[*RuCl*(*BoxTMS*)(*p-cymene*)][*Cl*]}/SiO_2 ***19***/SiO_2: NMR ^{13}C (75.5 MHz): 171 (CN); 138 ($Cq_{(C6H5)}$); 128 ($CH_{(C6H5)}$); 92 ($Cq_{(C6H4)}$); 83 (OCH; $CH_{(C6H4)}$); 76 (NCH); 61 (CH_2OSi); 49 ($CH_2CH_2CH_2$); 31 (NCCHCN; CH (p-cy)); 19 (CH_2CH_2CH; CH_3 (p-cy)); 12 (CH_2Si). Anal. [Found]: Ru 2.02, C 10.28, H 1.41, N 0.74, Cl 2.13 corresponding to 0.20 $mmol_{Ru}$/g.

{[*RuCl*(*BoxTMS*)(*p-cymene*)][*Cl*]}/*Pd@SiO*$_2$ ***19***/*Pd@SiO*$_2$: Anal. [Found]: Pd 0.50, Ru 1.92, C 10.43, H 1.37, N 0.73, Cl 1.6 corresponding to 0.19 $mmol_{Ru}$/g.

{[*RuCl*(*BoxPh*)(*p-cymene*)][*Cl*]}/SiO_2 ***17***/SiO_2: NMR ^{13}C (75.5 MHz): 172 (CN); 139 ($Cq_{(C6H5)}$); 128 ($CH_{(C6H5)}$); 92 ($Cq_{(C6H4)}$); 89 ($Cq_{(C6H4)}$); 76 (NCH; $CH_{(C6H4)}$); 58 (CH_2O); 49 ($CH_2CH_2CH_2$); 31 (NCCHCN; CH (p-cy)); 19 (CH_2CH_2CH; CH_3 (p-cy)); 13 (CH_2Si). Anal. [Found]: Ru 1.62, C 8.21, H 1.04, N 0.59, Cl 1.22 corresponding to 0.16 $mmol_{Ru}$/g.

{[*RuCl*(*BoxPh*)(*p-cymene*)][*Cl*]}/*Pd@SiO*$_2$ ***17***/*Pd@SiO*$_2$: Anal. [Found]: Pd 0.43, Ru 1.63, C 8.46, H 1.24, N 0.64, Cl 1.6 corresponding to 0.16 $mmol_{Ru}$/g.

4.4. Hydrogenation transfer with iPrOH/tBuOK

Under argon, 200 mg of substrate and 1 mol% of catalyst (homogeneous) were dissolved in 10 mL of dry iPrOH. 15 mol% of tBuOK was added. The mixture was stirred at 50 °C during 24 h.

The same protocol was performed with the grafted or combined catalysts using 3.5% [Ru] and, if apply, 1% [Pd].

A treatment was made on the sample before GC analysis: to a 0.4 mL sample was added 0.3 mL of dichloromethane. The mixture was washed with 0.2 mL of aqueous HCl 0.1N. The organic layer was filtered through a $MgSO_4$ pad and analyzed by chiral GC.

4.5. Reduction with iPrOH-H_2O/HCOOH

Under argon, 0.01 mmol of $[Ru(p\text{-cymene})Cl_2]_2$ and 0.022 mmol of ligand were dissolved in degazed H_2O/iPrOH (4/2) mixture. After

stirring for 1 h, 1 mmol of acetophenone and 5 mmol of HCOONa were introduced and the solution was heated at 50 °C for 24 h. After cooling, the solution was neutralized with HCl and extracted with CH_2Cl_2. The organic layer was dried over $MgSO_4$ and analyzed by GC.

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