Ketone transfer hydrogenation reactions catalyzed by a phosphinite ruthenium PCP complex
The X-ray crystal structure of [C$_6$H$_4$-1,3-(OPPh$_2$\{Ru(η^6-p-cymene)Cl$_2$\})$_2$]

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Abstract

The reaction of the potentially tridentate phosphinite PCP pincer type ligand [C$_6$H$_4$-1,3-(OPPh$_2$)$_2$] with [(η^6-p-cymene)RuCl$_2$]$_2$ affords the bimetallic species [C$_6$H$_4$-1,3-(OPPh$_2$\{Ru(η^6-p-cymene)Cl$_2$\})$_2$]. Several attempts, including the change of the ruthenium starting material (e.g. [(η^6-benzene)RuCl$_2$]$_2$) and reflux conditions to achieve the coordination of the diphosphinite [C$_6$H$_4$-1,3-(OPPh$_2$)$_2$] in a tridentate PCP pincer fashion failed. Complex [C$_6$H$_4$-1,3-(OPPh$_2$\{Ru(η^6-p-cymene)Cl$_2$\})$_2$] was tested in the transfer hydrogenation of ketones.
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1. Introduction

Since its discovery, transfer hydrogenation using ruthenium complexes as catalysts has been an increasingly useful tool in organic synthesis [1], allowing transformations otherwise very difficult or almost impossible to carry out. This process, has taken higher importance due to the mild conditions generally required, fact that has been important in the use of ruthenium chiral complexes for enantioselective transfer hydrogenations [2]. In addition, the chemistry of pincer type complexes has been having a steadily increasing interest in homogeneous catalysis [3], due the high thermal stability that these complexes exhibit and the potential alternative mechanistic routes they follow [4]. In fact, ruthenium PCP phosphino, NCN (amino) and *CNC* (*C*: carbene) pincer type complexes have already been employed in ketone transfer hydrogenation reactions [5] even in its asymmetric fashion using PCP phosphino complexes, affording good

yields and selectivities and when P-stereogenic centers have been included, good enantioselectivities [6].

Thus, following our continuous interest in the chemistry of phosphinite PCP pincer ligands [7] and the applications of cyclometalated ruthenium complexes [8], we report here our findings in the reactivity of ruthenium starting materials with the potentially tridentated PCP ligand [C$_6$H$_4$-1,3-(OPPh$_2$)$_2$] and the catalytic evaluation of the dinuclear complex [C$_6$H$_4$-1,3-(OPPh$_2$\{Ru(η^6-p-cymene)Cl$_2$\})$_2$] in the catalytic transfer hydrogenation of ketones.

2. Experimental

2.1. Materials and methods

Unless stated otherwise, all reactions were carried out under an atmosphere of dinitrogen using conventional Schlenk glassware, solvents were dried using established procedures and distilled under dinitrogen immediately prior to use. The IR spectra were recorded on a Bruker-Tensor 27 FT-IR spectrometer as KBr pellets. The ^{1}H NMR spectra were recorded on a JEOL GX300

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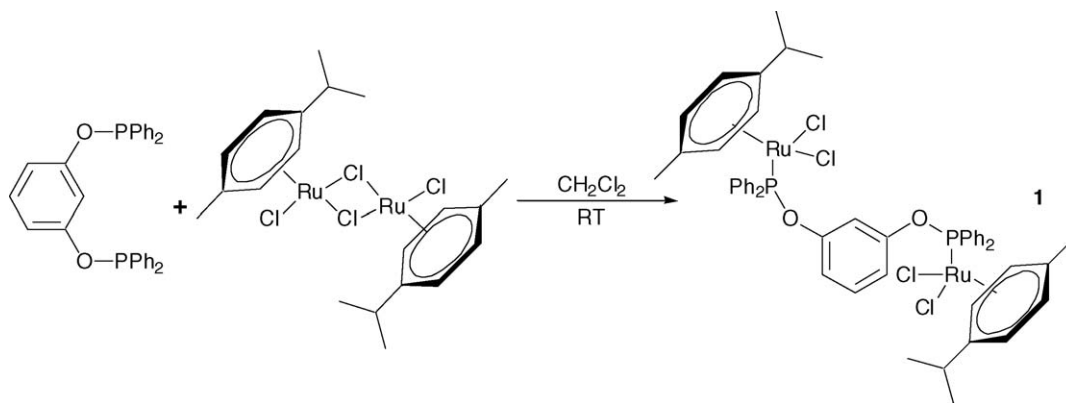
Scheme 1. Synthesis of [C$_6$H$_4$-1,3-(OPPh$_2$)$_2$] with [(η^6-*p*-cymene)RuCl$_2$]$_2$ (**1**).

spectrometer. Chemical shifts are reported in ppm down field of TMS using the solvent (CDCl$_3$, δ = 7.27) as internal standard. ^{31}P{^{1}H} NMR spectra were recorded with complete proton decoupling and are reported in ppm using 85% H$_3$PO$_4$ as external standard. Positive-ion FAB mass spectra were recorded on a JEOL JMS-SX102A mass spectrometer operated at an accelerating voltage of 10 kV. Samples were desorbed from a nitrobenzyl alcohol (NOBA) matrix using 3 KeV xenon atoms. Mass measurements in FAB are performed at a resolution of 3000 using magnetic field scans and the matrix ions as the reference material or, alternatively, by electric field scans with the sample peak bracketed by two (polyethylene glycol or cesium iodide) reference ions. Melting points were determined in a MEL-TEMP capillary melting point apparatus and are reported without correction. GC–MS analyses were performed on a Agilent 6890N GC with a 30.0 m DB-1MS capillary column coupled to an Agilent 5973 Inert Mass Selective detector.

The starting materials [(η^6-*p*-cymene)RuCl$_2$]$_2$, [(η^6-benzene)RuCl$_2$]$_2$ [9] and the ligand [C$_6$H$_4$-1,3-(OPPh$_2$)$_2$] [10] were prepared according to published procedures.

2.2. Synthesis of [C$_6$H$_4$-1,3-(OPPh$_2$ {Ru(η^6-p-cymene)Cl$_2$})$_2$] (1)

To a solution of [(η^6-*p*-cymene)RuCl$_2$]$_2$ (128 mg, 0.21 mmol) in CH$_2$Cl$_2$ (10 mL), a solution (CH$_2$Cl$_2$, 10 mL) of [C$_6$H$_4$-1,3-(OPPh$_2$)$_2$] (0.21 mmol) was added. The resulting reaction mixture was allowed to proceed under stirring at room temperature for 24 h. After this time, the solution was filtered off and the solvent evaporated under vacuum, the solid residue thus obtained is washed with diethyl ether (3 × 10 mL) and then dried under vacuum (Scheme 1). Following recrystalization from diethyl ether/CH$_2$Cl$_2$ a microcrystalline red powder was obtained (yield 127 mg, 56%), m.p. 180 °C (decomp.). ^{1}H NMR (300.53 MHz, CDCl$_3$) δ = 7.99–7.92 (m, 8H, arom), 7.27–7.19 (m, 13H, arom), 7.00–6.94 (m, 1H, arom), 6.80–6.77 (m, 2H, arom), 5.19 (d, 4H, ^3J = 6.4 Hz, C$_6$**H$_4$**), 5.08 (d, 4H, ^3J = 6.5 Hz, C$_6$**H$_4$**), 2.43 (m, 2H, C**H**(CH$_3$)$_2$), 1.42 (s, 6H, C**H$_3$**), 0.79 (d, 12H, ^3J = 6.5 Hz, CH(C**H$_3$)$_2$**); ^{31}P NMR (121.65 MHz, CDCl$_3$) δ = 114.78 (s). MS-FAB$^+$ [M + H]$^+$ = 1091 (<1%), [M + H − Cl]$^+$ = 1055 (1%) *m/z*, [M + H-(RuCl$_2$-η^6-*p*-cymene)]$^+$ = 784 (2%) *m/z*.

2.3. Synthesis of [C$_6$H$_4$-1,3-(OPPh$_2$ {Ru(η^6-benzene)Cl$_2$})$_2$] (2)

The title compound was synthesized in an analogous manner as that of complex **1** from a solution of [(η^6-benzene)RuCl$_2$]$_2$ (128 mg, 0.21 mmol) in CH$_2$Cl$_2$ (10 mL) and a solution (CH$_2$Cl$_2$, 10 mL) of [C$_6$H$_4$-1,3-(OPPh$_2$)$_2$] (0.21 mmol). A microcrystalline red powder was obtained after recrystalization from diethyl ether/CH$_2$Cl$_2$ (yield 106 mg, 52%). ^{1}H NMR (300.53 MHz, CDCl$_3$) δ = 8.03–7.81 (m, 8H, arom), 7.36–6.93 (m, 16H, arom), 5.37 (s, 12H, benzene); ^{31}P NMR (121.65 MHz, CDCl$_3$) δ = 116.86 (s). MS-FAB$^+$ [M + H − Cl]$^+$ = 943 (1%) *m/z*, [M + H − (Cl-benzene)]$^+$ = 864 (2%) *m/z*, [M + H − (2Cl-benzene)]$^+$ = 829 (2%) *m/z*, [M + H − (2Cl-2benzene)]$^+$ = 751 (1%) *m/z*.

2.4. Transfer hydrogenation of ketones

Typical procedure for the catalytic hydrogen-transfer reaction: a suspension of the ruthenium complex [C$_6$H$_4$-1,3-(OPPh$_2$ {Ru(η^6-*p*-cymene)Cl$_2$})$_2$] (**1**) (11.0 mg, 0.005 mmol), NaOH (0.5 mg, 0.012 mmol) and the corresponding ketone (0.5 mmol) in degassed *iso*-propanol (2.5 mL) was refluxed for 10 h. After this time a sample of the reaction mixture is taken off, diluted with acetone and analyzed by GC–MS, yields obtained are related to the residual unreacted ketone.

2.5. Data collection and refinement for [C$_6$H$_4$-1,3-(OPPh$_2${Ru(η^6-p-cymene)Cl$_2$})$_2$] (1)

A crystalline red-orange prism of [C$_6$H$_4$-1,3-(OPPh$_2${Ru(η^6-*p*-cymene)Cl$_2$})$_2$] (**1**), grown from CDCl$_3$ was glued to a glass fiber. The X-ray intensity data were measured at 291 K on a Bruker SMART APEX CCD-based X-ray diffractometer system equipped with a Mo-target X-ray tube (λ = 0.71073 Å). The detector was placed at a distance of 4.837 cm from the crystal. A total of 1800 frames were collected with a scan width of 0.3° in ω and an exposure time of 10 s/frame. The frames were integrated with the Bruker SAINT software package using a narrow-frame integration algorithm. The integration of the data using a monoclinic unit cell yielded a total of 42334 reflections to a maximum

Table 1
Summary of crystal structure data for complex [C$_6$H$_4$-1,3-(OPPh$_2$\{Ru(η^6-p-cymene)Cl$_2$\})$_2$] (**1**)

Empirical formula	C$_{51}$H$_{54}$Cl$_6$Ru$_2$O$_2$P$_2$
Formula weight	1175.72
Temperature	291 (2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	*P2(l)/c*
Unit cell dimensions	a = 15.9326 (10) Å, α = 90°
	b = 18.6537 (11) Å, β = 92.654 (2)°
	c = 17.6065 (11) Å, γ = 90°
Volume	5227.1 (6) Å^3
Z	4
Density (calculated)	1.494 g/cm^3
Absorption coefficient	0.984 mm^{-1}
F(0 0 0)	2384
Crystal size	0.38 mm × 0.09 mm × 0.08 mm
θ range for data collection	1.28–25.00°
Index ranges	$-18 \leq h \leq 18, -22 \leq k \leq 22, -20 \leq l \leq 20$
Reflections collected	42334
Independent reflections	9197 [R(int) = 0.0670]
Absorption correction	Analytical
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	9197/0/573
Goodness-of-fit on F^2	1.000*
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0585, wR2 = 0.1142**
R indices (all data)	R1 = 0.0976, wR2 = 0.1247**
Largest diff. peak and hole	0.638 and −0.570 eÅ^{-3}

* $S = [w(F_o)^2 - (F_c)^2)^2/(n - p)]^{1/2}$, where *n*: number of reflections and *p*: total number of parameters.
** $R1 = |F_o - F_c|/|F_o|, wR2 = [w((F_o)^2 - (F_c)^2)^2/w(F_o)^2]^{1/2}$.

2θ angle of 50.00° (0.93 Å resolution), of which 9197 were independent (R_{int} = 6.70%). Analysis of the data showed negligible decay during data collection. The structure was solved by Patterson method using SHELXS-97 [11] program. The remaining atoms were located via a few cycles of least squares refinements and difference Fourier maps, using the space group *P2(l)/c*, with Z = 4. Hydrogen atoms were input at calculated positions, and allowed to ride on the atoms to which they are attached. Thermal parameters were refined for hydrogen atoms on the phenyl groups using a Ueq = 1.2 Å to precedent atom. The final cycle of refinement was carried out on all non-zero data using SHELXL-97 [12] and anisotropic thermal parameters for all non-hydrogen atoms. The details of the structure determination are given in Table 1 and selected bond lengths (Å) and angles (°) in Table 2.

Table 2
Selected bond lengths and angles for [C$_6$H$_4$-1,3-(OPPh$_2$\{Ru(η^6-p-cymene)Cl$_2$\})$_2$] (**1**)

Bond lengths (Å)		Angles (°)	
Ru(1)—P(1)	2.2960 (15)	P(1)—Ru(1)—Cl(1)	90.65 (6)
Ru(1)—Cl(1)	2.3956 (16)	P(1)—Ru(1)—Cl(2)	85.03 (6)
Ru(1)—Cl(2)	2.4070 (16)	Cl(1)—Ru(1)—Cl(2)	87.48 (6)
Ru(2)—P(2)	2.3116 (17)	P(2)—Ru(2)—Cl(4)	86.62 (6)
Ru(2)—Cl(4)	2.4044 (17)	P(2)—Ru(2)—Cl(3)	94.69 (6)
Ru(2)—Cl(3)	2.4128 (16)	Cl(4)—Ru(2)—Cl(3)	87.75 (6)
P(1)—O(1)	1.625 (4)	O(1)—P(1)—Ru(1)	113.79 (15)
P(2)—O(2)	1.642 (4)	O(2)—P(2)—Ru(2)	113.63 (17)

The numbering of the atoms is shown in Fig. 1 (ORTEP). [13].

3. Results and discussion

The reaction of stoichiometric amounts of [(η^6-p-cymene)RuCl$_2$]$_2$ and [C$_6$H$_4$-1,3-(OPPh$_2$)$_2$] affords complex [C$_6$H$_4$-1,3-(OPPh$_2$\{Ru(η^6-p-cymene)Cl$_2$\})$_2$] (**1**) in good yield as a red microcrystalline powder, this compound being stable to the open atmosphere. Analysis by ^{1}H NMR reveals this compound to be diamagnetic, exhibiting signals corresponding to the aromatic rings for the phosphinite ligand at 6.77–7.99 ppm. Another set of signals consisting of two doblets centered at 5.19 and 5.08 ppm are due to the presence of the aromatic protons in the p-cymene group, this information is complemented by the presence of signals at 2.43 and 0.79 ppm due to the CH and CH$_3$ of the *iso*-propyl groups of the p-cymene moiety. Finally, a signal due to the presence of the methyl in the p-cymene group is observed at 1.42 ppm. Analysis by ^{31}P\{^{1}H\} NMR exhibits a unique signal in the spectrum, indicative of both phosphorus being equivalent as result of the high symmetry of the complex. The FAB$^+$ mass spectrometry analysis of this complex exhibits the molecular ion plus one unit [M + H]$^+$ at 1091 *m/z*, other important fragments are observed at 1055 and 784 *m/z* due to the consecutive loss of a Cl$^-$ ligand and the [RuCl-(η^6-p-cymene)] fragment, respectively.

Crystals of [C$_6$H$_4$-1,3-(OPPh$_2$\{Ru(η^6-p-cymene)Cl$_2$\})$_2$] (**1**) suitable for single crystal X-ray diffraction analyses (Table 1) were obtained by slow evaporation of a saturated solution of **1** in CDCl$_3$. The structure determined is quite unusual exhibiting a Ru(II) bimetallic species with the PCP phosphinite ligand acting as a bridge between the two ruthenium centers.

The geometry around the two ruthenium centers can be defined as slightly distorted pseudo tetrahedrons, exhibiting the typical "piano-stool" geometry around the ruthenium, having two chloride ligands and one diphenylphosphino group coordinated and completing the coordination sphere the p-cymene group occupying three coordination sites. To the best of our knowledge this is the first crystallographic determination of a bimetallic bridged structure using this sort of ligands, although a related structure has been invoked by Balakrishna and coworkers [14] for the formation of the ruthenium complex (**a**) where the ligand also serves as bridge between two metal centers (Scheme 2), however no crystallographic evidence was presented.

Another related structure (**b**) has been reported by Osborn and co-workers [15], where the phosphinite ligand PONOP [C$_6$H$_3$N-2,6-(CH$_2$OPPh$_2$)$_2$] behaves as bridging ligand between two platinum centers, forming a large 20 membered diplatina-macrocycle. This behavior was attributed to the length of the arms in the ligand, being one CH$_2$ longer that the ligand used in this work (Scheme 3).

Most recently [16] a similar structure (**c**), (Scheme 4) has been determined for a BINAP-based phosphinite ligand BINAPO, where as is the case for complex **1**, it is noted by the authors that compounds bearing binaphtyl-based ligands bridging two metal centers are very rare.
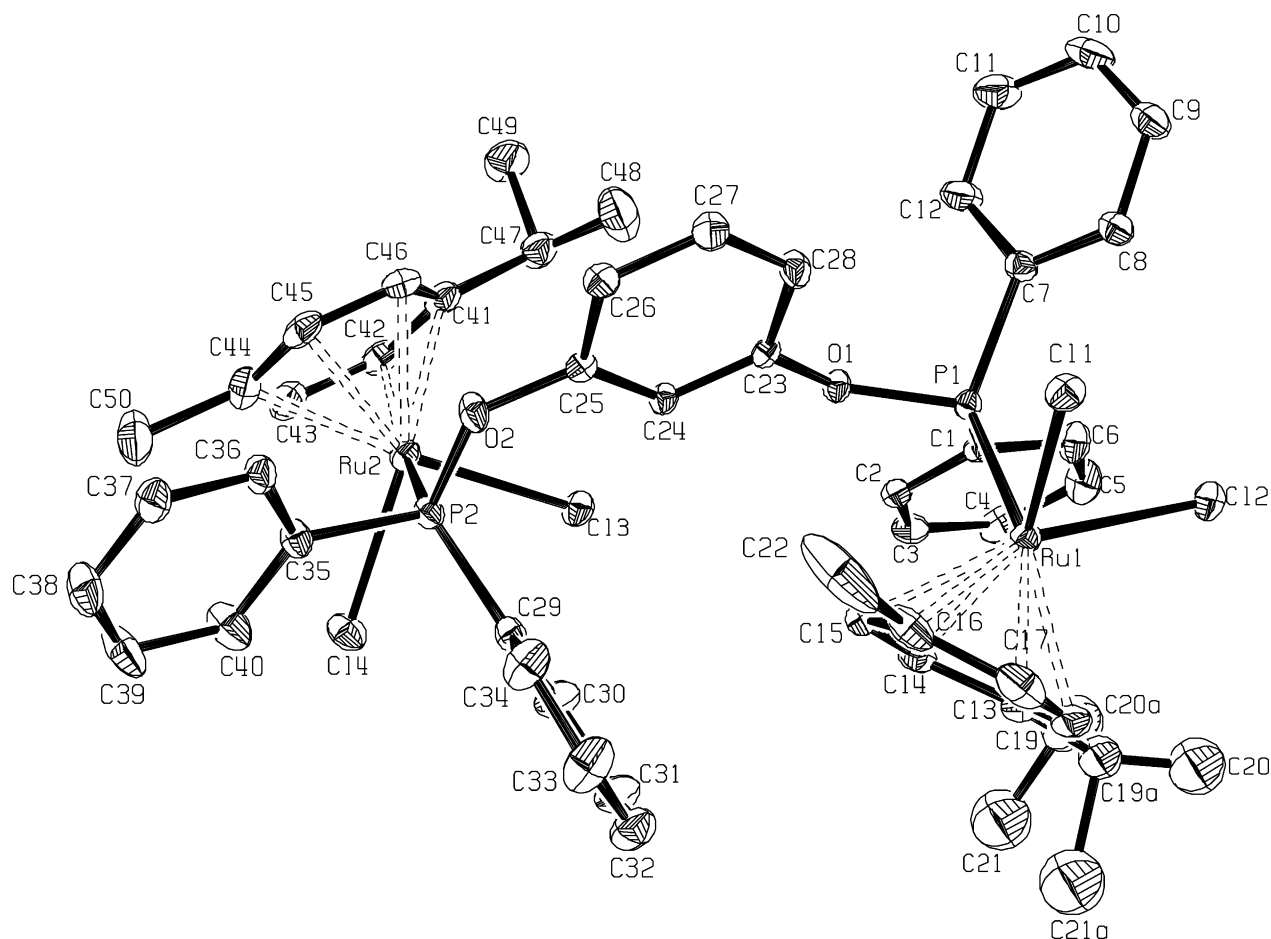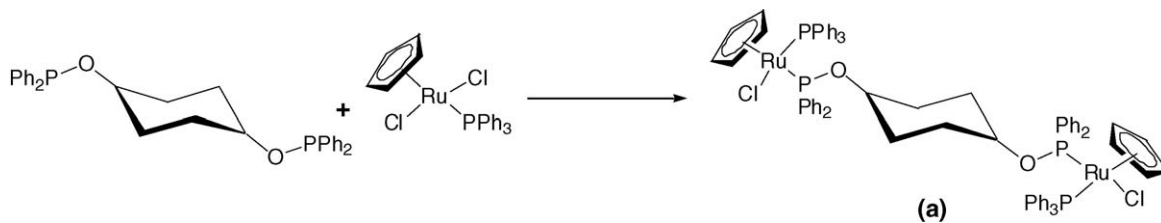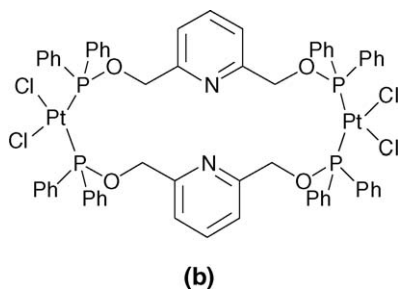
Fig. 1. An ORTEP representation of the structure of $[C_6H_4\text{-}1,3\text{-}(OPPh_2)_2]$ with $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$ (**1**) at 50% probability showing the atom labeling scheme.
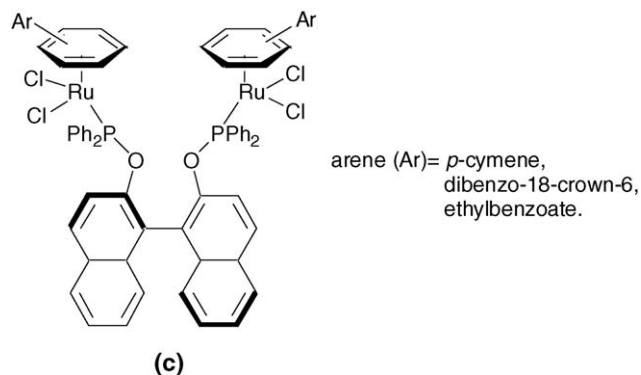

Scheme 2.

The Ru–P distances in $[C_6H_4\text{-}1,3\text{-}(OPPh_2\{Ru(\eta^6\text{-}p\text{-}cymene)Cl_2\})_2]$ (**1**) [Ru(1)–P(1) 2.2960 (15) Å and Ru(2)–P(2) 2.3116 (17) Å] are comparable to those found in the BINAPO derivative (**c**) (2.299 (4) Å), and a similar situation occurs in

Scheme 3.

the case of the Ru–Cl distances. In all other respects the bond distances and angles are within the expected values.

The PCP ligands can behave as potentially tridentate pincer type ligands [17], fact that has made their transition metal complexes very valuable in organic transformations [18] and activation of small molecules [19]. The thermal stability that these ligands confer to their complexes, allow them to withstand high temperatures and thus overcome the energy barriers to perform the corresponding activation. In an attempt to obtain ruthenium complexes with the ligand $[C_6H_4\text{-}1,3\text{-}(OPPh_2)_2]$ behaving as pincer ligand, the starting material $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$ was changed for $[(\eta^6\text{-benzene})RuCl_2]_2$ [9]. However, analysis of the resulting product reveals this compound to have a similar structure as that of $[C_6H_4\text{-}1,3\text{-}(OPPh_2\{Ru(\eta^6\text{-}p\text{-cymene})Cl_2\})_2]$ (**1**). Direct reaction of the ligand $[C_6H_4\text{-}1,3\text{-}(OPPh_2)_2]$ with $[RuCl_2(PPh_3)_3]$ [20] resulted

arene (Ar)= *p*-cymene,
dibenzo-18-crown-6,
ethylbenzoate.

(c)

Scheme 4.

in an intractable mixture of compounds that were not further characterized. More drastic conditions were also used. For example, a mixture of the ruthenium dimer, the $[C_6H_4(OPPh_2)_2$-1,3] ligand (in various amounts) and KPF_6 was refluxed (EtOH or MeCN) under basic (KOH) conditions. The use of silver salts ($AgBF_4$ for instance) was another strategy developed to lead to

the formation of the PCP complexes. However, in most of the cases unworkable mixtures were obtained, which often decomposed readily to dark green material. In other cases, compound **1** could be isolated in lower yields than under the "mild" conditions (CH_2Cl_2, RT) reported.

Following our continuous interest in the use of potentially tridentated PCP pincer ligands in relevant organic transformations, we have used complex $[C_6H_4$-1,3-(OPPh_2$\{Ru(\eta^6$-*p*-cymene)$Cl_2\})_2]$ (**1**) as catalyst in the transfer hydrogenation of ketones.

The results obtained are similar to those reported by van Koten with the PCP pincer complex $[(C_6H_3$-2,6-$(CH_2PPh_2)_2RuCl(PPh_3)]$ for benzophenone and acetophenone [5a]. Interestingly, our system is considerably faster, at least in the case of benzophenone, since we achieve 84% yield in only 10 h while van Koten's system affords 98% but only after 108 h of reaction [5a]. Other ketones like the propiophenone and 3-heptanone were also tested, however the yields under the same reaction conditions and reaction times were only of 34% and 58%, respectively. An interesting result occurs when the transfer hydrogenation of chalcone was attempted, afford-

Table 3
Reduction of ketones by $[C_6H_4$-1,3-(OPPh_2$\{Ru(\eta^6$-*p*-cymene)$Cl_2\})_2]$ (**1**) with Pr^{i}OH/NaOH as the reducing agent
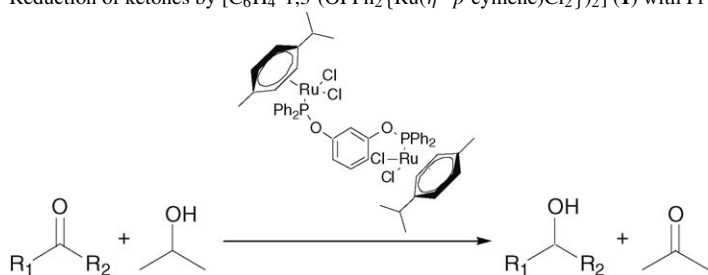
Entry	Substrate	Product	Yield[a] (%)
1			91
2			84
3			34
4			17
5			34

Reaction conditions: complex (**1**) (11.0 mg, 0.005 mmol), NaOH (0.5 mg, 0.012 mmol) and ketone (0.5 mmol) in degassed *iso*-propanol (2.5 mL), reflux for 10 h.
[a] Yields were determined by GC–MS and related to the unreacted ketone.

ing the hydrogenation of the alkene C=C bond, without any detectable (GC–MS) amount of the alcohol as hydrogenated product, which in fact may favor the use of this catalyst in the regioselective hydrogenation of conjugated enones. It is noteworthy that, extension of the reaction times up to 40 h affords in all cases quantitative yields (Table 3).

It is probable, as in the case for [(C$_6$H$_3$-2,6-(CH$_2$PPh$_2$)$_2$ RuCl(PPh$_3$)], that in the present case hydrido-alkoxo intermediates are the active species in the catalytic process [5a]. This hypothesis and other aspects of the reaction mechanism for the transfer hydrogenation of ketones using [C$_6$H$_4$-1,3-(OPPh$_2$\{Ru(η^6-*p*-cymene)Cl$_2$\})$_2$] (**1**) as catalyst are currently under study and will be matter of a further communication.

In summary, we have synthesized and unequivocally characterized a new bimetallic ruthenium complex having a phosphinite PCP ligand as a bridging ligand between the two ruthenium centers. This compound has proved to be an efficient catalyst in the transfer hydrogenation reaction of ketones in the presence of Pr^{i}OH and NaOH.

4. Supplementary material

Supplementary data for complex **1** have been deposited at the Cambridge Crystallographic Data Centre. Copies of this information are available free of charge on request from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336033; e-mail address: deposit@ccdc.cam.ac.uk or url: http://www.ccdc.cam.ac.uk) quoting the deposition number CCDC 284682.

Acknowledgements

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