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Ruthenium–benzocrownether complexes: Synthesis, structures, catalysis and immobilisation in ionic liquids

Tilmann J. Geldbach *, Melanie R.H. Brown, Rosario Scopelliti, Paul J. Dyson

Ecole Polytechnique Fédérale de Lausanne (EPFL), Institut des Sciences et Ingénierie Chimiques, CH-1015 Lausanne, Switzerland

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Abstract

A facile pathway to $[RuCl_2(\eta^6\text{-benzocrownether})]_2$ complexes is described and crystal structures of the complexes $[RuCl_2(\eta^6\text{-benzo-15-crown-5})]_2$ and $[RuCl_2(\eta^6\text{-dibenzo-18-crown-6})]_2$ are reported. The complexes were derivatised with (1*S*,2*R*)-2-amino-1,2-diphenylethanol and evaluated in the enantioselective transfer-hydrogenation of acetophenone. The effect of complexation of different alkaline metals (Na, K, Cs) within the crown on the selectivity and reaction rate was studied. Interaction of a sulfonated phosphine ligand with the crown was probed by NOESY-NMR and utilisation of the crownether to serve as an anchor for catalyst immobilisation was investigated.

Keywords: Crownether; Ruthenium; Transfer-hydrogenation; Crystal structure; Ionic liquids; Biphasic catalysis; NOESY

1. Introduction

The last decades have seen the development of a plethora of homogeneous catalysts that provide facile access to numerous products in excellent yield and selectivity [1]. Yet, catalyst separation and reuse in an easy and economical way are possible in only few cases and homogeneous industrial processes in which recycling of the catalyst is realised are sparse [2].

Accordingly, a range of different methodologies have been developed to address this problem which include, e.g., immobilisation of the catalyst onto solid supports or biphasic (aqueous, fluorous, ionic liquid, etc.) systems. In both cases, tedious ligand modifications are usually required to either sufficiently immobilise the catalyst in the liquid phase or to anchor the catalyst onto a support. For example, attaching charged moieties like $[SO_3]^-$ and $[NR_3]^+$ or fluorous chains to ligands renders a complex water or fluorous phase soluble. In enantioselective catalysis, however, different substrates often require slightly different chiral ligands and the adaptation of each ligand for biphasic catalysis is not practical. Synthesis of ruthenium precursors for biphasic catalysis which allow for the use of unmodified ligands may provide a relatively simple solution. Based on such a proposition, we recently synthesised the ionic liquid tagged derivative **I** of the widely used starting material into ruthenium chemistry, $[RuCl_2(\eta^6\text{-arene})]_2$ [3]. Bearing charged imidazolium moieties, **I** is virtually insoluble in most common organic solvents whereas in water and ionic liquids it is highly soluble. It can thus serve as precursor for a range of complexes aimed for biphasic catalysis.

* Corresponding author. Tel.: +41 216939862; fax: +41 216939885.
E-mail address: tilmann.geldbach@epfl.ch (T.J. Geldbach).

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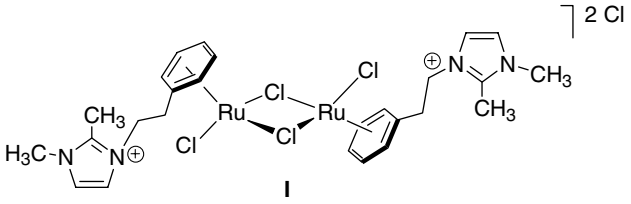
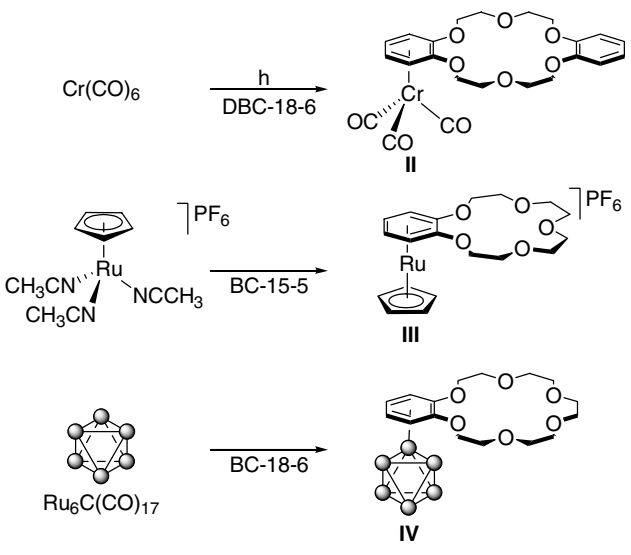


I

Complexes containing crownether moieties might provide an interesting alternative, especially, as they would offer the possibility to attach and detach a charge and, thus, transfer the complex back and forth between different solvent phases such as ionic liquids and organic solvents. While many ligands containing macrocyclic units exist [4], only few metal complexes with η^6-benzocrown ligands are known, and prominent examples are shown in Scheme 1. Irradiation of hexacarbonyl chromium with UV light in the presence of benzocrown afforded the tricarbonyl arene complex **II**, which has been used as an IR-readable sensor for alkali metal cations and aromatic analytes [5–7]. Heating 1,2-dichloroethane solutions of $RuCp(NCCH_3)_3$ containing two equivalents of benzo-15-crown-5 for 16 h at 80 °C led to the formation of $RuCp(\eta^6$-benzo-15-crown-5), **III**, in 68% yield [8]. Thermolysis of the ruthenium cluster $Ru_6C(CO)_{17}$ in dibutylether afforded compound **IV** in which one ruthenium atom is capped with a benzocrown ligand [9]. In this latter compound, the crown moiety was used to immobilise the cluster onto aminated mesoporous silica [9a], or onto aminated ArgoGel resins, the latter yielding a recyclable hydrogenation catalyst [9d].

Recently, a benzocrown ruthenium dimer, viz., $[RuCl_2(\eta^6$-benzo-18-crown-6)$]_2$, **V**, was synthesised from Ru(η^4-cyclooctadiene)(η^6-cyclooctatriene), see Scheme 2 [10]. Such dimeric arene–ruthenium complexes are versatile precursors for a number of interesting complexes even including ruthenium complexes for cancer treatment [11]. A serious drawback to the synthetic route outlined in Scheme 2 is that synthesis of Ru(cod)(cot) is not trivial, and that both the starting material and the intermediate Ru(η^4-cyclooctadiene)(η^6-benzo-18-crown-6) are highly air and moisture sensitive. Accordingly, both Ru(cod)(cot) as well as the dimeric complex are obtained at only low to moderate yield (42–53%) [10,12].



Scheme 1. Synthetic pathways to η^6-benzocrown complexes.

Here, we present a more facile pathway to dimeric η^6-benzocrown ruthenium complexes and examine the performance of their derivatives in transfer-hydrogenation, together with some studies on immobilisation in ionic liquids.

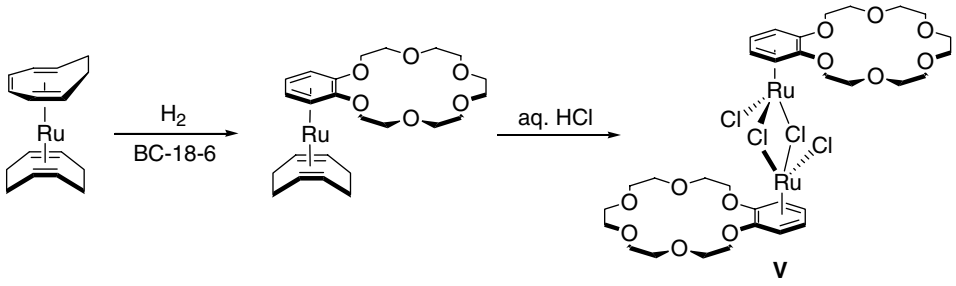
2. Results and discussion

2.1. Synthesis of dimeric ruthenium–crownether complexes

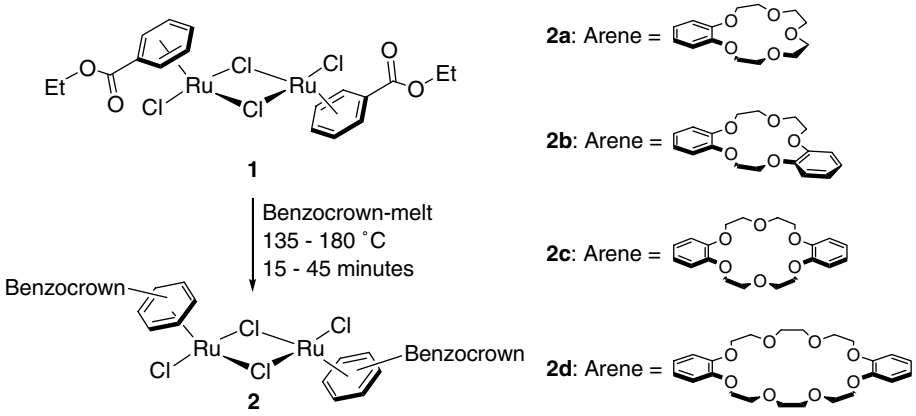
The ease with which coordinated arenes can be replaced depends on the substituents on the arene such that thermal exchange is sufficiently facile if electron-withdrawing groups like esters are present [13,14]. Accordingly, the weakly coordinated arene in $[RuCl_2(\eta^6$-ethyl benzoate$)]_2$, **1**, is lost above ca. 125 °C, and stirring a mixture of **1** in a 5–10-fold excess of molten benzocrown affords the corresponding crownether complexes in less than 1 h, see Scheme 3.

Depending on the melting point of the ether, reaction temperatures varied between 135 and 180 °C, with reaction times between 15 and 45 min (see Section 4). Although, yields are also only moderate and are typically around 50%, the synthesis is much less cumbersome compared to the route outlined in Scheme 2. The moderate yields are most likely due to fast decomposition of "naked" ruthenium(II) chloride once the coordination to the ethyl benzoate has been cleaved and indeed significant amounts of black deposits are formed in the course of the reaction. Following the pathway outlined in Scheme 3, ruthenium dimers with benzo-15-crown-5, dibenzo-15-crown-5, dibenzo-18-crown-6 and di-benzo-24-crown-8 could be obtained. Attempts to synthesise the benzo-18-crown-6 derivative in this manner gave only very low yields, presumably due to the lower thermal stability of the envisaged product. Ionic liquids might turn out to be a suitable matrix for such arene-exchange reactions, already having been used in Cp-arene exchange reactions involving ferrocene [15], and research is currently underway to evaluate their viability here.

The course of the reaction may be followed by ^{1}H NMR spectroscopy in that small amounts of the melt



Scheme 2.



Scheme 3.

are dissolved in $CDCl_3$ and the disappearance of the diagnostic arene-resonances of the η^6-ethyl benzoate are monitored. After complete conversion of the starting material, the product was extracted from the melt, leaving behind crude excess benzocrown, which can be reused without further purification. All of the crownether-dimer complexes are air-stable and highly soluble in donor solvents such as water and acetonitrile. The NMR data of complexes **2a**–**d** are routine with chemical shifts of the coordinated arene being essentially unaffected by the size of the crown. At room temperature, the proton resonances are rather broad, indicating pronounced dynamic behaviour of the crown moiety on the NMR time scale. Electrospray mass spectra of aqueous solutions of **2a**–**d** give $[RuCl(\eta^6\text{-benzocrown})]^+$ as the most prominent peak. Aqueous solutions of **2c** and **2d** were further studied by ESI-MS in the presence of a 5-fold excess of either NaCl, KCl or CsCl, respectively. For both compounds additional peaks are observed which correspond to $[RuCl_2(\eta^6\text{-benzocrown}) + \text{alkali metal}]^+$ and are found for **2c** at $m/z = 555$ (Na), 573 (K) and 665 (Cs) and **2d** at $m/z = 643$ (Na), 659 (K) and 753 (Cs). In addition, signals for adducts of alkali metal and uncomplexed benzocrown ligand are also present.

2.2. Characterisation in the solid state

Crystals suitable for X-ray diffraction were grown from slow diffusion of diethyl ether into chloroform solutions of **2a** and **2c**. Views of the structures of **2a** and **2c** are shown in Figs. 1 and 2, respectively, and selected bond lengths and angles are listed in Table 1.

Bonding parameters around the metal centre are in good agreement with related dimeric ruthenium–arene complexes [16]. In both compounds, coordination of the arene is slightly asymmetric with larger Ru–C distances to the quaternary carbon atoms C1 and C6. The most striking difference between the two structures lies in the orientation of the crownether moiety relative to that of complexed arene. In **2a**, the 15-crown-5 is oriented towards the chloride ligands, whereas in **2c** the benzo-18-crown-6 part is almost perpendicular to the plane of the complexed arene, pointing away from the chloro-ligands, which can be appreciated from Fig. 3. This difference is probably due to the presence of a solvent chloroform molecule in **2c**, which hydrogen bonds to some of the crown-oxygen atoms and also to some extent the reflection of crystal packing effects, see Fig. 4. While for **2a**, all molecules have the same orientation, those in **2c** adopt two orientations, which differ

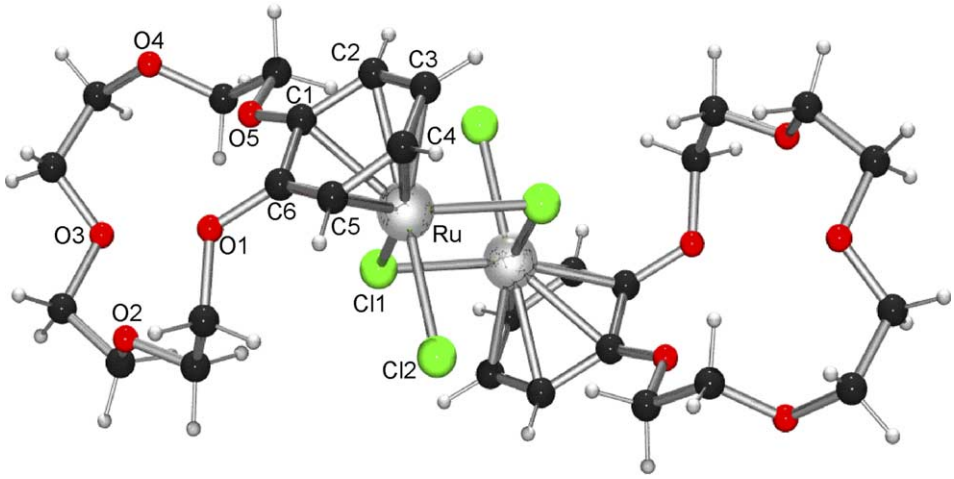


Fig. 1. Ball-and-stick representation of **2a**. Symmetry equivalent atoms are obtained by the operation $-x, -y + 2, -z$.

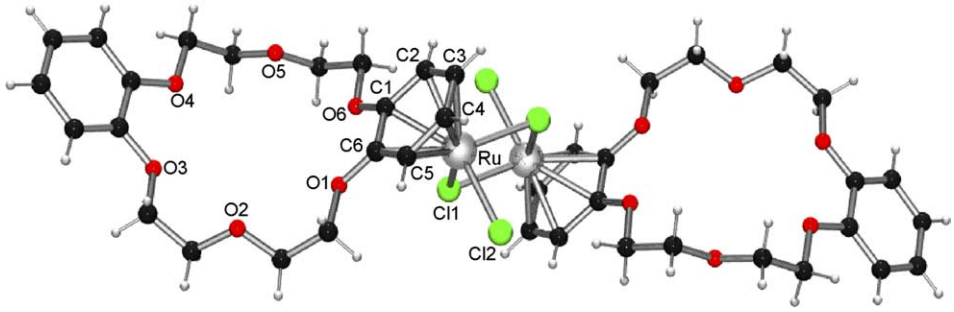


Fig. 2. Ball-and-stick representation of **2c**. Symmetry equivalent atoms are obtained by the operation $-x + 1, -y, -z + 2$.

Table 1
Selected bond lengths and angles for **2a** and **2c**

	2a	**2c**
Ru–C1	2.27(1)	2.241(6)
Ru–C2	2.21(1)	2.160(6)
Ru–C3	2.14(1)	2.162(6)
Ru–C4	2.17(1)	2.130(6)
Ru–C5	2.15(1)	2.173(6)
Ru–C6	2.23(1)	2.250(6)
Ru–Cl1	2.476(3)	2.458(2)
Ru–Cl2	2.416(3)	2.405(2)
Cl1–Ru–Cl2	86.9(1)	89.19(6)
Cl2–Ru–Cl1*	87.1(1)	89.66(5)
Cl1–Ru–Cl1*	81.8(1)	81.05(5)

by a 180° rotation along the *b*-axis. In the crystal, the crown ether moieties are stacked to form channel-like structures. Similarly, aligned crownethers have recently been reported as proton conductors [17].

2.3. Catalysis and immobilisation studies

As part of our ongoing research in ruthenium catalysed (transfer) hydrogenation [3,18], the benzocrown complexes were reacted with the chiral ligand (1*S*,2*R*)-2-amino-1,2-diphenylethanol to afford complexes **3a**–**d** in near quantitative yield, see Scheme 4.

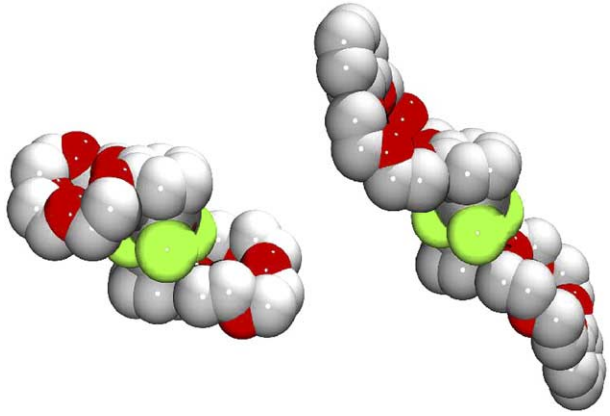


Fig. 3. Space-filling view of **2a** and **2c**, showing the different orientation of the crownether moiety. Hydrogen atoms have been omitted for clarity.

All compounds were fully characterised by ESI-MS and NMR spectroscopy and selected ^{13}C NMR data are listed in Table 2 compared to data for the known η^6-*p*-cymene complex, **4**, and the η^6-ethyl benzoate complex, **5** (see Scheme 4 for numbering). The presence of the chiral amino alcohol ligand renders the nuclei of the complexed arene diastereotopic and accordingly six different signals are observed. As one might expect there

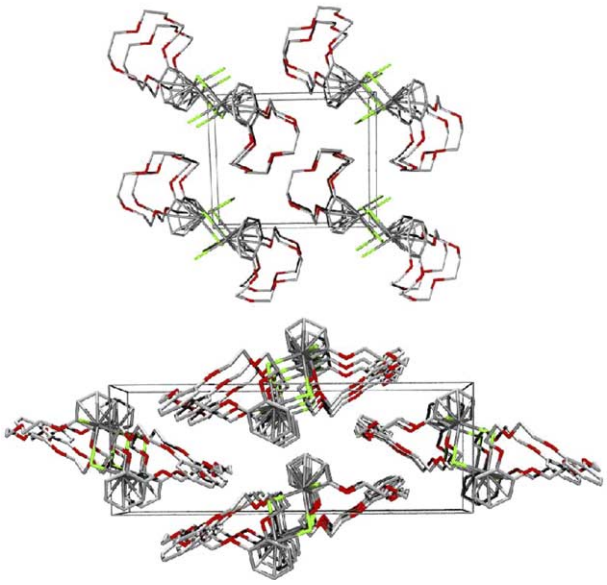
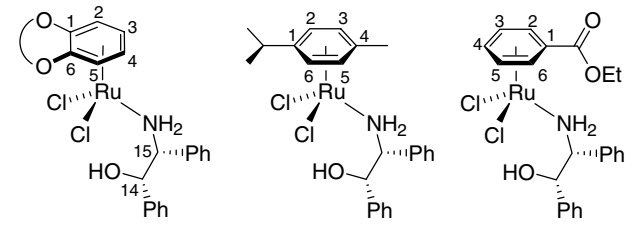


Fig. 4. Unit cells of **2a** (top) and **2c** (bottom). Note the channel-like alignment of the crownether moieties.



3a: Arene = Benzo-15-crown-5
3b: Arene = Dibenzo-15-crown-5
3c: Arene = Dibenzo-18-crown-6
3d: Arene = Dibenzo-24-crown-8

Scheme 4.

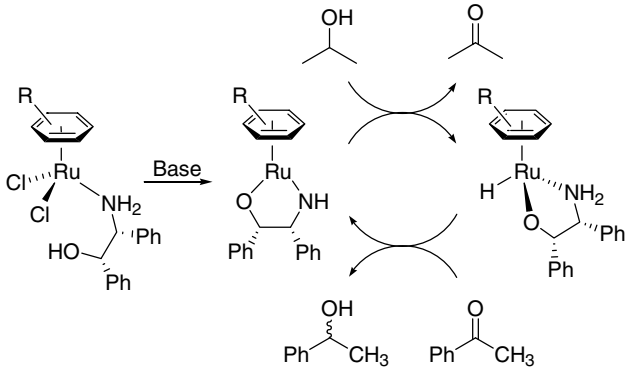
is close resemblance with respect to the ^{13}C NMR chemical shift of the different crownether pre-catalysts. Complex **3b** is obtained as a mixture of isomers, which differ with respect to the orientation of the η^6-arene relative to the aminoalcohol, therefore no assignment of the NMR-signals was attempted for this compound.

The benzocrown complexes with the aminoalcohol ligand, **3**, were tested as pre-catalysts in the enantioselective reduction of acetophenone with 2-propanol and the results compared to the known complex **4** and the ester derivative **5**. Of particular interest is to what degree catalyst activity and selectivity are influenced by the presence of different alkali metal cations. It is conceivable that coordination of the alkali metal cation to the crown-moiety may alter the steric (preferred orientation of the crown) and electronic properties of the complexes. The active catalyst was prepared in situ in 2-propanol from reaction of **3**–**5** with excess alkali metal hydroxide (four equivalents), see Scheme 5, and the reaction monitored by GC using a chiral column. This catalytic cycle is now well-established [19] and crystal structures of the 16-electron species as well as the hydride complex have been obtained previously for a related diamine complex [20]. Results from the reduction of acetophenone with **3c**, **4** and **5** are shown in Fig. 5; data for **3a**, **3b** and **3d** is compiled in Supplementary.

Table 2
Selected ^{13}C NMR chemical shifts for the transfer-hydrogenation pre-catalysts **3a**, **3b**, **3c**, **4** and **5** ($CDCl_3$; 100 MHz)

Pos[a]	3a	3c	3d	4	5
1	118.5	117.9	119.0	102.7	78.2
2	69.1	68.1	68.0	81.2	88.1
3	79.3	78.8	78.0	79.4	79.3
4	77.6	77.3	77.0	95.7	89.3
5	67.5	66.5	67.7	79.7	78.8
6	118.0	117.3	118.1	80.7	87.8
14	73.9	74.1	75.2	76.7	76.3
15	63.7	63.5	65.0	67.1	66.4

[a] In **3**, values for positions 1/6, 2/5 and 3/4, and in **4** and **5**, values for positions 2/6 and 3/5, are interchangeable as the absolute configuration was not determined.



Scheme 5. Formation of the catalytically active species and catalytic cycle.

Compound **4** is essentially insensitive to the nature of the base (as is expected), whereas there are some significant differences in the performance of the benzocrown complex **3c**. Here, the enantioselectivity is ca. 20% lower with KOH than with either NaOH or CsOH. There are also some cation effects for **3a**, **3b** and **3d**, but not to the same extent. It is difficult to rationalise these effects as complexation of a metal cation could both alter the orientation of the crown with respect to the aminoalcohol ligand as well as interact with the substrate [21]. It is, however, clear that dibenzo-18-crown-6 is more selective than the other crownethers which might explain the pronounced effect with potassium which is more tightly bound in the cavity. In addition to the selectivity of the reaction, rates in **3** are also affected although to only a small degree. The catalyst solution of **3c** was investigated using electrospray mass spectroscopy. After addition of four equivalents KOH, major peaks are found at

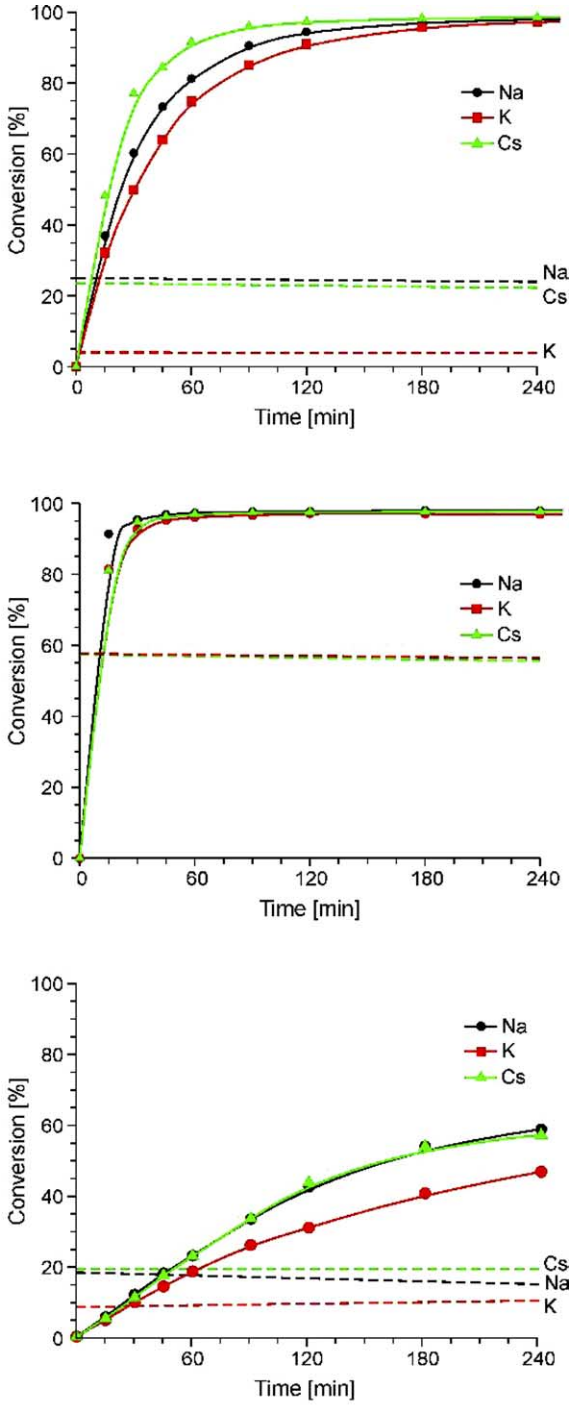


Fig. 5. Reaction profiles and ee (dotted lines) in the transfer-hydrogenation of acetophenone with **3c** (top), **4** (middle) and **5** (bottom) with either NaOH, KOH or CsOH as base. Reaction conditions: 0.125 M acetophenone in 2-propanol, S/C 200, 4 equivalents base, at 30 °C.

m/z = 674 and 714, which may be attributed to the catalytically active 16-electron complex, [Ru(η^6-dibenzo-18-crown-6)(aminoalcohol)]$^+$, and the hydride-complex [RuH(η^6-dibenzo-18-crown-6)(aminoalcohol)K]$^+$. Once acetophenone is added to this solution, new prominent signals are observed at m/z = 710 and 748. From the isotope pattern, the former was assigned to the chloride complex [RuCl(η^6-dibenzo-18-crown-6)(aminoalcohol)]$^+$, and the latter to [RuCl(η^6-dibenzo-18-crown-6)-(aminoalcohol)K]$^+$. The reason why signals for a chloro-complex become more prominent upon addition of acetophenone is not yet understood.

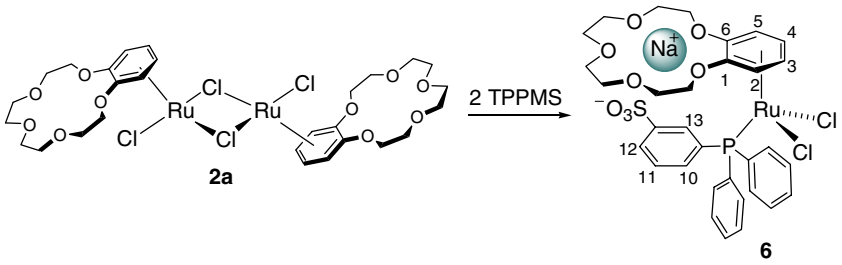
Cation effects are also observed for the benzylethylester derivative **5**. It is noteworthy that with this pre-catalyst the *R*-enantiomer is predominantly formed, though at very low ee, while **3** and **4** afford the *S*-enantiomer. It is therefore conceivable that the coordination sphere in **5** undergoes major change upon addition of excess base and substrate. Carboxylic esters can undergo hydrolysis in the presence of a base to afford alcohols and a carboxylate and the latter could interact with the alkaline metal. Alternatively, base-induced cleavage of the relatively weak metal–arene bond could occur which would explain the poor catalytic performance.

To better understand possible interactions between complexed alkali metals and polar ligands, **2a** was reacted with two equivalents triphenylphosphine monosulfonate, TPPMS, to afford the mono-phosphine complex **6**, see Scheme 6. The sulfonato-substituted phosphines are among the most widely used ligands employed to make a complex water-soluble [22]. Although, the crownether complexes described herein are water soluble, it was of interest to establish whether a complexed TPPMS ligand would interact with the crown ether.

As in the other benzocrown complexes, ^{1}H NMR resonances of the arene ligand in **6** are very broad at ambient temperature. Below ca. 260 K motion of the ligand is sufficiently slow to afford four resolved signals for the arene-protons, as shown in Fig. 6. Of these, one is shifted to unusually low frequency, 3.15 ppm (at 218 K). These observations are already indicative that indeed the sulfate-substituted phenyl ring adopts a preferred orientation. To gain further insight, a NOESY spectrum was run at 205 K and a section showing the cross-peaks arising from contacts of the phenyl protons is shown in Fig. 7.

From this measurement, it is evident that only the *ortho*-proton H^{13}, which was assigned on the basis of a H,H-COSY spectrum, approaches the crown ether sufficiently to give NOE-signals. No such cross-peaks are observed for the two unsubstituted phenyl rings which accordingly point away from the crown. Thus, charge attraction between Na^+ and SO_3^- is sufficient to steer the sulfonated phenyl group into a specific position. It is conceivable, that hydrogen-bonding between the SO_3^- and CH_2-groups from the crown ether also contribute to the observed preferred conformation. However, both of these forces are too weak to keep the phenyl ring in place above ca. 258 K.

Within the context of biphasic catalysis, the effect of crownether-complexed cations on the retention in ionic



Scheme 6.

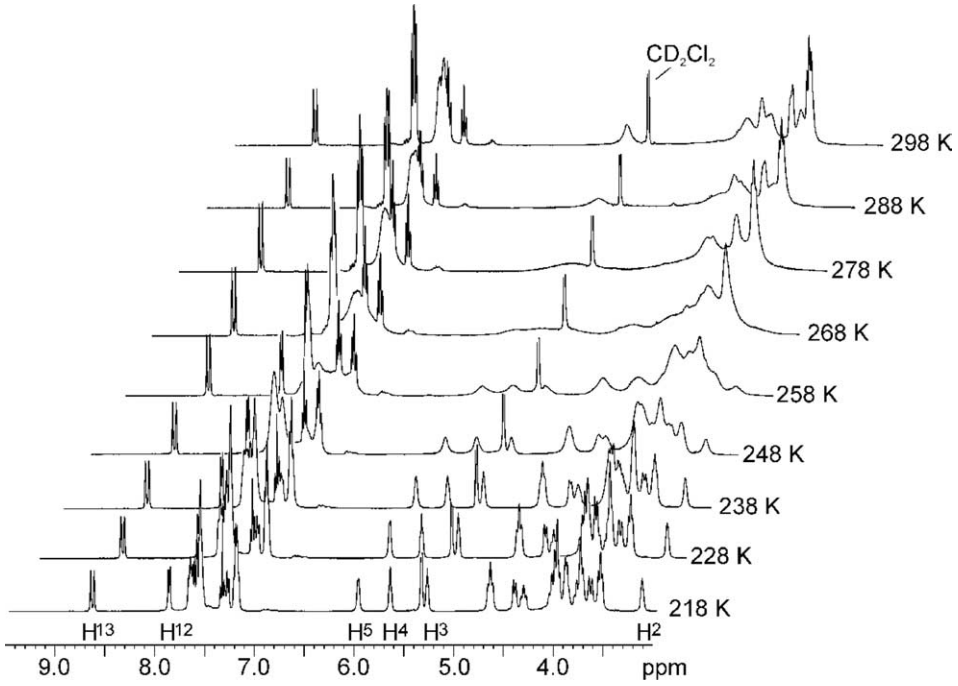


Fig. 6. ^{1}H NMR spectra of **6** in the range of 218–298 K in CD_2Cl_2. Note the resolution of the protons of the coordinated arene at low temperature. The solvent signal has been reduced for clarity; (CD_2Cl_2, 400 MHz).

liquids was studied. Immobilisation of the ruthenium dimer **2c** in the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate, $[C_4C_1im][PF_6]$, was studied in the presence of excess KCl and subsequent extraction with water. The amount of extracted complex was established by UV–Vis spectroscopy and compared to a calibration curve of **2c** in water. While in the absence of potassium chloride, ca. 46% of the total amount of the complex was extracted, addition of 10 equivalents of KCl significantly improved the immobilisation in that only ca. 18% were found in the aqueous phase. Further increasing the amount of KCl to 100 equivalents only had a minor effect with ca. 10% being extracted.

Although, these results are not satisfactory in terms of catalyst recycling (i.e., 10% catalyst loss is not tolerable) one has to bear in mind that water as extractant itself is a highly suitable solvent for charged molecules, and the improved retention nevertheless nicely demonstrates the potential such crownether complexes might offer in terms of catalyst immobilisation. If the second phase is an organic solvent of low polarity, i.e., toluene or diethyl ether, then catalyst leaching approaches zero. Of special interest would be a system in which the immobilisation of the catalyst were reversible, as outlined in Scheme 7. By using the dicationic *N*-aminopropylimidazolium as an "anchor", retention in imidazolium-based ionic liquids should be further improved. In such a system, complexation to the crown ether could be switched on and off by simply adjusting the pH of the solution. While it was possible to complex the imidazolium salt to the crownether in analogy to a method described previously [9d], the envisaged system suffered from several limitations. An ionic liquid like $[C_4C_1im][PF_6]$ or polar solvents such as water or methanol are required to dissolve such a dicationic complex, and in these media

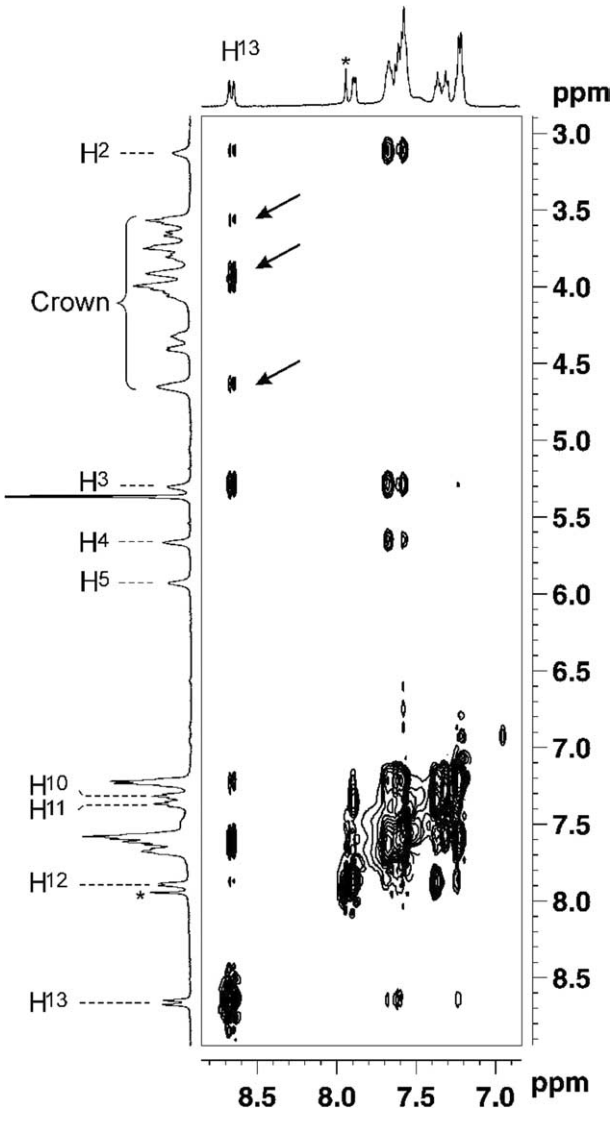


Fig. 7. Slice through the NOESY spectrum of **6** at 205 K. Note that only H^{13} shows cross-peaks to the crown-moiety. * = residual DMF; (CD_2Cl_2, 500 MHz).

the binding of *N*-aminopropylimidazolium to the crownether was not sufficiently strong. In addition, once the ammonium salt was deprotonated, it represented a reasonably good ligand that competed for the metal centre and thereby altered the coordination sphere around the metal.

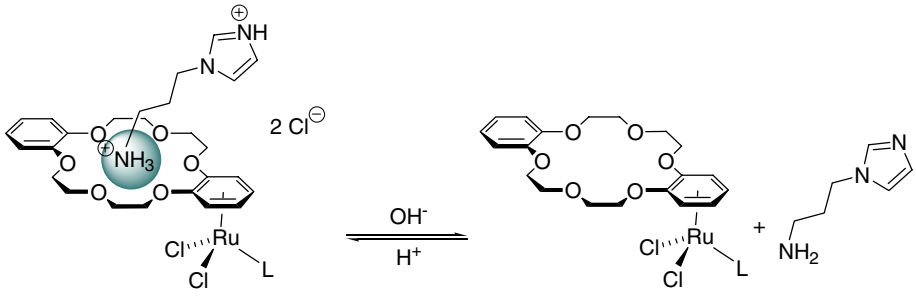
3. Conclusions

An easy and general pathway to η^6-benzocrownether ruthenium complexes has been devised. Such compounds have been tested in the asymmetric transfer-hydrogenation of acetophenone and dependence of both the selectivity and the reaction rate on the nature of the alkali metal present was demonstrated. Work is in progress to evaluate the effect of lanthanide cations in close proximity to the ruthenium centre in catalysis. As was demonstrated for complex of **6**, these crownether complexes are highly dynamic and charge attraction is not sufficient to lead to a stable conformation at ambient temperature. To fully benefit from such crownether moieties in the context of catalysis, more rigidity is desirable to allow for more specific interactions between substrate, ligand and crown. By complexation of cations to the crown, the solubility of the complexes could be tuned, which could be utilised to adapt complexes for the purpose of biphasic catalysis.

4. Experimental

4.1. General

All organometallic manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques. Diethyl ether was distilled from sodium–potassium alloy, 2-propanol, DMF and dichloromethane from CaH_2. Acetophenone was distilled and stored over molecular sieves. The ionic liquid $[C_4C_1Im]PF_6$ [23] and the ruthenium complexes **1** [16d] and **4** [24] were prepared as described elsewhere. All other chemicals are commercial products and were used as received. Spectra were recorded with Bruker Avance 400 and 500 spectrometers. Chemical shifts are given in ppm and coupling constants (*J*) in Hz. Elemental analyses



Scheme 7. Concept of a pH-switch to immobilise crownether complexes.

were performed at the EPFL. Electrospray mass spectra were measured on a Thermo Finnigan LCQ Deca XPplus spectrometer. Catalyst solutions before and after addition of acetophenone were diluted with four parts 2-propanol and introduced at 5 kV at a rate of 5 μl min^{-1} according to a literature protocol [25]. UV–Vis spectra were recorded on a Jasco V-550.

4.2. Transfer hydrogenation of acetophenone in 2-propanol

Under inert atmosphere, a solution of the catalyst (0.00625 mmol) in 2-propanol (10 ml) was treated with 4 equivalents 0.05 M *i*-PrOM/*i*-PrOH (M = Na, K, Cs) and stirred for 5 min at 30 °C, then acetophenone (120 μl, 1.25 mmol) was added and stirring continued. The conversion and ee were monitored by GC. (Chromapack CP-Cyclodex B.)

4.3. Immobilisation studies

To a solution of **2c** (2.7 mg, 0.003 mmol) in $[C_4C_1im][PF_6]$ (0.5 g) was added KCl (either 10 or 100 equivalents) and the mixture stirred at 50 °C in a sonic bath. Then bi-distilled water (3 ml) was added and the two phases stirred for 30 min. The aqueous layer was separated and the amount of extracted crownether complex established by UV–Vis, comparing the measured absorbance at 324 and 406 nm to a calibration curve. The calibration was made by measuring the absorbance of aqueous solutions of **2c** at concentrations of 0.003, 0.0015, 0.00075 and 0.000375 mmol l^{-1}.

4.4. Synthesis of *2–6*

4.4.1. Synthesis of *2a*

A mixture of $[RuCl_2(\eta^6\text{-}C_6H_5CO_2Et)]_2$ (300 mg, 0.47 mmol) and benzo-15-crown-5 (2.0 g, 7.45 mmol) was heated to 135 °C and the melt stirred for 45 min. Et_2O was carefully added to the still molten mixture to extract any unreacted crown ether of which 1.6 g was recovered. The residue was dried and then extracted with $CHCl_3$ to afford the product as an orange sold. Yield: 205 mg (50%). ^1H NMR (CD_2Cl_2, 400 MHz): 5.54 (dd, $^3J_{HH}$ = 4.1, $^4J_{HH}$ = 2.2 4H, $H^{2/5}$), 5.26 (dd, $^3J_{HH}$ = 4.1, $^4J_{HH}$ = 2.1 4H, $H^{3/4}$), 4.68 (m, 4H), 4.11 (m, 4H), 3.96 (m, 4H), 3.83–3.66 (m, 20 H). ^{13}C NMR (CD_2Cl_2, 100 MHz): 117.9 ($C^{1/6}$), 76.1 ($C^{3/4}$), 70.7, 70.6, 69.9, 68.9, 68.0 ($C^{2/5}$). MS (ESI): *m*/*z* = 405.1 $[RuCl(\eta^6\text{-benzo-15-crown-5})]^+$. Anal. Calc. for $C_{28}H_{40}Cl_4O_{10}Ru_2$: C, 38.19; H, 4.58. Found: C, 38.06; H, 4.65%.

4.4.2. Synthesis of *2b*

To a melt of dibenzo-15-crown-5 (1 g, 3.16 mmol) was added at 150 °C $[\{RuCl_2(\eta^6\text{-}C_6H_5CO_2Et)\}_2]$ (100 mg, 0.155 mmol) and the mixture stirred for 10 min. After cooling to room temperature, the residue was thoroughly extracted with degassed water. The solvent was pumped off, the crude product re-dissolved in $CHCl_3$, filtered and precipitated by addition of Et_2O. Yield: 62 mg (41%). ^1H NMR ($CDCl_3$, 400 MHz): 6.97–6.90 (m, 8H), 5.67 (br, 2H, $H^{2/5}$), 5.61 (br, 2H, $H^{2/5}$), 5.27 (br, 4H, $H^{3/4}$), 5.03 (br, 2H), 4.81 (br, 2H), 4.49–4.41 (m, 4H), 4.23–3.91 (m, 16H). ^{13}C NMR (CD_2Cl_2, 100 MHz): 149.6, 122.6, 121.8, 117.7 ($C^{1/6}$), 117.2 ($C^{1/6}$), 117.0, 115.7, 76.9 ($C^{3/4}$), 76.2 ($C^{3/4}$), 71.3, 70.6, 70.4, 69.6 ($C^{2/5}$), 69.5 ($C^{2/5}$), 69.4, 69.2, 68.7. MS (ESI): *m*/*z* = 453.1 $[RuCl(\eta^6\text{-dibenzo-15-crown-5})]^+$. Anal. Calc. for $C_{36}H_{40}Cl_4O_{10}Ru_2$: C, 44.27; H, 4.13. Found: C, 44.53; H, 4.22%.

4.4.3. Synthesis of *2c*

As described for **2b** but with dibenzo-18-crown-6 for 15 min at 180 °C. Yield: 51%. ^1H NMR ($CDCl_3$, 400 MHz): 6.93–6.83 (m, 8H), 5.49 (br, 4H, $H^{2/5}$), 5.24 (br, 4H, $H^{3/4}$), 4.73 (br, 4H), 4.21–3.80 (m, 4H), 3.83–3.64 (m, 28 H). ^{13}C NMR ($CDCl_3$, 100 MHz): 148.8, 121.3, 117.8 ($C^{1/6}$), 113.5, 76.2 ($C^{3/4}$), 70.9, 70.1, 69.5, 68.4, 67.1 ($C^{2/5}$). MS (ESI): *m*/*z* = 497.1 $[RuCl(\eta^6\text{-dibenzo-18-crown-6})]^+$. UV–Vis ($H_2O$): 324, 406. Anal. Calc. for $C_{40}H_{48}Cl_4O_{12}Ru_2 \cdot 2CHCl_3$: C, 38.70; H, 3.87. Found: C, 38.86; H, 4.02%.

4.4.4. Synthesis of *2d*

As described for **2b** but with dibenzo-24-crown-8 for 15 min. at 150 °C. Yield: 53%. ^1H NMR ($CDCl_3$, 400 MHz): 6.87 (br, 8H), 5.47 (br, 4H, $H^{2/5}$), 5.20 (br, 4H, $H^{3/4}$), 4.64 (br, 4H), 4.22–4.13 (m, 12H), 3.88–3.70 (m, 32 H). ^{13}C NMR ($CDCl_3$, 100 MHz): 148.9, 121.7, 118.2 ($C^{1/6}$), 114.2, 76.7 ($C^{3/4}$), 71.5, 71.4, 71.1, 69.9, 69.6, 69.4, 67.1 ($C^{2/5}$). MS (ESI): *m*/*z* = 585.2 $[RuCl(\eta^6\text{-dibenzo-24-crown-8})]^+$. Anal. Calc. for $C_{48}H_{64}Cl_4O_{16}Ru_2 \cdot Et_2O$: C, 47.49; H, 5.67. Found: C, 47.59; H, 5.50%.

4.4.5. Synthesis of *3a*

A suspension of $[RuCl_2(\eta^6\text{-benzo-15-crown-5})]_2$ (80 mg, 0.09 mmol) and (1*S*,2*R*)-2-amino-1,2-diphenylethanol (39 mg, 0.18 mmol) in dichloromethane (7 ml) was stirred at RT for 30 min. The orange solution was concentrated and then Et_2O added which afforded the product as yellow-orange powder. Yield: 108 mg (91%). ^1H NMR ($CDCl_3$, 400 MHz): 7.28–7.13 (m, 10H), 5.42 (br, 1H, H^{14}), 5.36 (br, 1H, $H^{2/5}$), 5.19 (br, 1H, $H^{2/5}$), 5.12 (br, 2H, $H^{3,4}$), 4.52 (br, 1H, H^{15}), 4.47 (br, m, 3H), 4.10–3.65 (m, br, 19H). ^{13}C NMR (CD_3Cl, 100 MHz): 140.8, 129.0, 127.8, 127.7, 127.1, 126.3, 118.5 ($C^{1/6}$), 118.0 ($C^{1/6}$), 79.3 ($C^{3/4}$), 77.6 ($C^{3/4}$), 73.9 (C^{14}), 70.7, 70.6 70.4, 69.7, 69.1 ($C^{2/5}$), 68.8, 67.5 ($C^{2/5}$), 63.7

(C^{15}). MS (ESI): $m/z = 617.7$ ($M^+ - Cl$), 528.2 ($M^+ - 2Cl$). Anal. Calc. for $C_{28}H_{35}Cl_2NO_6Ru$: C, 51.46; H, 5.40; N, 2.14. Found: C, 50.83; H, 5.41; N, 2.15%.

4.4.6. Synthesis of **3c**

As described for **3a**. Yield: 92%. ^{1}H NMR ($CDCl_3$, 400 MHz): 7.20–7.05 (m, 8H), 6.96–6.84 (m, 5H), 6.80 (m, 1H), 5.37 (br, 1H, $H^{2/5}$), 5.32 (br, 1H, H^{14}), 5.17 (br, 1H, $H^{2/5}$), 5.05 (br, 1H, $H^{3/4}$), 5.00 (br, 1H, $H^{3/4}$), 4.46 (br, m, 4H), 4.21–3.80 (m, br, 17H). ^{13}C NMR (CD_3Cl, 100 MHz): 148.4 (br), 137.9, 129.0, 127.8, 127.7, 127.6, 127.0, 126.4, 121.1, 121.0, 117.9 ($C^{1/6}$), 117.3 ($C^{1/6}$), 112.9 (br), 112.7 (br), 78.8 ($C^{3/4}$), 77.3 ($C^{3/4}$), 74.1 (C^{14}), 70.4, 70.3 70.0, 69.9, 69.3, 69.1, 68.1 ($C^{2/5}$), 67.9, 67.6, 66.5 ($C^{2/5}$), 63.5 (C^{15}). MS (ESI, CH_2Cl_2): $m/z = 709.9$ ($M^+ - Cl$), 674.2 ($M^+ - 2Cl$). Anal. Calc. for $C_{34}H_{39}Cl_2NO_7Ru$: C, 54.77; H, 5.27; N, 1.88. Found: C, 54.06; H, 5.19; N, 1.95%.

4.4.7. Synthesis of **3d**

As described for **3a**. Yield: 93%. ^{1}H NMR (CD_2Cl_2, 400 MHz): 7.73–7.22 (m, 8H), 7.00 (br, 2H), 6.88 (br, 4H), 5.33 (br, 1H, H^{14}), 5.17 (br, 1H, $H^{2/5}$), 5.10 (br, 1H, $H^{2/5}$), 5.00 (br, 1H, $H^{3/4}$), 4.97 (br, 1H, $H^{3/4}$), 4.57 (br, 1H, H^{15}), 4.43 (m, 2H), 4.13–3.73 (m, 25H). ^{13}C NMR (CD_3Cl, 100 MHz): 148.9 (br), 140.0, 137.5, 129.0, 128.0, 127.8, 127.3, 126.3, 121.7, 121.5, 119.0 ($C^{1/6}$), 118.1 ($C^{1/6}$), 114.2, 78.0 ($C^{3/4}$), 77.0 ($C^{3/4}$), 75.2 (C^{14}), 71.4, 71.3, 71.1, 69.8, 69.6, 69.2, 68.0 ($C^{2/5}$), 67.7 ($C^{2/5}$), 65.0 (C^{15}). MS (ESI): $m/z = 797.9$ ($M^+ - Cl$), 762.2 ($M^+ - 2Cl$). Anal. Calc. for $C_{38}H_{47}Cl_2NO_9Ru$: C, 54.74; H, 5.68; N, 1.68. Found: C, 54.54; H, 6.11; N, 1.66%.

4.4.8. Synthesis of **5**

As described for **3a**. Yield: 96%. ^{1}H NMR ($CDCl_3$, 400 MHz): 7.35–7.17 (m, 8H), 7.01 (m, 2H), 6.30 (d, $^3J_{HH} = 5.6$, $H^{2/6}$), 6.22 (d, $^3J_{HH} = 5.9$, $H^{2/6}$), 5.68 (m, H^4), 5.35 (m, $H^{3/5}$), 5.25 (br, H^{14}), 5.17 (m, $H^{3/5}$), 4.58 (m, H^{15}), 4.46 (q, $^3J_{HH} = 7.0$, 2H, CH_2), 4.14 (m, N*H*), 3.79 (m, N*H*), 3.35 (br, O*H*), 1.42 (t, $^3J_{HH} = 7.0$, 3H, CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): 165.4 (C^7), 139.3, 136.3, 129.0, 128.6, 128.3, 128.0, 127.7, 126.3, 89.3 (C^4), 88.1 ($C^{2/6}$), 87.8 ($C^{2/6}$), 79.3 ($C^{3/5}$), 78.8 ($C^{3/5}$), 78.2 (C^1), 76.3 (C^{14}), 66.4 (C^{15}), 63.1 (CH_2), 14.5 (CH_3). MS (ESI, MeOH): $m/z = 499.9$ [RuCl(η^6-ethyl benzoate)(2-amino-1,2-diphenylethanol)]$^+$. Anal. Calc. for $C_{23}H_{25}Cl_2NO_3Ru$: C, 51.59; H, 4.71; N, 2.62. Found: C, 51.60; H, 4.90; N, 2.74%.

4.4.9. Synthesis of **6**

To $[RuCl_2(\eta^6$-benzo-15-crown-5)$]_2$ (140 mg, 0.16 mmol) in DMF (10 ml) was added TPPMS (118 mg, 0.32 mmol) and the solution stirred at room temperature of 30 min. The solvent was removed and the residue washed with Et_2O to afford the product as pale orange solid. Yield: 217 mg (85%). ^{1}H NMR (CD_2Cl_2, 400 MHz, 293 K): 8.69 (d, $^3J_{PH} = 13.1$, H^{13}), 8.10 (d, $^3J_{HH} = 7.6$, H^{12}), 7.69 (m, 4H), 7.44–7.30 (m, 7H), 7.13 (dd, H^{10}), 5.50 (br, 2H), 4.46–4.02 (m, br, 8H), 3.89–3.62 (m, br, 8H); (CD_2Cl_2, 400 MHz, 218 K): 8.66 (d, $^3J_{PH} = 14.6$, H^{13}), 7.89 (d, $^3J_{HH} = 7.9$, H^{12}), 7.71–7.53 (m, 7H), 7.36 (m, 1H), 7.32 (m, 1H), 7.21 (m, 3H), 5.99 (br, H^5), 5.67 (H^4), 5.30 (H^3), 4.67 (br, 2H), 4.42 (br, 1H), 4.33 (br, 1H), 4.08-3.71 (m, 12H), 3.15 (br, H^2). ^{13}C NMR (CD_2Cl_2, 100 MHz, 293 K): 134.9 (d, $^3J_{PC} = 22$, C^{13}), 133.9 (d, $^3J_{PC} = 2$, C^{10}), 133.5 (d, $^4J_{PC} = 9$), 131.0 (d, $^1J_{PC} = 46$), 130.5, 129.1 (d, $^5J_{PC} = 2$, C^{12}), 128.2 (d, $^4J_{PC} = 7$, C^{11}), 128.1 (d, $^3J_{PC} = 10$), 75.4 (br), 72.5 (br), 68.2, 67.6, 67.5. ^{31}P NMR (CD_2Cl_2, 162 MHz, 293 K): 30.9. MS (ESI, MeOH): $m/z = 768.8$ [RuCl(η^6-benzo-15-crown-5)(TPPMS)Na]$^+$, 746.9 [RuCl(η^6-benzo-15-crown-5)(TPPMS)]$^+$, 405.1 [RuCl(η^6-benzo-15-crown-5)]$^+$. Anal. cacld. for $C_{32}H_{34}Cl_2NaO_8PRuS \cdot H_2O$: C, 46.72; H, 4.41. Found: C, 46.84; H, 4.28%.

4.5. Crystallography

Data collection for the X-ray structure determinations was performed on a KUMA 4 CCD diffractometer system by using graphite-monochromated Mo Kα (0.71070 Å) radiation and a low temperature device [$T = 140(2)$ K]. Crystals of **2a** and **2c**, suitable for X-ray diffraction, were obtained from slow diffusion of diethyl ether into chloroform solutions. Data reduction was performed by CrysAlis RED [26]. Structure solution and refinement was performed on PCs by using the

Table 3
Crystallographic data for compounds **2a** and **2c**

	2a	**2c**
Formula	$C_{28}H_{40}Cl_4O_{10}Ru_2$	$C_{42}H_{50}Cl_{10}O_{12}Ru_2$
M	880.54	1303.36
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$
a (Å)	7.8250(15)	8.1350(6)
b (Å)	9.918(2)	23.8086(15)
c (Å)	10.9567(18)	12.7701(8)
α (°)	89.140(17)	90
β (°)	85.836(14)	98.154(6)
γ (°)	72.080(19)	90
V (Å^3)	806.9(3)	2448.3(3)
Z	1	2
Density (Mg/m^3)	1.812	1.768
T (K)	140(2)	293(2)
Θ range (°)	3.37–25.02	2.93–25.02
μ (mm^{-1})	1.322	1.222
Reflections measured	4819	14,131
Unique reflections [$I > 2\sigma(I)$]	2491 [0.0957]	4322 [0.0554]
Final R_1, $wR_2[I > 2\sigma(I)]$	0.0664, 0.1917	0.0364, 0.0764

SHELX97 [27] software package, graphical representations of the structures were made with ORTEP32 [28]. Structures were solved by direct methods and successive interpretation of the difference Fourier maps, followed by full matrix least-squares refinement (against F^2). An empirical absorption correction (DELABS) [29] was applied for **2a**. All atoms were refined anisotropically. The contribution of the hydrogen atoms, in their calculated positions, was included in the refinement using a riding model.

Relevant crystallographic data are compiled in Table 3. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publication Nos. CCDC 260313 and CCDC 260314. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk, Internet: www.ccdc.cam.ac.uk/conts/retrieving.html).

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Appendix A. Supplementary data

Graphs showing the reaction profile and selectivity for the transfer-hydrogenation of acetophenone with **3a**, **3b** and **3d** as pre-catalysts. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2005.03.019.

References

[1] P.W.N.M. van Leeuwen, Homogeneous Catalysis: Understanding the Art, Kluwer Academic, Dordrecht, 2004.
[2] Examples include aqueous biphasic hydroformylation and the Shell Higher Olefin Process (SHOP), which can be run with the nickel-catalyst immobilised in a butanediol phase. See for example: B. Cornils, W.A. Herrmann (Eds.), Applied Homogeneous Catalysis with Organometallic Compounds, Wiley-VCH, Weinheim, 2002.
[3] T.J. Geldbach, P.J. Dyson, J. Am. Chem. Soc. 126 (2004) 8114.
[4] C.R. Rice, A. Guerrero, Z.R. Bell, R.L. Paul, G.R. Motson, J.C. Jeffery, M.D. Ward, New J. Chem. 25 (2001) 185.
[5] K.H. Pannell, D.C. Hambrick, G.S. Lewandos, J. Organomet. Chem. 99 (1975) C21.
[6] C.E. Anson, C.S. Creaser, G.R. Stephenson, J. Chem. Soc., Chem. Commun. (1994) 2175.
[7] C.E. Anson, C.S. Creaser, G.R. Stephenson, Spectrochim. Acta A 52 (1996) 1183.
[8] D.S. Glueck, A.R. Brough, P. Mountford, M.L.H. Green, Inorg. Chem. 32 (1993) 1893.
[9] (a) D.S. Shepard, W. Zhou, T. Maschmeyer, J.M. Matters, C.L. Roper, S. Parsons, B.F.G. Johnson, M.J. Duer, Angew. Chem. Int. Ed. 37 (1998) 2719;
(b) B.F.G. Johnson, C.M.G. Judkins, J.M. Matters, D.S. Shepard, S. Parsons, Chem. Commun. (2000) 1549;
(c) D.S. Shepard, B.F.G. Johnson, J.M. Matters, S. Parsons, J. Chem. Soc., Dalton Trans. (1998) 2289;
(d) C.M.G. Judkins, K.A. Knights, B.F.G. Johnson, Y.R. de Miguel, R. Raja, T.J. Meurig, Chem. Commun. (2001) 2624.
[10] R. Hartmann, Dissertation Nr. 15231, ETH Zürich, 2003.
[11] C. Scolaro, A. Bergamo, L. Brescacin, R. Delfino, M. Cocchietto, G. Laurenczy, T.J. Geldbach, G. Sava, P.J. Dyson, J. Med. Chem. (accepted).
[12] P. Pertici, G. Vitulli, R. Lazzaroni, P. Salvadori, P.L. Barili, J. Chem. Soc., Dalton Trans. (1982) 1019.
[13] A. Fürstner, T. Müller, J. Am. Chem. Soc. 121 (1999) 7814.
[14] A. Hafner, A. Mühlebach, P.A. Van Der Schaaf, Angew. Chem. Int. Ed. 36 (1997) 2121.
[15] (a) P.J. Dyson, M.C. Grossel, N. Srinivasan, T. Vine, T. Welton, D.J. Williams, A.J. White, T. Zigras, J. Chem. Soc., Dalton Trans. (1997) 3465;
(b) D. Crofts, P.J. Dyson, K.M. Sanderson, N. Srinivasan, T. Welton, J. Organomet. Chem. 573 (1999) 292.
[16] (a) M. Bown, M.A. Bennett, Acta Crystallogr. C C55 (1999) 852;
(b) F.B. McCormick, W.B. Gleason, Acta Crystallogr. C C44 (1988) 603;
(c) C.S. Allardyce, P.J. Dyson, D.J. Ellis, P.A. Salter, R. Scopelliti, J. Organomet. Chem. 668 (2003) 35;
(d) B. Therrien, T.R. Ward, M. Pilkington, C. Hoffann, F. Gilardoni, J. Weber, Organometallics 17 (1998) 330;
(e) L. Vieille-Petit, B. Therrien, G. Süss-Fink, Acta Crystallogr. E 58 (2002) m656.
[17] A. Akutsu-Sato, H. Akutsu, S.S. Turner, P. Day, M.R. Probert, J.A.K. Howard, T. Akutagawa, S. Takeda, T. Nakamura, T. Mori, Angew. Chem. Int. Ed. 44 (2005) 292.
[18] (a) C. Daguenet, R. Scopelliti, P.J. Dyson, Organometallics 23 (2004) 4849;
(b) C. Daguenet, P.J. Dyson, Organometallics 23 (2004) 6080;
(c) P.J. Dyson, Dalton Trans. (2003) 2964;
(d) C. Daguenet, P.J. Dyson, Catal. Commun. 4 (2003) 153;
(e) P.J. Dyson, D.J. Ellis, G. Laurenczy, Adv. Syth. Catal. 345 (2003) 211.
[19] R. Noyori, Angew. Chem. Int. Ed. 41 (2002) 2008.
[20] K.-J. Haack, S. Hashiguchi, A. Fujii, T. Ikariya, R. Noyori, Angew. Chem. Int. Ed. 36 (1997) 285.
[21] R. Hartmann, P. Chen, Angew. Chem. Int. Ed. 40 (2001) 3581.
[22] F. Joó, Aqueous Organometallic Chemistry, Kluwer Academic Publishers, Dordrecht, 2001.
[23] J.G. Huddleston, H.D. Willauer, R.P. Swatloski, A.E. Visser, R.D. Rogers, J. Chem. Soc., Chem. Commun. (1998) 1765.
[24] M. Henning, K. Püntener, M. Scalone, Tetrahedron: Asym. 11 (2000) 1849.
[25] P.J. Dyson, J.S. McIndoe, Inorg. Chim. Acta 354 (2003) 68.
[26] Oxford Diffraction Ltd, M.P., Abingdon, OX14 4 RX, UK, 2003.
[27] G.M. Sheldrick, SHELX97, Structure Solution and Refinement Package, Universität Göttingen, Göttingen, 1997.
[28] L.J. Farrugia, J. Appl. Crystallogr. 30 (1997) 565.
[29] N. Walker, D. Stuart, Acta Crystallogr. A 39 (1983) 158.