Water-Soluble Arene Ruthenium Complexes Containing a *trans*-1,2-Diaminocyclohexane Ligand as Enantioselective Transfer Hydrogenation Catalysts in Aqueous Solution

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The cationic chloro complexes $[(arene)Ru(H_2N\cap NH_2)Cl]^+$ (**1**: arene = C_6H_6; **2**: arene = *p*-MeC_6H_4iPr; **3**: arene = C_6Me_6) have been synthesised from the corresponding arene ruthenium dichloride dimers and enantiopure (*R*,*R* or *S*,*S*) *trans*-1,2-diaminocyclohexane ($H_2N\cap NH_2$) and isolated as the chloride salts. The compounds are all water-soluble and, in the case of the hexamethylbenzene derivative **3**, the aqua complex formed upon hydrolysis $[(C_6Me_6)Ru(H_2N\cap NH_2)OH_2]^{2+}$ (**4**) could be isolated as the tetrafluoroborate salt. The molecular structures of **3** and **4** have been determined by single-crystal X-ray diffraction analyses of $[(C_6Me_6)Ru(H_2N\cap NH_2)Cl]Cl$ and $[(C_6Me_6)Ru(H_2N\cap NH_2)OH_2][BF_4]_2$. Treatment of $[Ru_2(arene)_2Cl_4]$ with the monotosylated *trans*-1,2-diaminocyclohexane derivative ($TsHN\cap NH_2$) does not yield the expected cationic complexes, analogous to **1**–**3** but the neutral deprotonated complexes $[(arene)Ru(TsN\cap NH_2)Cl]$ (**5**: arene = C_6H_6; **6**: arene = *p*-MeC_6H_4iPr; **7**: arene = C_6Me_6; **8**: arene = C_6H_5COOMe). Hydrolysis of the chloro complex **7** in aqueous solution gave, upon precipitation of silver chloride, the corresponding monocationic aqua complex $[(C_6Me_6)Ru(TsHN\cap NH_2)(OH_2)]^+$ (**9**) which was isolated and characterised as its tetrafluoroborate salt. The enantiopure complexes **1**–**9** have been employed as catalysts for the transfer hydrogenation of acetophenone in aqueous solution using sodium formate and water as a hydrogen source. The best results were obtained (60 °C) with **7**, giving a catalytic turnover frequency of 43 h^{-1} and an enantiomeric excess of 93 %.

Introduction

Water-soluble organometallic complexes continue to attract growing interest for applications in catalysis because of environmentally friendly processing, simple product separation and pH dependent selectivity in aqueous media.

The first arene ruthenium aqua complexes were observed by NMR spectroscopy in 1972 when Zelonka and Baird dissolved $[(C_6H_6)Ru_2Cl_4]$ in D_2O.[1] The osmium complex $[(C_6H_6)Os(H_2O)_3]^{2+}$ was synthesised in an analogous manner and characterised spectroscopically by Hung et al.[2] Stebler-Röthlisberger et al. finally succeeded in isolating the first cationic benzene aqua complexes $[(C_6H_6)Ru(H_2O)_3]^{2+}$ and $[(C_6H_6)Os(H_2O)_3]^{2+}$ as the tosylate salts. The structure of the triaqua(benzene)ruthenium(II) cation was confirmed by a single-crystal X-ray structure analysis of the sulfate.[3]

Since these early reports, the chemistry of organometallic aqua ions of the transition metals has steadily grown during the 1980s and this topic was comprehensively reviewed by Koelle.[4] Related reviews deal with water-soluble organometallics complexed by hydrophilic ligands,[5] metal-mediated organic synthesis in water[6] and catalysis by water-soluble organometallic complexes in biphasic systems.[7] Recently, Ogo reported the transfer hydrogenation of ketones with HCO_2Na as a hydrogen donor, catalysed by achiral water-soluble Ru(II) complexes.[8] The intermediary formato and hydrido complexes $[(C_6Me_6)Ru(bipy)(OCHO)]^+$ and $[(C_6Me_6)Ru(bipy)H]^+$ could be isolated and structurally characterised.[8,9] We have also described the synthesis and catalytic activity of cationic arene ruthenium complexes containing 1,10-phenanthroline and its derivatives as chelating *N*,*N*-donor ligands.[10]

Several recent reports deal with asymmetric transfer hydrogenation of ketones with formate in aqueous media using active catalytic systems based on $[(p\text{-}MeC_6H_4iPr)RuCl_2]_2$ and *N*-(*p*-toluenesulfonyl)-1,2-diphenyl-ethylenediamine and its derivatives[11–14] 2-(*N*-anilinocarboxy)-pyrrolidine[15] or aminoethanol attached to cyclodextrin.[16] These catalytic systems show good activities and enantioselectivities but the catalysts are formed in situ from precursors and are not isolated. 1,2-dephenylethylendiamine ("Noyori's ligand")[17,18] and also *trans*-1,2-diaminocyclohexane form, in combination with $[(p\text{-}MeC_6H_4iPr)RuCl_2]_2$, an active catalytic system for the transfer hydrogenation of ketones in 2-propanol or in an Et_3N/HCOOH azeotropic mixture.[19]

In this paper we report a series of water-soluble arene ruthenium complexes containing enantiopure *trans*-1,2-di-

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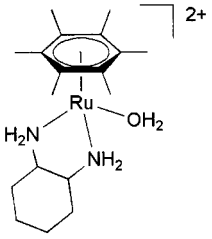
aminocyclohexane and derivatives thereof as chelating *N*,*N*-donor ligands. We also describe the catalytic activity of these complexes in the transfer hydrogenation of aromatic ketones to give the corresponding chiral secondary alcohol with sodium formate as a hydrogen donor in aqueous solution.



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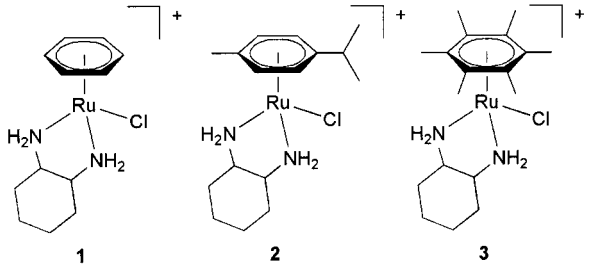
Results and Discussion

Synthesis of Enantiopure Arene Ruthenium Complexes Containing the *trans*-1,2-Diaminocyclohexane Ligand (1–4)

The monocationic chloro complexes $[(arene)Ru(H_2N\cap NH_2)Cl]^+$ (**1**–**3**) containing the *N*,*N* donor as a chelating ligand are accessible by treatment of the dimeric arene ruthenium complexes $[(arene)RuCl_2]_2$ with enantiopure (*R*,*R* or *S*,*S*) *trans*-1,2-diaminocyclohexane ($H_2N\cap NH_2$) at room temperature in dichloromethane solution [Equation (1)].

$$0.5\ [(arene)RuCl_2]_2 + H_2N\cap NH_2 \rightarrow [(arene)Ru(H_2N\cap NH_2)Cl]^+ + Cl^- \quad (1)$$



1 **2** **3**

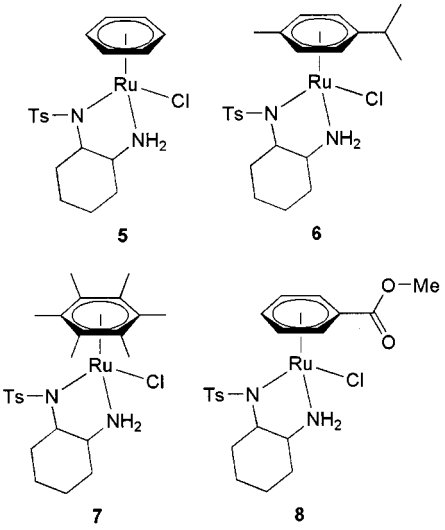
The chloride salts of **1**–**3** are orange solids that dissolve well in water, a property which can be used to remove unreacted materials. Since there is a risk of hydrolysis in water, the aqueous solutions were filtered immediately and then evaporated to dryness to give the analytically pure salts [**1**–**3**]Cl. All compounds were obtained for both *trans*-1,2-diaminocyclohexane enantiomers (*R*,*R* or *S*,*S*) and were subsequently characterised by ^1H and ^{13}C spectroscopy, mass spectroscopy and elemental analysis. The molecular structure of **3** has been confirmed by a single-crystal X-ray structure analysis.

The chloro complex $[(C_6Me_6)Ru(H_2N\cap NH_2)Cl]^+$ (**3**) undergoes hydrolysis in aqueous solution and gives, upon precipitation of silver chloride, the enantiopure dicationic aqua complex $[(C_6Me_6)Ru(H_2N\cap NH_2)(OH_2)]^+$ (**4**). Both enantiomers (*R*,*R* or *S*,*S*) have been isolated as tetrafluoroborate salts and characterised by ^1H and ^{13}C spectroscopy, mass spectroscopy, elemental analysis and single-crystal X-ray structure analysis.

Synthesis of Enantiopure Arene Ruthenium Complexes Containing the *N*-Tosyl-*trans*-1,2-diaminocyclohexane Ligand (5–9)

The reaction of $[Ru_2(arene)_2Cl_4]$ with the monotosylated *trans*-1,2-diaminocyclohexane[20] ($TsHN\cap NH_2$) at room temperature in dichloromethane solution does not give the expected cationic complexes, analogous to **1**–**3**, but the deprotonated neutral complexes $[(arene)Ru(TsN\cap NH_2)Cl]$ (**5**–**8**) [Equation (2)].

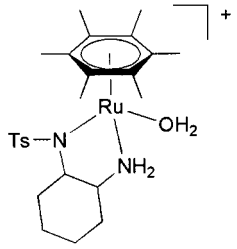
$$0.5\ [(arene)RuCl_2]_2 + TsHN\cap NH_2 \rightarrow [(arene)Ru(TsN\cap NH_2)Cl] \quad (2)$$



5 **6** **7** **8**

Similar to the known complex **6**,[21] complexes **5**, **7** and **8** are orange solids. The products obtained are quite soluble in water but in order to avoid hydrolysis they were purified by column chromatography on aluminium oxide using methanol as eluent. All compounds were obtained for both the *N*-Tosyl-*trans*-1,2-diaminocyclohexane enantiomers (*R*,*R* or *S*,*S*) and were subsequently characterised by ^1H and ^{13}C spectroscopy, mass spectroscopy and elemental analysis.

The chloro complex $[(C_6Me_6)Ru(TsN\cap NH_2)Cl]$ (**7**) undergoes hydrolysis in aqueous solution and gives, upon precipitation of silver chloride, the enantiopure monocationic aqua complex $[(C_6Me_6)Ru(TsN\cap NH_2)(OH_2)]^+$ (**9**). Both enantiomers (*R*,*R* or *S*,*S*) were isolated as the tetrafluoroborate salts and characterised by ^1H and ^{13}C spectroscopy, mass spectroscopy and elemental analysis.



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Molecular Structures of $[(C_6Me_6)Ru(R,R\text{-}H_2N\cap NH_2)Cl]^+$ (*R*,*R*-3) and $[(C_6Me_6)Ru(S,S\text{-}H_2N\cap NH_2)(OH_2)]^{2+}$ (*S*,*S*-4)

The compound $[R,R\text{-}3][Cl]\cdot 2CHCl_3$ crystallises in the orthorhombic non-centrosymmetric space group $P2_12_12_1$. The molecular structure of $[R,R\text{-}3][Cl]\cdot 2CHCl_3$ is depicted in Figure 1. The structure of the cation consists of a pseudo-tetrahedral arrangement of a ruthenium atom coordinated to the η^6-hexamethylbenzene ligand, the two nitrogen atoms of the (*R*,*R*) *trans*-1,2-diaminocyclohexane ligand and a chlorine atom. Ru–C distances fall within the range 2.183(2)–2.218(2) Å. As expected, the two amino groups of the (*R*,*R*) *trans*-1,2-diaminocyclohexane ligand are in equatorial positions which is the more stable conformation.

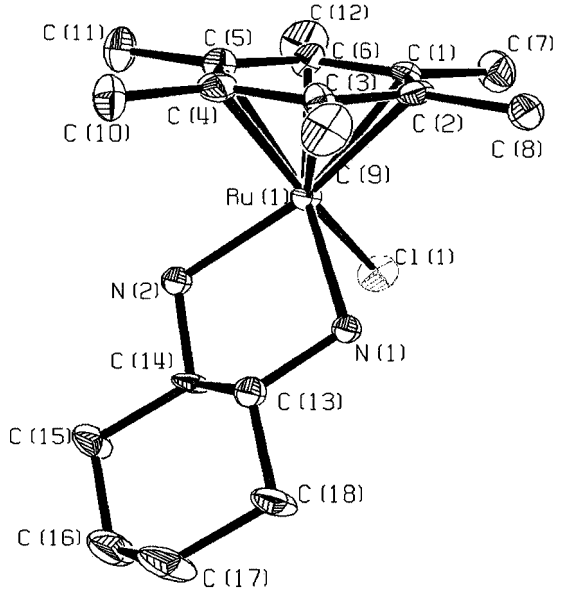


Figure 1. Molecular structure of *R*,*R*-**3**; displacement ellipsoids are shown at the 50% probability level; hydrogen atoms, the chloride counter anion and chloroform molecule are omitted for clarity; selected bond lengths [Å] and angles [°]: Ru(1)–N(1) 2.129(4), Ru(1)–N(2) 2.130(4), Ru(1)–Cl(1) 2.4052(16); N(1)–Ru(1)–N(2) 79.26(16), N(1)–Ru(1)–Cl(1) 83.06(15), N(2)–Ru(1)–Cl(1) 84.89(14).

The compound $[S,S\text{-}4][BF_4]_2\cdot H_2O$ crystallises in the orthorhombic noncentrosymmetric space group $P2_12_12_1$. The molecular structure of $[S,S\text{-}4][BF_4]_2\cdot H_2O$ is depicted in Figure 2. The structure of the cation consists of a pseudo-tetrahedral arrangement of a ruthenium atom coordinated to the η^6-hexamethylbenzene ligand, the two nitrogen atoms of the (*S*,*S*) *trans*-1,2-diaminocyclohexane ligand and a water molecule. Ru–C distances fall within the range 2.183(2)–2.218(2) Å. As expected, the two amino groups of the (*S*,*S*) *trans*-1,2-diaminocyclohexane ligand are in equatorial positions which is the more stable conformation.

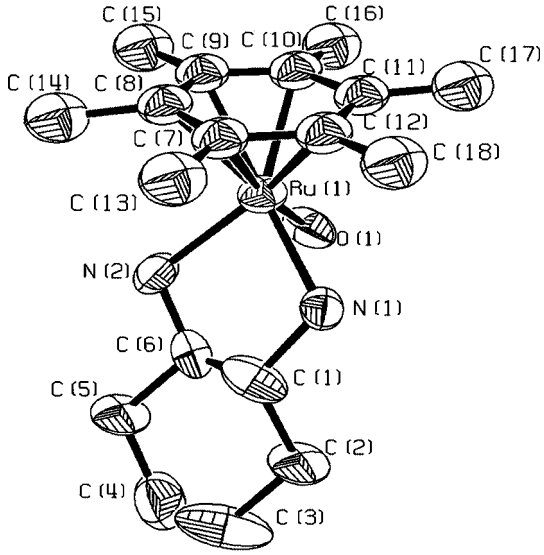
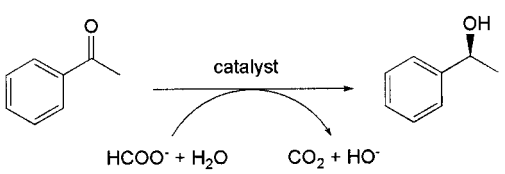


Figure 2. Molecular structure of *S*,*S*-**4**; displacement ellipsoids are shown at the 50% probability level; hydrogen atoms, tetrafluoroborate counter anions and water molecule are omitted for clarity; selected bond lengths [Å] and angles [°]: Ru(1)–N(1) 2.127(10), Ru(1)–N(2) 2.125(11), Ru(1)–O(1) 2.188(7); N(1)–Ru(1)–N(2) 78.8(3), N(1)–Ru(1)–O(1) 81.9(4), N(2)–Ru(1)–O(1) 82.6(4).

Catalytic Application of 1–9 for the Transfer Hydrogenation of Acetophenone and Derivatives with Sodium Formate in Aqueous Solution

Based on the studies using a catalytic system composed of the tosylated diphenylethanediamine (TsDPEN) with $[(p\text{-}MeC_6H_4iPr)RuCl_2]_2$ for the asymmetric transfer hydrogenation of ketones with sodium formate as hydrogen donor in water,[11–14] we evaluated the catalytic potential of the *trans*-diaminocyclohexane complexes **1**–**9** for this reaction using acetophenone as a test substrate. The solubility of the catalysts in water varies from 10 $\mu mol\,mL^{-1}$ for the neutral complexes **5**–**8** to 40 $\mu mol\,mL^{-1}$ for the ionic compounds **1**–**4** and **9** at 60 °C.



All *trans*-diaminocyclohexane complexes **1**–**9** (both *R*,*R* *and* *S*,*S* enantiomers) were found to catalyse the transfer hydrogenation reaction of acetophenone to give phenylethanol in aqueous solution with sodium formate as a hy-

drogen source (Table 1). However, the tosylated derivatives **5**–**7** and **9** shown higher activities and selectivities than the non-tosylated complexes. The contribution of the donor effect of the substituents on the arene ligand is also obvious as the enantiomeric excess (*ee*) increases from 54% for the benzene complex **5** to 93% for the hexamethylbenzene complex **7**. This result is also consistent with the CH/π attraction model reported by Noyori.[22] The beneficial effect of the donor substituents at the arene ligand was confirmed by the use of complex **8** which gave a lower activity and selectivity than those observed for the benzene complex **5**.

Table 1. Catalytic enantioselective transfer hydrogenation of acetophenone using the (1*R*,2*R*)-diaminocyclohexane ruthenium complexes as catalysts and HCOONa as a hydrogen donor in water.[a]

Catalyst	Conversion % (h)[b]	*ee* %[b]	TOF [h^{-1}][c]
1	74 (16)	29	4.6
2	89 (16)	17	5.6
3	82 (16)	47	5.1
4	86 (16)	38	5.4
5	94 (2)	54	47
6	93 (2)	81	46.5
7	86 (2)	93	43
8	7 (2)	44	3.5
9	85 (2)	91	42.5

[a] Conditions: Reactions were carried out at 60 °C, pH = 9, in 5 mL of water and with acetophenone (1 mmol); the ratio catalyst/substrate/formate was 1:100:500. [b] The conversion and the enantiomeric excesses were determined by chiral HPLC analysis. [c] TOF: turnover frequencies (mol of acetophenone converted to phenylethanol per mol of catalyst per hour) were taken after 60% conversion.

It may be assumed that the chloro complexes **1**–**3** and **5**–**8** undergo hydrolysis to the corresponding aqua complexes under catalytic conditions. Thus, the isolated aqua complex **9** shows the same activity and selectivity as the corresponding chloro complex **7**. We believe that the aqua complexes react with the formate anion to give the corresponding formato complexes as the catalytically active species. A proposed catalytic cycle for derivative **9**, based on the pioneering work of Noyori[17c] and Ogo[8] is shown in Figure 3.

The hypothesis of an η^4 transition state (Figure 3) postulated by Ogo, in the case of the $[(C_6Me_6)Ru(bipy)(OH_2)]^{2+}$ complex[8] (bipy = 2,2' bipyrimidine) is substantiated by the arene substituent dependence of the catalytic activity described above. Indeed, complex **7** containing donor substituents on the arene ligand (arene = C_6Me_6, TOF = 43 h^{-1}), which would stabilise the transition species, shows activity more than ten times greater than that of the analogue **8** with an electron-withdrawing substituent at the arene ligand (arene = $C_6H_4CO_2Me$, TOF = 3.5 h^{-1}).

The pH dependence of the catalytic activity[8,10] of **7** was studied for the transfer hydrogenation of acetophenone to give phenylethanol in aqueous solution. As Figure 4 reveals, the best pH conditions were found to be around 9 which corresponds to the pH obtained by addition of sodium formate in water under catalytic conditions.

The temperature dependence of the catalytic activity of **7** was also studied for the same reaction. The curve obtained (Figure 5) clearly shows that the catalytic conditions for the activity of this reaction were found to be the best at 60 °C without significant modification to the selectivity.

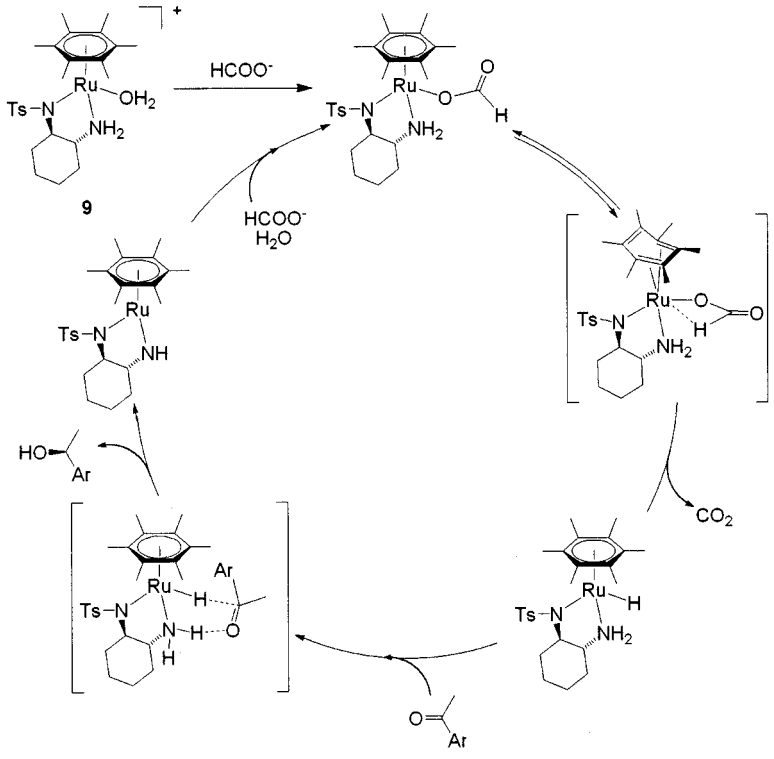


Figure 3. Postulated catalytic cycle for transfer hydrogenation catalysed by **9**.

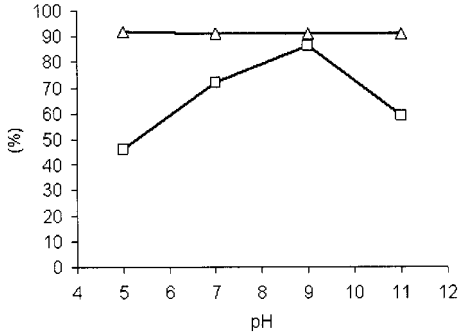


Figure 4. pH-dependent profile of conversion (□) and enantiomeric excess (ρ) for transfer hydrogenation of acetophenone (1 mmol) using complex **7** as the catalyst and HCOONa as a hydrogen donor in water (5 mL), at 60 °C, for 2 h, the catalyst/substrate/formate ratio being 1:100:500.

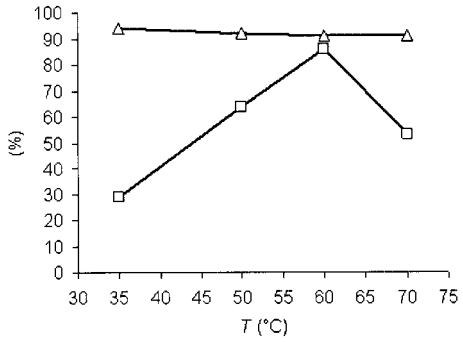


Figure 5. Temperature-dependent profile of conversion (□) and enantiomeric excess (Δ) for transfer hydrogenation of acetophenone (1 mmol) using complex **7** as catalyst and HCOONa as hydrogen donor in water (5 mL), at pH = 9, for 2 h, the catalyst/substrate/formate ratio being 1:100:500.

The kinetic plot (Figure 6) shows that under these conditions the reaction is almost complete after 3 h. The turnover frequency calculated in this case, using the best catalyst precursor **7**, is 43 h^{-1}, comparable to those found for the TsDPEN catalysts.[11–14]

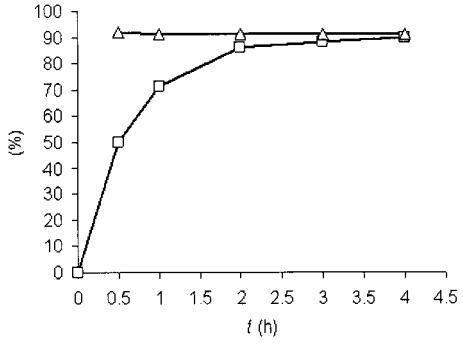


Figure 6. Time dependence of conversion (□) and enantiomeric excess (Δ) for transfer hydrogenation of acetophenone (1 mmol) using complex **7** as catalyst and HCOONa as hydrogen donor in water (5 mL), at 60 °C, pH = 9, the catalyst/substrate/formate ratio being 1:100:500.

The catalytic activity and selectivity of complex **7** have also been determined for the transfer hydrogenation reaction of *para*-substituted acetophenone under the same catalytic conditions (Table 2).

Table 2. Enantioselective catalytic transfer hydrogenation of *para*-substituted acetophenone using complex **7** as catalyst and HCOONa as a hydrogen donor in water.[a]

Substituent	Conversion % (h)	*ee* %	TOF [h^{-1}][d]
CF_3	70 (2)[c]	90[c]	35
NO_2	57 (2)[c]	79[c]	28.5
Br	88 (2)[b]	90[b]	44
Me	84 (2)[b]	92[b]	42
OMe	65 (2)[c]	93[c]	32.5

[a] Conditions: reactions were carried out at 60 °C, at pH = 9, in 5 mL of water, acetophenone (1 mmol), the ratio catalyst/substrate/formate being 1:100:500. [b] The conversion and the enantiomeric excess were determined by chiral HPLC analysis. [c] The conversion and the enantiomeric excess were determined by chiral GC analysis. [d] TOF: turnover frequencies (mol of acetophenone converted to phenylethanol per mol of catalyst per hour) were taken at 50% conversion.

The catalytic system is rather tolerant with respect to the substrate. There is no substantial limitation by electronic effects of the substituents at the substrate molecule. Thus, the enantioselectivity varies only slightly from 79% (*para*-nitroacetophenone) to 93% (*para*-methoxyacetophenone) with dramatically varying electronic densities in the aromatic rings of the substrates. The variation of the catalytic activity from 28.5 h^{-1} (*para*-nitroacetophenone) to 44 h^{-1} (*para*-bromoacetophenone) is also not very pronounced.

Conclusions

In conclusion, we report here nine water-soluble chiral arene ruthenium complexes containing *trans*-1,2-diaminocyclohexane or derivatives thereof as chelating ligands. All these complexes were found to catalyse the enantioselective transfer hydrogenation of acetophenone to give 1-phenylethanol using sodium formate as a hydrogen source in aqueous solution. The best results were obtained for **7** at 60 °C, giving a turnover frequency of 43 h^{-1} and an enantiomeric excess of 93%. The corresponding aqua complex **9**, presumed to be the catalytic species, has been isolated and characterised as its tetrafluoroborate salt.

Experimental Section

General: All manipulations were carried out in an inert atmosphere using standard Schlenk techniques and freshly distilled solvents saturated with nitrogen prior to use. The starting dimer [(arene)Ru-$Cl_2]_2$[23,24] and the monotosylated diaminocyclohexane ($TsHN\cap NH_2$)[20] were prepared according to the published methods. All other reagents were commercially available and were used without further purification. NMR spectra were recorded on a Bruker 400 MHz spectrometer using sodium 2,2-dimethyl-2-silapentane-5-sulfonate in D_2O as a ^{13}C locking agent. Electrospray mass spectra were obtained in the positive-ion mode with an LCQ Finnigan mass spectrometer. Microanalyses were carried out by the Laboratoire de Chimie Pharmaceutique, Université de Genève

(Switzerland). All chemical characterisations given below were found for both *R,R* and *S,S* enantiomers.

Preparation of the Enantiopure Chloro Complexes [(arene)-Ru($H_2N\cap NH_2$)Cl]$^+$ (arene = C_6H_6, *p*-MeC_6H_4iPr or C_6Me_6; $H_2N\cap NH_2$ = *trans*-1,2-diaminocyclohexane): Two equiv. (0.30 mmol) of the appropriate enantiomer of *trans*-1,2-diaminocyclohexane ($H_2N\cap NH_2$) were added to a suspension of [(arene)-$RuCl_2]_2$ (0.15 mmol) in dichloromethane (30 mL). The mixture was stirred for 4 h at room temperature, during this time the orange colour became darker. After evaporation to dryness, the residue was dissolved in water (20 mL). The solution was filtered, washed with diethyl ether (2× 10 mL), and the aqueous solution was evaporated to dryness giving the product in 75–85% yield.

[(C_6H_6)Ru($H_2N\cap NH_2$)Cl]Cl ([1]Cl): Yield 74%, 80.8 mg. ^{1}H NMR (400 MHz, D_2O, 21 °C): δ = 1.03 (m, CH_2), 1.18 (m, $^3J_{cis}$ = 3.96, $^3J_{trans}$ = 11.36 Hz, CH), 1.57 (m, CH_2), 1.83 (m, $^3J_{cis}$ = 3.72, $^3J_{trans}$ = 12.28 Hz, CH), 1.94 (m, CH_2), 5.78 (s, C_6H_6) ppm. ^{13}C NMR (200 MHz, D_2O, 21 °C): δ = 24.1 (CH_2), 24.3 (CH_2), 32.9 (CH_2), 34.4 (CH_2), 56.7 (CH), 61.0 (CH), 84.4 (C_6H_6) ppm. MS (ESI) *m*/*z* = 329 [M]$^+$. $C_{12}H_{20}Cl_2N_2Ru$ (364.28): calcd. C 39.57, H 5.53, N 7.69; found N 39.63, H 5.48, N 7.58.

[(*p*-$MeC_6H_4Pr^i$)Ru($H_2N\cap NH_2$)Cl]Cl ([2]Cl): Yield 85%, 107.1 mg. ^{1}H NMR (400 MHz, D_2O, 21 °C): δ = 1.07 (m, CH_2), 1.21 (m, CH), 1.28 (d, $^3J_{H,H}$ = 7 Hz, $(CH_3)_2CH$), 1.55 (m, CH_2), 1.78 (m, CH), 1.92 (m, CH_2), 2.84 (m, $^3J_{H,H}$ = 7 Hz, $CH(CH_3)_2$), 5.61 (d, $^3J_{H,H}$ = 6 Hz, C_6H_4), 5.75 (d, $^3J_{H,H}$ = 6 Hz, C_6H_4) ppm. ^{13}C NMR (200 MHz, D_2O, 21 °C): δ = 18.4 (CH_3), 21.4 ($CH(CH_3)_2$), 24.1 (CH_2), 24.3 (CH_2), 31.0 ($CH(CH_3)_2$), 32.9 (CH_2), 34.4 (CH_2), 57.2 (CH), 61.1 (CH), 86.7 (C_6H_4), 103.9 (C_6H_4), 105.6 (C_6H_4) ppm. MS (ESI): *m*/*z* = 385 [M$^+$]. $C_{16}H_{28}Cl_2N_2Ru$ (420.38): calcd. C 45.71, H 6.71, N 6.66; found N 45.58, H 6.69, N 6.58.

[(C_6Me_6)Ru($H_2N\cap NH_2$)Cl]Cl ([3]Cl): Yield 81%, 108.9 mg. ^{1}H NMR (400 MHz, D_2O, 21 °C): δ = 1.11 (m, CH_2), 1.21 (m, CH), 1.53 (m, CH_2), 1.85 (m, CH), 1.98 (m, CH_2), 2.08 (s, $C_6(CH_3)_6$) ppm. ^{13}C NMR (200 MHz, D_2O, 21 °C): δ = 15.2 ($C_6(CH_3)_6$), 24.0 (CH_2), 24.2 (CH_2), 33.5 (CH_2), 34.3 (CH_2), 57.0 (CH), 60.9 (CH), 92.1 ($C_6(CH_3)_6$) ppm. MS (ESI): *m*/*z* = 413 [M$^+$]. $C_{18}H_{32}N_2Cl_2Ru$ (448.44): calcd. C 48.21, H 7.19, N 6.25; found N 48.07, H 7.22, N 6.23.

Preparation of the Enantiopure Chloro [(arene)Ru(TsN∩NH_2)Cl] (arene = C_6H_6, *p*-MeC_6H_4iPr, C_6Me_6 or C_6H_4COOMe; TsHN∩NH_2 = *N*-tosyl-*trans*-1,2-diaminocyclohexane): Two equiv. (0.30 mmol) of the appropriate enantiomer of *N*-tosyl-*trans*-1,2-diaminocyclohexane (TsHN∩NH_2) were added to a suspension of [(arene)$RuCl_2]_2$ (0.15 mmol) in dichloromethane (30 mL). The mixture was stirred for 4 h at room temperature, during this time the orange colour became darker. After evaporation to dryness the residue was dissolved in a minimum of dichloromethane and then submitted to column chromatography on aluminium oxide using methanol as eluent. The orange-yellow fraction was collected and the solvent was evaporated to dryness giving the product in 70–75% yield.

[(C_6H_6)Ru(TsN∩NH_2)Cl] (5): Yield 70%, 93.9 mg. ^{1}H NMR (400 MHz, $CDCl_3$, 21 °C): δ = 0.95 (m, CH_2), 1.22 (m, 2 CH_2), 1.43 (m, CH), 1.60 (m, CH_2), 1.88 (m, CH), 2.28 (s, *p*-$(CH_3)C_6H_4SO_2$), 5.78 (s, C_6H_6), 7.17 (d, *J* = 7.3 Hz, *p*-$(CH_3)C_6H_4SO_2$), 7.71 (d, *J* = 7.3 Hz, *p*-$(CH_3)C_6H_4SO_2$) ppm. ^{13}C NMR (200 MHz, $CDCl_3$, 21 °C): δ = 21.5 (*p*-$(CH_3)C_6H_4SO_2$), 24.4 (CH_2), 25.0 (CH_2), 31.8 (CH_2), 32.5 (CH_2), 59.3 (CH), 60.0 (CH), 83.4 (C_6H_6), 127.2 (2 CH), 128.3 (2 CH), 137.9 (*p*-$(CH_3)C_6H_4SO_2$), 143.3 (*p*-$(CH_3)C_6H_4SO_2$) ppm. MS (ESI): *m*/*z* = 447 [M – Cl]$^+$. $C_{19}H_{25}ClN_2O_2RuS$ (482): calcd. C 47.34, H 5.23, N 5.81; found N 47.13, H 5.32, N 5.69.

[(*p*-MeC_6H_4iPr)Ru(TsN∩NH_2)Cl] (6): Yield 73%, 110.2 mg. ^{1}H NMR (400 MHz, $CDCl_3$, 21 °C): δ = 1.05 (m, CH_2), 1.25 (m, 2 CH_2), 1.32 (d, $^3J_{H,H}$ = 7 Hz, $(CH_3)_2CH$), 1.53 (m, CH), 1.71 (m, CH_2), 1.99 (m, CH), 2.36 (s, *p*-$(CH_3)C_6H_4SO_2$), 2.86 (m, $^3J_{H,H}$ = 7 Hz, $(CH_3)_2CH$), 5.57 (d, $^3J_{H,H}$ = 6 Hz, C_6H_4), 5.77 (d, $^3J_{H,H}$ = 6 Hz, C_6H_4), 7.17 (d, $^3J_{H,H}$ = 8 Hz, *p*-$(CH_3)C_6H_4SO_2$), 7.71 (d, $^3J_{H,H}$ = 8 Hz, *p*-$(CH_3)C_6H_4SO_2$) ppm. ^{13}C NMR (200 MHz, $CDCl_3$, 21 °C): δ = 18.4 (CH_3), 21.4 ($CH(CH_3)_2$), 21.5 (*p*-$(CH_3)C_6H_4SO_2$), 24.1 (CH_2), 24.3 (CH_2), 31.0 ($CH(CH_3)_2$), 33.5 (CH_2), 34.2 (CH_2), 57.2 (CH), 60.6 (CH), 86.8 (C_6H_4), 104.0 (C_6H_4), 105.5 (C_6H_4), 127.1 (*p*-$(CH_3)C_6H_4SO_2$), 128.3 (*p*-$(CH_3)C_6H_4SO_2$), 138.0 (*p*-$(CH_3)C_6H_4SO_2$), 142.7 (*p*-$(CH_3)C_6H_4SO_2$) ppm. MS (ESI): *m*/*z* = 503 [M – Cl]$^+$. $C_{23}H_{33}ClN_2O_2RuS$ (538): calcd. C 51.34, H 6.18, N 5.21; found N 51,28, H 6.06, N 5.16.

[(C_6Me_6)Ru(TsN∩NH_2)Cl] (7): Yield 76%, 121.1 mg. ^{1}H NMR (400 MHz, $CDCl_3$, 21 °C): δ = 1.05 (m, CH_2), 1.23 (m, CH), 1.33 (m, CH_2), 1.44 (m, $CH–CH_2$), 1.80 (m, CH), 2.09 (s, $C_6(CH_3)_6$), 2.39 (s, *p*-$(CH_3)C_6H_4SO_2$), 7.28 (d, $^3J_{H,H}$ = 8 Hz, *p*-$(CH_3)C_6H_4SO_2$), 7.77 (d, $^3J_{H,H}$ = 8 Hz, *p*-$(CH_3)C_6H_4SO_2$) ppm. ^{13}C NMR (200 MHz, $CDCl_3$, 21 °C): δ = 15.1 ($C_6(CH_3)_6$), 21.4 (*p*-$(CH_3)C_6H_4SO_2$), 24.1 (CH_2), 24.1 (CH_2), 33.4 (CH_2), 34.2 (CH_2), 57.1 (CH), 61.1 (CH), 92.1 ($C_6(CH_3)_6$), 127.1 (*p*-$(CH_3)C_6H_4SO_2$), 128.1 (*p*-$(CH_3)C_6H_4SO_2$), 137.8 (*p*-$(CH_3)C_6H_4SO_2$), 143.0 (*p*-$(CH_3)C_6H_4SO_2$) ppm. MS (ESI): *m*/*z* = 531 [M – Cl]$^+$. $C_{25}H_{37}ClN_2O_2RuS$ (566.16): calcd. C 53.04, H 6.59, N 4.95; found N 52.96, H 6.48, N 5.12.

[(C_6H_4COOMe)Ru(TsN∩NH_2)Cl] (8): Yield 71%, 110.8 mg. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.95 (m, CH_2), 1.18 (m, CH_2), 1.37 (m, CH), 1.65 (m, CH_2), 1.92 (m, CH), 2.26 (s, *p*-$(CH_3)C_6H_4SO_2$), 3.81 (s, $C_6H_5COOCH_3$), 5.26 (dd, $^3J_{H,H}$ = 7.5, *J* = 8 Hz, $C_6H_5COOCH_3$), 5.86 (t, $^3J_{H,H}$ = 8 Hz, $C_6H_5COOCH_3$), 6.32 (d, $^3J_{H,H}$ = 7.5 Hz, $C_6H_5COOCH_3$), 7.21 (d, $^3J_{H,H}$ = 7.3 Hz, *p*-$(CH_3)C_6H_4SO_2$), 7.68 (d, $^3J_{H,H}$ = 7.3 Hz, *p*-$(CH_3)C_6H_4SO_2$), ppm. ^{13}C NMR (200 MHz, $CDCl_3$, 25 °C): δ = 21.5 (*p*-$(CH_3)C_6H_4SO_2$), 24.4 (CH_2), 25.0 (CH_2), 31.7 (CH_2), 32.48 (CH_2), 52.9 ($C_6H_5COOCH_3$), 59.3 (CH), 60.01 (CH), 80.5 ($C_6H_5COOCH_3$), 82.1 ($C_6H_5COOCH_3$), 88.6 ($C_6H_5COOCH_3$), 90.0 ($C_6H_5COOCH_3$), 127.2 (2 CH), 128.3 (2 CH), 138.0 (*p*-$(CH_3)C_6H_4SO_2$), 142.8 (*p*-$(CH_3)C_6H_4SO_2$), 165.4 ($C_6H_5COOCH_3$) ppm. MS (ESI): *m*/*z* = 520 [M – Cl]$^+$. $C_{22}H_{30}ClN_2O_4RuS$ (555): calcd. C 47.60, H 5.45, N 5.05; found N 47.48, H 5.28, N 4.96.

Preparation of the Enantiopure Aqua Complex [(C_6Me_6)-Ru($H_2N\cap NH_2$)(OH_2)]$^{2+}$ (4) and [(C_6Me_6)Ru(TsN∩NH_2)(OH_2)]$^+$ (9) ($H_2N\cap NH_2$ = *trans*-1,2-diaminocyclohexane; TsHN∩NH_2 = *N*-tosyl-*trans*-1,2-diaminocyclohexane): To an aqueous solution of the appropriate chloro complex, [(arene)Ru($H_2N\cap NH_2$)Cl]$^+$ or [(arene)Ru(TsN∩NH_2)Cl], was added one equiv. of silver sulfate (0.30 mmol, 93.6 mg) in water (30 mL). After stirring for 1 h in the dark at room temperature the white precipitate (AgCl) was removed by filtration from the yellow solution. Solid $NaBF_4$ was added until saturation and a yellow precipitate appeared. The suspension was then centrifuged, the solid dissolved in dry acetonitrile (10 mL) and the resultant solution filtered through celite to eliminate the excess $NaBF_4$. After evaporation of the solvent, the tetrafluoroborate salt was obtained as a yellow-orange powder in quantitative yield.

[(C_6Me_6)Ru($H_2N\cap NH_2$)(OH_2)](BF_4)$_2$ ([4](BF_4)$_2$): Yield 98%, 167.6 mg. ^{1}H NMR (400 MHz, D_2O, 21 °C): δ = 1.09 (m, CH_2), 1.22 (m, CH), 1.63 (m, CH_2), 1.85 (m, CH), 1.89 (m, CH_2), 2.12 (s, $C_6(CH_3)_6$). ^{13}C NMR (200 MHz, D_2O, 21 °C): δ = 15.2 ($C_6(CH_3)_6$),

24.0 (CH_2), 24.2 (CH_2), 33.5 (CH_2), 34.2 (CH_2), 57.0 (CH), 60.9 (CH), 92.1 ($C_6(CH_3)_6$). MS (ESI): m/z = 396 $[M]^+$. $C_{18}H_{34}B_2F_8N_2ORu$ (569.15): calcd. C 37.98, H 6.02, N 4.92; found N 38.06, H 6.08, N 4.95.

$[(C_6Me_6)Ru(TsN\cap NH_2)(OH_2)](BF_4)$ ([9]BF_4): Yield 97%, 185.4 mg. ^{1}H NMR (400 MHz, D_2O, 21 °C): δ = 1.03 (m, 2 CH_2), 1.21 (m, CH_2), 1.29 (m, CH), 1.39 (m, CH_2), 1.78 (m, CH), 2.11 (s, $C_6(CH_3)_6$), 2.42 (s, CH_3), 7.26 (d, $^3J_{H,H}$ = 7 Hz, C_6H_4), 7.74 (d, $^3J_{H,H}$ = 7 Hz, C_6H_4). ^{13}C NMR (200 MHz, D_2O, 21 °C): δ = 15.1 ($C_6(CH_3)_6$), 21.3 (p-$(CH_3)C_6H_4SO_2$), 24.1 (CH_2), 24.1 (CH_2), 33.3 (CH_2), 34.1 (CH_2), 57.2 (CH), 61.0 (CH), 92.0 (C_6Me_6), 127.0 (p-$(CH_3)C_6H_4SO_2$), 128.0 (p-$(CH_3)C_6H_4SO_2$), 137.8 (p-$(CH_3)C_6H_4SO_2$), 143.0 (p-$(CH_3)C_6H_4SO_2$). MS (ESI): m/z = 550 $[M]^+$. $C_{25}H_{39}BF_4N_2O_3RuS$ (635.53): calcd. C 47.25, H 6.19, N 4.41; found N 47.41, H 6.31, N 4.32.

Single Crystal X-ray Structure Analyses: A yellow crystal of compound [*R*,*R*-**3**][Cl]·2$CHCl_3$, obtained from recrystallisation of [*R*,*R*-**3**][Cl] with chloroform by slow evaporation, was mounted on a Stoe Imaging Plate Diffractometer System (Stoe & Cie, 1995) equipped with a one-circle φ goniometer and a graphite-monochromator. Data collection was performed at –100 °C using Mo-K_α radiation (λ = 0.71073 Å). 133 exposures (6 min per exposure) were obtained at an image plate distance of 70 mm with $0 < \varphi < 198°$ and with the crystal oscillating through 1.5° in φ. The resolution was D_{min}–D_{max} 12.45–0.81 Å. This compound crystallised in a noncentrosymmetric orthorhombic cell [$P2_12_12_1$, Flack parameter x = 0.00(5)]. The molecular formula of this compound is {[RuCl($C_{12}H_{18}$)($C_6H_{14}N_2$)]Cl($CHCl_3$)$_2$}. The structure was solved by direct methods using the program SHELXS-97[25] and refined by full-matrix least-squares on F^2 with SHELXL-97.[26] The positions of the protons N2H3 and N2H4 were derived from difference Fourier maps and refined with the N–H distance constrained to the theoretical value, the remaining hydrogen atoms were included in calculated positions and treated as riding atoms using SHELXL-97 default parameters. All non-hydrogen atoms, were refined anisotropically. A semi-empirical absorption correction was applied using MULABS (PLATON03, $T_{min.}$ = 0.804, $T_{max.}$ = 0.839). Selected crystallographic data for the complex are summarised in Table 3.

A yellow crystal of compound [*S*,*S*-**4**][BF_4]$_2$·H_2O, obtained by recrystallisation of [*S*,*S*-**4**][BF_4]$_2$ from water, was mounted on a Stoe Mark II-Imaging Plate Diffractometer System (Stoe & Cie, 2002) equipped with a graphite monochromator. Data collection was performed at –100 °C using Mo-K_α radiation (λ = 0.71073 Å). 171 exposures (6 min per exposure) were obtained at an image plate distance of 135 mm, 171 frames with φ = 0° and $0 < \omega < 171°$, with the crystal oscillating through 1° in ω. The resolution was $D_{min.} - D_{max.}$ 17.78–0.72 Å. This compound crystallises in a noncentrosymmetric space group with an orthorhombic cell ($P2_12_12_1$). The absolute structure could not be defined [Flack parameter = 0.16(12)]. The molecular formula of this compound is {[Ru($C_{12}H_{18}$)($C_6H_{14}N_2$)(H_2O)](BF_4)$_2$.(H_2O)}. As a result of the high disorder found in the anions and solvent molecules, the SQUEEZE instruction in PLATON03[27] was used to calculate the remaining potential solvent accessible area in the unit cell; 602.1 Å^3 was calculated containing about 173 electrons. Therefore, one BF_4 (4×41 electrons) per asymmetric unit was included in all further calculations. The structure was solved by direct methods using the program SHELXS-97[25] and refined by full-matrix least-squares on F^2 with SHELXL-97.[26] The hydrogen atoms were included in calculated positions and treated as riding atoms using SHELXL-97 default parameters. All non-hydrogen atoms were refined anisotropically.

Table 3. Crystallographic data for the structure of [*R*,*R*-**3**]-[Cl]·2$CHCl_3$.

Chemical formula	$C_{20}H_{34}Cl_8N_2Ru$
Formula mass	687.16
Crystal colour and shape	yellow block
Crystal size	0.30×0.20×0.10
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a [Å]	9.04557(8)
b [Å]	15.5966(9)
c [Å]	20.1964(12)
α [°]	90
β [°]	90
γ [°]	90
V [Å^3]	2849.4(3)
Z	4
$D_{calcd.}$ [g·cm^{-3}]	1.602
μ (Mo-K_α) [mm^{-1}]	1.313
Temperature [K]	173(2)
F(000)	1392
Scan range [°]	$2< \theta < 25.75$
Cell refinement parameters reflections	8000
Reflections measured	22511
Independent reflections	5556
Reflections observed [$I > 2\sigma(I)$]	3385
R_{int}	0.1068
Final R indices [$I > 2\sigma(I)$]	0.0369
R indices (all data)	0.0820
Goodness-of-fit	0.747
Residual density: max., min. $\Delta\rho$ [e·Å^{-3}]	0.524, –1.200
The structure was refined on F_o^2: wR_2 = $\{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2\}^{1/2}$, where w^{-1} = $[\Sigma(F_o^2) + (aP)^2 + bP]$ and P = $[\max(F_o^2,0) + 2F_c^2]/3$	

Table 4. Crystallographic data for the structure of [*S*,*S*-**4**][BF_4]$_2$·H_2O.

Chemical formula	$C_{18}H_{36}B_2F_8N_2O_2Ru$
Formula mass	587.18
Crystal colour and shape	yellow block
Crystal size [mm]	0.25×0.18×0.10
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a [Å]	10.4410(8)
b [Å]	15.2988(16)
c [Å]	15.9586(13)
α [°]	90
β [°]	90
γ [°]	90
V [Å^3]	2549.1(4)
Z	4
$D_{calcd.}$ [g cm^{-3}]	1.530
μ (Mo-K_α) [mm^{-1}]	0.690
Temperature [K]	173(2)
F(000)	1200
Scan range [°]	$1.84 < \theta < 25.18$
Cell refinement parameters reflections	8869
Reflections measured	15808
Independent reflections	4528
Reflections observed [$I > 2\sigma(I)$]	2748
R_{int}	0.1083
Final R indices [$I > 2\sigma(I)$]	0.0743
R indices (all data)	0.1122
Goodness-of-fit	0.968
Residual density: max., min. $\Delta\rho$ [e Å^{-3}]	0.774, –1.471
The structure was refined on F_o^2: wR_2 = $\{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2\}^{1/2}$, where w^{-1} = $[\Sigma(F_o^2) + (aP)^2 + bP]$ and P = $[\max(F_o^2,0) + 2F_c^2]/3$	

tropically. Selected crystallographic data for the complex are summarised in Table 4.

CCDC-273653 (for [**3**]Cl·2CHCl$_3$) and -273652 (for [**4**](BF$_4$)$_2$·H$_2$O) contain supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336033.

Transfer Hydrogenation Catalysis: The transfer hydrogenation reactions of acetophenone (1 mmol), using **1–9** as their chloride (**1–3** and **5–8**) or sulfate (**4** and **9**) salts (10 μmol) with HCOONa (5 mmol), were carried out in water (5 mL) in an inert atmosphere. The reactions were quenched by cooling the mixtures to 0 °C. The products were extracted with Et$_2$O, filtered through silica and identified (and conversion and enantiomeric excesses were determined) by HPLC on a Chiracel OB-H capillary column for acetophenone and its Br and Me *para*-substituted derivatives or by gas chromatography on a 6-*tert*-butyl-2,3-diethyl-β-cyclodextrin (30% in 5% phenyl polymer) capillary column for the CF_3, NO_2 and MeO *para*-substituted substrates. The pH was monitored using a pH meter (Mettler Toledo InLab® 413) and adjusted using HNO_3 (for pH = 4 to 9) or NaOH (for pH = 10).

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