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(H₂N\(\text{NH}_2\))Cl]^+ (1: arene = C₆H₆; 2: arene = p-MeC₆H₄)Pr; 3: arene = C₆Me₆) have been synthesised from the corresponding arene ruthenium dichloride dimers and enantiopure (R,R or S,S) trans-1,2-diaminocyclohexane (H₂N\(\text{NH}_2\)) 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 [(C₆Me₆)Ru(H₂N\(\text{NH}_2\))Cl\(\text{OH}_2\)]^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 [(C₆Me₆)Ru(H₂N\(\text{NH}_2\))Cl] and [(C₆Me₆)Ru(H₂N\(\text{NH}_2\))OH₂][BF₄]₂. Treatment of [Ru₂(arene)Cl₂] with the monotosylated trans-1,2-diaminocyclohexane derivative (TsHN\(\text{NH}_2\)) does not yield the expected cationic complexes, analogous to 1–3 but the neutral deprotonated complexes [(arene)Ru(TsHN\(\text{NH}_2\))Cl] [5: arene = C₆H₆; 6: arene = p-MeC₆H₄]Pr; 7: arene = C₆Me₆; 8: arene = C₆H₄COOMe]. Hydrolysis of the chloro complex 7 in aqueous solution gave, upon precipitation of silver chloride, the corresponding monocationic aqua complex [(C₆Me₆)Ru(TsHN\(\text{NH}_2\))(OH₂)]^+ (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 Zelenka and Baird dissolved [(C₆H₆)Ru₂Cl₂] in D₂O.[1] The osmium complex [(C₆H₆)Os(H₂O)]^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 [(C₆H₆)Ru(H₂O)]^2+ and [(C₆H₆)Os(H₂O)]^2+ as the tosylate salts. The structure of the triaquabenzene 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 HCO₂Na as a hydrogen donor, catalysed by achiral water-soluble Ru(II) complexes.[8] The intermediary formated and hydrido complexes [(C₆Me₆)Ru(bipryl)(CHO)]^+ and [(C₆Me₆)Ru(bipryl)H]^+ could be isolated and structurally characterised.[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-MeC₆H₄)Pr-RuCl₂] and N-(p-toluenesulfonyl)-1,2-diphenyl-ethylenediamine and its derivatives[11–14] 2-(N-anilinocarboxy)-pyrroline[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-diphenylethylendiamine ("Noyori’s ligand")[17,18] and also trans-1,2-diaminocyclohexane form, in combination with [(p-MeC₆H₄)Pr-RuCl₂], an active catalytic system for the transfer hydrogenation of ketones in 2-propanol or in an Et₃N/HCOOH azeotrope 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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[a‡] Crystal structure analysis.
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.

Results and Discussion

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

The monocationic chloro complexes [(arene)Ru(H₂N\(\backslash\)NH₃)Cl]⁺ (1–3) containing the N,N donor as a chelating ligand are accessible by treatment of the dimeric arene ruthenium complexes [(arene)RuCl₂]₂ with enantiopure (R,R or S,S) trans-1,2-diaminocyclohexane (H₂N\(\backslash\)NH₂) at room temperature in dichloromethane solution [Equation (1)].

\[
0.5 \text{(arene)RuCl}_2 + H_2N\backslash NH_2 \rightarrow \text{(arene)Ru(H}_2N\backslash NH_2)\text{Cl]}^+ + \text{Cl}^-
\]  

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 \(^1\)H 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 [(C₆Me₆)Ru(H₂N\(\backslash\)NH₂)Cl]⁺ (3) undergoes hydrolysis in aqueous solution and gives, upon precipitation of silver chloride, the enantiopure dicationic aqua complex [[(C₆Me₆)Ru(H₂N\(\backslash\)NH₂)(OH₂)]²⁺ (4). Both enantiomers (R,R or S,S) have been isolated as tetrafluoroborate salts and characterised by \(^1\)H and \(^{13}\)C spectroscopy, mass spectroscopy, elemental analysis and single-crystal X-ray structure analysis.

\[
\text{Synthesis of Enantiopure Arene Ruthenium Complexes Containing the N-Tosyl-trans-1,2-diaminocyclohexane Ligand (5–9)}
\]

The reaction of [Ru₂(arene)₂Cl₄] with the monotosylated trans-1,2-diaminocyclohexane \(^{(20)}\) (TsHN\(\backslash\)NH₂) 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\(\backslash\)NH₂)Cl] (5–8) [Equation (2)].

\[
0.5 \text{(arene)RuCl}_2 + \text{TsHN}\backslash\text{NH}_2 \rightarrow \text{[arene]Ru(TsN}\backslash\text{NH}_2)\text{Cl]} 
\]  

Similar to the known complex \(^{(21)}\) 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 \(^1\)H and \(^{13}\)C spectroscopy, mass spectroscopy and elemental analysis.

The chloro complex [(C₆Me₆)Ru(TsN\(\backslash\)NH₂)Cl] (7) undergoes hydrolysis in aqueous solution and gives, upon precipitation of silver chloride, the enantiopure monocationic aqua complex [[(C₆Me₆)Ru(TsN\(\backslash\)NH₂)(OH₂)]²⁺ (9). Both enantiomers (R,R or S,S) were isolated as the tetrafluoroborate salts and characterised by \(^1\)H and \(^{13}\)C spectroscopy, mass spectroscopy and elemental analysis.
Molecular Structures of [(C₆H₅)₂Ru(R,R-H₂N=NH₂)Cl]⁺ (R,R-3) and [(C₆H₅)₂Ru(S,S-H₂N=NH₂)(OH₂)]²⁺ (S,S-4)

The compound [R,R-3][Cl]₂CHCl₃ crystallises in the orthorhombic non-centrosymmetric space group P2₁2₁2₁. The molecular structure of [R,R-3][Cl]₂CHCl₃ is depicted in Figure 1. The structure of the cation consists of a pseudo-tetrahedral arrangement of a ruthenium atom coordinated to the η⁶-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 (S,S) trans-1,2-diaminocyclohexane ligand are in equatorial positions which is the more stable conformation.

![Figure 1](image1.png)

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-4][BF₄]₂·H₂O crystallises in the orthorhombic non-centrosymmetric space group P2₁2₁2₁. The molecular structure of [S,S-4][BF₄]₂·H₂O is depicted in Figure 2. The structure of the cation consists of a pseudo-tetrahedral arrangement of a ruthenium atom coordinated to the η⁶-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](image2.png)

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-MeC₆H₄H₂Pr)₂RuCl₂] 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 μmol·L⁻¹ for the neutral complexes 5–8 to 40 μmol·L⁻¹ for the ionic compounds 1–4 and 9 at 60 °C.

![Catalytic Reaction](image3.png)

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-
hydrogen 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. 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 (1R,2R)-diaminocyclohexane ruthenium complexes as catalysts and HCOONa as a hydrogen donor in water.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conversion % (h)[b]</th>
<th>ee [%][b]</th>
<th>TOF [h⁻¹][c]</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>74 (16)</td>
<td>29</td>
<td>4.6</td>
</tr>
<tr>
<td>2</td>
<td>89 (16)</td>
<td>17</td>
<td>5.6</td>
</tr>
<tr>
<td>3</td>
<td>82 (16)</td>
<td>47</td>
<td>5.1</td>
</tr>
<tr>
<td>4</td>
<td>86 (16)</td>
<td>38</td>
<td>5.4</td>
</tr>
<tr>
<td>5</td>
<td>94 (2)</td>
<td>54</td>
<td>47</td>
</tr>
<tr>
<td>6</td>
<td>93 (2)</td>
<td>81</td>
<td>46.5</td>
</tr>
<tr>
<td>7</td>
<td>86 (2)</td>
<td>93</td>
<td>43</td>
</tr>
<tr>
<td>8</td>
<td>7 (2)</td>
<td>44</td>
<td>3.5</td>
</tr>
<tr>
<td>9</td>
<td>85 (2)</td>
<td>91</td>
<td>42.5</td>
</tr>
</tbody>
</table>

[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 formate 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 η⁴ transition state (Figure 3) postulated by Ogo, in the case of the [(C₅Me₅)Ru(bipy)-(OH₂)]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 = C₅Me₅, 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 = C₅H₅CO₂Me, 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 (Δ) for transfer hydrogenation of acetonaphone (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 acetonaphone (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>
<thead>
<tr>
<th>Substituent</th>
<th>Conversion % (h)</th>
<th>ee %</th>
<th>TOF [h⁻¹][d]</th>
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</thead>
<tbody>
<tr>
<td>CF₃</td>
<td>70 (2)[c]</td>
<td>90[c]</td>
<td>35</td>
</tr>
<tr>
<td>NO₂</td>
<td>57 (2)[d]</td>
<td>79[b]</td>
<td>28.5</td>
</tr>
<tr>
<td>Br</td>
<td>88 (2)[b]</td>
<td>90[b]</td>
<td>44</td>
</tr>
<tr>
<td>Me</td>
<td>84 (2)[b]</td>
<td>92[b]</td>
<td>42</td>
</tr>
<tr>
<td>OMe</td>
<td>65 (2)[b]</td>
<td>93[b]</td>
<td>32.5</td>
</tr>
</tbody>
</table>

[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 arenare 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]Ru₂Cl₅[23,24] and the monosubstituted diaminocyclohexane (TsHN=NH₃)²⁺ 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 D₂O as a ¹H 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.
Preparation of the Enantiopure Chloro Complexes [(arene)-RuH(N=NNH)]Cl (6): Yield 73%, 110.2 mg. 1H NMR (400 MHz, CDC13, 21 °C): δ = 1.05 (m, CH2), 1.25 (m, 2 CH2), 1.32 (d, J = 7.7 Hz, (CH2)2CH), 1.53 (m, 1.71 (m, CH2), 1.99 (m, CH2), 2.36 (s, p-(CH3)C6H12SO3), 2.86 (m, J2H = 7 Hz, (CH2)2CH), 5.57 (d, J3H = 6 Hz, CH2), 5.77 (d, J3H = 6 Hz, CH2), 7.17 (d, J4H = 8 Hz, p-(CH3)C6H12SO3), 7.71 (d, J4H = 8 Hz, p-(CH3)C6H12SO3) ppm. 13C NMR (200 MHz, CDC13, 21 °C): δ = 18.4 (CH2), 21.4 (CH(CH2)), 21.5 (p-(CH3)C6H12SO3), 24.1 (CH3), 24.3 (CH3), 31.0 (CH(CH2)), 33.5 (CH3), 34.2 (CH2), 57.2 (CH2), 60.6 (CH2), 86.8 (CH2), 104.0 (CH2), 105.5 (CH2), 127.1 (p-(CH3)C6H12SO3), 128.3 (p-(CH3)C6H12SO3), 138.0 (p-(CH3)C6H12SO3), 142.7 (p-(CH3)C6H12SO3) ppm. MS (ESI): m/z = 503 [M - Cl]⁺. C25H17Cl3O2RuS (538): calc'd. C 51.34, H 6.18, N 5.21; found N 51.28, H 6.06, N 5.16.

Preparation of the Enantiopure Chloro Complexes [(arene)RuHCl(CCl2)(OAc)2] (4) and [(arene)RuHCl(CCl2)(OAc)2] (9): To an aqueous solution of the appropriate chloro complex, [(arene)RuHCl(CCl2)(OAc)2] or [(arene)RuHCl(CCl2)(OAc)2], 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 NaBF4 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 NaBF4. After evaporation of the solvent, the tetrafluoroborate salt was obtained as a yellow-orange powder in quantitative yield.

[(arene)Me2RuH(CCl2)(OAc)]2 (5): Yield 70%, 93.9 mg. 1H NMR (400 MHz, CDCl3, 21 °C): δ = 0.95 (m, CH2), 1.22 (m, 2 CH2), 1.43 (m, CH2), 1.60 (m, CH2), 1.88 (m, CH2), 2.28 (s, p-(CH3)C6H12SO3), 5.76 (s, CH2), 7.17 (d, J = 7.3 Hz, p-(CH3)C6H12SO3), 7.71 (d, J = 7.3 Hz, p-(CH3)C6H12SO3) ppm. 13C NMR (200 MHz, CDCl3, 21 °C): δ = 21.5 (p-(CH3)C6H12SO3), 24.4 (CH2), 25.0 (CH2), 31.8 (CH2), 32.5 (CH2), 59.3 (CH), 60.0 (CH), 83.4 (Cl), 127.2 (2 CH2), 128.3 (2 CH2), 137.9 (p-(CH3)C6H12SO3), 143.3 (p-(CH3)C6H12SO3) ppm. MS (ESI): m/z = 447 [M - Cl]⁻, C47H25Cl3O2RuS (482): calculated C 47.34, H 5.23, N 5.81; found N 47.13, H 5.32, N 5.69.
Single Crystal X-ray Structure Analyses: A yellow crystal of compound [R.R-3][Cl]2CHCl₃, 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 g goniometer and a graphite-monochromator. Data collection was performed at −100 °C using Mo-Kα radiation (λ = 0.71073 Å). 133 exposures (6 min per exposure) were obtained at an image plate distance of 70 mm with 0 < φ < 180° and with the crystal oscillating through 1.5° in φ. The resolution was D_{min} – D_{max} 12.45 – 81.81 Å. This compound crystallised in a noncentrosymmetric orthorhombic cell (P2₁2₁2₁, Flack parameter x = 0.005(5)).

The molecular formula of this compound is [(RuCl(C₂H₅)(CH₂=CH₂)](Cl(CHCl₃)). The structure was solved by direct methods using the program SHELXS-97[23] and refined by full-matrix least-squares on F² with SHELXL-97.[24] 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.
tropically. Selected crystallographic data for the complex are summarised in Table 4.

CCDC-273653 (for [3Cl-2CHCl]_2 and -273652 (for [4](BF_4)_2H_2O) 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 mmol) 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_2O, filtered through silica and identified (and conversion and enantiomeric excesses were determined) by HPLC on a Chiralcel OB-H column for acetophenone and its Br and Me para-substituted derivatives or by gas chromatography on a 6-tetra-tert-butyl-2,3-diethyl-β-cycloexdrin (30% in 5% phenyl polymer 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).

Acknowledgments

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