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Ruthenium (II) thiacrown complexes as hydrogen-transfer reduction catalysts

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Abstract

An investigation into the potential of a series of Ruthenium (II) thiacrown complexes with general formula $[Ru([9]aneS_3)Cl_2(L)]$ and $[Ru([n]aneS_4)Cl(L)]^+$, where L = DMSO or Ph_3P, n = 12, 14, or 16, as hydrogen transfer reduction catalysts is reported. As part of these studies two new complexes incorporating $[Ru([12]aneS_4)]$ and $[Ru([16]aneS_4)]$ metal centres have been synthesised and fully characterised. The X-ray structure of one of these complexes is also reported. The UV/Vis spectra of these complexes are dominated by $\pi \rightarrow \pi^*$ transitions, with weaker $d \rightarrow d$ transitions also being apparent. Using these eight structurally related complexes, studies on the transfer hydrogenation of acetophenone using propan-2-ol as the hydride source were carried out. This work revealed that the complexes displayed catalytic activity in the presence of a base promoter. Although the activity of these complexes were considerably lower than that of structurally related mixed-donor ligand systems, there was some evidence that the flexibility of the ligand did have an effect on initial catalytic activity.

Keywords: Ruthenium; Thiacrowns; Catalysis; Macrocyclic ligands

1. Introduction

Historically, hydrogen-transfer reduction with homogenous catalysts has attracted much less attention than homogenous hydrogenation [1]. This may be in part due to the low catalytic activity displayed by the first generation catalysts, e.g. $[RuCl_2(PPh_3)_3]$ requires high reaction temperature [2], whereas homogenous hydrogenation catalysts like $[RhCl(PPh_3)_3]$ are active under much milder conditions [3]. However, in recent years, major advances have been achieved in this field. The discovery of more active catalysts [4] and more efficient hydrogen donors [5] has led to the possibility of obtaining high reaction rates under mild conditions.

Catalytic asymmetric reduction of prochiral ketones to produce chiral secondary alcohols can be carried out using transfer hydrogenation [6]. In view of the low cost of the reducing agent and its operational simplicity, transition-metal catalysed hydrogenation, either with propan-2-ol or with a formic acid/triethylamine mixture as a hydride source, has emerged as an attractive alternative to asymmetric hydrogenation with H_2.

One of the most efficient systems has been reported by the group of Noyoril [7]. Utilising a Ru^{II} catalyst, propan-2-ol as a donor, and potassium hydroxide as a promoter, Noyori and co-workers have demonstrated that high yielding and highly enantioselective transfer hydrogenation reactions of aromatic ketones can occur at room temperature.

More recently, Braunstein et al. [8] have reported on the use of Ru^{II} complexes incorporating a new achiral tridentate facially coordinating ligand, bis(2-oxazolin-

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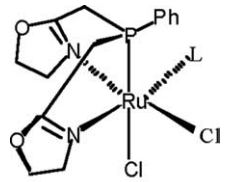


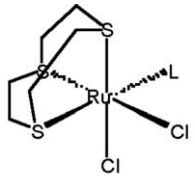
1 L = PPh_3
2 L = DMSO

Scheme 1. Braunstein's Ru^{II} complexes incorporating the bopp ligand.

2-ylmethyl)phenylphosphine (bopp) in the catalytic transfer hydrogenation of ketones – Scheme 1. Both complexes **1** and **2** catalyse the transfer hydrogenation of acetophenone and cyclohexanone using propan-2-ol as the hydrogen donor. The most efficient of these base promoted catalysts is **1**, producing a 94% conversion with a turn over frequency (TOF) per hour of 1,12,800. In contrast, TOF for **2** is 990. This difference in activity is attributed to the change in the ancillary ligand: it was postulated that dissociation of a neutral ligand is necessary during the catalytic cycle and that, since PPh_3 is bulkier than DMSO, its ease of dissociation is reflected in the differences in reactivity between complexes **1** and **2**.

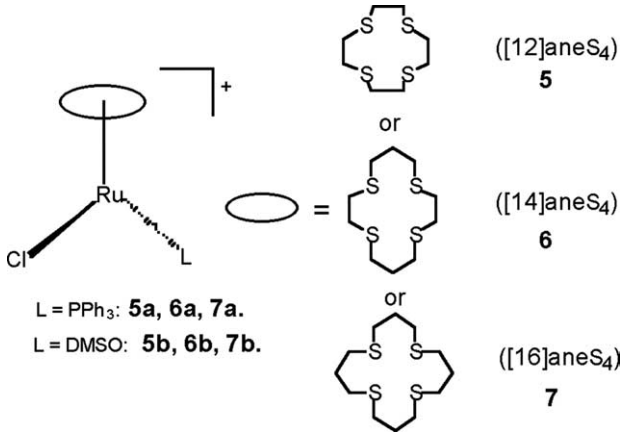
Although they have been investigated less than ligands with other donor atoms, it is well established that transition metal complexes of thioether ligands can function as active catalysts in a considerable number of homogenous reactions. They possess unusual σ-donor/π-acceptor properties and their *trans* influence is considered to be lower than that of phosphines and higher than that of primary amines [9]. It has been suggested that this combination of properties means that thioethers stabilise lower oxidation states of metal ions more than amines but less than phosphines, and are thus capable of yielding complexes with unusual reactivities.

In recent years, we have been investigating the properties of thiacrown ruthenium moieties to function as building blocks for the construction of oligomeric systems with unusual electronic properties [10] and reactivities [11], as well as templates for the self-assembly of novel metallomacrocycles [10c,12]. It struck us that several of the starting materials we have employed in these studies possess many of the structural features seen in complexes **1** and **2**. For example, readily accessible complexes **3** [13] and **4** [14] (Scheme 2) are facially capped, ruthenium (II) systems with the same combination of facially coordinated monodentate ligands in the same geometric arrangement (*cis*-dihalides) as **1** and **2**.



L = PPh_3: **3** L = DMSO:**4**

Scheme 2. Thiacrown complexes structurally related to **1** and **2**.



L = PPh_3: **5a, 6a, 7a.**
L = DMSO: **5b, 6b, 7b.**

Scheme 3.

Given these observations, and the established interest in thioether based catalysts outlined above, we decided to investigate possible catalytic properties transfer hydrogenation of **3** and **4**. These studies were also extended to include a series of structurally related [Ru([*n*]aneS$_4$)] (*n* = 12, 14, 16) mono-anionic complexes – Scheme 3.

2. Experimental

Solvents were dried and purified using standard literature methods, while other commercially available materials were used as received. Standard ^{1}H NMR spectra were recorded on a Bruker AM250 machine. FAB spectra were obtained on a Kratos MS80 machine working positive ion mode, with *m*-nitrobenzyl alcohol matrix. UV/Vis spectra were recorded on a Unicam UV2 spectrometer in twin beam mode. Spectra were recorded in matched quartz cells and were baseline corrected.

Complexes **3**, [13] **4**, [14] **6a**, [13] **5b**, [15] **6b**, [16] and **7b** [17] were synthesised using literature procedures.

3. Catalytic experiments

Typical procedure for the catalytic transfer hydrogenation of acetophenone: each reaction was performed in a four-chambered flask to allow comparison of results under identical conditions.

Ruthenium complex (0.01 mmol) and 4 ml of degassed propan-2-ol were added together and the solution was heated at 82 °C for 5–10 min under nitrogen. Acetophenone (1.201 g, 10.0 mmol) was added dropwise to the refluxing mixture. The resulting yellow mixture was stirred for 10 min and then a solution of NaOH, 60 eq. (0.60 mmol) in 5 ml of propan-2-ol, was added dropwise. The yellow solution turned slight brown after the addition of base. The extent of conversion was deter-

mined by gas chromatography using a Zebron 1500 column. One millilitre samples were removed from the reaction vessel using a syringe and stored in sample tubes. These samples were then loaded onto the column and the extent of conversion was determined.

4. Syntheses

4.1. [RuCl([12]aneS$_4$)(PPh$_3$)][PF$_6$] (**5a**)

A suspension of [$RuCl_2(PPh_3)_3$] [18] (0.356 g, 0.37 mmol) and [12]aneS$_4$ (0.09 g, 0.37 mmol) in degassed dichloromethane (20 ml) was stirred under nitrogen for 1 h. Addition of a mixture of NH_4PF_6 (0.110 g, 2 eq.) in water (1 ml) and ethanol (20 ml) to the resulting solution gave a yellow–brown precipitate. The suspension was concentrated to approximately 10 ml, filtered and ethanol (20 ml) was added to the filtrate to give the desired product, which was isolated by filtration, and washed with ethanol (20 ml) and diethyl ether (20 ml) and allowed to dry in vacuo. Yellow powder: Yield 0.236 g (81%). UV/Vis (H_2O): λ_{max} (ε dm^3 mol^{-1} cm^{-1}) = 212.00 nm (37,694), 405 nm (710). ^{1}H NMR (d^6-acetone) δ_H 7.5–7.3 (m, 15H), 3.40–2.05 (m, 16H). ^{31}P NMR δ_P 35.0 (s, 1P). Elemental analysis obtained (expected $RuC_{26}H_{31}S_4ClPF_6$): C, 39.05% (39.82%); H, 3.74% (3.98%); Cl, 4.81% (4.52%); S, 16.69% (16.36%). MS (FAB): *m/z* (%) = 639 (100) [M$^+$ − PF$_6$].

4.2. [RuCl([16]aneS$_4$)(PPh$_3$)][PF$_6$] (**7a**)

A suspension of [$RuCl_2(PPh_3)_3$] (0.356 g, 0.37 mmol) and [16]aneS$_4$ (0.11 g, 0.37 mmol) in degassed dichloromethane (20 ml) was stirred under nitrogen for 1 h. Addition of a mixture of NH_4PF_6 (0.110 g, 2 eq.) in water (1 ml) and ethanol (20 ml) to the resulting solution gave a yellow–brown precipitate. The suspension was concentrated to approximately 10 ml, filtered and ethanol (20 ml) was added to the filtrate to give the desired product, which was isolated by filtration, and washed with ethanol (20 ml) and diethyl ether (20 ml) and allowed to dry in vacuo. Yellow powder: Yield 0.245 g (79%). UV/Vis (H_2O): λ_{max} (ε dm^3 mol^{-1} cm^{-1}) = 215.00 nm (28,255), 350 nm (310). ^{1}H NMR (d^6-acetone) δ_H 7.55–7.4 (m, 15H), 3.75–2.25 (m, 24H). ^{31}P NMR δ_P 35.0 (s, 1P). Elemental analysis obtained (expected $RuC_{30}H_{42}S_4ClPF_6$): C, 42.09% (42.72%); H, 4.85% (5.02%); Cl, 4.31% (4.02%); S, 15.54% (15.21%). MS (FAB): *m/z* (%) = 695 (60) [M$^+$ − PF$_6$].

5. X-ray crystallography

Crystallographic data for **5a** are summarised in Table 1. Data collected were measured on a Bruker Smart CCD area detector with Oxford Cryosystems low temperature system and complex scattering factors were taken from the program package SHELXTL[1] as implemented on the Viglen Pentium computer. Hydrogen atoms were placed geometrically and refined with a riding model and with U_{iso} constrained to be 1.2 times U_{eq} of the carrier atom. The structures were refined against F^2 by least-squares methods using a weighting scheme.

Table 1
Summary of crystallographic data for [**5a**][PF$_6$]

Empirical formula	$C_{26}H_{31}ClF_6P_2RuS_4$
M	784.21
Crystal system	monoclinic
Space group	$P2_1/n$
Crystal dimensions (mm)	$0.16 \times 0.10 \times 0.06$
a (Å)	8.3260(15)
b (Å)	28.369(5)
c (Å)	15.441(3)
β (°)	101.622(4)
U (Å^3)	3572.4(11)
Z	4
D_c (Mg/m^3)	1.458
F(000)	1584
μ(Mo Kα) (mm^{-1})	0.884
Final R_1 (on *F*)	0.0532

6. Results and discussion

6.1. Synthetic studies

Complexes **3**, **4**, **6a**, **5b**, **6b**, and **7b** were synthesised using previously reported procedures, while **5a** and **7a** were synthesised for the first time. The reaction of [12]aneS$_4$ with [$RuCl_2(PPh_3)_3$] in degassed dichloromethane led to the isolation of **5a** as a yellow hexafluorophosphate salt in good yields. An analogous procedure with [16]aneS$_4$ led to the isolation of **7a**. Both complexes were fully characterised by a combination of ^{1}H NMR, ^{31}P NMR, and mass spectroscopy, and also elemental analysis.

6.2. X-ray crystallography studies

The structure of [**5a**][(PF_6)] was solved through X-ray studies on yellow crystals grown by vapour diffusion of diethyl ether into a nitromethane solution – Fig. 1.

The adoption of *cis* geometry for the chloride and phosphine ligands is consistent with a stepwise chelation of the four sulfur donor atoms, following successive

[1] SHELXTL version, An integrated system for solving and refining crystal structures from diffraction data (Revision 5.1), Bruker AXS Ltd.

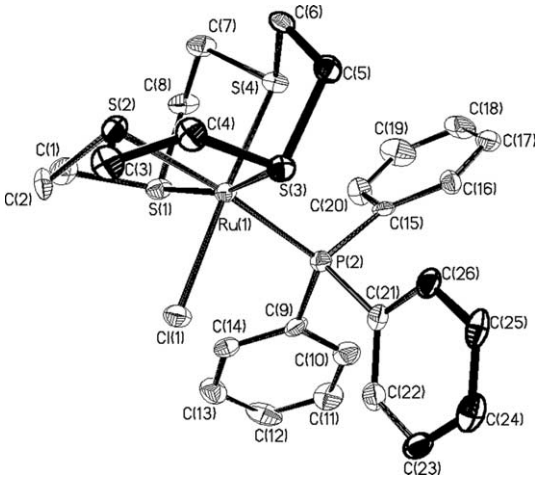


Fig. 1. ORTEP plot of the cation in [**5a**][(PF_6)]. Hydrogen atoms are removed for clarity.

removal of ligands at the ruthenium centre. The adoption of a *trans* geometry in octahedral complexes is not favoured due to the small ring size of [12]aneS_4.

The X-ray structure of **5a** shows subtle differences to that previously reported for **6a** [13]. This is reflected in the data within Table 2 where the bond lengths and angles between the ruthenium (II) centre and the atoms bound to it are shown.

The *trans* influence of the phosphine and chloride ligands are seen in the relative Ru–S bond lengths. The longest Ru–S interactions occur for the sulfur *trans* to the phosphine ligand even though the steric bulk of the PPh_3 would be expected to result in an increase of Ru(1)–S(2) and Ru(1)–S(4). The Ru–S interactions are shortest for that *trans* to the chloride.

Inspection of the angles between ligands reveals differences between the structures of **5a** and **6a**. The *cis* octahedral geometry of **5a** shows greater distortion compared to **6a**. The thiacrowns ligands are not symmetrically coordinated; instead the carbon linkages are

Table 2
A comparison of selected bond lengths and angles for complex **5a** with those of **6a**

	5a	**6a**
Bond lengths (Å)		
Ru(1)–Cl(1)	2.444(13)	2.425(1)
Ru(1)–P(2)	2.325(14)	2.344(2)
Ru(1)–S(1)	2.365(14)	2.359(2)
Ru(1)–S(2)	2.377(13)	2.383(2)
Ru(1)–S(3)	2.357(14)	2.344(2)
Ru(1)–S(4)	2.287(14)	2.286(2)
Bond angles (°)		
P(2)–Ru(1)–Cl(1)	85.32(5)	91.5(1)
P(2)–Ru(1)–S(4)	93.83(5)	90.0(1)
P(2)–Ru(1)–S(1)	95.78(5)	89.7(1)
P(2)–Ru(1)–S(3)	98.54(5)	94.3(1)

Table 3
UV/Vis absorption spectra of complexes in water

Complex	λ_{max} (nm), ε_{max} ($dm^3\ mol^{-1}\ cm^{-1}$), assignment
3	206 (25,100) $\pi \rightarrow \pi^*$, 406 (730) d → d
4	213 (20,300) $\pi \rightarrow \pi^*$, 365 (370) d → d
5a[a]	212 (37,700) $\pi \rightarrow \pi^*$, 405 (710) d → d
5b[a]	215 (20,700) $\pi \rightarrow \pi^*$, 396 (830) d → d
6a[a]	213 (35,200) $\pi \rightarrow \pi^*$, 375 (670) d → d
6b[a]	218 (21,600) $\pi \rightarrow \pi^*$, 368 (350) d → d
7a[a]	202 (28,250) $\pi \rightarrow \pi^*$, 350 (310) d → d
7b[a]	215 (20,750) $\pi \rightarrow \pi^*$, 373 (410) d → d

[a] Chloride salt.

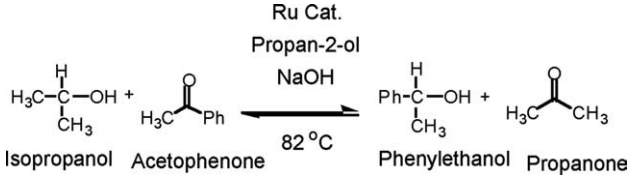
folded. The ring size of [12]aneS_4 is smaller compared to [14]aneS_4 and it is the reduced flexibility of the ethyl linkages which produces greater distortion of the octahedral geometry.

Coordination of [16]aneS_4 to octahedral metal ions can lead to *cis* or *trans* geometries Although X-ray quality crystals of **7a** were not obtained, NMR studies involving comparisons to related systems confirm that the complex is exclusively formed as the *cis*-isomer.

6.3. Absorption spectroscopy

All UV/Vis spectra were recorded in water on chloride salts obtained from anion metathesis. The complexes display similar features in their spectra – Table 3. In all cases, intense relatively high energy transitions are observed. Each complex shows a band at around 200–220 nm with a large absorption coefficient which, through comparison with similar structures [10], has been assigned to a $\pi \rightarrow \pi^*$ transition on the thiacrown, PPh_3 or DMSO ligands. Weaker bands are also observed at around 350–400 nm. Comparison with structurally similar complexes allows these bands to be assigned as d–d transitions [19].

The high-energy bands for all eight complexes vary by less than 20 nm. This suggests that there is very little energy difference between the π and π* orbitals of PPh_3 and DMSO upon coordination to the different ruthenium (II) centres. Likewise, the energy differences between d–d transitions of the complexes are very small, particularly between complexes containing the same thiacrown.



Scheme 4.

7. Catalysis studies

Catalytic studies with the complexes **3**, **4**, **5**, **6**, and **7** were performed for the transfer hydrogenation of acetophenone by propan-2-ol – Scheme 4. Reactions were performed in a four-chambered flask to allow comparison of results under identical conditions.

Preliminary studies were carried out using **3** as a catalyst as this complex is most structurally analogous to **1**. Initial experiments using **3** with ketone:Ru:base in the ratio 1000:1:25 showed limited reactivity with conversions as low as 10% after a 24 h period. Since the reduction of ketones with propan-2-ol is influenced by base concentration [20], it was decided to vary its concentration in order to determine the optimum conditions – Fig. 2.

There was found to be an upper limit of 60 eq. of NaOH beyond which there was little further enhancement observed over a 24 h period. Bubbling nitrogen through the mixture, intended to remove the acetone product and push the reaction equilibrium towards the right-hand side, did increase the conversion by approximately 10% and push the reaction nearer to completion.

It is known that replacement of [9]aneS_3 with [*n*]aneS_4 (*n* = 12, 14, 16) thiacrowns gives ruthenium complexes showing more distorted *cis*-octahedral geometries [13–17]. In *cis*-complexes such as **5**, **6**, and **7**, two sulfur atoms of the macrocyclic ligand, one chlorine and one sulfur or phosphorous atom from the third ligand lie on the equatorial plane. Two remaining sulfur donor atoms of the macrocyclic ligand occupy the axial octahedral positions. To investigate whether the increased steric strain imposed by S_4 macrocyclic coordination would enhance catalytic activity, the properties of **5**, **6**, and **7** were investigated. Again, components were found to give optimised results in the mixing ratio 1000:1:60 (ketone:Ru:base).

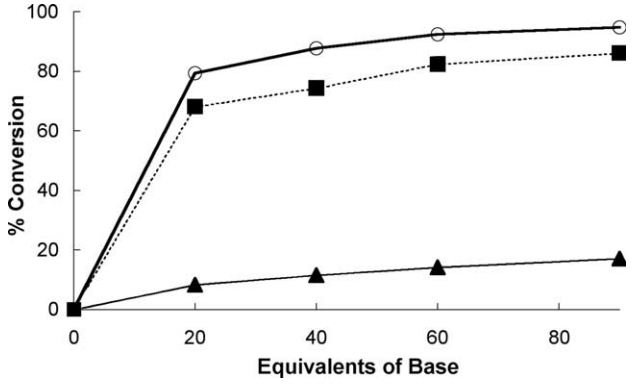


Fig. 2. Effect of base concentration on the transfer hydrogenation of acetophenone using **3** as a catalyst: (▲) percentage conversion in 1 h, (■) percentage conversion in 24 h, (○) percentage conversion in 24 h + N_2.

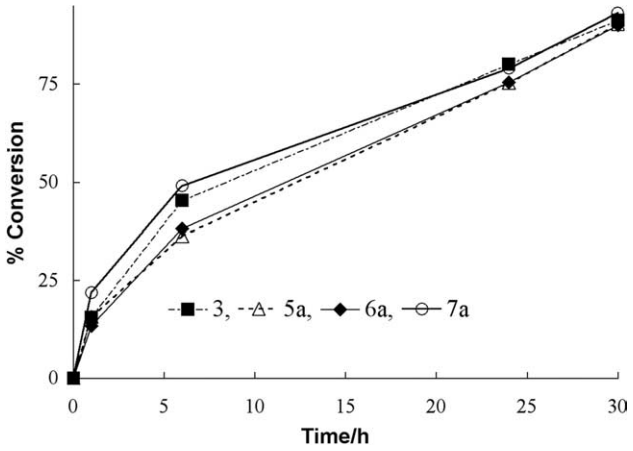


Fig. 3. Catalytic transfer hydrogenation of acetophenone using complexes **3**, **5a**, **6a**, and **7a**.

Using these conditions, a comparison of the Ph_3P coordinated systems, including **3**, was first carried out – Fig. 3. Complex **7a** seems to show greatest initial catalytic activity. However, given the relatively small differences in activity and the fact that error values cannot be fully assessed, it is not possible to conclude that it is the most reactive. Indeed, the observation of "cross-over plots" suggests rates are not statistically significantly different, and over 24 h all the complexes show essentially identical activity.

To investigate the effect of auxiliary ligands on catalytic activity the properties of DMSO coordinated complexes **4**, **5b**, **6b**, and **7b** in the same conditions were also investigated – Fig. 4.

Under these conditions, **4** shows comparable reactivity to that of **3**: after 24 h 76% conversion was observed compared with 80% for **3**. Again, there is evidence that the complex bearing the larger 16-membered macrocycle, in this case **7b**, displaying greater initial reactivity,

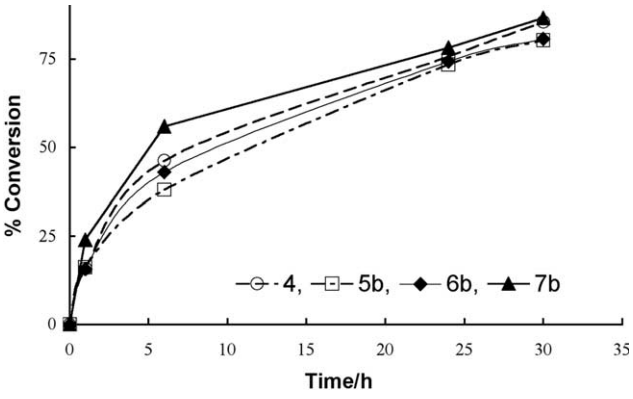


Fig. 4. Catalytic transfer hydrogenation of acetophenone using complexes **4**, **5b**, **6b**, and **7b**.

Table 4
Transfer hydrogenation of acetophenone by the ruthenium (II) complexes **3**–**7**

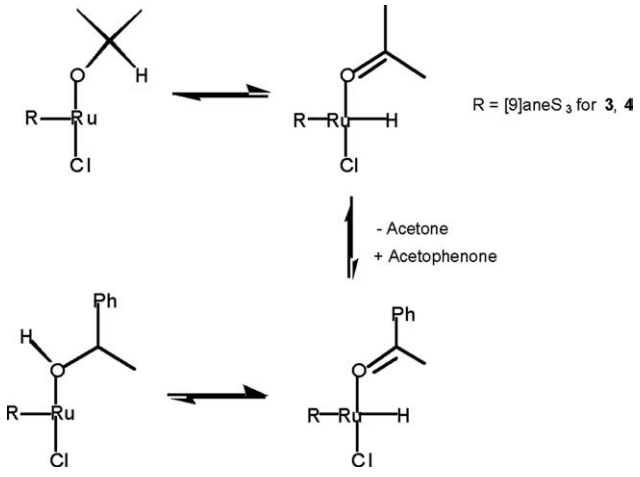
Catalyst	t (h^{-1})	Yield (%)	Turnover (h^{-1})
3	1	16	160
	24	83	35
4	1	15	150
	24	75	31
5a	1	15	150
	24	75	31
5b	1	16	160
	24	75	31
6a	1	13	130
	24	72	30
6b	1	16	160
	24	80	33
7a	1	21	210
	24	79	33
7b	1	23	230
	24	86	36

however after 24 h all the complexes show similar activity, with substrate conversion being around 80%. Table 4 summarises the data obtained on the catalytic properties of all eight complexes.

8. Discussion

Complexes **3** and **4** are similar in structure to **1** and **2** with bopp being replaced by [9]aneS$_3$. However, turnover numbers in comparison with those obtained by Braunstein et al. [8] are much lower, suggesting that the change in electronic properties relayed to the ruthenium centre is the major factor in the reduction of the activity of the catalyst.

Further factor in activity seems to be the flexibility of the thiacrown ligands. Complexes **7a** and **7b**, which incorporate the more flexible [16]aneS$_4$ ligand, display higher TON after 1 h compared with **3** and **4**. All reactions reach completion after 24 h at which point nitrogen is required to remove acetone in order to raise% conversion further. TOF after this period is approximately the same for all eight complexes.



Scheme 5. Possible catalytic mechanism for thiacrown complexes.

Further studies using a formic acid/triethylamine [21] azeotrope as an alternative source of hydrogen yielded poor results with conversions not greater than 15% over a 24 h period.

Although no studies have been carried out to determine the mechanism for these particular catalytic processes, it is known that transition metal complexes prefer transfer hydrogenation via hydride formation [4]. Thus, using complexes **3** and **4** as an example, it may be reasonable to propose that hydrogenation takes place via the mechanism shown in Scheme 5.

The same mechanism may be proposed for complexes **5**–**7**. Since four coordination sites on the ruthenium centre are occupied by the sulfur macrocycle, the chloride ligand will be absent in order to maintain a six-coordinate metal centre.

9. Conclusions

Ruthenium (II) complexes incorporating facially bound sulfur macrocycles have been investigated to determine their efficiency as catalysts in the transfer hydrogenation of acetophenone using propan-2-ol as the source for hydrogen.

The reduction of acetophenone is influenced by the concentration of base. An upper limit of 60 eq. of NaOH was found beyond which little rate enhancement was observed over a 24 h period. Bubbling nitrogen through the reaction mixture raised conversion by approximately 10% so pushing reactions nearer to completion.

Ligand substitution studies found little difference in reactivity between complexes containing PPh_3 or DMSO ligands. This suggests that dissociation of a neutral ligand during the catalytic cycle is not important.

Complexes bearing [n]aneS$_4$ (n = 12, 14, 16) did appear to display greater initial reactivity in comparison with their [9]aneS$_3$ counterparts. However, these slight differences are within experimental error and after a 24 h period, all complexes produce similar percentage conversions suggesting that that there is very little difference in overall reactivity between them.

The low reactivity of these complexes may be a result of the electronic properties relayed to the ruthenium centre by the thiacrown. Furthermore, the coordination of sulfur macrocycles to metals is known to enhance the acidity of C–H bonds α to sulfur. This may also compromise the ability of such complexes to perform as catalysts.

Nevertheless, this work demonstrates that macrocyclic ligand complexes of transition metals can display catalytic behaviour. By judiciously selecting donors and tuning the flexibility of the coordinated macrocycle

it may be possible to produce systems with new or novel activity. Furthermore, by using molecular building blocks related to the systems described here, it may be possible to self-assemble novel multi-site and/or multi-function catalysts.

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