

Asymmetric Catalysis

Easy To Synthesize, Robust, Organo-Osmium Asymmetric Transfer Hydrogenation Catalysts

James P. C. Coverdale, Carlos Sanchez-Cano, Guy J. Clarkson, Rina Soni, Martin Wills,* and Peter J. Sadler*^[a]

Abstract: Asymmetric transfer hydrogenation (ATH) is an important process in organic synthesis for which the Noyori-type Ru^{II} catalysts [(arene)Ru(Tsdiimine)] are now well established and widely used. We now demonstrate for the first time the catalytic activity of the osmium analogues. X-ray crystal structures of the 16-electron Os^{II} catalysts are almost identical to those of Ru^{II}. Intriguingly the precursor complex was isolated as a dichlorido complex with a monodentate amine ligand. The Os^{II} catalysts are readily synthesised (within 1 h) and exhibit excellent enantioselectivity in ATH reactions of ketones.

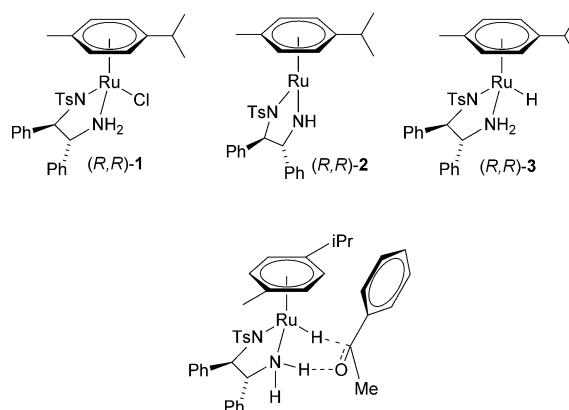


Figure 1. Ruthenium pre-catalyst (R,R)-1, active amido catalyst (R,R)-2 and hydrido species (R,R)-3 shown together with the transition state for reduction of ketones by (R,R)-3. The catalyst derived from the diamine of R,R configuration gives the acetophenone product of R-configuration.

Maintaining control over chirality is essential during many chemical syntheses and so it has become necessary to obtain enantiopure products cost-effectively. Selective reduction of prochiral starting materials provides a simple route to such compounds.^[1] The Noyori catalyst [Ru(*p*-cymene)(TsDPEN)Cl], (H)TsDPEN = *N*-*p*-tosyl-1,2-diphenylethylenediamine, **1** celebrates two decades of use in the asymmetric transfer hydrogenation (ATH) of ketones and imines, often achieving high enantioselectivities (*ee*) and full conversions in under 24 h.^[1–2]

Upon treatment with base in the course of a catalytic application, Ru pre-catalyst **1** eliminates HCl, forming the active 16-electron amido complex **2**. During the reduction, the catalyst cycles between **2** which contains a pseudo-planar chelated ligand and an 18-electron 'hydride' species **3** (bearing hydrido and amine ligands).^[2,3] The catalysis is considered to be an outer-sphere ligand-assisted process^[3] since the substrate has no direct interaction with the metal centre (Figure 1). Instead, chiral components on the diamine ligand bring about a six-membered transition state using both steric and electronic effects,^[2,3] allowing hydrogenation from both the Ru–H and N–H centres to occur directly with the substrate. Because a favoured diastereoisomer of hydride is regenerated during each cycle, the catalyst is configurationally defined at the metal centre, and this chirality is relayed to the product in the reduction.^[2c]

X-ray crystallographic structures of the pre-catalyst, catalyst and hydrido species have been reported.^[3a]

Although research on transfer hydrogenation catalysts has largely been centred on Ru^{II} complexes,^[2–4] and to some extent those of Rh and Ir,^[5] little attention has been paid to the potential of closely related osmium(II) complexes. The first examples of osmium complexes for asymmetric transfer hydrogenation (and the reverse reaction of alcohol oxidation) were reported by Faller et al., using *cis*-aminoindanol as the chiral ligand.^[6] Several chiral Os^{II} complexes have been reported for asymmetric reductions including those containing L- α -amino carboxylates^[7] and pybox ligands.^[8] Monophosphinite complexes,^[9] iminopyridine complexes,^[10] and pincer complexes^[11] have also been described. Many of these reduce ketones with high enantioselectivities at very low loadings. In addition, Os^{II} catalysts containing nonchiral ligands have been reported.^[12] Other low-spin d⁶ organometallic analogues [M(Cp*)(Tsdiimine)Cl] with M = Rh^{III} or Ir^{III} have shown promise in their robustness and performance whilst maintaining the high enantioselectivities and conversions observed with the Ru^{II} catalysts,^[5] yet the chemistry of an Os-centred analogue of the Noyori catalyst has never been explored. Here we report the first preparation of osmium analogues (**4/5**) of Noyori-type catalysts (**1/2**). Importantly we find that the osmium catalysts are easy to synthesise, are stable, and yet still retain high enantioselectivity in asymmetric reductions of prochiral ketones.

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Ruthenium Noyori-type catalysts are readily prepared using the dimer precursor $[\text{RuCl}_2(\eta^6\text{-arene})]_2$ (arene most commonly *p*-cymene) forming a chlorido pre-catalyst when combined with the chiral ligand (1*S*,2*S*)-(H)TsDPEN in 2-propanol with a base.^[2e] This method was unsuccessful for the Os complexes since the dimer was poorly soluble in 2-propanol and decomposition products were observed by NMR spectroscopy. However, Os^{II} pre-catalysts were readily synthesised by microwave methods, combining the dimer $[\text{OsCl}_2(\eta^6\text{-p-cymene})]_2$ with a chiral diamine: either (1*R*,2*R*)-(H)TsDPEN or (1*S*,2*S*)-(H)TsDPEN, to produce both enantiomers: (*R,R*)-**4a** and (*S,S*)-**4b** (Figure 2).

Owing to the absence of base, it was anticipated that these complexes would differ structurally from the chelated ruthenium species.^[3a] Indeed, NMR spectroscopy, mass spectrometry, infrared spectroscopy

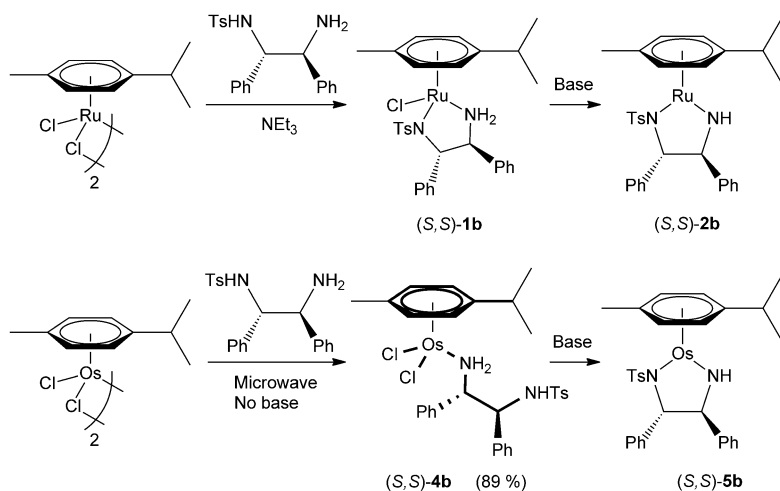


Figure 2. Noyori Ru pre-catalyst formation (top)^[2c,3a] The route to the osmium pre-catalyst (bottom) differs in the absence of base to form **4b**. Upon subsequent treatment with a base they both form structurally similar 16-electron active catalysts (**2b/5b**).^[2c,3a] Osmium catalysts **4a/5a** (the opposite configuration) were synthesised by using (1*R*,2*R*)-(H)TsDPEN.

and elemental analysis suggested that **4** contained the diamine coordinated only by the terminal amine, while two chlorido ligands remained complexed to the metal centre (Figure 2 and Supporting Information).

Treatment of either enantiomer of **4** with base yielded a red solution of active amido catalysts **5a** and **5b**, highly stable analogues of reported ruthenium complexes.^[3a] The ability of **4** to still undergo activation by a Noyori-type HCl elimination mechanism demonstrated that it was a suitable Os pre-catalyst for ATH reactions. Alternatively, direct reaction of the Os-dimer with either enantiomer of (H)TsDPEN with a base at room temperature provided a facile route to **5a** and **5b** (Figure 3), synthesised in less than an hour. Hence, although the osmium chloride complexes analogous to **1** remained elusive, their 16e amido derivatives **5** could be readily prepared. Moreover there is no need for an inert atmosphere during synthesis or storage.

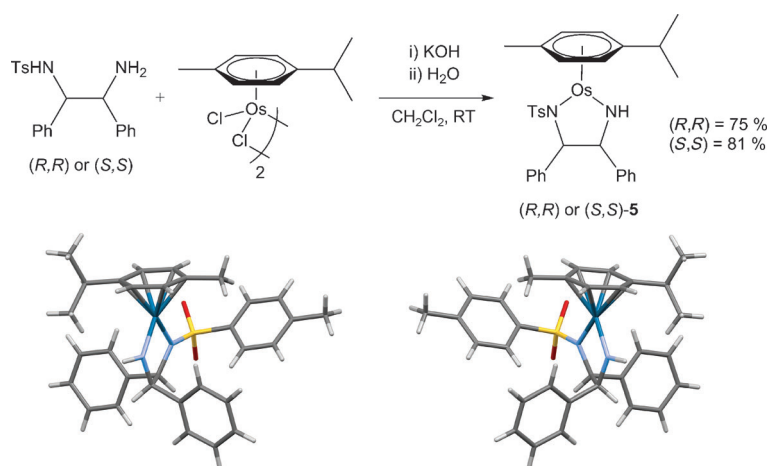


Figure 3. Facile route for direct formation of 16-electron amido Os^{II} catalysts, with X-ray crystal structures of both enantiomers: **5a** (left) and **5b** (right). All hydrogen atoms except those on the diamine and amide have been omitted for clarity.

Though adapted ruthenium protocols to isolate the hydride using 2-propanol^[3a] and direct hydrogenation were not successful, the osmium hydride intermediate was observed in solution by NMR spectroscopy by treatment of **4** or **5** with triethylamine and formic acid. ¹H NMR resonances of Os–H species were observed as two singlets at $\delta = -5.89$ and -6.04 ppm each with ¹⁸⁷Os satellites (¹*J*(¹⁸⁷Os,¹H) = 44 Hz). This suggests that hydride transfer to **5** is not fully stereoselective. Subsequent enantioselectivity in substrate reduction may result from the greater reactivity of one of the two hydride diastereomers, as previously speculated in the

case of Ru^{II} complexes.^[4a,13] Alternatively, selectivity may be controlled by an alternate interaction of the substrate with the chiral ligand rather than a dependence on the configuration of the metal hydride.

The X-ray crystal structures of catalysts **5a** and **5b** were determined (Figure 3). The distorted octahedral Os^{II} structures are remarkably similar to the Ru analogue **2**.^[3a] Particularly, the terminal amido N–H bond was found to be similar in length (0.96(3) Å compared to 0.88(6) Å in the Noyori catalyst). This bond is known to be important in the Ru^{II} catalysis mechanism^[14] and so its comparable length may help to explain the activities observed with Os^{II}.

The catalytic activity of **4a** and **4b** and their 16-electron active counterparts **5a** and **5b** towards acetophenone reduction were studied in a formic acid/triethylamine azeotrope to give irreversible kinetic enantioselectivity.^[1–2] Catalyst loading

was defined by the substrate/catalyst molar ratio, S/C. A Noyori-type ATH cycle and hydrogen-transfer mechanism was assumed based on the structural similarities between amido complex **5b** and its Ru^{II} counterpart **2**. Complexes **4a/4b** would be first converted into **5a/5b**, respectively, before entering the catalytic cycle, hence the use of either **4** or **5** would be expected to give identical results.

Complexes **4** and **5** were highly enantioselective for ATH, with > 94% ee controlled by the fixed chirality of the diamine. (*S,S*)-Configured **4b/5b** established reduction on the *Si*-face, similarly to **2**,^[1–2] while *R,R*-configured **4a/5a** selected for the *Re*-face (reduction through an analogous transition state to that in Figure 1).

Further reductions were undertaken using **4a/4b** and selected acetophenone derivatives **6–10** (Tables 1 and 2). Enantiose-

lectivities seem to be the result of both steric and electronic factors, consistent with observations for Ru,^[1–2] and a slight reduction of enantioselectivity for substrates bearing electron-withdrawing substituents was observed.

Since reactions using the amido catalysts remained bright yellow, the reduction of acetophenone using **4b** was continued for a longer time. As anticipated, the conversion continued to increase with time (to 88% after 48 h and 94% after 72 h, Table 2), as the catalyst had not become deactivated. A high enantiomeric excess (95%) was maintained, providing evidence for ATH irreversibility when using formic acid/triethylamine. The enantioselectivity compares well to ruthenium analogues but the reaction proceeded at a slower rate, for example, the conversion of ketone **6** at S/C=200 for Os complex **5b** to 94% took 72 h, whilst Ru analogue **2** reached 99% after 20 h at 28 °C (Table 2). In general the kinetics of substitution reactions at Os^{II} arene centres are approximately 40–100× slower than at Ru^{II}.^[15]

Though the osmium catalysts may not compete with the extent of conversion observed for ruthenium, they can be prepared easily in under an hour, and do not require an inert atmosphere during synthesis or storage. The 16-electron amido complexes **5a** and **5b** are particularly stable in air, and can be prepared well in advance of requirement. This may be particularly useful in a laboratory setting, in which a chiral alcohol can be produced overnight (with high enantioselectivity) using a catalyst that may be synthesised and stored well in advance.

These novel osmium–arene TsDPEN catalysts have been fully characterised and catalyse ATH reductions of acetophenone-derived substrates with high enantioselectivity. The Os catalysts appear to follow a Noyori-type ATH mechanism, with similar X-ray crystal structures, hydrido intermediates observed by NMR and mass spectrometry, and behaviour in catalytic reductions. The ease and speed of preparation combined with high stability on storage of the osmium catalysts makes them attractive alternatives to existing ruthenium catalysts.

Experimental Section

General

The synthesis and characterisation of complexes **4a**, **4b**, **5a** and **5b**, catalytic reductions, ¹H NMR spectroscopy of osmium hydride species, and determination of the X-ray structures of **5a** and **5b** are described in the Supporting Information.

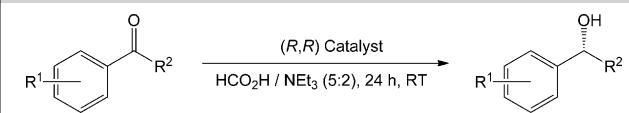
X-ray crystallographic data

CCDC-1035611 (**5a**), -1035612 (**5b**) and -686925 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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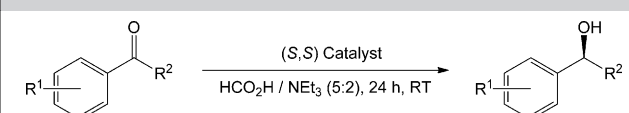
Table 1. Reduction of prochiral ketones **6–10** by *R,R* pre-catalysts **4a/5a**.



Ketone	R ¹	R ²	Cat.	S/C	Conv. ^[a]	ee [%] ^[a]
6	H	Me	4a	100	98	98
6	H	Me	4a	200	62	98
6	H	Me	5a	100	83	98
6	H	Me	5a	200	67	97
7	<i>p</i> -Cl	Me	4a	100	98	96
8	<i>p</i> -MeO	Me	4a	100	67	— ^[b]
9	H	CH ₂ Cl	4a	100	97	94
10	H	Et	4a	100	56	96

[a] Determined by GC analysis. [b] ee undetermined for the reduction of **8** due to poor separation of enantiomers.

Table 2. Reduction of ketones **6–10** by *S,S* Os (pre)catalysts **4b/5b** compared to Ru analogue **2**.^[2a,b]



Ketone	R ¹	R ²	Cat.	S/C	Conv. ^[a]	ee [%] ^[a]
6	H	Me	4b	100	93	98
6	H	Me	4b	200	54	95
6	H	Me	5b	100	79	94
6	H	Me	5b	200	59	95
6	H	Me	2 ^[2a, 2b]	200	99	98
7	<i>p</i> -Cl	Me	4b	100	97	94
7	<i>p</i> -Cl	Me	2 ^[2a, 2b]	200	99	95
8	<i>p</i> -MeO	Me	4b	100	70	99
8	<i>p</i> -MeO	Me	2 ^[2a, 2b]	200	99	97
9	H	CH ₂ Cl	4b	100	92	84
9	H	CH ₂ Cl	2 ^[2b]	1000	36 ^[b]	91 ^[b]
10	H	Et	4b	100	54	95
10	H	Et	2 ^[2a, 2b]	200	96	97
6	H	Me	5b	200	88 ^[c]	95
6	H	Me	5b	200	94 ^[d]	95

[a] Determined by GC analysis. Ru reductions for 20 h at 28 °C. [b] Reduction of **9** with ruthenium catalyst **2** was conducted in 1.0 M EtOAc with S/C = 1000. [c] After 48 h. [d] After 72 h.

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Keywords: asymmetric catalysis • hydrogen transfer • ketone reduction • organometallic complexes • osmium

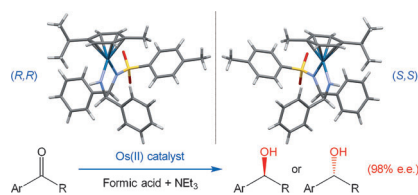
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COMMUNICATION

Transferable methods: Asymmetric transfer hydrogenation (ATH) is an important process in organic synthesis for which the Noyori-type Ru^{II} catalysts [(arene)Ru(Tsdiimine)] are now well established and widely used. We now demonstrate for the first time the catalytic activity of the osmium analogues (see scheme).

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Easy To Synthesize, Robust, Organo-Osmium Asymmetric Transfer Hydrogenation Catalysts

