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PERSPECTIVE

The development of aqueous transfer hydrogenation catalysts

Andrew Robertson,[a] Takahiro Matsumoto[b,c] and Seiji Ogo*[b,c,d]

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This review discusses the development of aqueous phase, homogeneous, transfer hydrogenation catalysis. Transfer hydrogenation catalysts, based on Ru, Ir and Rh, reduce organic substrates in water by assisting the transfer of hydrogen from simple donor species. These catalysts are expected to have significant benefits when compared with organic phase catalysts, including greater activity, greater selectivity and smaller environmental impact. They will therefore be expected to make a significant contribution to homogeneous catalysis and 'green chemistry'. Here, we comprehensively examine these catalysts, paying special attention to structural features.

Introduction

Transfer hydrogenation is an important form of catalytic reduction involving the transfer of a hydrogen atom, or hydride ion, from a donor molecule to a substrate. The catalysts involved are typically based on transition metal complexes, which allow for specificity, such as chemo- and regiospecificity, above and beyond that achievable by heterogeneous, surface methods or simple reducing agents. The employment of simple hydrogen donors, such as formic acid (HCOOH), results in an abundant and relatively safe source of reductant.

Transfer hydrogenation has a history that goes back to 1952 when Braude and Linstead reported the catalytic hydrogen transfer from cyclohexene to a variety of organic acceptors, mediated by a palladium black catalyst.[1] This led to a wide variety of transfer hydrogenation reactions depending on heterogeneous, homogeneous and biochemical systems.[2–8] In recent years, a variety of transfer hydrogenation catalysts have been developed that promote direct transfer hydrogenation in water. It is these systems that will form the focus of this review.

[a]*International Education Center, Kyushu University, 744 Moto-oka, Nishi-ku, Fukuoka, 819-0395, Japan*
[b]*Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, 744 Moto-oka, Nishi-ku, Fukuoka, 819-0395, Japan. E-mail: ogotcm@mail.cstm.kyushu-u.ac.jp; Fax: +81-92-802-2823; Tel: +81-92-802-2818*
[c]*International Institute for Carbon-Neutral Energy Research (I²CNER), 744 Moto-oka, Nishi-ku, Fukuoka, 819-0395, Japan*
[d]*Core Research for Evolutional Science and Technology (CREST), Japan Science and Technology Agency (JST), Kawaguchi Center Building, 4-1-8 Honcho, Kawaguchi-shi, Saitama, 332-0012, Japan*

Andrew Robertson

Andrew Robertson graduated from the University of Manchester Institute of Science and Technology in 1993 and obtained his PhD from the University of Birmingham in 1998. Thereafter, he undertook two years of post-doctoral research with Prof. Seiji Shinkai at Kyushu University. For the following ten years, he worked in the private sector in fields related to science education before returning to Kyushu University as part of the Global 30 International Education Project. His research interests lie in applying principles of organometallic chemistry to systems chemistry.

Takahiro Matsumoto

Takahiro Matsumoto graduated from Kanazawa University in 2002 and received his PhD on O_2-activation by copper complexes from Kanazawa University in 2007. After a post-doctoral internship at Kyushu University, he was made Assistant Professor in 2009. He currently works on the development of catalysts for small molecule activation.

Transfer hydrogenation performed in water has many attractions.[9] Firstly, water is a cheap and environmentally benign solvent. Secondly, many reactions have been found to be significantly accelerated in water, compared with organic solvents.[10–13] Finally, performing the reactions in water may result in pH-dependence, allowing for fine-tuning of selectivity and limiting side reactions. In short, running transfer hydrogenation reactions in water allows us to perform highly selective reductions, using relatively safe reductants, in a cheap and benign solvent. For these reasons, we believe that aqueous transfer hydrogenation will facilitate the synthesis of a wide range of challenging target materials without costing the Earth.

Aqueous transfer hydrogenation catalysts are reviewed here in terms of their structural development. All of these catalysts are based on one or more members of the Ru/Ir/Rh series. As we shall see later, the exact choice of metal within this series follows a sensitive dependence on the nature of the surrounding ligands and the overall reaction conditions.

We have organised the systems into types based on a progression of design: the first system has few characteristics in common with later complexes and has been labeled type I. Subsequent complexes all bear an aromatic π-acceptor ligand and a simple, labile σ-donor. Two of these that have little similarity to other designs have been grouped into type II. Two systems that use pyridine-based ligands have been labeled type III and the remaining systems, which all use amine-based ligands, have been labeled type IV. All of these systems use HCOOH as the hydride donor, in either the acid or $HCOO^-$ form, since they produce only CO_2 or HCO_3^- as by-products.

Discussion

Type I

The pioneering work of aqueous transfer hydrogenation by a water-soluble catalyst was reported in 1989.[14,15] Joó and Bényei reported a simple Ru^{II} complex, $[Ru^{II}(Cl)_2(TPPMS)_2]$ {TPPMS = 4-(diphenylphosphino)benzenesulfonic acid}, based on monosulfonated triphenylphosphine and chloro ligands (Fig. 1). This system used HCOONa as the hydride donor and benzaldehyde as the substrate. Although the catalysis itself was reported as being aqueous-phase, the reaction conditions were biphasic since they involved large amounts of water-insoluble benzaldehyde. The reaction was reported to be independent of pH over the range 7.8–9.2.

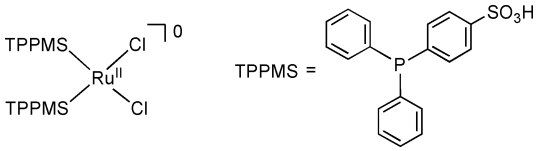

Fig. 1 A Ru^{II} complex based on monosulfonated triphenylphosphine and chloro ligands. Reported by Joó and coworkers.[14,15]

The design was based on a system originally reported by Sasson and Blum who used a water-insoluble catalyst $[Ru^{II}(Cl)_2(PPh_3)_3]$ and a phase-transfer agent for the biphasic reduction of aldehydes with aqueous sodium formate.[16] The monosulphonated phosphine ligand imparts water solubility and stability whilst the choice of Ru followed transfer hydrogenation experiments which showed that a Rh^I catalyst was much less efficient and an Ir^I catalyst lost activity within 25 cycles.

An excess of TPPMS was shown to have a positive effect on the rate of reaction. Using only two equivalents of phosphine ligand resulted in a low reaction rate and low conversion. Whilst increasing to three equivalents did not improve the rate of reaction, it did result in quantitative conversion. Thereafter, additional amounts of TPPMS increased the rate of reaction until the limit of solubility. The reason for this additional rate increase remains unclear, though it is possible that TPPMS behaves as a form of phase transfer catalyst to shuttle benzaldehyde into the aqueous phase. Phase transfer catalysts based on cyclodextrins, however, were found to inhibit the reaction, probably as a result of direct interactions with the catalyst.

The positive correlation between phosphine ligand concentration and reaction rate seems to raise further questions, however. The authors had previously assumed that displacement of the phosphine ligand was a necessary first step in the coordination of substrate and/or donor molecules.[17] This requirement would lead one to expect greater concentrations of phosphine to inhibit catalysis at some point. It is therefore likely that phosphine ligands act to suppress the formation of catalytically inactive bis-aldehyde complexes,[17] *i.e.* they reduce substrate inhibition.

Though the reaction conditions are notionally biphasic, it is most likely that the catalyst itself is active either in the aqueous phase alone or at the organic/water boundary. When the Ru^{II} complex is shuttled into the organic phase by quaternary ammonium salts, a distinct inhibition is observed. Furthermore, changing the organic solvent did not affect the rate of reaction. The reported mechanism is reproduced in Fig. 2.

Type II

In 1999, we reported a transfer hydrogenation catalyst based on a seemingly simple Ir^{III} system, $[Ir^{III}(Cp^*)(H_2O)_3]^{2+}$ (Cp^* = pentamethylcyclopentadienyl, Fig. 3).[18] This system involved a

Seiji Ogo

Seiji Ogo received his PhD from the Graduate University for Advanced Studies in 1996. After working in the Institute for Molecular Science (IMS) at Okazaki (1996–2001), Nagoya University (2001–2002), and Osaka University (2002–2005), in 2005 he joined Kyushu University as a full Professor. He is currently a leader of the CREST (Core Research for Evolutional Science and Technology) project of the Japan Science and Technology Agency (JST). His research interests are in the activation of H_2, N_2, CO_2, O_2, and H_2O in water. He received the Japan Society for the Promotion of Science (JSPS) Prizes in 2008.

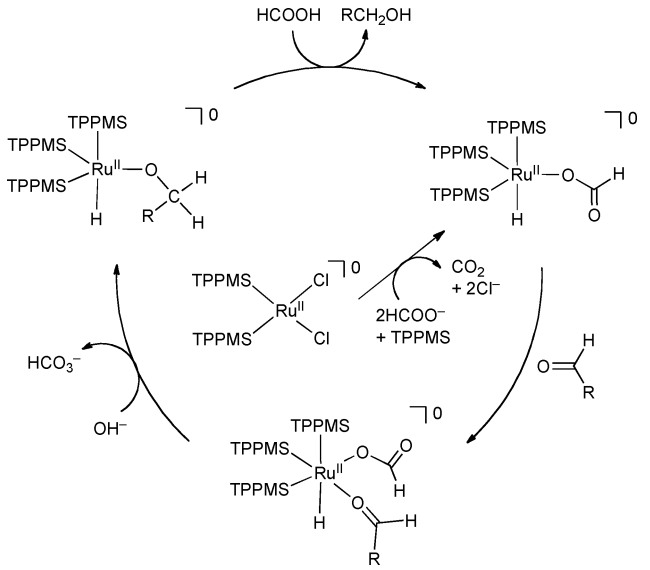

Fig. 2 Proposed mechanism for transfer hydrogenation by $[Ru^{II}(Cl)_2(TPPMS)_2]$ {TPPMS = 4-(diphenylphosphino)benzenesulfonic acid}.[15]

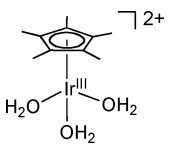

Fig. 3 An Ir^{III} pentamethylcyclopentadienyl (Cp*) piano-stool complex. Reported by Ogo and coworkers.[18]

piano-stool complex composed of the Ir^{III} centre, a Cp* π-acceptor and three labile, aqua σ-donor ligands.

The choice of the Cp* ligand initiated a trend that was followed in all subsequent aqueous transfer hydrogenation catalysts, that is the requirement for an aromatic π-acceptor. The choice of the most appropriate ligand from the library of common aromatic ligands depends on the exact nature of the complex and reaction conditions.

The aqua ligands play several significant roles. Firstly, they impart water solubility to the metal complex. Secondly, they are, of course, labile in water and provide easy access to a vacant site for incoming substrates and donors. Finally, they impart pH-dependence since they can be deprotonated at high pH to form hydroxo ligands and thereby change the nature of the whole complex. Indeed, aqua ligands form a central part of our most noteworthy chemistry.[19]

$[Ir^{III}(Cp^*)(H_2O)_3]^{2+}$ forms dinuclear complexes, in common with other piano-stool complexes,[20] and we believe that a related structure forms a key part of the reaction mechanism (Fig. 4). Here, two molecules of $HCOO^-$ form a bridge between two Ir^{III} centres with the remaining position being occupied by a bridging hydroxo ligand. β-Hydrogen elimination releases CO_2 and leaves a three-centre, two-electron bond which incorporates the hydride between the two Ir^{III} centres. It is this hydride that functions as the reducing agent.

This simple complex had relatively straightforward catalytic properties. For instance, cyclic aldehydes were reduced faster

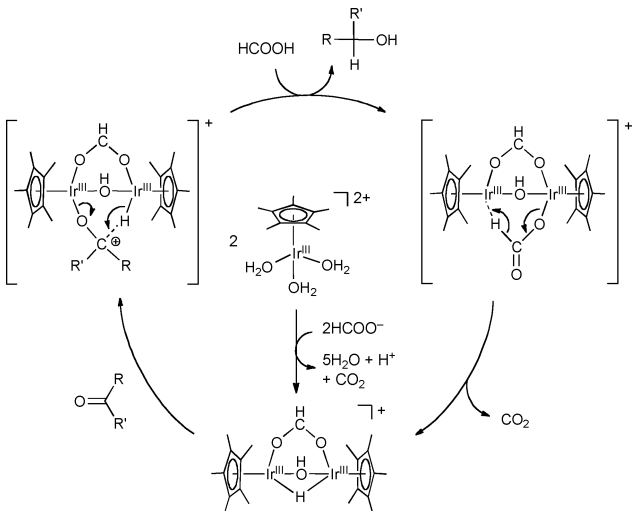

Fig. 4 Proposed mechanism for transfer hydrogenation by Ir^{III} pentamethylcyclopentadienyl (Cp*) complexes.[18]

than linear aldehydes and all aldehydes were reduced faster than ketones.

Phosphorous ligands were revived in 2007 by Frost and coworkers who conducted a study on a wide range of Ru^{II} complexes in water or mixtures of water and methanol (Fig. 5).[21] These complexes included a labile chloro ligand, one of three types of aromatic π-acceptor ligand and one or two 1,3,5-triaza-7-phosphaadamantane (PTA) ligands. PTA ligands had previously been successfully employed by Darensbourg and Joó in biphasic transfer hydrogentation.[22,23]

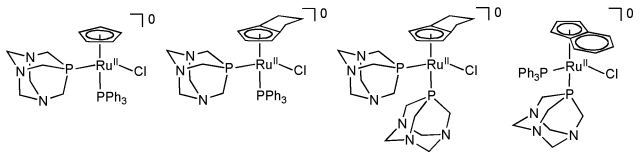

Fig. 5 A library of Ru^{II} complexes. Reported by Frost and coworkers.[21]

The Ru^{II} complexes were tested for their ability to reduce α-β unsaturated aldehydes and the wide range of complexes demonstrated a variety of behaviours, not easily attributable to any one feature. For instance, hydride exchange with CD_3OD is not observed for $[Ru^{II}(Cp)(PTA)_2(H)]$ (Cp = cyclopentadienyl) though it is observed with the closely related $[Ru^{II}(Cp)(PTA)(PPh_3)(H)]$. Indeed, the authors' conclusions sum up the paper by saying that the conversions and selectivity were dependent on the precise combination of ligands, substrate and pH.

Type III

In 2003, we introduced the bipyridine (bpy) ligand to aqueous transfer hydrogenation complexes by incorporating it into an Ir^{III} aqua catalyst bearing a Cp* ligand, $[Ir^{III}(Cp^*)(bpy)(H_2O)]^{2+}$ (Fig. 6).[24] Bpy ligands have well known functions: they act simultaneously as σ-donor and π-acceptor ligands, have significant steric properties and even trivial modifications allow improvements in performance.[25] As before, we included the labile aqua ligand to perform the function of a vacant site for easy substrate docking. Whilst the aromatic group functions primarily

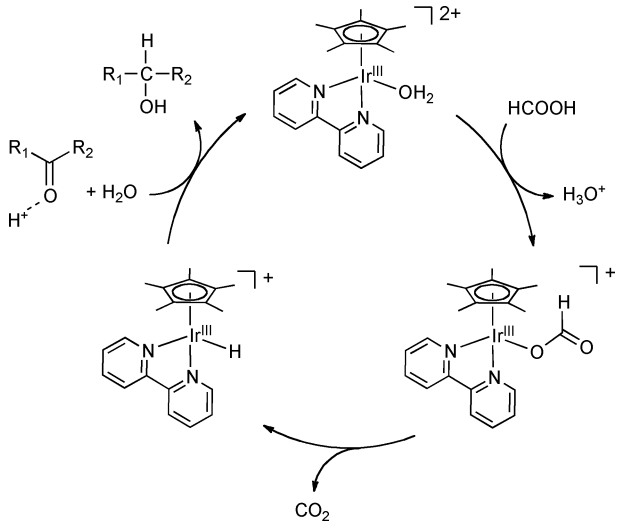

Fig. 6 Proposed mechanism for transfer hydrogenation by Ir^{III} catalysts bearing pentamethylcyclopentadienyl (Cp*) and bipyridine (bpy) ligands.[24]

as a π-acceptor, we also presumed the bulky methyl substituents contributed to the steric environment of the Ir^{III} complex. A further advantage of the aromatic π-acceptor ligand is that β-hydrogen elimination is promoted by a ring slippage mechanism from η^6 to η^4 coordination, as suggested by the crystal structure of the formate adduct of a related Ru^{II} complex (Fig. 7).[26]

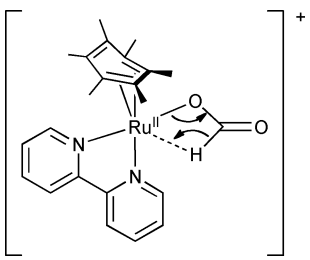

Fig. 7 β-Hydrogen elimination promoted by ring slippage and η^4 coordination.[26]

$[Ir^{III}(Cp^*)(bpy)(H)]^+$ was particularly notable for two reasons. Firstly, it demonstrated a very marked dependence on pH when performing transfer hydrogenation reactions. Secondly, the catalyst was remarkably stable, so much so that we were able to grow crystals and determine the first crystal structure of a highly active catalyst for aqueous transfer hydrogenations.

As mentioned, the behaviour of $[Ir^{III}(Cp^*)(bpy)(H_2O)]^{2+}$ was pH-dependent, being significantly more active at low pH than high pH, with the peak of activity being observed at pH 2.0. Although the hydride is unusually stable, at pH < 1.0 it can be protonated to form H_2, thereby breaking the catalytic cycle. This also has the additional consequences of wasting one equivalent of HCOOH and simultaneously raising the pH. The reduction of activity at high pHs can be rationalised by considering that, at pH > 6.6, the aqua ligand is deprotonated to a hydroxo ligand, which is significantly less labile and thus less able to act as a vacant site.

The hydride intermediate is interesting in itself as it was stable enough to be isolated and crystallised as the PF_6^- salt. This great stability is attributed to a significant protic character, in other words, the hydride moiety has donated much of its electron density to the Ir^{III} centre making it significantly less reactive than conventional hydrides. Such behaviour was evidenced by H^+/D^+ exchange in D_2O, with faster exchange occurring at lower values of pD. This was an occasion that such a stable, protic hydride complex had been observed and isolated. We have since made use of this behaviour in some of our most significant advances.[18–20]

We were also able to demonstrate that the transfer hydrogenation reaction required carbonyl activation to proceed. When the reaction was performed in methanol, thereby reducing the availability of protons, no reaction was observed until trifluoroacetic acid was added. Furthermore, carbonyl compounds activated by α-electron withdrawing groups were more reactive than those without such groups. As might be expected for such a complex system, the exact ratios of substrate : catalyst : HCOOH required significant optimisation to realise the highest possible efficiency.

In 2010, a related Ru^{II} system was reported by Fischmeister, Renaud and coworkers (Fig. 8).[27] In this case, the bpy ligand was replaced by a NH-bridged pyridine ligand, which is reported to be more soluble than bpy or phenanthroline. Four aromatic π-acceptor ligands were used to generate a library of four complexes.

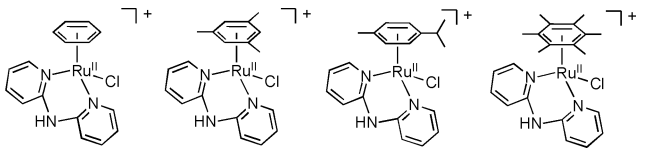

Fig. 8 A library of catalysts bearing a NH-bridged pyridine ligand. Reported by Fischmeister, Renaud and coworkers.[27]

Type IV

In 2004, aqueous transfer hydrogenation catalysts were developed by Xiao and coworkers that made use of diamine ligands. They reported the development of a tosylated 1,2-diphenylethylenediamine (Ts-DPEN) system[28,29] that used chloro-bound Ru^{II} and *p*-cymene as the aromatic π-acceptor ligand. Notably, reactions performed in water were considerably faster than those performed in a common HCOOH-NEt_3 azeotrope.

This system also demonstrated pH-dependence in the reduction of acetophenone. There was barely any activity below pH 3.5, followed by a steady increase in reaction rate from pH 4.8 up to pH 5.2 with the rate levelling off thereafter. This behaviour was partly attributed to a requirement for $HCOO^-$ as the hydrogen donor. The Ts-DPEN ligand also appeared to be less sensitive to high pHs than bpy, which was ascribed to the higher basicity of the diamine ligand.

Interestingly, Xiao and coworkers proposed that the increase in reaction rate upon increasing pH was not simply the result of an increasing concentration of $HCOO^-$ but also resulted from the suppression of competing pH-dependent reaction paths. This proposal was based on an increase in enantioselectivity with increasing pH, accompanied by a concomitant colour change from yellow to orange.

The two pathways were proposed as shown in Fig. 9. At high pH, the cycle follows the conventional pathway. As mentioned above, this cycle involves simultaneous coordination of the substrate to the hydride and amine moieties. At low pHs, however, one of

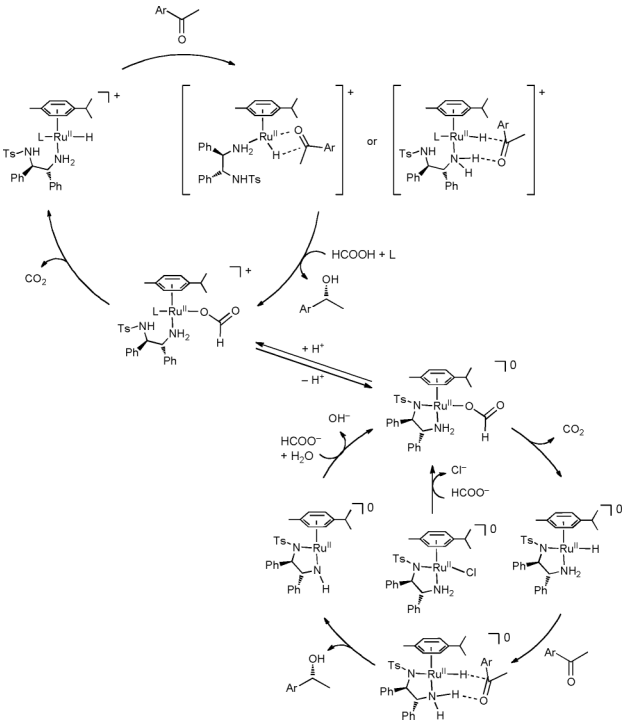

Fig. 9 Competing, pH-dependent catalytic cycles for asymmetric transfer hydrogenation. The authors propose that L may be a water molecule.[28,29]

the amines is protonated, ultimately being replaced by a labile, possibly aqua, ligand. In this case, the substrate binds directly to the Ru^{II} centre, resulting in slower activation and reduced enantioselectivity.

Xiao and coworkers later developed this system to study the behaviour of a tosylated cyclohexanediamine (Ts-CYDN) system.[30] This time, all three metal centres of the catalytic series were tested, as well as the Cp* and *p*-cymene aromatic π-acceptor ligands. In this case, the Rh^{III} and Ir^{III} centres were coordinated to a Cp* ligand and the Ru^{II} centre was bound to a *p*-cymene ligand, though this difference was not accounted for.

In 2005, Süss-Fink and coworkers reported the synthesis of a simple library of Ru^{II} transfer hydrogenation catalysts. The library was divided into complexes that bore either simple *trans*-1,2-diaminocyclohexane ligands or *N*-tosylated diamine ligands (*N*-tosyl-*trans*-1,2-diaminocylohexane). Within each division, the complexes made use of one of four different aromatic π-acceptor ligands. Transfer hydrogenation of acetophenone in water was used to probe the effects of these variations.[31]

This study found that all of the Ru^{II} complexes were catalytically active but the library allowed comparisons of certain ligand effects. Firstly, *N*-tosylated complexes were more active and more selective than simple complexes. Secondly, aromatic substitution effects were also noticeable as hexamethylbenzene (HMB) was more active than simple benzene, which was in turn more active than methyl benzoate. No differences between chloro and aqua ligated complexes were found, leading the authors to propose that the chloro ligands hydrolyse to aqua ligands under the reaction conditions.

The authors attributed the effect of aromatic substitution to two causes. Firstly, the greater activity of HMB over benzene can be justified in terms of a CH/π attraction model, where hydrogen bonding is facilitated between the protons of the HMB methyl groups and the π system of the substrate.[32] Secondly, electron donating groups would be expected to stabilise the η^4 intermediate, originally proposed in our mechanism for the action of $[Ru^{II}(HMB)(bpy)(H_2O)]^{2+}$.[26]

The proposal of the catalytic mechanism is shown in Fig. 10. The key steps are ring slippage to generate the hydride, followed by simultaneous binding of the substrate to the hydride and amine hydrogen as an intermediate step before reduction. The rate-determining step has not been elucidated.

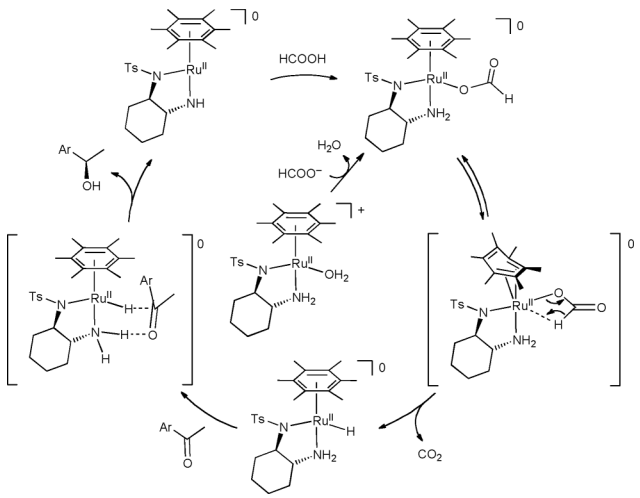

Fig. 10 Proposed mechanism for transfer hydrogenation by Ru^{II} complexes bearing hexamethylbenzene (HMB) and *N*-tosylated diamines.[31]

This system also showed pH-dependence. The maximum activity was observed at pH 9.0 demonstrating that $HCOO^-$, rather than HCOOH, is the hydrogen donor in this case. Enantioselectivity, however, was not dependent on pH.

In 2006, a diamine ligand was employed in a slightly modified manner by Wills and coworkers.[33] They tethered the diamine ligands directly to the aromatic π-acceptor ligands to prevent rotation of the aromatic ligand and improve the stability of the catalyst.[34] Their tethered catalyst was able to achieve very high conversions with high enantiomeric excesses. Catalyst loadings were in line with that of Xiao's systems, achieving ratios of 1000 : 1 to 10 000 : 1 and enantiomeric excesses of 99.5%.

In 2007, Süss-Fink produced a rich library of Ru catalysts, bearing variations in aromatic π-acceptor ligand and sulfonated diamine ligand (Fig. 11). All compounds were air and water stable and able to reduce aryl ketones in water.[35]

This study was extensive and therefore enabled the elucidation of important properties. It was found, for instance, that use of the rigid cyclohexane-bearing diamines resulted in higher enantioselectivity than the use of the more flexible pyrollidine-bearing ligands. This difference was more pronounced for more rigid substrates. Whilst changing from cyclohexane-type to pyrrolidine-type made little difference to the turnover frequencies (TOFs) for each particular substrate, there were large differences in TOFs between different substrates. Specifically, the more flexible substrates had higher TOFs than the more rigid substrates.

All systems were pH-dependent in terms of TOF, with the highest conversions at pH 9.0. pH-Dependency was not observed

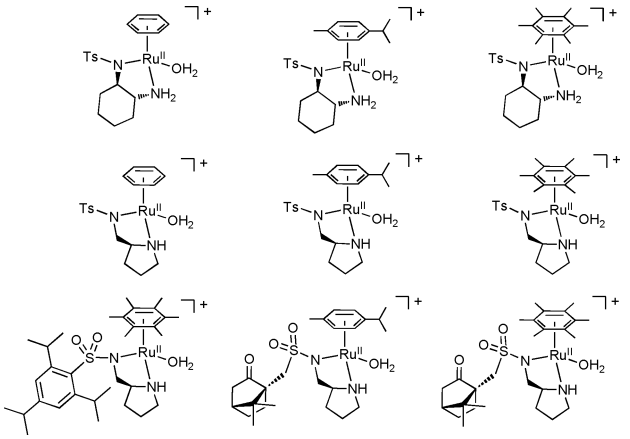

Fig. 11 Library of sulfonated diamines. Reported by Süss-Fink and coworkers.[35]

in the enantioselectivities, suggesting only one reaction mechanism across the pH range.

Another interesting property was that all substrates produced the *R*-enantiomer on reduction, regardless of the chirality of the diamine ligand. This behaviour was explained in terms of CH/π interactions between the aromatic π-acceptor ligand of the Ru^{II} complex and the phenyl moieties of the substrates.

In 2009 and 2010, Carreira and coworkers reported the effect on transfer hydrogenation catalysis of fluorinated Ts-DPEN ligands (Fig. 12).[36,37] The first catalyst was used for the transfer hydrogenation of cyano- and nitro-alkenes. The reaction was conducted at pH 2.0 to reduce side reactions, though no other pH-dependency was reported. The fluorinated ligands resulted in improved selectivity and reactivity, in contrast to previous fluorinated diamine systems studied in organic media.

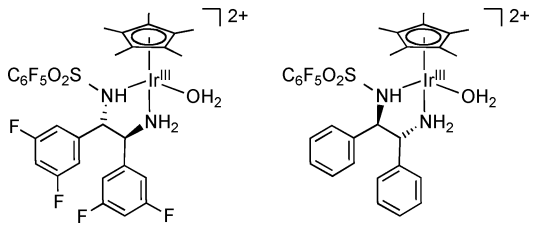

Fig. 12 Fluorinated Ir^{III} catalysts. Reported by Carreira and coworkers.[36,37]

Their second, closely related, system was used for transfer hydrogenation of α-activated aryl ketones. In this study, the Ts-DPEN was no longer bearing fluorine substituents on the phenyl moieties, though no comment was made on this change. In common with most of the systems studied here, the catalyst was air stable, water-soluble and functional at ambient temperatures.

A range of α-substituted acetophenones was tested and trends examined. Although aryl substituents made little difference to TOFs, heterocyclic ketones were particularly good substrates. Substrates bearing bulky substituents in the *para* position demonstrated enhanced selectivities. Whilst α-cyano aryl ketones were reduced at pH 3.5, α-nitro aryl ketones had to be reduced at pH 2.0 to reduce side reactions. This ability to reduce side reactions by a change in pH is a useful demonstration of the benefits of pH-dependency in aqueous media.

Conclusions

Although chemistry often requires the use of dangerous reagents in toxic organic solvents, the research discussed in this review shows how we can develop our chemistry to use mild reagents for transformations in water. These innovations demonstrate the importance of advancing homogeneous catalysis so we can synthesise challenging molecules whilst reducing harmful consequences both to ourselves and to our environment. By means of aqueous transfer hydrogenation, we are now able to perform more efficient reactions, without the need for explosive hydrogen, whilst using nature's favourite solvent. As the development of catalysts for benign chemistry advances, so will the harmful impact of our industry recede.

Acknowledgements

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