

Outer sphere hydrogenation catalysis†

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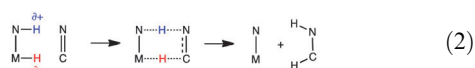
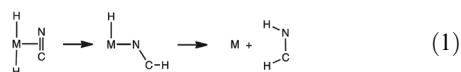
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In the title catalysts, the substrate, typically a ketone, imine or N-heterocycle, remains in the outer sphere (OS). The catalyst transfers hydride and a proton to the unbound substrate either by a concerted or by a stepwise path. These include catalysts not always considered together, such as Bullock's ionic hydrogenation catalysts, bifunctional catalysts in the tradition of Shvo and Noyori and Stephan's frustrated Lewis pair catalysts. By omitting the oxidative addition, insertion and reductive elimination pathways of conventional inner sphere (IS) catalysts, these OS pathways are in principle equally open to inexpensive metals and even nonmetal catalysts. These OS pathways lead to useful selectivity properties, particularly Noyori's asymmetric catalysis, but much more remains to be done in this rapidly developing field.

Introduction

The majority of homogeneous hydrogenation catalysts operate by an inner sphere (IS) mechanism.¹ In this case, an unsaturated organic substrate binds directly to the catalyst, typically by π -bonding between the C=X double bond and the metal (X = C, N, O). Subsequent insertion, elimination and H₂ oxidative addition steps complete the cycle (eqn (1)). In outer sphere (OS) catalysts, in contrast, the substrate does not bind to the metal

but H⁺ and H[−] are instead transferred, either together or stepwise, from the catalyst to the unbound substrate. Eqn (2) shows a common case of OS catalysis where an adjacent NH acts as the proton donor. The implications of OS catalysis, currently of rising importance, are discussed in this review.



The OS (H⁺ + H[−]) transfer mechanism has been suggested for three classes of catalyst not always considered together. (1) Ionic hydrogenation catalysts, typically based on Mo and W

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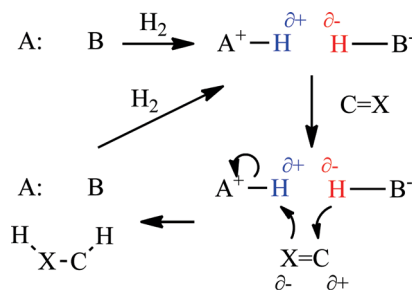


Fig. 1 General reaction pattern.

hydrides, acting together with a variety of strong Brønsted acids as the proton donor.² (2) Bifunctional catalysts in the tradition of Shvo and of Noyori,^{3,4} typically based on Ru complexes that contain both proton donor sites and hydride donor sites. (3) Frustrated Lewis pair (FLP) catalysts, typically based on bulky main group pairs such as NR_3 and Ar_3B . Heterolytic H_2 activation generates an $[\text{Ar}_3\text{BH}][\text{HNR}_3]$ ion pair that acts as $(\text{H}^+ + \text{H}^-)$ transfer agent.^{5–9} Fig. 1 illustrates the general pattern in OS hydrogenation.

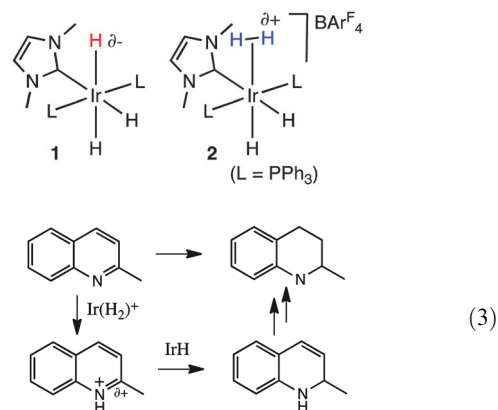
While all three classes are of mechanistic interest, Noyori catalysts have also been of great practical use for the catalytic asymmetric reduction of ketones,⁴ an important problem in organic synthesis. By the early 2000s, this had focused attention on the Ru catalysts rather than the ionic hydrogenation class. With the perspective afforded by the passage of time, we can now better appreciate the mechanistic analogies across the whole series. In each case, we have a frustrated proton–hydride pair, consisting of a proton donor A–H and a weak hydride donor H–B pair, where A is an electronegative element such as N or O and B is an electropositive element such as a d-block metal or boron. These are frustrated in the sense that they do not exclusively react to form H_2 , as $\text{CaH}_2 + \text{H}_2\text{O}$ would do, for example. They tend instead to form a dihydrogen bond $\text{A}-\text{H} \cdots \text{H}-\text{B}$, an attractive proton–hydride interaction with a bond strength comparable with that of traditional hydrogen bonds.¹⁰

Ionic hydrogenation

Ionic hydrogenation, initially stoichiometric,^{11,12} but later² catalytic, requires a combination of a metal hydride and acid, such as $\text{CpW}(\text{CO})_3\text{H} + \text{HOTf}$, leading to initial formation of a protonated form that seems to be a dihydride^{12b} but a dihydrogen complex $[\text{CpW}(\text{CO})_3(\text{H}_2)]^+$ OTf may be in equilibrium with it. Such complexes are excellent proton donors^{13,14} and, following proton transfer to the $\text{C}=\text{X}$ substrate, the carbocation center ($^+\text{C}-\text{XH}$) of the resulting protonated substrate abstracts hydride from $\text{CpW}(\text{CO})_3\text{H}$ to complete the hydrogenation. If it involves a single molecule of the complex, the process necessarily involves stepwise rather than concerted $(\text{H}^+ + \text{H}^-)$ transfer. The protonated complex, whether $[\text{L}_n\text{M}(\text{H}_2)]^+$ or $[\text{L}_n\text{M}(\text{H})_2]^+$ can only act as a proton donor and the hydride donor, neutral $[\text{L}_n\text{MH}]$, is only formed after proton transfer. Kinetic studies for the $\text{CpW}(\text{CO})_3\text{H}$ case by Bullock, Norton and their coworkers, suggest a pre-equilibrium protonation of the complex is followed by proton transfer to substrate, then rate-determining hydride transfer.^{12c}

Irreversible adduct formation between the metal and the conjugate base of the acid is avoided by having an acid such as TfOH with a noncoordinating or reversibly coordinating anion. Magee and Norton¹⁵ introduced an enantioselective reduction of an iminium cation with $\text{CpRu}(\text{chiraphos})\text{H}$ as hydride donor and H_2 as the reductant to regenerate the active hydride, and Bullock¹⁶ has recently extended his work to the acid-catalyzed dehydration of vicinal diols to give aldehydes that are subsequently hydrogenated to the monohydric alcohols. In the main group, combinations of $\text{R}_3\text{SiH} + \text{acid}$ give stoichiometric ionic hydrogenation.¹⁷

A recent ionic hydrogenation¹⁸ involves reduction of 2-methyl quinoline and acridine by catalyst **2** formed from **1** and $\text{H}[\text{B}\{3,5-(\text{CF}_3)_2\text{C}_6\text{H}_3\}_4]$. In each case the heterocyclic ring but not the carbocyclic ring(s) are reduced. DFT calculations suggest that the intermediacy of dihydrogen complex **2** with stepwise proton transfer to the N lone pair of the heterocycle, followed by hydride transfer to the 2-position in the quinoline but to the 4-position for acridine (eqn (3)). The catalysts are very active, operating at near-ambient conditions with high TOF. Contrary to the usual case of having faster catalysis with lower steric hindrance, unsubstituted pyridine requires harsher conditions, for reasons discussed below.



Shvo and Noyori catalysts

Moving to the second class,^{19–21} the Shvo³ and Noyori⁴ catalysts incorporate both AH and BH sites within the same complex. The proton donor site is typically a ligand OH or NH unit adjacent to the metal, and the hydride donor is a metal hydride, typically Ru–H. The two sites being adjacent and coupled electronically facilitates concerted $(\text{H}^+ + \text{H}^-)$ transfer (Fig. 2).

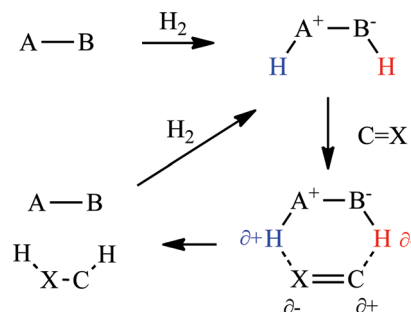
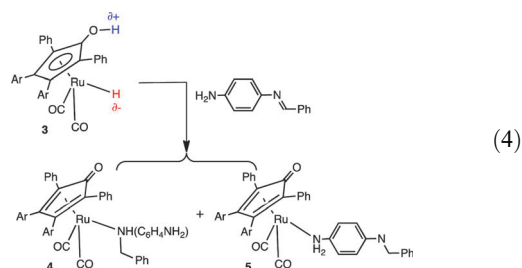


Fig. 2 Noyori catalyst mechanism.

The Shvo catalyst (**3** in eqn (4)) has attracted detailed mechanistic study, notably by the groups of Bäckvall and of Casey.^{22–24} The key question was whether the reaction really is OS. Casey and coworkers saw significant H/D isotope effects for both RuH and OH sites, consistent with concerted ($H^+ + H^-$) transfer; DFT calculations also supported this conclusion with the OS mechanism being favored by at least 10 kcal mol^{−1}.²⁵ A mechanism involving η^5 - to η^3 -slip of the cyclopentadienyl and inner sphere coordination of the substrate C=X bond was hard to exclude, however. An elegant trapping experiment by Casey's group probed the problem.²⁶ On the IS hypothesis, the C=N bond of the substrate imine in eqn (4) is reduced to amine while the imine nitrogen remains bound. In that case the coordinatively inert Ru should retain that same nitrogen to give **4** as the final product. If OS reduction occurs, then nothing should prevent binding at the alternative $-NH_2$ binding site of the substrate from giving product **5** as well. In an experiment run below -20°C in toluene, a 50:50 kinetic mixture of **4** and **5** was found, consistent with the OS path. On warming to 25° , where kinetic lability has already set in, a thermodynamic 94:6 ratio was found (eqn (4)). Bäckvall²² argued that Ru migration across the arene ring could reconcile the results with the IS hypothesis and so some doubt still remained. Casey²⁴ responded with a study of a saturated substrate with results again strongly supporting the OS mechanism. This important point now seems to be definitely established for imines and, until counter-examples are found, by inference for all the substrates and catalysts in this class.



Moving to the Noyori catalysts, the AH and BH sites being combined within the same structure allows them no conformational freedom. The transition state for concerted ($H^+ + H^-$) transfer (Fig. 2)²⁷ has much greater rigidity than for cases in which A and B are unconnected, conformationally mobile or where stepwise H^+/H^- transfer takes place. This rigidity allows efficient transfer of the chiral information to differentiate the diastereomeric transition states involved for a substrate such as $RR'C=O$. A judicious ligand choice can give an extremely high level of asymmetric induction. Fig. 3 shows the hydrogenated form of typical catalysts. With the key NH sites methylated, however, all activity is lost.^{28a} In one case,^{28b} asymmetric OS and IS mechanisms were followed depending on the presence of acid or base.

The hydrogenation step is reversible for many of the OS catalysts, so that transfer hydrogenation is an alternative means of recycling the catalyst, avoiding H_2 . Isopropanol is a classic ($H^+ + H^-$) donor because of its high driving force for production of acetone, a byproduct that is easily removed. Transfer hydrogenation has been successfully employed in

reduction of ketones, although the reversibility of the process with $i\text{-PrOH}/\text{Me}_2\text{CO}$ militates against obtaining high enantiomeric excesses, since the undesired 50:50 thermodynamic enantiomer ratio is necessarily slowly approached under reversible conditions. Formic acid, as a 1:1 mixture with NEt_3 , is a better ($H^+ + H^-$) donor since the resulting loss of CO_2 makes the process irreversible. For example, benzils, ArCOCOAr , were successfully reduced in this way to the *dl* diols, ArCH(OH)CH(OH)Ar , with up to 99% ee.²⁰

Many other reactions have been carried out asymmetrically with Noyori catalysts.⁴ Chloromethyl ketones can be reduced to the asymmetric alcohols; base treatment then gives the chiral epoxides with retention of configuration at the carbinol carbon. If H_2 is replaced by a nucleophile such as dimethyl malonate, asymmetric addition of the Nu-H takes place across the C=C bond of a suitable Michael acceptor such as 2-cyclopentenone or a nitroalkene; ees in the 90–98% range were achieved. To show practical utility a gram scale synthesis was carried out with 95% ee and 94% yield involving dimethyl malonate and an aromatic nitroalkene to give an intermediate in the synthesis of the anti-inflammatory neuroprotective drug, Rolipram. The structure of the η^6 -arene in the arene ruthenium catalysts had a big effect on the ee obtained, C_6Me_6 being preferred. The malonate is believed to bind as Ru-CH(COOMe)_2 , with the accompanying proton binding at the adjacent N; an OS mechanism is envisaged for the subsequent reaction with the Michael acceptor.

Once the hydride transfers to the substrate from the metal in a Noyori or Shvo catalyst, the remaining metal center is left as an unsaturated 16e fragment. Any factors stabilizing this fragment help the hydride depart. This role is played by the deprotonated amine adjacent to M, which acts as a π -donor and partially compensates for the unsaturation (eqn (5)). Stabilization of coordinative unsaturation by an adjacent heteroatom lone pair along with relief of steric pressure is well documented.²⁹

Hydrogen activation can convert the unsaturated form of the catalyst back to the 18e starting complexes (Fig. 3). This can happen by coordination of H_2 to the unsaturated metal to give an H_2 complex. These are good proton donors, and so the adjacent base can deprotonate the H_2 to restore the original structure for the next cycle of catalysis (eqn (5)). The enhanced acidity of bound H_2 arises from the contrast between the relatively weak binding in M-H_2 versus the very much stronger binding of the hydride left behind after proton transfer. This

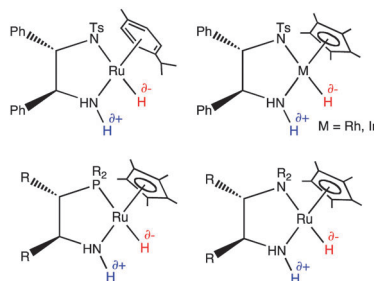
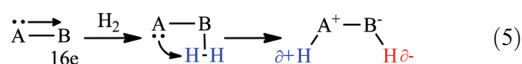


Fig. 3 Some Noyori catalyst types.

provides a high driving force for H^+ transfer even to a weak base such as the ketones typical in ionic hydrogenation.



Morris *et al.* reported a series of $Cp^*Ir(NHC)$ and $Cp^*Ru(NHC)$ complexes that hydrogenate ketones by a Noyori mechanism.³⁰ Hydricity of $M-H$ is important because an otherwise analogous cationic Ir complex was inactive. Nitriles were reduced to the saturated amines with the Ru catalyst.³¹ Other ketone reduction catalysts have structural features analogous to the bifunctional catalysts discussed above and may therefore go by an OS pathway.³² Sola, Oro and coworkers see hydrogenation of an aromatic imine by an $Ir(III)$ complex. The initially formed amine binds in η^6 -fashion to iridium and the adduct mediates OS reduction of the imine, benefiting from the NH bond of the coordinated amine as proton donor.³³

Frustrated Lewis pair catalysts

In the third class, an FLP pair such as a borane of type BR_3 and a Lewis base of type AR_3' ($A = P$ or N) reacts with hydrogen to give a transient ion pair, $[R_3B-H][H-AR_3']$, that transfers ($H^+ + H^-$) to the substrate. The acid and base sites can either combine in the same molecule or remain separate.^{8,9} Spectroscopic and computational work shows the importance of inter and intramolecular phosphine borane interactions in FLPs.³⁴ Concerted addition was shown to be possible by DFT calculations³⁵ and heterolytic cleavage of an N-heterocyclic carbene (NHC) borane adduct to an FLP was also shown to have a low energy barrier.³⁶ A frontier orbital analysis showed the importance of polarization of the H_2 by the FLP in facilitating the $H-H$ cleavage.³⁷ This was emphasized by showing that H_2 could be cleaved in a sufficiently strong electric field even without new bonds being formed to H^+ and H^- .³⁸

For catalysis, the acidic and basic sites of the FLP pair must avoid deactivation by irreversible adduct formation as would occur for NH_3 and BH_3 combining to give the catalytically inert H_3N-BH_3 . Unless any such adduct formation is reversible, the Lewis acid-base pair will lose the ability to activate H_2 and thus fail to act as a catalyst. Steric bulk is typically involved in preventing this deactivation, or at least promoting its reversibility.

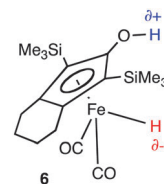
In a somewhat related case, Miller, Labinger and Bercaw have proposed an FLP activation of H_2 by a ligand-centered boron Lewis acid site in the stoichiometric hydrogenation of CO by a Re complex.³⁹

Inexpensive metal catalysts

With increasing prices for precious metals, an urgent goal is their replacement by the inexpensive metals, Mo, W and the 1st row transition metals. Such catalysts are also less likely to leave toxic residues.^{2,40} The precious metals have provided extremely useful catalysts, many of which operate by IS mechanisms *via* oxidative addition and reductive elimination (OA/RE). As

2e processes, OA and RE are appropriate for precious metals because they have stable oxidation states two units apart (*e.g.*, $Ir(I)$, (III) and (V)). In contrast, first row transition metals tend to have stable oxidation states only one unit apart ($M(I)$, (II) and (III) for Cu and Ni).

OS hydrogenation requires no change of oxidation state during the cycle. In principle, this should open the field to first row transition metals and even to main group elements. Indeed the known main group FLP catalysts confirms the potential in this area; in addition, Shvo-type catalysts include one (6) based on a first row transition metal, iron.^{41,42} Morris *et al.*⁴³ also have a series of Fe catalysts that adopt an OS mechanism. For the moment the efficiency of the first row and main group catalysts is limited, but the relative youth of the field gives hope for future progress. First row metals with their lower $M-H$ bond strengths and greater tolerance for coordinative unsaturation may even be better suited than heavier metals to act as hydride donors. Bullock² has emphasized the suitability of inexpensive metals for ionic hydrogenation.

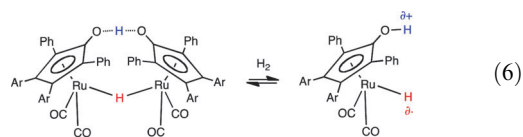


One barrier to progress is the greater stress laid on high efficiency catalysts that have the potential for immediate application *versus* the progressive development of inexpensive catalysts of much lower initial efficiency. If turnover activity per unit cost were adopted as a 'green' metric in comparisons, however, inexpensive catalysts would look far more attractive.

Nature of the catalyst

The pK_a data for the proton donor, AH , can aid in catalyst design and ligand tuning. The hydride donor function is quantified in terms of hydricity, both thermodynamic and kinetic.^{44,45} From equilibrium electrochemical and calorimetric data, Rakowski-Dubois, DuBois, and co-workers report a thermodynamic hydricity range of well over 30 $kcal\ mol^{-1}$.⁴⁶ As a broad guide, a hydride is expected to become more hydridic when located *trans* to a high *trans* effect ligand, a situation that also facilitates H^- transfer since a vacancy is more easily accessed in such a site.

Since the hydrogenated and dehydrogenated catalyst are both present together, formation of an adduct between them is in principle possible, as in the Shvo catalyst (eqn (6)). This dimerization is clearly reversible with H_2 for catalysis to occur. Additional steric bulk may promote dissociation and no such dimerization is seen for the Noyori catalysts.



Main group bifunctional catalysts such as $(Me)_2P(CH_2)_2B(C_6F_5)_2$ hydrogenate enamines and imines, so H_2 activation and ($H^+ + H^-$)

transfer to the substrate are both possible without a d-block metal.⁹ Relatively few metals have yet been reported as active; these include Mo, W, Ir and predominantly, Ru. This may be a legacy effect in that studies tend to be carried out on metals already shown to be active. Much remains to be done in expanding the range of applicable metals.

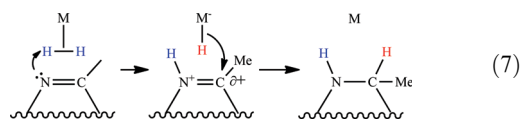
The H⁺ and H[−] donors

A variety of proton donors is seen for OS hydrogenation catalysts. In ionic hydrogenation, these are dihydrogen complexes formed from strong acids. In Shvo and Noyori systems, the proton donors are ligand –OH or –NH groups and for FLP catalysts, the conjugate acids of the bulky base. The substrate is likely to pre-associate with these groups *via* C=X...H–A hydrogen bonds (X=O, N; AH = proton donor). The great majority of hydride donors are hydrides either of a transition metal or of a main group element, typically boron. For pre-association, a nonpolar solvent may favor the formation of hydrogen bonds and indeed toluene seems to be the most common solvent choice.

Substrates

Organic carbonyls are the most common substrates. C=O bonds are highly polar and very suitable to act as (H⁺ + H[−]) acceptors. More importantly, they and their reduction products have only a weak tendency to bind to the metal site. If binding were strong, H₂ activation would be difficult, since H₂ is a rather poor ligand.

OS hydrogenation is therefore less often seen for imines and for N-heterocycles. The N lone pairs of these failed substrates do bind strongly to the metal and can suppress the catalysis. H₂ is sterically small, so by introducing sufficient bulk in the system, we can block the substrate, but not H₂, from the metal and permit catalysis. In a recent case,¹⁸ for example, quinoline blocked the metal site but the much more bulky 2-methyl quinoline did not do so and was successfully reduced by an OS route. Initial protonation of the N lone pair polarizes the C=N bond, decreases the aromaticity of the heterocyclic ring and facilitates H[−] transfer to carbon (eqn (7)). On protonation, the substrate's affinity for H[−] greatly increases.



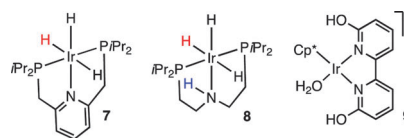
In the hydrogenation of quinoline by Ir(III) hydrides, the IS reaction has been calculated to have a significantly higher energy barrier than the OS reaction. In the IS case the migratory insertion of the quinoline into the Ir–H bond occurs in a substrate that maintains aromaticity.¹⁸ In the case of the hydrogenation of substrates other than aromatics, the OS and IS mechanisms have comparable energy barriers, suggesting that the OS mechanism may occur competitively with the IS.⁴⁷ Bulky aromatic heterocycles are also successfully reduced by B(C₆F₅)₃, where a catalytically active FLP is formed with the

substrate.⁴⁸ Imine reduction with **3** was possible only with a bulky Ph group at nitrogen that prevents direct binding of the N lone pair to Fe.¹⁹

An advantage of OS hydrogenation is its ability to reduce very hindered substrates. Another advantage is its selectivity for polar C=X bonds over C=C bonds.⁴² Noyori catalysts with adjacent AH and BH sites would be expected to favor 1,2-addition to double bonds. This would no longer apply for ionic and FLP catalysts where stepwise (H⁺ + H[−]) transfer would permit 1,4-addition as has been seen for acridine reduction.¹⁸

CO₂ is not at all bulky but relatively hard to reduce. While the molecule as a whole is nonpolar, it contains polar C=O bonds that lend themselves to OS reduction by H[−] transfer to the CO₂ carbon.⁵⁰ The mechanism then typically converts to inner sphere in the sense that the formate ion produced in the H[−] transfer is thought to subsequently bind to the metal.

An important advance by Nozaki *et al.*⁵¹ was the introduction of complex **7** as an extremely active CO₂ reduction catalyst to give HCOOH with TOFs up to 1.5 × 10⁵ h^{−1} and operating by an OS H[−] transfer. The structures of **1** and **7** are obviously related, but in the case of **7** the H[−] transfer occurs first, rather than protonation being needed as for **1**.



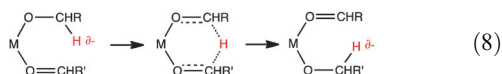
Hazari *et al.* introduced a similar catalyst, **8**, for which DFT calculations suggested that the ligand NH proton is involved in polarizing the CO₂ by an OS interaction.⁵² Fujita, Himeda *et al.* have recently described a water soluble catalyst, **9**, in which H₂ activation is believed to be accelerated by the pendant base effect of a deprotonated OH.⁵³ Although these catalysts are not fully OS, since formate binds to the metal, yet they seem to be OS in the key H[−] transfer.^{50a}

For esters and nitriles, Grey, Pez *et al.* saw hydrogenation with the anionic hydride salts, K[RuH₂L₂L'] (L = PPh₃; L' = cyclometalated L) and plausibly proposed H[−] transfer to the substrate with simultaneous polarization of the C=X bond by the potassium counterion within an ion pair.⁵⁴

Intermediate IS/OS cases

In strict IS hydrogenation, all the chemistry occurs at the metal and the C=X substrate binds in the η²-form (eqn (1)). In the OS case, (H⁺ + H[−]) transfer occurs between the catalyst and the unbound substrate (eqn (2)). An intermediate situation applies in the case of the Meerwein–Ponndorf–Verley (MPV) mechanism of hydrogen transfer catalysis by catalysts such as Al(III). In this case a substrate C=O binds in the η¹-form *via* O and a H[−] transfer occurs from the CH bond of the alkoxide co-reactant, typically O*i*Pr, remote from the metal in the intermediate sphere (eqn (8)). The MPV pathway has been proposed for several transition metal catalysts but is hard to distinguish

experimentally from IS and OS routes, so calculations have taken a central place. For example, hydrogen-transfer from alcohols to ketones with Ir(cod) complexes of aminoalcohols as catalysts was proposed to go by the MPV mechanism on the basis of DFT calculations by Meijer and colleagues.⁴⁹ In a highly effective asymmetric peptide catalyst series based on (arene)Ru complexes, an MPV-like mechanism involved the alkali metal cation deriving from the base needed for activity.⁵⁵ An MPV pathway may easily escape detection because it seems to be considered much less often by workers in the field. Computational work is powerless if a potentially applicable mechanism is not considered.



The MPV mechanism has also been proposed for a number of heterogeneous catalysts, such as MgO, ZrO₂, SiO₂, Al₂O₃ and even solid K₃PO₄.⁵⁶ Certain zeolites can be highly stereoselective OS catalysts, for example in the conversion of 4-*tert*-butylcyclohexanone to *cis*-4-*tert*-butylcyclohexanol rather than the thermodynamically more stable *trans* alcohol.⁵⁷

OS H atom transfer

Outer sphere hydrogenation goes back to the earliest days of homogeneous transition metal catalysis. In 1942, Iguchi looked at the reaction of cobalt cyanide solutions under an H₂ atmosphere originally intended as an inert blanket.⁵⁸ A fast reaction occurred that eventually led to the discovery that the solution catalyzed the reduction of a wide range of compounds, both organic and inorganic. [Co^{III}(CN)₅H]³⁻ was later identified as the main species in solution under H₂,⁵⁹ with an OS transfer of a hydrogen atom to the substrate as the mechanism of hydrogenation.⁶⁰ Styrene, for example, is a good substrate because it can form a stabilized benzylic radical after H transfer. A second H atom transfer from another molecule of cobalt hydride then completes the reduction to ethylbenzene.

Conclusion

Outer sphere hydrogenation provides important advantages not all of which have yet been exploited. In particular, a much wider variety of catalysts involving inexpensive metals should be viable. The analogy between FLP, Shvo–Noyori and ionic hydrogenation catalysts is likely to make for cross-fertilization between these fields, hitherto somewhat isolated from one another. The area has so far shown the most dramatic applications of these catalysts in the current rich development of the Noyori asymmetric hydrogenation, but much remains to be done in this rapidly developing field.

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