

Multiple-Metal Catalysis

Multiple-Metal (De-)Hydrogenation-Catalysed Processes

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Abstract: The use of different metals acting together in a synergistic way allows synthetic transformations that are not achievable by other means. Metal cooperation becomes important in catalytic processes for the synthesis of compounds with sophisticated structures or for difficult transformations. Rational design of multiple-metal-catalysed processes requires that the metal complexes and reaction conditions are compatible, which in general is not straightforward. A key feature for success

found in all systems involving multimetallic processes is catalyst stability. The use of robust metal complexes increases the probability of success in the search for tandem catalytic processes. This microreview is based on the recent and most important findings of multiple-metal-catalysed processes that have involved (de-)hydrogenation reactions. The field constitutes a research area that is full of potential, and it can be foreseen that relevant applications will be described in the near future.


1. Introduction

This microreview reports recent advances in the use of multiple organometallic complexes applied to catalytic reactions involving at least one hydrogenation or dehydrogenation process.^[1–5] There are multiple-metal-catalysed processes in which the hydrogen released in the first catalytic cycle is then used for a catalytic hydrogenation reaction in a second catalytic cycle. The presence of two catalysts based on different metals allows the rational design of tandem processes through the combination of two independent catalytic cycles.^[6,7] The processes allow organic transformations that are not achievable by other means. Although the concept of multiple-metal-catalysed processes

has been known for a long time, it still needs further development and improvement. A number of important transformations are based on combinations of different metal complexes acting in a synergistic way.

Hydrogenation is a basic transformation related to reduction, whereas dehydrogenation, the reverse process, is related to oxidation processes.^[8–10] The combination of both processes constitutes an interesting way of performing oxidation/reduction reaction sequences without the need for molecular hydrogen. This methodology has been widely studied in the case of transfer hydrogenation. In the catalytic version of this process, the hydrogen is abstracted and transferred to another molecule, normally by the same catalyst. Further, more challenging, development of this dual activity involves the use of two or more different metal complexes in the design of multiple-metal-catalysed hydrogenation processes.^[11] In a transfer hydrogenation, the first catalyst will carry out the dehydrogenation and a second catalyst will serve in the transfer of the two hydrogen atoms to the other molecule.

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J. A. Mata received a B.S. in chemistry from the University of Valencia (1997) and completed his Ph.D. with honours at the University Jaume I under the supervision of Profs. R. Llusar and E. Peris in 2002, working on functionalised ferrocenes with nonlinear optical (NLO) properties. He was a postdoctoral fellow at Yale University with Prof. Robert Crabtree (2002–2003) working on rhodium complexes with N-heterocyclic carbene ligands. In 2004 he moved to Toulouse as a postdoctoral fellow at the Laboratoire de Chimie de Coordination (CNRS) with Prof. Rinaldo Poli and worked on atom transfer radical polymerisation (ATRP). He returned to the University Jaume I with the “Ramón y Cajal” program (2005–2008) and became assistant professor of chemistry in 2008 and associate professor in 2010. His research interests are focused on development of new catalysts, design of tandem catalytic processes and immobilisation of molecular complexes on graphene surfaces with applications in supported catalysis.

Other catalytic processes are those requiring the presence of two different metal catalysts. In this case, the presence of the two metals is required in order to complete the catalytic cycle.

The use of multiple catalysts for concatenated multistep processes should allow the simple preparation of compounds with sophisticated molecular structures in one-pot synthesis. A straightforward approach to the design of tandem processes is through the combination of two different metal catalysts. Each catalyst should facilitate a mechanistically independent catalytic cycle. An alternative is the use of heterobimetallic catalysts containing two or more different metals. In both cases synergism or cooperativity between the different metal centres may occur, facilitating a complicated catalytic reaction.^[12] The presence of two metal centres would increase the scope of the reaction exponentially. In nature there are many enzymes that contain two metal ions that operate in a synergistic way in complex biological transformations.^[13] Tandem catalytic cycles similar to those that operate in some enzymes have been described and are discussed below.

Multiple-metal-catalysed processes should be developed for those cases in which a single metal fails to promote a selective or efficient catalytic process. A major drawback in the design of tandem catalytic systems is the requirement for catalyst compatibility and stability in the presence of all of the components of the reaction. The different catalysts should be tolerant under the same reaction conditions and the reaction kinetics should be consistent.

This microreview focuses on hydrogenation/dehydrogenation processes combined with other catalytic transformations performed through the action of multiple catalyst systems (Figure 1). Several examples in which the use of two metal complexes or one heterobimetallic catalyst results in a clear enhancement of catalytic outcome are given. The field constitutes a research area that is full of potential.

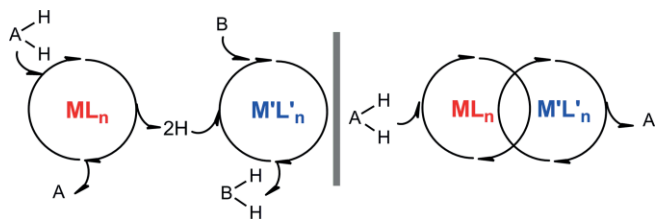
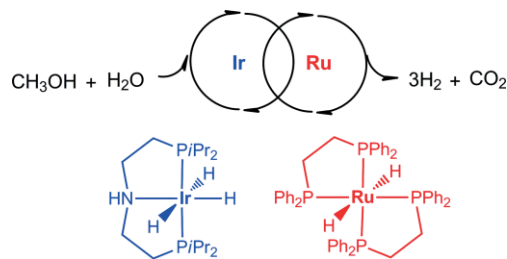


Figure 1. Multiple-metal (de-)hydrogenation-catalysed processes.

2. Dehydrogenation of Alcohols

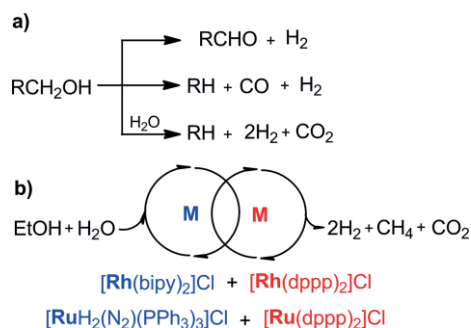
Acceptorless dehydrogenation of alcohols is an interesting green process for the synthesis of ketones, aldehydes, esters and even carboxylic acids, with the concomitant formation of molecular hydrogen.^[14–17] The production of hydrogen from alcohols is highly desirable because they are readily available from the fermentation of biomass. The most effective and intensively studied systems for the dehydrogenation of alcohols are based on ruthenium pincer complexes.^[18,19] In the search for more efficient catalytic systems, an iridium/ruthenium two-component-catalysed process was developed for the genera-

tion of hydrogen from methanol and water under base-free conditions.^[20] The combination of an Ir-PNP catalyst with a Ru hydride complex is an efficient two-component system for producing hydrogen and CO₂ with only trace amounts of CO contamination (Scheme 1). The sequential catalytic process involves the formation of formaldehyde and formic acid. The iridium and ruthenium catalysts interact in a synergistic manner that favours the dehydrogenation of formic acid and allows the reaction to proceed under mild reaction conditions.



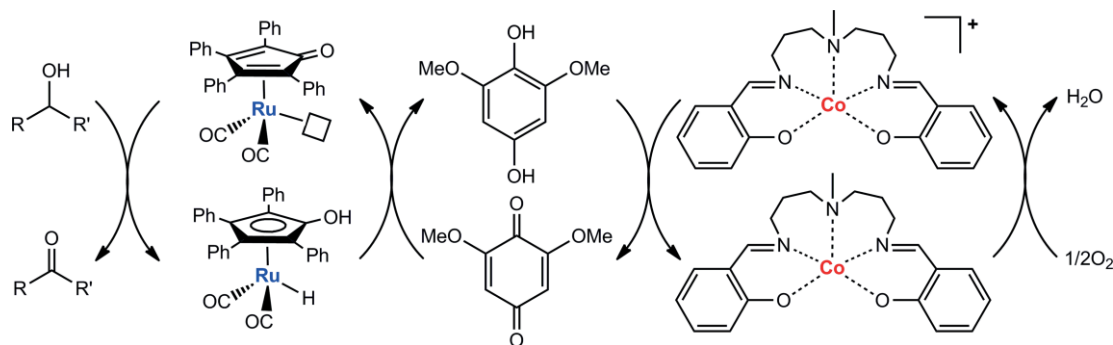
Scheme 1. Dehydrogenation of methanol in the presence of a combination of an Ir-PNP and Ru hydride as a dual catalyst system.

Different strategies for the production of hydrogen from ethanol with the aid of two-component catalytic systems based on well-known rhodium and ruthenium complexes have been described (Scheme 2). The proof of concept was based on the principle of microscopic reversibility, which demands that a catalyst active in hydrogenation should also be active for dehydrogenation. The synergistic effect of two different rhodium or ruthenium catalysts favours the reaction by avoiding decomposition. Removal of CO from a metal centre is achieved by the second metal, thus avoiding catalyst poisoning (Scheme 2).^[21] Hydrogen is obtained at good rates and in good yields through the use of the combination of the Rh catalysts. The mechanism involves the dehydrogenation of ethanol to ethanal through the action of the [Rh(bipy)₂]Cl complex and the decarbonylation through the action of the [Rh(dppp)₂]Cl complex, which does not itself dehydrogenate ethanol. In the case of the ruthenium system, catalytic hydrogen production is particularly improved under irradiation with visible light.



Scheme 2. Alcohol dehydrogenation catalysed by combinations of different metal complexes.

Oxidation of alcohols has been carried out with the aid of a multiple-metal-catalysed system in three catalytic steps performed in one-pot.^[22] The process is reminiscent of biological oxidation of alcohols through the respiratory chain and involves selective electron/proton transfer (Scheme 3). The Shvo ruth-



Scheme 3. Multiple-metal-catalysed system for the dehydrogenation of alcohols, based on the Shvo catalyst and a cobalt-salen-type complex.

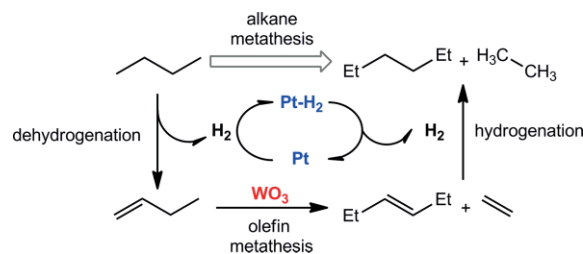
enium catalyst dehydrogenates the alcohol, and the hydrogen atoms are used for the reduction of a quinone into the corresponding hydroquinone. The hydroquinone is re-oxidised by air with the assistance of an oxygen-activated cobalt-salen-type complex. In the net reaction, alcohols plus oxygen are converted into the corresponding ketones and water. The system is very active at 100 °C, giving quantitative yields in short reaction times at catalyst loadings of 0.5 mol-% Ru, 20 mol-% quinone and 2 mol-% Co. The reaction is air-compatible and allows the oxidation of both aromatic and aliphatic alcohols. The three-component system is general and has also been applied in the oxidation of amino alcohols to produce lactams^[23] and in the oxidative coupling or benzylamines and aminophenols to produce benzoxazoles.^[24]

3. Alkane Dehydrogenation/Metathesis

The activation of inert C–H bonds by transition-metal complexes is a major area of interest in organometallic chemistry.^[25–31] The use of metal complexes for C–H activation is particularly interesting for the conversion of lighter alkanes into added-value alkane products, normally in the form of liquid fuels.^[32] The combination of lighter alkanes to afford C9 – C19 *n*-alkanes is an example of the importance of C–H activation and represents a big challenge in the field of energy production. The combination of alkanes to afford *n*-alkanes of different chain lengths is known variously as alkane metathesis, light hydrocarbon upgrading or alkane disproportionation.

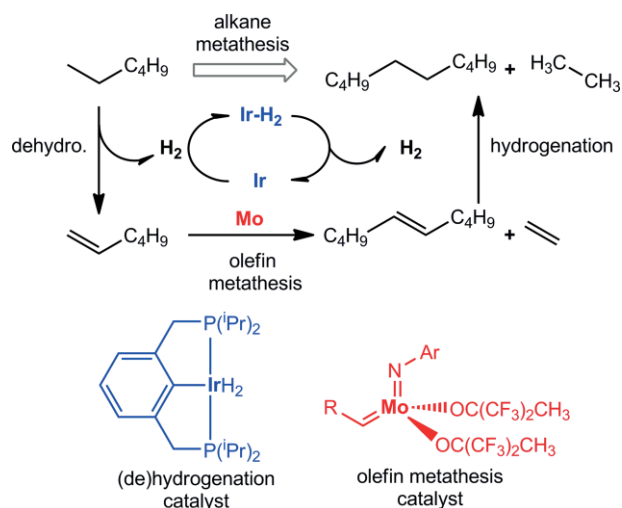
Alkane disproportionation resembles the pioneering work developed in alkene metathesis in which linear alkenes containing three to eight carbon atoms were converted into homologues of shorter and longer carbon chains.^[33] A decade later, Brunett and Hugues developed the first process for alkane disproportionation at Chevron Research.^[34] The process was known as disproportionation of alkanes, and the key point was the use of multiple-metal catalysis. The combination of two different metal complexes, based on platinum and on tungsten, allowed three catalytic reactions to be carried out in a one-pot process. The Pt/ γ -Al₂O₃ catalyst facilitated the dehydrogenation of alkanes and the hydrogenation of alkenes, whereas the WO₃/

SiO₂ catalyst facilitated the alkene metathesis. In a typical reaction, butane is dehydrogenated to but-1-ene, and this is in turn converted into a mixture of hex-3-ene and ethylene by alkene metathesis. Finally, both alkenes are hydrogenated to form *n*-hexane and ethane by the hydrogen released in the first step of the reaction (Scheme 4). In an ideal system, *n*-butane is converted into *n*-hexane and ethane, but in practice a broad distribution of products is obtained, due to isomerisation of the but-1-ene double bond along the chain.



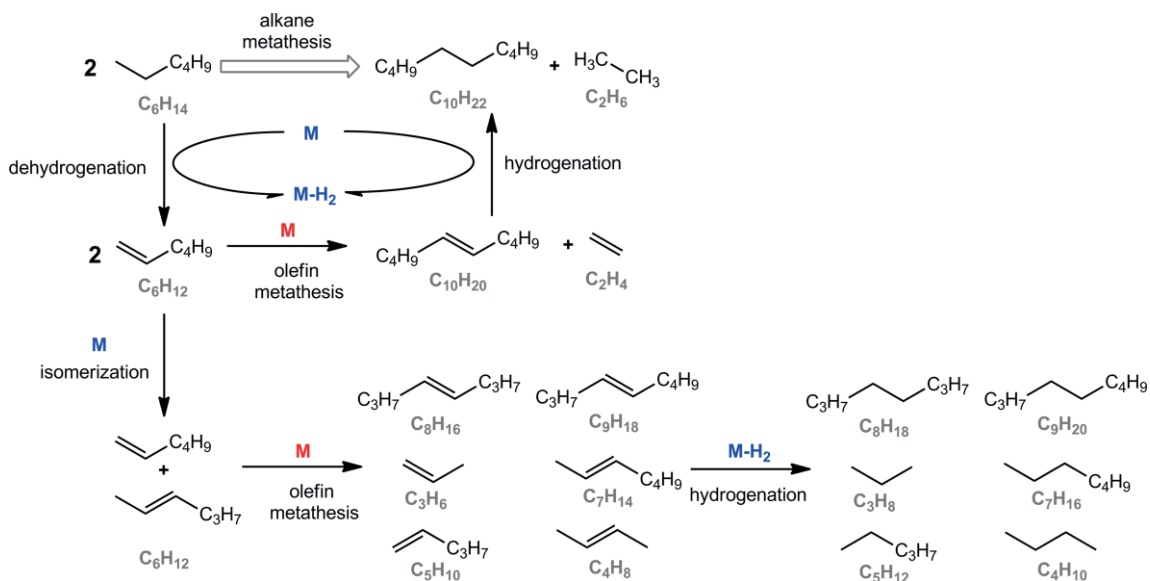
Scheme 4. Alkane disproportionation developed by Brunett and Hugues.

The alkane metathesis proposed by Goldman consists of dehydrogenation of an *n*-alkane at the terminal position, followed by alkene metathesis and then by hydrogenation of the metathesised alkene products, yielding a longer-carbon-chain *n*-alkane and ethane (Scheme 5).^[35] The tandem process is based on the utilisation of two different catalysts. The system requires a (de-)hydrogenation catalyst and an alkene metathesis catalyst. The first combination of metals was that of an iridium pincer catalyst, active in hydrogenation and dehydrogenation, and the Grubbs catalyst, to produce the alkene metathesis. Unfortunately, no reaction occurred because of incompatibility of the organometallic complexes, leading to deactivation of the iridium catalytic species. The main drawback in alkane metathesis is that it requires high temperatures and long reaction times. For these reasons, catalyst stability is one of the major challenges in the development of practical alkane metathesis processes. Alkane metathesis was achieved by use of a pincer iridium complex combined with a Schrock-type catalyst. With these two metal complexes, *n*-hexane was converted into a range of C2 to C15 *n*-alkanes in high yield. Importantly, no branched or cyclic alkanes were detected.



Scheme 5. Alkane metathesis in the presence of an iridium pincer catalyst and a Schrock-type catalyst.

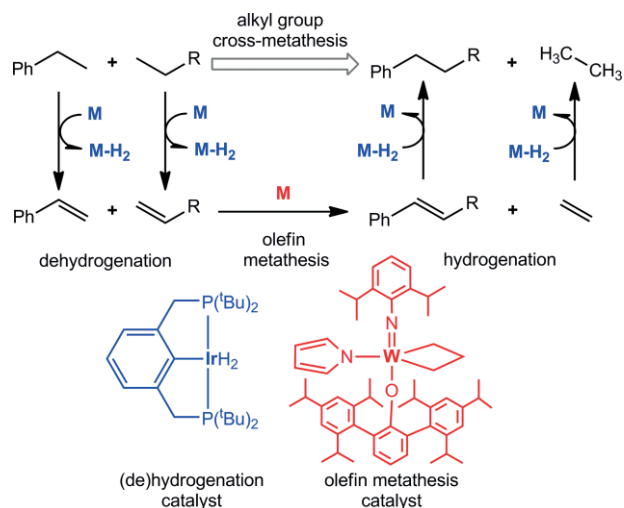
Product distribution in alkane metathesis is an important and difficult issue, especially when branched or cyclic alkanes are obtained. One of the main advantages of using molecular catalysts in alkane metathesis is that only linear products are obtained. However, selectivity is still the key factor that needs to be addressed. In alkane metathesis, when starting from a single C_n n -alkane, the expected products are $C_{2n-2}H_{4n-2}$ and ethane (Scheme 6, top). However, the process is not selective, and different compounds are obtained as a consequence of double bond isomerisation prior to alkene metathesis (Scheme 6, down). Alkane metathesis always leads to a product distribution of n -alkanes. The highest selectivity for n -decane when starting from n -hexane has been reported by Goldman (50 % of total C7–C10 product), with a combination of the irid-



Scheme 6. Product distribution of alkane metathesis.

ium pincer catalyst ($t\text{BuPCP}$)Ir and the Schrock catalyst Mo-F12 for alkene metathesis.^[36]

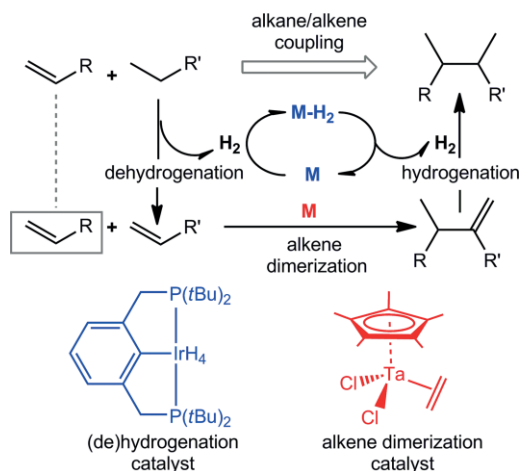
A new process based on the same tandem strategy as described for alkane metathesis and named alkyl group cross-metathesis (AGCM) has been described.^[37] Alkyl-substituted arenes are prepared in a one-pot tandem (de-)hydrogenation and alkene metathesis process starting from alkanes and ethylbenzene (Scheme 7). A highly active catalytic system was obtained by combination of an iridium pincer catalyst and a tungsten monoaryloxide complex. The system showed excellent selectivity in favour of the formation of n -alkyl-substituted arenes over alkane metathesis. The high stability of the alkene metathesis catalyst allows high working temperatures (180 °C) for days.



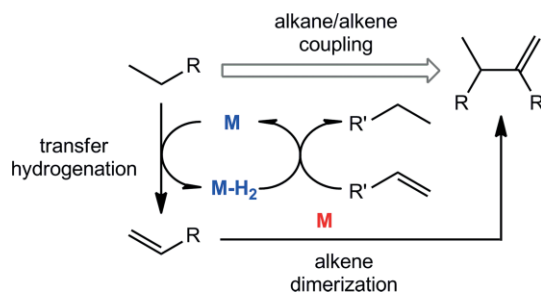
Scheme 7. Catalytic reactions involved in alkyl group cross-metathesis.

Bercaw et al. have developed a complementary approach for light hydrocarbon upgrading based on a tandem alkane–alkene

coupling.^[38] The proof of concept of the process consisted of alkane dehydrogenation through the action of a pincer iridium complex, alkene dimerisation assisted by a Cp*Ta catalyst and hydrogenation of the dimerisation product through the action of the pincer iridium complex (Scheme 8). The net reaction is an alkane/alkene coupling for the upgrading of hydrocarbons without generation of byproducts.^[39] Calculations indicate that the overall process is thermodynamically favoured below 250 °C. The complete catalytic cycle has not been developed and only works with use of a sacrificial hydrogen acceptor (Scheme 9).



Scheme 8. Tandem alkane–alkene coupling through the action of iridium and tantalum catalysts. Printed with permission from ref.^[38] Copyright (2010) American Chemical Society.

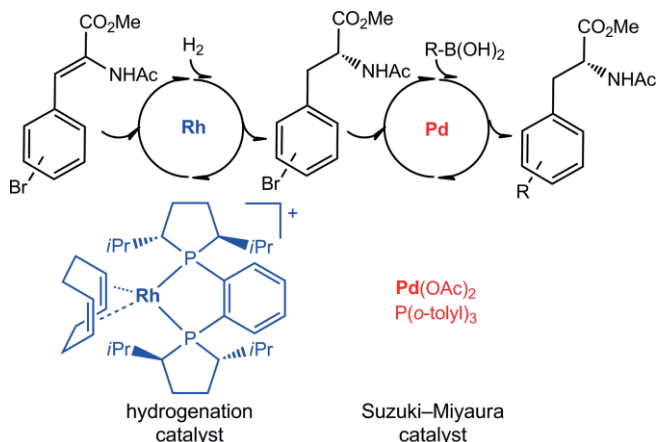


Scheme 9. Alkane–alkene coupling with use of a sacrificial hydrogen acceptor.

4. Other Tandem Processes Based on Two Different Metal Catalysts

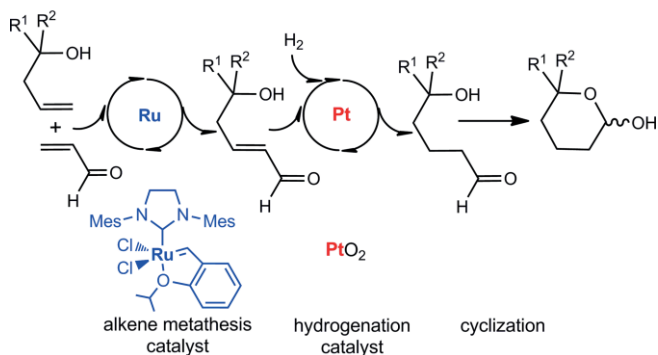
A tandem catalytic procedure for the preparation of amino acids and peptides in the presence of a combination of rhodium and palladium catalysts has been developed (Scheme 10).^[40] The general strategy involves a chiral hydrogenation catalyst (Pr-DuPHOS-Rh) and a Suzuki–Miyaura coupling catalyst. Prochiral α -enamides are hydrogenated with excellent enantioselectivities to afford the corresponding α -amino acids in the presence of molecular hydrogen. These chiral amino acids are converted into the final products by cross-

coupling with a variety of substituted boronic acids including heteroatom-containing and heterocyclic boronic acids. Good yields (75–99 %) of unconventional α -amino acids have been obtained, with no detectable racemisation of the intermediates.



Scheme 10. Tandem catalytic procedure for the preparation of amino acids assisted by a combination of a rhodium and a palladium catalyst.

The compatibility of the second-generation Grubbs catalyst with PtO_2 allows the design of a tandem process consisting of a cross-metathesis followed by hydrogenation with molecular hydrogen and cyclisation.^[41] By starting from acrylic acid and acrolein, substituted lactones and lactols are obtained in high yields under mild reaction conditions (room temperature and 1 atm of H_2) and at low catalyst loadings (Scheme 11).

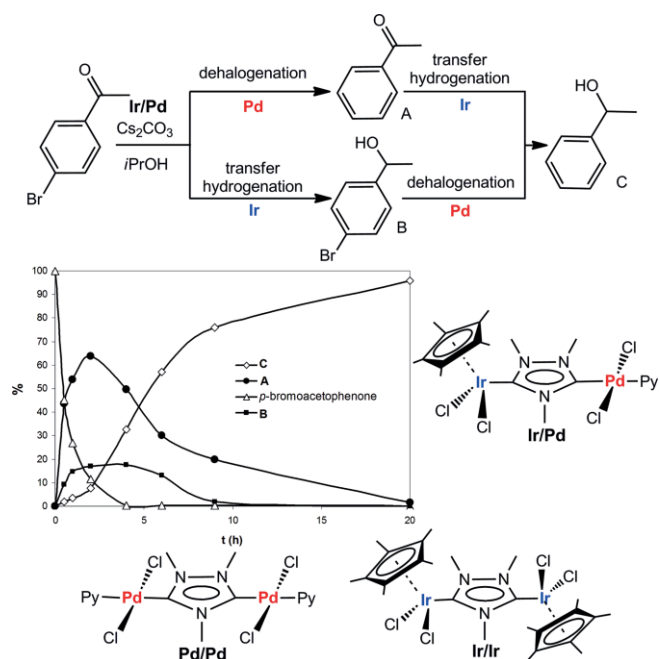


Scheme 11. Sequential synthesis of lactols with the aid of a combination of ruthenium and platinum catalysts.

5. Tandem Processes Based on Heterobimetallic Catalysts

Heterobimetallic catalysts represent an interesting alternative to the use of two different metal catalysts in hydrogenation tandem processes. The presence of two metals connected through a single ligand can induce “intermetallic cooperativity” that can improve or modify the catalytic activity. Several examples in which the activity of the heterobimetallic catalyst is enhanced over the sum of those of the homobimetallic catalysts are described in this section. An iridium/palladium heterobimetallic catalyst has been synthesised and used as catalyst in different

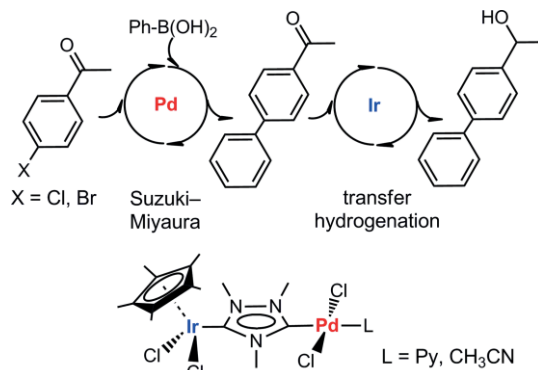
tandem processes involving hydrogenation.^[42] For the proof of concept *p*-bromoacetophenone was used as benchmark substrate. The presence of two functional groups – an aryl halide and a C=O system – in the same molecule provided a library of transformations in which the palladium was active through oxidative addition and the iridium through transfer hydrogenation. The first tandem process consisted of the dehalogenation/transfer hydrogenation of *p*-bromoacetophenone to afford 1-phenylethanol (Scheme 12). The reaction time course showed that the two processes – dehalogenation and transfer hydrogenation – are simultaneous and afford the two reaction intermediates A and B (Scheme 12). Dehalogenation is faster, as can be seen in the formation of acetophenone (A) in a maximum yield of 65 % after 2.5 h (the maximum yield for B is 17 %). Then both reaction intermediates are converted into the final 1-phenylethanol (C) in quantitative yield. When the reaction was attempted in the presence of the homobimetallic iridium catalyst (Ir/Ir), only 1-(4-bromophenyl)ethanol (B) was obtained. Alternatively, when the homobimetallic palladium catalyst (Pd/Pd) was used only acetophenone (A) was obtained. These two experiments clearly illustrate that each metal is performing one catalytic reaction. Interestingly, when the reaction is carried out in the presence of a combination of equimolar amounts of the homobimetallic iridium catalyst (Ir/Ir) and the homobimetallic palladium catalyst (Pd/Pd) under the same conditions, the yield of 1-phenylethanol is significantly lower. This result suggests catalytic cooperativity between the two different metals contained in the Ir/Pd heterobimetallic catalyst.



Scheme 12. Reaction time course for the transformation of *p*-bromoacetophenone in the presence of the Ir/Pd catalyst (*i*PrOH, 100 °C, cat 2 mol-%). Adapted, with permission, from reference.^[42] Copyright 2009, American Chemical Society.

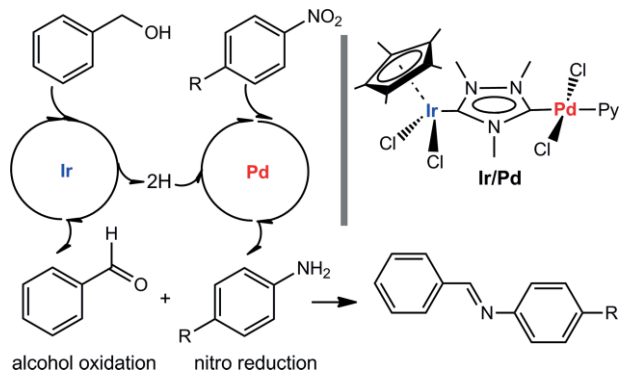
Through a slight modification of the reaction conditions and addition of a phenylboronic acid, a new tandem process was developed (Scheme 13). In this process the transfer hydrogen-

ation is combined with a Suzuki–Miyaura coupling to afford a biphenylated secondary alcohol. All of these reactions constituted a clear advance over other alternative procedures to afford the same final products, by combining two catalytic reactions in a one-pot procedure using a single catalyst containing two different metals.



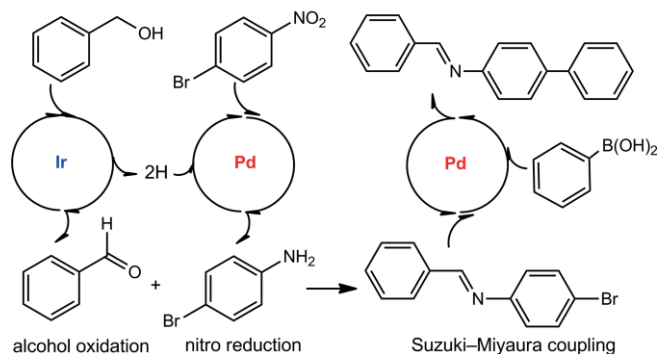
Scheme 13. Tandem catalytic reaction based on an iridium/palladium heterobimetallic catalyst.

The same heterobimetallic Ir/Pd catalyst was used for the synthesis of imines through direct reaction between nitroarenes and primary alcohols under basic conditions. The reaction presumably proceeds through a two-step tandem process, in which the nitroarene is reduced to an aniline by the primary alcohol, which is subsequently oxidised to the corresponding aldehyde (Scheme 14).^[43] The reduction of the nitro group is achieved by the hydrogen obtained from the oxidation of the alcohol. The coupling of the aldehyde and the amine selectively yields the final imine. The iridium component facilitates the oxidation of the alcohol to the aldehyde, with release of hydrogen. The hydrogen is then consumed through the action of the palladium component in the reduction of the nitroarene to the corresponding aromatic amine. The stoichiometric coupling between the amine and the aldehyde affords the final imine. Control experiments carried out with the analogous homobimetallic Ir/Ir and Pd/Pd catalysts confirmed the independent role of the two metals in the overall reaction process. The same catalytic process was studied in the case of a heterobimetallic Ir/Au complex.^[44]



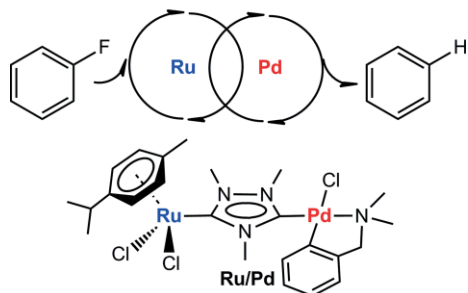
Scheme 14. Heterobimetallic Ir/Pd catalyst for tandem catalytic nitro reduction with alcohols.

The tandem reaction shown in Scheme 14 could be combined with other catalytic processes such as palladium-catalysed Suzuki–Miyaura coupling. Transfer hydrogenation is facilitated by iridium, and dehalogenation and Suzuki–Miyaura coupling by palladium. *p*-Bromonitrobenzene and benzyl alcohol in the presence of phenylboronic acid were used as benchmark substrates (Scheme 15). This reaction afforded the corresponding bisarylated imine in 77 % yield.^[45]



Scheme 15. One-pot reaction based on multiple-metal catalysis with an Ir/Pd heterobimetallic catalyst.

The combination of Ru and Pd in a single heterobimetallic catalyst (Ru/Pd) provided an interesting tandem process for the activation of C–F bonds through hydrodefluorination of organic molecules.^[46–48] In this reaction two different processes occur: the C–F bond is broken, and then a hydrogen atom is introduced with the aid of a convenient hydrogen source such as *i*PrOH under basic conditions (Scheme 16).

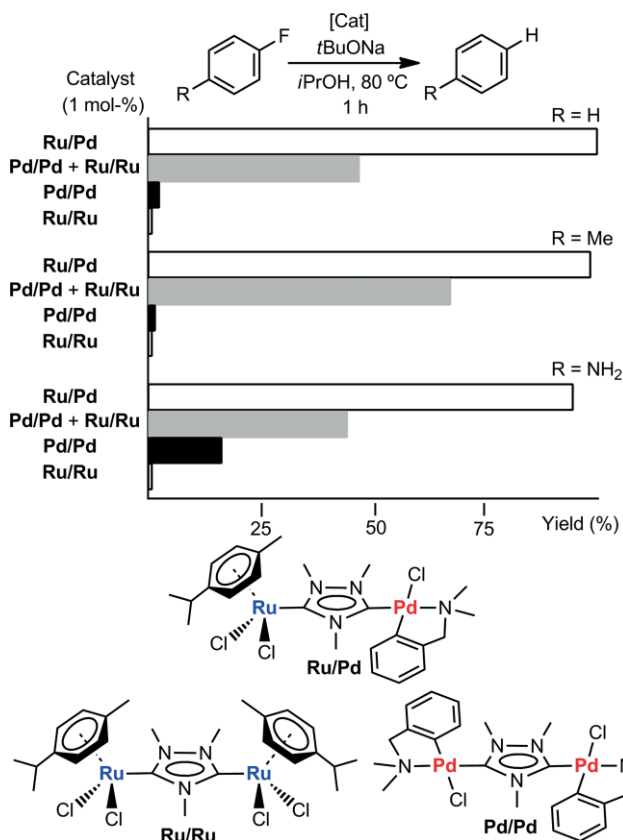


Scheme 16. Hydrodefluorination promoted by a Ru/Pd catalyst. Adapted from ref.^[6] with permission from The Royal Society of Chemistry.

The heterobimetallic Ru/Pd complex proved to be very efficient for the hydrodefluorination of a variety of fluoroarenes, affording quantitative yields in very short reaction times and under mild reaction conditions.^[49] Interestingly the combination of the two different metals is necessary to promote the tandem process. The independent use of the homobimetallic complexes of palladium and ruthenium afforded negligible yields of the final product.

The combination of the two homobimetallic complexes of palladium and ruthenium (Pd/Pd + Ru/Ru) is also active in the hydrodefluorination process, but less so than the heterobimetallic single catalyst (Scheme 17). The reaction clearly benefits when the two different metal fragments are linked to the

single-frame ligand. This enhancement of the catalyst activity is in line with the results described above in support of the idea of catalytic cooperativity between the two vicinal metals.^[49]



Scheme 17. Comparative study in the hydrodefluorination of aromatic substrates. Adapted from ref.^[6] with permission from The Royal Society of Chemistry.

The mechanism in the hydrodefluorination process is unknown, but the results show that ruthenium and palladium need to be present either in a single catalyst or in a combination of a ruthenium catalyst plus a palladium catalyst.

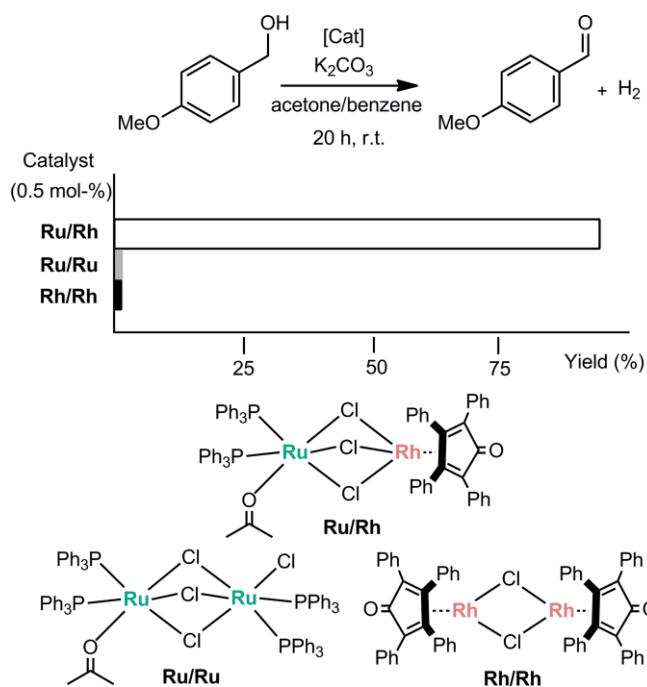
The activity of the Ru/Pd catalyst can be extended to the hydrodefluorination of aliphatic C–F bonds. The reaction behaviour with a series of trifluoromethyl-substituted aryl derivatives suggested that the Ru/Pd catalyst acts as an effective two-component catalyst, which provides clear benefits in the hydrodefluorination of a wide set of organic substrates (Table 1).

A heterobimetallic Rh/Ru catalyst is active for the dehydrogenation of primary and secondary alcohols. The ruthenium(II) component – RuCl₂(acetone)(PPh₃)₂ – is connected to the rhodium(I) fragment – (η⁴-C₄Ph₄CO)RhCl – through chloro ligands.^[50,51] The heterobimetallic complex produces aldehydes and ketones at room temperature in the presence of a catalyst loading of 0.5 mol-% in acetone/benzene as solvent. Although no clear mechanism is described, both metals seem to participate, as evidenced by the fact that the corresponding homobimetallic complexes are almost completely inactive in the Oppenauer-type alcohol oxidation under the same reaction conditions (Scheme 18).

Table 1. Hydrodefluorination of trifluoro-substituted aryl derivatives in the presence of the Ru/Pd catalyst.^[a] Adapted from ref.^[6] with permission from The Royal Society of Chemistry.

Substrate	Product	Yield (%) ^[b]
		50
		99
		90
		90
		96

[a] Reactions were carried out with 0.3 mmol of the trifluoromethylarene, *t*BuONa (0.9 mmol), catalyst (5 mol-%), and 2 mL of propan-2-ol at 80 °C, reaction time 2–12 h. [b] Yields determined by GC analyses with use of anisole as internal standard.



Scheme 18. Comparative activity of the Ru/Rh heterobimetallic catalyst in relation to Ru/Ru and Rh/Rh homobimetallic catalysts.

6. Conclusions and Future Perspectives

In the search for more efficient ways to prepare complex organic molecules, there have been increasing efforts in the design of more sophisticated catalysts. In this microreview, an alternative approach has been shown, based on combination of different catalytic cycles performed by different metal complexes. The use of multiple-metal catalysts has provided a wide set of organic transformations in one-pot processes. The combination of fundamental catalytic steps with simple and accessible substrates can then lead to compounds with sophisticated molecular structures. The design of effective multiple-metal catalysts for tandem processes represents a clear example of this approach. From the very simple idea of using different metal complexes, or two metals connected through a single-frame ligand, a series of tandem processes based on combination of the catalytic activities associated with each metal fragment have been described. The combination of two metals into a single compound provides an extra benefit, as shown by the better catalytic outcome of the heterobimetallic catalysts in relation to the activity provided by mixtures of related homobimetallic complexes. The catalytic cooperativity still needs further study in order to explain and understand the mechanisms and to develop more sophisticated multiple-metal catalysts. It can be foreseen that the work described in this microreview will serve to inspire future research in the design of efficient multiple-metal catalysts that might be used for simple access to sophisticated organic molecules.

Acknowledgments

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Keywords: Multiple-metal catalysis · Heterobimetallic catalysts · Tandem catalysis · Metathesis · Hydrogenation · Dehydrogenation

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