Multimetallic (de)hydrogenation catalysed processes

David Ventura-Espinosa[a] and Jose A. Mata*[a]

Abstract: The use of different metals working together in a synergistic way, allows synthetic transformations that are not achievable by other means. The metal cooperation becomes important in catalytic processes for the synthesis of sophisticated molecules or difficult transformations. A rationale design of multimetallic catalysed processes entails metal complexes and reaction conditions being compatible, which in general is not straightforward. A key feature for success found in all systems dealing with multimetallic processes is catalyst stability. The use of robust metal complexes increases the probability of success in the search of tandem catalytic processes. This microreview is based on the recent and most important findings of multimetallic catalysed processes that involved (de)hydrogenation reactions. The field constitutes a research area that is full of potential and can be foreseen that relevant applications will be described in the near future.

1. Introduction

This microreview reports the 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 multimetallic catalysed processes were the hydrogen released in the first catalytic cycle is then used for a hydrogenation catalytic reaction in a second catalytic cycle. The presence of two catalysts based on different metals allows the rational design of tandem processes by combining two independent catalytic cycles.[6,7] The processes allow organic transformations that are not achievable by other means. Although the concept of multimetallic catalysed processes is known for a long time still needs further development and improvement. Important transformations are based on the combination of different metal complexes working 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 reactions without the need of using molecular hydrogen. This methodology has been widely studied in the case of the transfer hydrogenation. In the catalytic version of this process, the hydrogen is used and transferred to other molecule normally by the same catalyst. Based on the idea of this dual activity, more challenging is the use of two or more different metal complexes in the design of multimetallic hydrogenation catalysed processes.[11] For transfer hydrogenation, the first catalyst will carry out the dehydrogenation and a second catalyst will be used in the transfer of the two hydrogen atoms to the other molecule. Other catalytic processes will be those requiring the presence of two different metal catalysts. In this latter case, the presence of the two metals is required to complete the catalytic cycle. The use of multiple catalysts for concatenated multistep processes will allow the simple preparation of sophisticated molecules in one-pot synthesis. A straightforward approach to the design of tandem processes is to combine two different metal catalysts. Each catalyst should facilitate a mechanistically independent catalytic cycle. An alternative is the use of heterobimetallic catalysts composed of two or more different metals. In both cases synergism or cooperativity between the different metal centers may occur facilitating a complicated catalytic reaction.[12] The presence of two metal centers would increase exponentially the scope of the reaction. In nature there are many enzymes that contain two metal ions that operate in a synergistic way in complex biological transformations.[13] Similar to some enzymes, tandem catalytic cycles have been described and will be discussed.

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Multimetallic catalysed processes should be developed for the 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 of catalyst

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compatibility and stability with all 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 by multiple catalysts systems (Figure 1). Several examples in which the use of two metal complexes or one heterobimetallic catalyst results in a clear enhancement of the catalytic outcomes are shown. The field constitutes a research area that is full of potential.

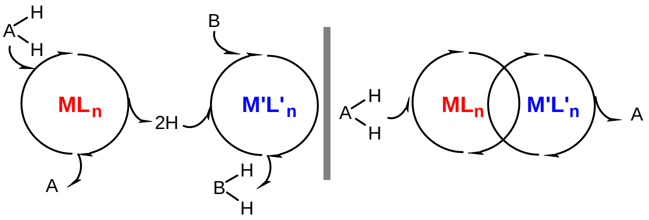
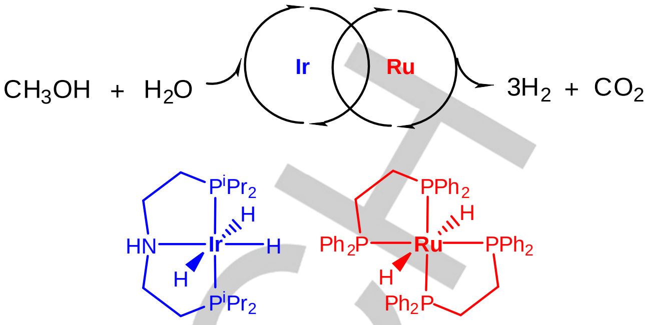


Figure 1. Multimetallic (de)hydrogenation catalysed processes.

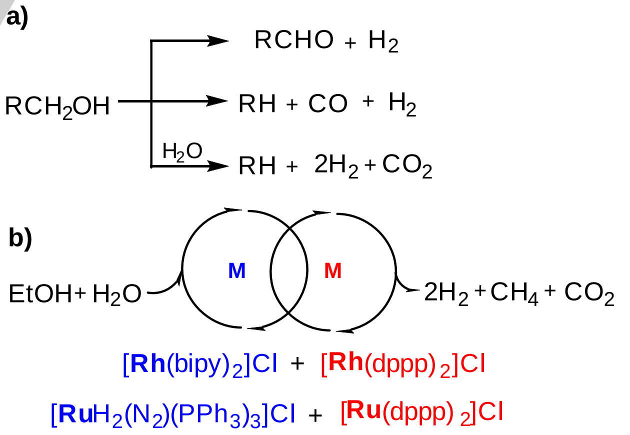
2. Dehydrogenation of alcohols

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 as they are readily available from the fermentation of biomass. The most effective and studied systems for the dehydrogenation of alcohols are based on ruthenium pincer complexes.[18,19] In the search of more efficient catalytic systems, an iridium/ruthenium two-component catalysed process was developed for the generation 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 to produce hydrogen and CO_2 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 favors the dehydrogenation of formic acid and allows the reaction to proceed under mild reaction conditions.



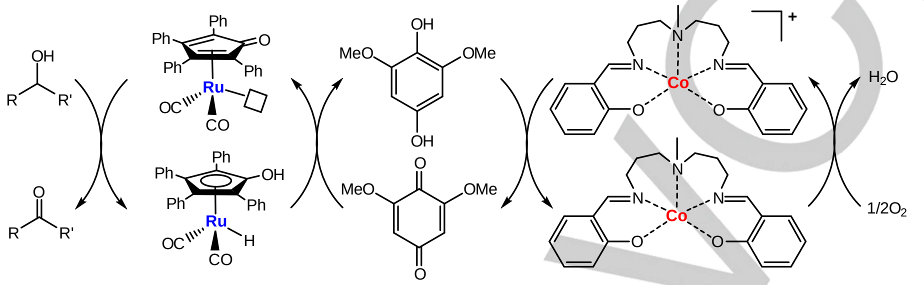
Scheme 1. Dehydrogenation of methanol using the combination of an Ir-PNP and Ru hydride as catalyst.

Different strategies for the hydrogen production from ethanol using a two-component catalytic system have been described using well-known rhodium and ruthenium complexes (Scheme 2). The proof of concept was based in the principle of microscopic reversibility that ensures that a catalyst active in hydrogenation should be active for dehydrogenation. The synergistic effect of two different rhodium or ruthenium catalysts favors the reaction by avoiding decomposition. Removal of CO from a metal center is achieved by the second metal avoiding catalyst poisoning (Scheme 2).[21] Hydrogen is obtained in good rates and yields using the combination of the Rh catalysts. The mechanism involves the dehydrogenation of ethanol to ethanal by the $[Rh(bipy)_2]Cl$ complex and the decarbonylation by the $[Rh(dppp)_2]Cl$ complex, which itself does not dehydrogenate ethanol. The catalytic hydrogen production in the case of the ruthenium system is particularly improved when irradiating with visible light.



Scheme 2. Alcohol dehydrogenation catalysed by the combination of different metal complexes.

Oxidation of alcohols has been carried out by a multimetallic catalysed system based on three catalytic steps performed in one-pot system.[22] The process is reminiscent of biological oxidation of alcohols via the respiratory chain and involves selective electron/proton transfer (Scheme 3). The Shvo's ruthenium catalyst dehydrogenates the alcohol and the hydrogen atoms are used for the reduction of a quinone into the corresponding hydroquinone. The hydroquinone is reoxidized by air with an oxygen activated cobalt-salen type complex. In the net reaction, alcohols plus oxygen are converted to the corresponding ketones and water. The system is very active at 100 ºC yielding quantitative yields in short reaction times at a catalyst loading of 0.5 mol% of Ru, 20 mol% of quinone and 2 mol% of Co. The reaction is air compatible and allows the oxidation of aromatic and aliphatic alcohols. The three component system is general and it has also been applied to the oxidation of amino alcohols to produce lactams[23] or to the oxidative coupling or benzylamines and aminophenols to produce benzoxaszoles.[24]

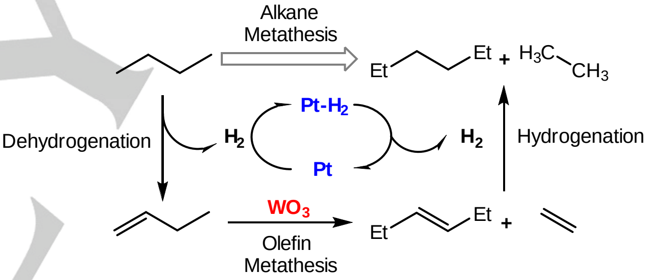


Scheme 3. Multimetallic catalysed system for the dehydrogenation of alcohols based on the Shvo's catalyst and a cobalt-salen type complex.

3. Alkane dehydrogenation/metathesis

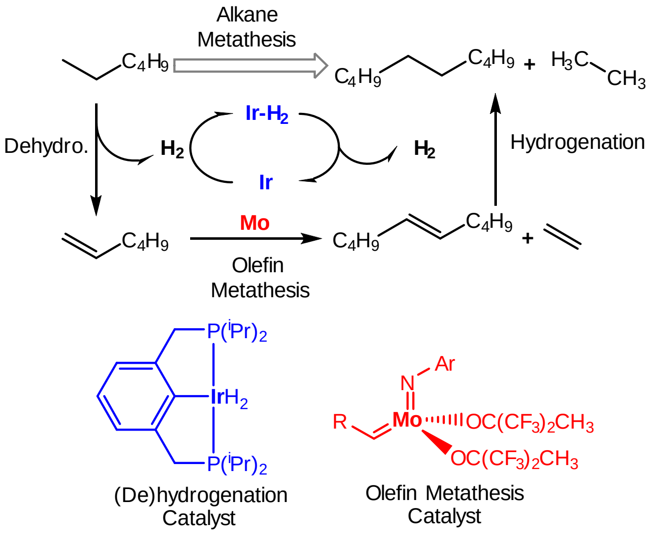
The activation of inert C-H bonds by transition metal complexes is a major interest in organometallic chemistry.[25–31] The use of metal complexes for C-H activation is particularly interesting for the conversion of lighter alkanes into added value alkane products, normally in the form of liquid fuels.[32] 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 as alkane metathesis, light hydrocarbon upgrading or alkane disproportionation.

Alkane disproportionation resembles the pioneering work developed in alkene metathesis in which linear alkenes of three to eight carbon atoms were converted to homologues of shorter and longer carbon chains.[33] A decade after, Brunett and Hugues developed the first process for alkane disproportionation at Chevron Research Company.[34] The process was known as disproportionation of alkanes and the key point was the use of multimetallic catalysis. The combination of two different metal complexes comprising platinum and tungsten performed three catalytic reactions in one pot. The $Pt/\gamma\text{-}Al_2O_3$ catalyst facilitated the dehydrogenation of alkanes and hydrogenation of alkenes and the WO_3/SiO_2 catalyst facilitated the alkene metathesis. In a typical reaction, butane is dehydrogenated to 1-butene that in turn is converted to a mixture of 3-hexene and ethylene by alkene metathesis. Finally both alkenes are hydrogenated to 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 to n-hexane and ethane, but in practice, a broad distribution of products is obtained due to isomerization of the double bond along the chain in 1-butene.



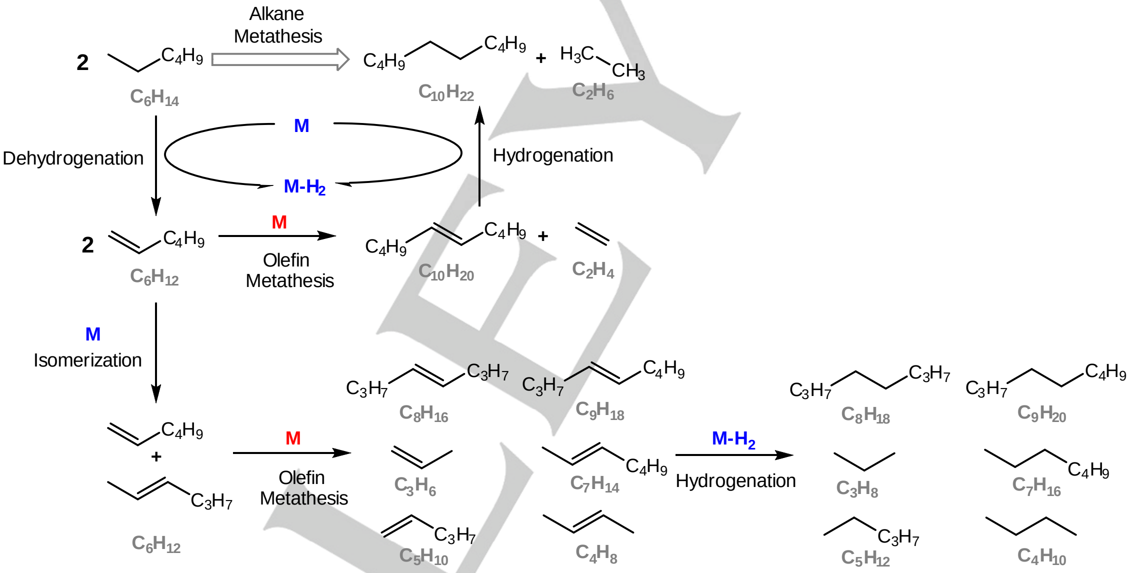
Scheme 4. Alkane disproportionation developed by Brunett and Hugues.

The alkane metathesis proposed by Goldman consist of dehydrogenation of an n-alkane at the terminal position followed by alkene metathesis and then hydrogenation of the metathesized alkene products, yielding a longer carbon chain n-alkane and ethane (Scheme 5).[35] The tandem process is based on the utilization of two different catalysts. The system requires a (de)hydrogenation and an alkene metathesis catalyst. The first combination of metals was an iridium pincer catalyst, active in hydrogenation and dehydrogenation, with the Grubbs catalyst to produce the alkene metathesis. Unfortunately, no reaction occurred because incompatibility of organometallic complexes leading to inactive 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. The alkane metathesis was achieved by using a pincer iridium complex combined with the Schrock molybdenum catalyst. By the use of these two metal complexes n-hexane was converted to a range of C2 to C15 n-alkanes in high yield and importantly no branched or cyclic alkanes were detected.



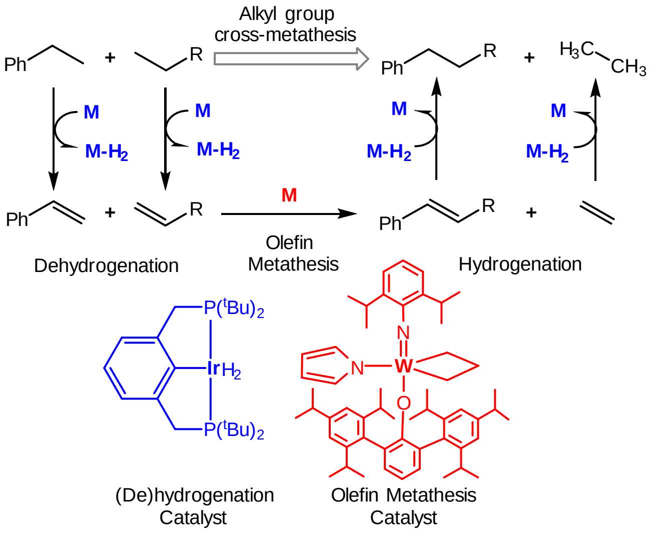
Scheme 5. Alkane metathesis by an iridium pincer and Schrock type catalyst.

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 catalyst 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, 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 isomerization prior to alkene metathesis (Scheme 6, down). Alkane metathesis always leads to a product distribution of n-alkanes. The highest selectivity for n-decane starting from n-hexane has been reported by Goldman (50% of total C7-C10 product) for a combination of an iridium pincer (tBuPCP)Ir and the Schrock catalyst Mo-F12 for alkene metathesis.[36]



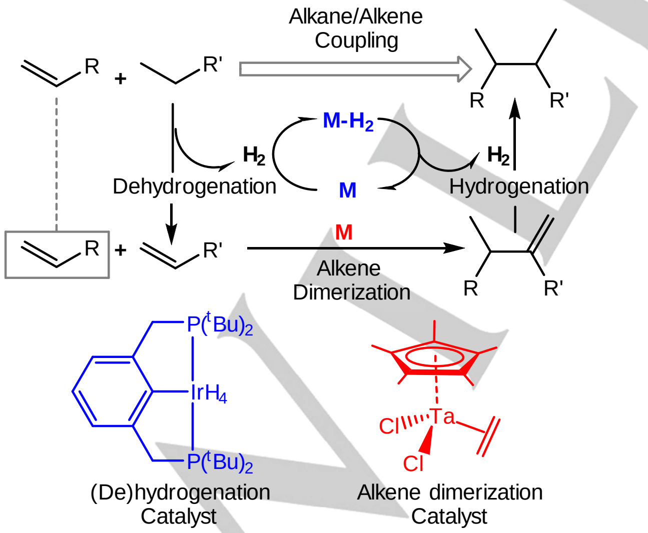
Scheme 6. Product distribution of alkane metathesis.

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

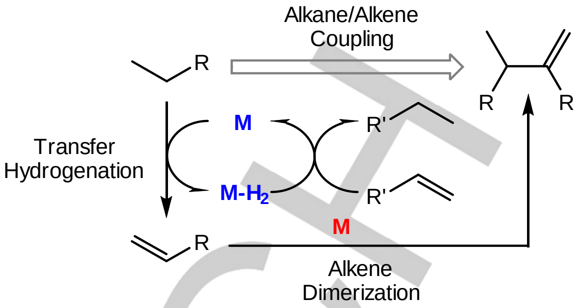


Scheme 7. Catalytic reactions involved in the alkyl group cross-metathesis.

Bercaw et al. have developed a complementary approach toward light hydrocarbon upgrading based on a tandem alkane-alkene coupling.[38] The proof of concept of the process consist of alkane dehydrogenation by a pincer iridium complex, alkene dimerization by a Cp*Ta catalyst and hydrogenation of the dimerization product by 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 favored below 250 ºC. The complete catalytic cycle has not been developed and only works using a sacrificial hydrogen acceptor (Scheme 9).



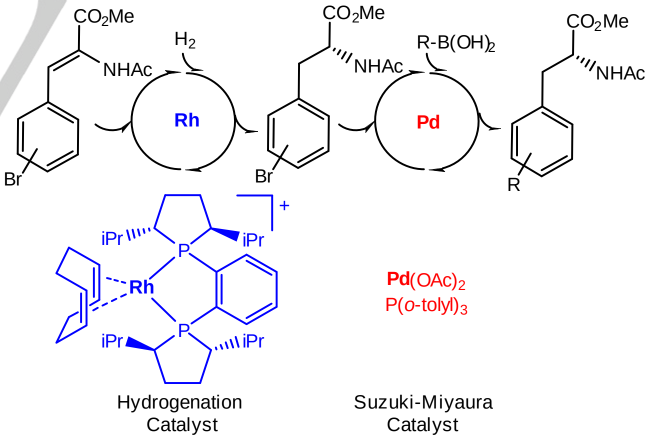
Scheme 8. Tandem alkane-alkene coupling by iridium and tantalum catalyst.



Scheme 9. Alkane-alkene coupling using a sacrificial hydrogen acceptor.

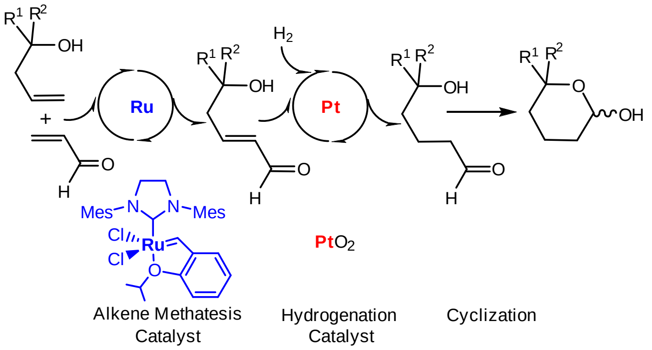
4. Other tandem processes based on two different metal catalysts.

A tandem catalysis procedure for the preparation of amino acids and peptides has been developed by the combination of rhodium and palladium catalysts (Scheme 10).[40] The general strategy involves a chiral hydrogenation catalyst, Pr-DuPHOS-Rh, and a Suzuki-Miyaura coupling catalyst. The prochiral α-enamides are hydrogenated in excellent enantioselectivities to the corresponding α-amino acids using molecular hydrogen. These chiral amino acids are converted to the final products by a cross coupling reaction using a variety of substituted boronic acids including heteroatom-containing and heterocyclic boronic acids. Good yields (75 - 99%) of novel α-amino acids have been obtained with no detectable racemization of the intermediates.



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

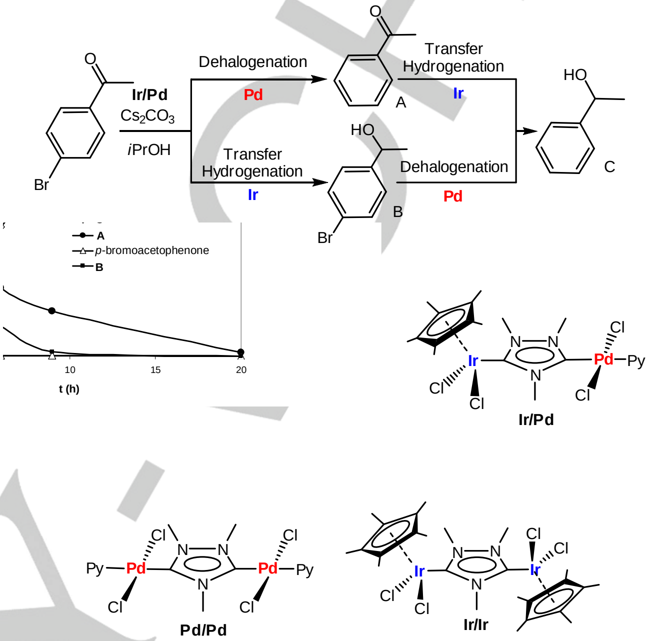
The compatibility of the second generation of Grubbs' catalyst with PtO_2 allows the design of a tandem process that consist of a cross-metathesis followed by hydrogenation using molecular hydrogen and cyclization.[41] Starting form acrylic acid and acrolein, substituted lactones and lactols are obtained 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 lactones by the combination of ruthenium and platinum.

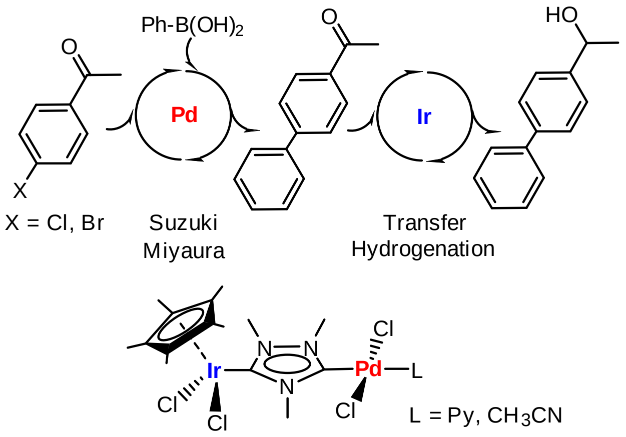
5. Tandem processes based on heterobimetallic catalysts

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 may induce ‘intermetallic cooperativity’ that can improve or modify the catalytic activity. Several examples where the activity of the heterobimetallic catalyst is enhanced over the sum of the homobimetallic catalysts are described in this section. An Iridium/Palladium heterobimetallic catalyst has been synthesized 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 in the same molecule, aryl halide and a C=O, provided a library of transformations in which the palladium through oxidative addition and iridium through transfer hydrogenation were active. The first tandem process consisted of the dehalogenation/transfer hydrogenation of p-bromoacetophenone to obtain 1-phenyl-ethanol (Scheme 12). The reaction time course showed that both processes, dehalogenation and transfer hydrogenation, are simultaneous and afford the two reaction intermediates A and B (Scheme 12). Debromination is faster as seen by the formation of acetophenone (A) in a maximum yield of 65% after 2.5h (the maximum yield for B is 17 %). Then both reaction intermediates are converted to the final 1-phenylethanol C in quantitative yield. When the reaction is carried out using the homobimetallic iridium catalyst (Ir/Ir), only the p-bromo-1-phenylethanol (B) was obtained, and alternatively, when using the homobimetallic palladium catalyst (Pd/Pd) only the acetophenone was obtained (A). Both these experiments, clearly illustrate that each metal is performing one catalytic reaction. Interestingly, when the reaction is carried out using the combination of an equimolecular amount of the homobimetallic iridium catalyst (Ir/Ir) and homobimetallic palladium catalyst (Pd/Pd) under the same conditions, the yield of 1-phenylethanol is significantly lower. This result suggests a catalytic cooperativity between the two different metals contained in the Ir/Pd heterobimetallic catalyst.



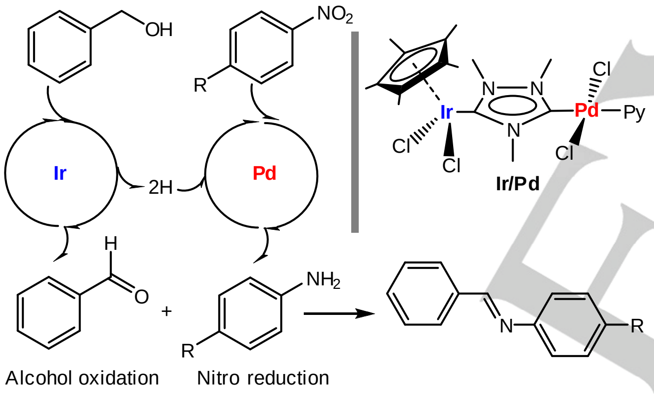
Scheme 12. Time reaction course of the transformation of *p*-bromoacetophenone with the Ir/Pd catalyst (*i*PrOH, 100 ºC, cat 2 mol %). Adapted with permission from reference [42]. Copyright 2009 American Chemical Society.

By slightly modifying the reaction conditions and adding a phenylboronic acid, a new tandem process was developed (Scheme 13). In this process the transfer hydrogenation is connected with a Suzuki-Miyaura coupling to afford biphenylated secondary alcohols. All these reactions constituted a clear advance over other alternative procedures to afford the same final products, by combining two catalytic reactions in one-pot procedure using a single catalyst with two different metals.



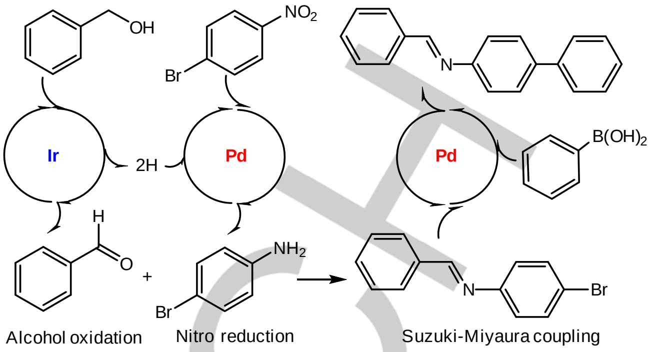
Scheme 13. Tandem catalytic reaction based on an iridium/palladium heterobimetallic catalyst.

The same heterobimetallic Ir/Pd catalyst was used for the synthesis of imines by direct reaction between nitroarenes and primary alcohols under basic conditions. The reaction implies a two-step tandem process, in which the nitroarene is reduced to aniline by the primary alcohol, which is subsequently oxidized to the aldehyde (Scheme 14).[43] The reduction of the nitro group is produced by the hydrogen obtained from the oxidation of the alcohol. The coupling of the aldehyde and the amine selectively yield the final imine. The iridium fragment facilitates the oxidation of the alcohol to aldehyde, with release of hydrogen. The hydrogen is used by the palladium fragment 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 by using the analogous homobimetallic Ir/Ir and Pd/Pd catalyst confirmed the independent role of the two metals in the overall reaction process. The same catalytic process was studied using an heterobimetallic Ir/Au complex.[44]



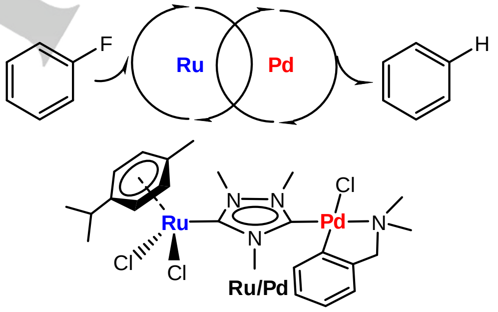
Scheme 14. Heterobimetallic Ir/Pd catalyst for tandem catalytic nitro reduction using alcohols.

The tandem reaction shown in scheme 14 could be combined with other catalytic process such as the palladium-catalysed Suzuki-Miyaura coupling. Transfer hydrogenation is facilitated by iridium and dehalogenation and Suzuki-Miyaura coupling by palladium. p-Bromonitrobenzene and benzylalcohol in the presence of phenylboronic acid were used as benchmark subtrates (Scheme 15).This reaction affords the corresponding bisarylated imine in 77% yield.[45]



Scheme 15. One-pot reaction multimetallic catalysis using an Ir/Pd heterobimetallic catalyst.

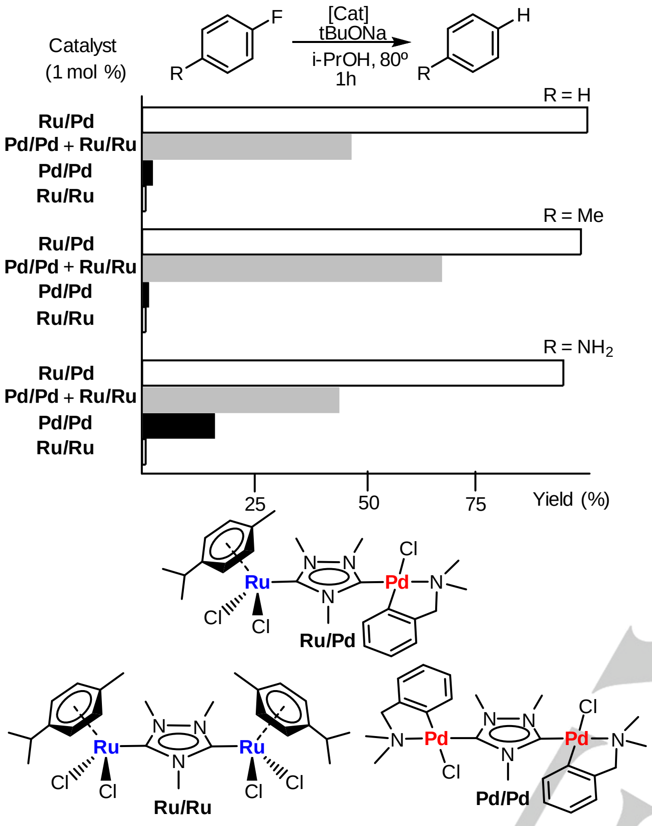
The combination of Ru and Pd in a single heterobimetallic catalyst (Ru/Pd) provided an interesting tandem process for the activation of C-F bond via hydrodefluorination of organic molecules.[46–48] In this reaction two different processes occur: the C-F is broken, and then a hydrogen atom is introduced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



Scheme 16. Hydrodefluorination promoted by a Ru/Pd catalyst.

The heterobimetallic Ru/Pd complex resulted very efficient for the hydrodefluorination of a variety of fluoroarenes, affording quantitative yields in very short reaction times and 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 active than the heterobimetallic single catalyst (Scheme 17). The reaction is clearly benefited when the two different metal fragments are linked to the single-frame ligand. This enhancement of the catalyst activity is in line with the above mentioned results that support the idea of the catalytic cooperativity between the two vicinal metals.[49]



Scheme 17. Comparative study in the hydrodeflurination of aromatic substrates.

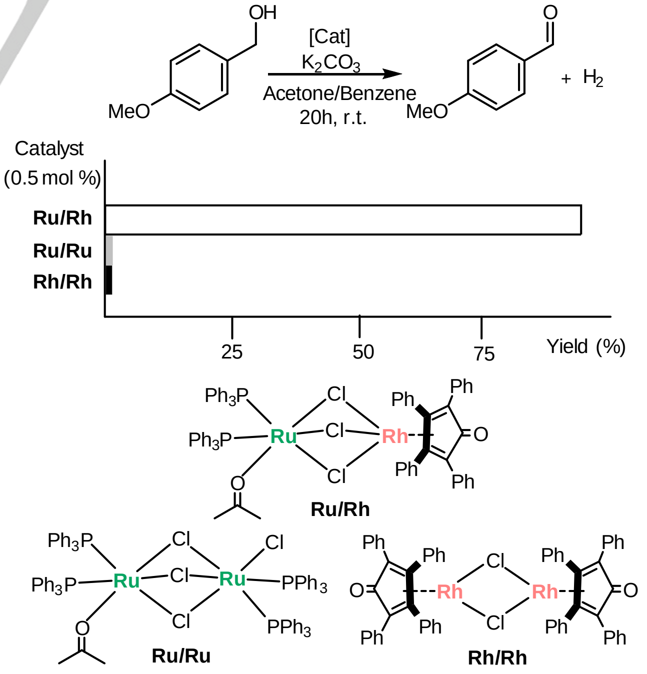
The mechanism in the hydrodefluorination process is unknown but the results show that ruthenium and palladium need to be present in a single catalyst or the combination of a ruthenium catalyst plus a palladium catalyst. The activity of the Ru/Pd catalyst can be extended to the hydrodefluorination of aliphatic C-F bonds. The reaction with a series of trifluoromethyl-toluenes suggested that the Ru/Pd catalyst behaves as an effective two-component catalyst, which provides clear benefits in the hydrodefluorination of a wide set of organic substrates (Table 1).

Table 1. Hydrodefluorination of trifluorotoluenes with the Ru/Pd catalyst.[a]

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

[a] Reactions were carried out with 0.3 mmol of trifluomethylarene, tBuONa (0.9 mmol), catalyst (5 mol%), 2 mL of 2-propanol at 80 ºC, reaction time 2 – 12h. [b] Yields determined by GC analyses using anisole as internal standard.

A heterobimetallic Rh/Ru catalyst is active for the dehydrogenation of primary and secondary alcohols. The ruthenium(II) fragment $RuCl_2(acetone)(PPh_3)_2$ is connected to the rhodium(I) fragment $(\eta^4\text{-}C_4Ph_4CO)RhCl$ by chloro ligands.[50,51] The heterobimetallic complex produces aldehydes and ketones at room temperature using a catalyst loading of 0.5 mol% using 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 completely inactive in the Oppenauer type alcohol oxidation under the same reaction conditions (Scheme 18).



Scheme 18. Comparative activity of Ru/Rh heterobimetallic catalyst versus Ru/Ru and Rh/Rh homobimetallic catalysts.

6. Conclusions and Future Perspectives

In the search of more efficient ways for preparing complex organic molecules, there has been an increasing effort in the design of more sophisticated catalysts. In this microreview, an alternative approach has been shown based on the combination of different catalytic cycles performed by different metal complexes. The use of multimetallic catalysts has provided a wide set of organic transformations in a one-pot process. The combination of fundamental catalytic steps implying simple and accessible substrates can then lead to sophisticated molecules. The design of effective multimetallic catalysts for tandem processes represents a clear example for 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 by combination of the catalytic activities associated with each metal fragment have been described. The combination of the two metals into a single compound provides an extra benefit, as shown by the better catalytic outcome of the heterobimetallic catalyst, when compared to the activity provided by the mixture of the related homobimetallic complexes. The catalytic cooperativity still needs further study in order to rationalize and understand the mechanisms and to develop more sophisticated multimetallic catalysts. It can be foreseen that the work described in this microreview will serve to inspire future research in the design of efficient multimetallic catalysts that may be used for the simple access to sophisticated organic molecules.

Acknowledgements

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Keywords: Multimetallic catalysis • hydrogenation • dehydrogenation • tandem catalysis • heterobimetallic catalysts

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Entry for the Table of Contents

MICROREVIEW

Two or more metals working together to accomplish difficult transformations. The unveiling of an old concept with actual potential applications in (de)hydrogenation.

Multimetallic catalysis

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