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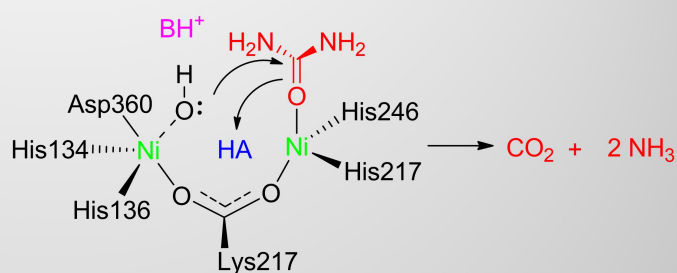# Cooperative Effects in Multimetallic Complexes Applied in Catalysis

Ramananda Maity,*[a] Bernhard S. Birenheide,[b] Frank Breher,*[b] and Biprajit Sarkar*[c]

The field of multimetallic catalysis is rapidly developing and some multimetallic complexes catalyze organic transformations to yield the desired products in more efficient ways owing to the combined action of different metals in a cooperative fashion. This Concept article describes the recent advances of cooperative catalysis playing in multimetallic systems such as homo-multimetallic complexes with short metal-metal distances, homo-multimetallic complexes with long metal-metal distances, hetero-multimetallic complexes and metallocene-based multimetallic complexes with special attention towards redox-switchable catalysis. Examples are illustrated in which the use of multimetallic complexes show clear enhancement of catalytic outcomes when compared with the sum of their corresponding mononuclear counterparts. Furthermore, several examples are discussed showing the effects of electronic communication in cooperative systems.

1. Introduction

Metal-based catalysts are conventionally prepared and used in most cases for a specific single step organic transformation. In contrast to the traditional approach towards organic transformations with a single mononuclear metal catalyst, some multimetallic catalysts show enhanced catalytic activities owing to the combined action of different metals. A close proximity of the metal centers and their consecutive or sequential action with the substrate molecule in multimetallic systems offers cooperativity in both homogeneous and heterogeneous catalysis. Therefore, an augmented reactivity can be observed when the binding affinity of a substrate to the metal increases upon fixation with another metal. As a result, the multimetallic catalysts produce an augmented combined effect, which is greater than the sum of their corresponding mononuclear counterparts.

The gradually increasing demand of environmentally friendly and more economical organic transformations to yield the desired products in more efficient ways need the development of multimetallic catalyst systems[1], as this synthetic strategy could minimize both the product costs and waste formation. Examples with the rapidly increasing development of multimetallic catalysts have been demonstrated during the past few decades. However, the applications of this concept and its practice could be directly learned from Mother Nature,

which offers a wide range of metalloenzymes possessing more than one metal center. The metal centers in these metalloenzymes interact in a cooperative fashion to achieve efficient catalytic activity.[2] The natural enzyme urease catalyzes the conversion of urea to ammonia and carbon dioxide in a cooperative fashion utilizing two nickel(II) centers, which is depicted in Figure 1.[3]

A large number of bio-transformations are also known to be achieved in a single reaction via the subsequent and ingenious action of more than one enzyme in an ordered fashion.[4] Therefore, mimicking the natural bio-transformations by enzyme catalysts has received tremendous attention by chemists in both industry and academia. One of such examples is the industrial preparation of acetic acid from methanol by the Cativa process involving the carbonylation of methanol by a promoted iridium/iodide catalyst.[5,6] The Cativa process also offers remarkable improvements over rhodium based catalysts. The presence of a ruthenium carbonyl catalyst promotes the Ir-catalyzed carbonylation of methanol to acetic acid. NMR spectroscopic data indicates that combination of the ruthenium and iridium complexes leads to an intermediate, in which both metals are connected together by a halide bridge.[7] A mixture of platinum and iridium complexes have also been successfully utilized for the carbonylation of methanol to acetic acid with a positive combined effect of dual metals[8] and the activity of rhodium based systems could be drastically increased by employing a dinuclear catalyst supported by a macrocyclic ligand framework (Scheme 1).[9] Bimetallic catalyst systems such as Mo—Co[10], Re—Pt[11] and Mo—Ni[10] have also been used in industry for naphtha reforming and hydro desulfurization processes.

In this context, a wide range of developments have been initiated on the synthesis and functionalization of multimetallic catalyst systems to facilitate complicated catalytic transformations in a more convenient way by combining several catalytic transformations in a single-pot tandem fashion. However, the establishment of a method for the quantitative measurement of cooperativity is still in its infancy. Recent reports demonstrated the measurement of cooperativity for the simpler systems at the molecular level could be achieved by energy consideration.[12,13] Therefore, the measurement of interaction energies of the entire system with respect to the interaction energies between all individual subsystems will allow determination of cooperativity for a system in which no chemical transformations occur. For the systems where chemical transformations occur, the cooperativity can be measured by considering the energy of activation in the synergistic system

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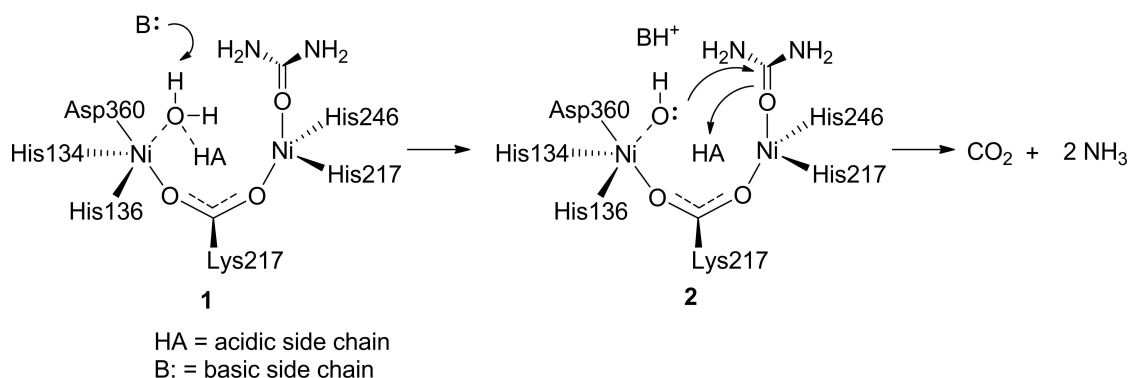Homepage: https://www.iac.uni-stuttgart.de/en/research/aksarkar/

Figure 1. Urea hydrolysis assisted by urease enzyme.

Ramananda Maity completed BSc in Chemistry (honours) from University of Calcutta in 2007 and received his MSc degree in Chemistry from IIT Madras in 2009. Afterwards, he joined Prof. F. Ekkehardt Hahn's research group to pursue his Ph.D. developing poly-NHC ligands for orthometalated heterobimetallic complexes. After the first postdoctoral stay with Prof. B. Sarkar at Freie Universität Berlin, he joined the group of Prof. S. Inoue at Technische Universitatät Berlin for his second postdoctoral work. After a short stay in Dibrugarh University, R. Maity began his career at University of Calcutta, where he is currently an Assistant Professor in the Department of Chemistry. The research interests of his group are primarily in the area of cooperative catalysis using poly-NHC complexes.
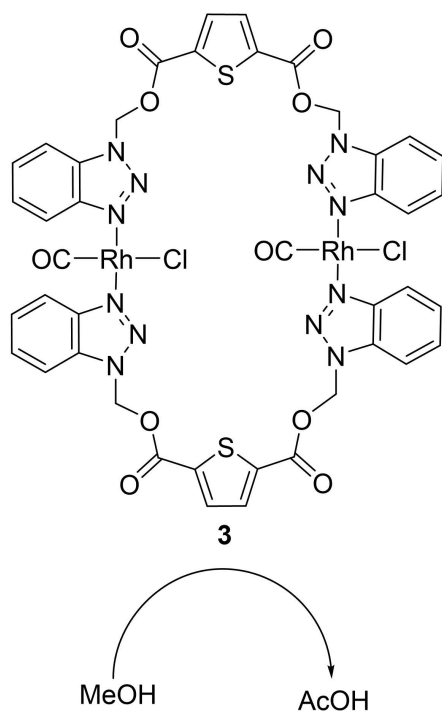
Frank Breher performed his Ph.D. studies at the Universities of Oldenburg and Marburg (10.1998 to 03.2001) under the supervision of Prof. W. Uhl. He spent his postdoctoral period in the research group of Prof. H. Grützmacher at the ETH Zürich, Switzerland, where he became an independent researcher in 2002 supported by a Liebig fellowship. In 2005 he accepted a faculty position at the Universität Karlsruhe (TH) and became Assistant Professor in January 2006. Subsequently, he was promoted to W3-Professor for Inorganic Chemistry at the Karlsruhe Institute of Technology (KIT) in April 2010. His research interests center around the synthesis, structure, bonding and reactivity of organometallic and coordination compounds of unusual Main Group element cages/clusters and transition metal complexes. Spectroscopic techniques including cyclic voltammetry, EPR spectroscopy, and advanced NMR methods as well as density functional theory calculations are also of interest. In 2016, he was awarded the faculty teaching award. Since October 2016, he is Dean of Study Affairs (Chemistry).
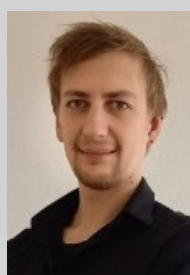
Bernhard Birenheide started his studies in chemistry at the Karlsruhe Institute of Technology (KIT) in 2012 in which he was supported by a scholarship of the Studienstiftung des deutschen Volkes. In 2017 he worked as a guest researcher in the group of Prof. K. Mashima at Osaka University for three months. He obtained his Master's degree at the KIT in 2018 and subsequently joined the research group of Prof. F. Breher as a doctoral student. His current research is focused on the synthesis of multimetallic iron complexes and their catalytic applications.

Biprajit Sarkar studied at the University of Delhi and the Indian Institute of Technology Bombay. At the end of 2001, he moved to Germany to work on his PhD under the guidance of Prof. W. Kaim at the University of Stuttgart. Between 2005 and 2006 he was a post-doctoral researcher in the group of Prof. P. Braunstein at the Université de Strasbourg. From 2006 to 2011, Biprajit worked on his habilitation at the University of Stuttgart. Between 2012 and 2019, he was a W2-Proffesor at the Freie Universität Berlin. At the end of 2019, he shifted to the University of Stuttgart as a W3-Professor and chair of inorganic coordination chemistry. His research interests lie in the areas of catalysis and optically/magnetically switchable molecular materials. Apart from synthesis, his group is heavily involved in using a combination of electrochemical, spectroelectrochemical, spectroscopic and theoretical methods for elucidating the electronic structures of organic and inorganic compounds, and for understand catalysis and switching.

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Scheme 1. Carbonylation of methanol catalyzed by dinuclear rhodium(I) complex.[6,9]

compared with the activation energies of the corresponding subsystems bearing no such activating moiety. However, for more complicated systems, cooperativity can be determined in general only at a qualitative level.[12]

In contrast to monometallic system (Figure 2, A), multi-metallic systems must be comprised of at least three chemical entities (substrate and two identical or different metal centers) to show cooperativity. The substrate gets activated by simultaneous or sequential action of at least two functional entities in a cooperative chemical reaction. The active functional entities may or may not be part of the same molecule. Cooperativity in multimetallic systems can be considered to take place when the combined effect arising from the interaction of the substrate with the multimetallic system is greater than the combined individual effects of their corresponding mononuclear complexes. Both electronic and ligand effects may be responsible for the observed specific reactivity of multimetallic catalysts.[14] The second metal can either interact directly with the substrate (**C**), or only with the other metal center (**B**), for example by means of electronic communication or stabilization of inter-
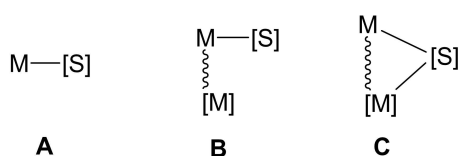
mediates. Binding of the substrate to one metal influences the interaction of this metal to the other metal center. Alternatively, the second metal can also be viewed as a ligand on the first metal, which influences the stereoelectronic interactions of the first metal with the substrate in comparison to the mononuclear complex.[14] A more sensitive case arises when the substrate binds two or more metal centers at the same time (Figure 2, **C**). In this particular process the relative participation of ligand versus electronic effects depends on the nature of the individual system.[14]
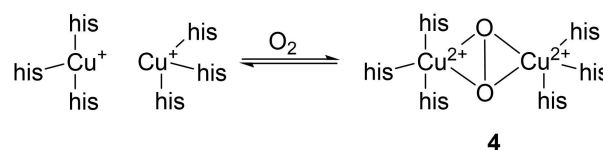
A number of reviews on the topic of cooperativity in catalysis have already been published,[14,15,16] this article aims to describe different types of cooperativity in 1.) homo-multi-metallic complexes with short metal-metal distances, 2.) homo-multimetallic complexes with long metal-metal distances, 3.) hetero-multimetallic complexes, and 4.) metallocene-based multimetallic complexes with special attention towards redox-switchable catalysis. The scope of this review is to demonstrate the importance of electronic cooperativity in multimetallic systems with selected examples and not to give a complete overview on the advances in this field. Furthermore, ligand-assisted cooperativity or complexes bearing non-innocent ligands are not discussed.[17]

2. Cooperative effects in homo-multimetallic complexes with short metal-metal distances
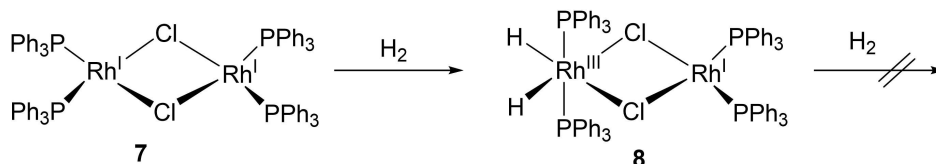
2.1. Cooperative activation of small molecules

A widespread interest in polynuclear complexes has been developed since the pioneer work on bimetallic systems by Jack Halpern.[18] It was assumed that multimetallic systems would show augmented reactivity patterns compared to those observed for monometallic complexes.[19] The interest on this topic was further inspired by the behavior of certain multi-metallic enzymes acting in a cooperative fashion to reduce oxygen (Scheme 2).[20,21] Numerous bimetallic complexes of this kind have emerged afterwards and were studied thoroughly for their cooperative redox activities.[21,22,23]

There are also several reports demonstrating the applications of multimetallic complexes towards various organic transformations.[19,23,24,25] A major difficulty with these complexes is that the electronic effects have to be precisely controlled to observe the cooperativity. However, numerous examples of multimetallic systems bearing transition metals have been studied well for the above mentioned purpose.

Figure 2. Different interactions lead to cooperativity in multimetallic systems.[12]

Scheme 2. Cooperative binding of dioxygen by hemocyanin.

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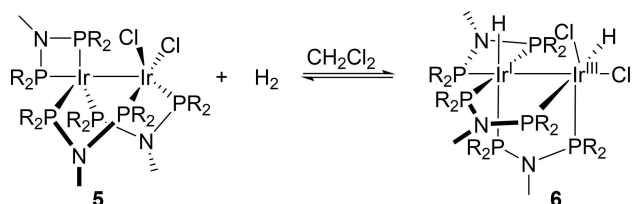European Chemical
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Scheme 4. Cooperative activation of dihydrogen by a bimetallic rhodium complex.

Metallobiomolecules are well known naturally existing catalysts with metal sites working in a cooperative fashion to activate small molecules by multielectron transformations for biological function.[26] Similar intermetallic redox cooperation in bimetallic complexes has potentially been achieved by judicial ligand design. Nocera and co-workers have demonstrated the activation of molecular hydrogen by a dinuclear mixed-valence Ir^0/Ir^{II} complex **5** through bimetallic cooperative reactivity (Scheme 3).[27] Their theoretical calculation models have also established that the flexibility of the supporting ligand framework has a tremendous impact on the observed bimetallic cooperativity. It was shown that the essential deformation energy for a metal-metal bond stretching mechanism (from 2.780 to 2.923 Å in possible intermediates) has a strong influence in the phosphazane-bridged Ir–Ir system. The ligand thus enables easy and reversible hydrogenation.

Dinuclear complexes bearing halogen bridging ligands, which could be synthesized from easily available starting materials, also show augmented reactivity and high structural variability. The influence of the second metal on the reactivity of the first metal towards the substrate has also been well documented.[28] The reaction of the dinuclear rhodium(I) complex **7** with dihydrogen yields the mixed-valence dirhodium complex **8**, where one of the metals undergoes oxidative addition reaction and the second one remains unchanged (Scheme 4). Interestingly, the reaction of this dinuclear Rh^{III}/Rh^I complex with dihydrogen even under high pressure does not show the expected oxidative addition product on the second metal. This certainly indicates that the rhodium(III) center regulates the reactivity of the adjacent rhodium(I) center, probably by the electronic communication through the chlorido-bridging units.[29]

Heterobimetallic complexes of similar type also show moderate to better activity in different catalytic conversions.[30]

Meyer and co-workers have reported a dinuclear copper(II) complex **9** based on a pyrazolate framework. The imidazole-containing ligand scaffold encompasses two copper centers in close proximity (4.34 Å)[31] to emulate the cooperativity in the bimetallic system. The complex has been anticipated in the oxidative C–C coupling reaction in a bioinspired synergistic approach (Scheme 5).[32]
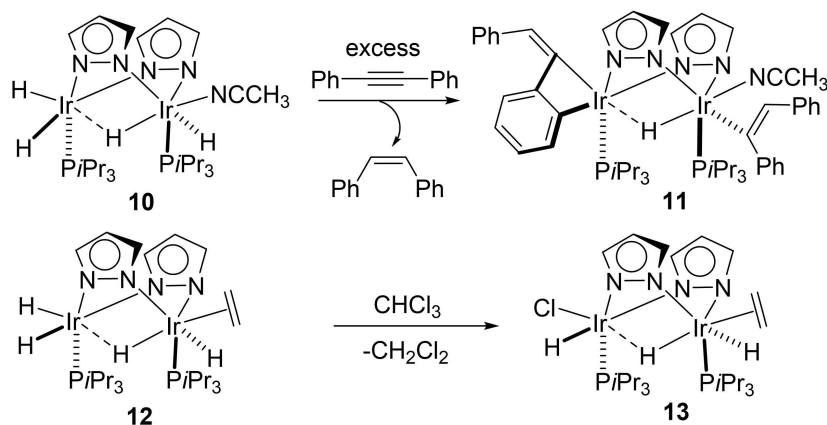
Pyrazolate-bridged dinuclear iridium(III) complexes have been known to catalyze the alkyne hydrogenation reactions in a dinuclear mechanistic fashion (Scheme 6).

The reaction of the dinuclear iridium complex **10** bearing pyrazolate ligands with excess of diphenyl acetylene yields the cyclometalated dinuclear complex **11** along with one equivalent *cis*-stilbene molecule (Scheme 6).[33] However, the formation of cyclometallated complex **11** involves many intermediate species, of which some have been characterized by spectroscopic methods. The novelty of these dinuclear compounds is that each iridium center possesses one labile coordination site, and both coordination sites are being used for substrate coordination and therefore the product is released in a concerted way.

The same research group has also investigated bimetallic cooperative activities with coordinatively unsaturated dinuclear iridium(III) complexes, which can be synthesized easily from the dinuclear iridium complex **10**. These new dinuclear iridium catalysts successfully carried out the H–H, C–H, and C–Cl bond activations in addition to alkene hydrogenation. One example of C–Cl bond activation using dinuclear complex **12** is shown in Scheme 6.[34]

Scheme 3. Various cooperative activation of dihydrogen by iridium complex.
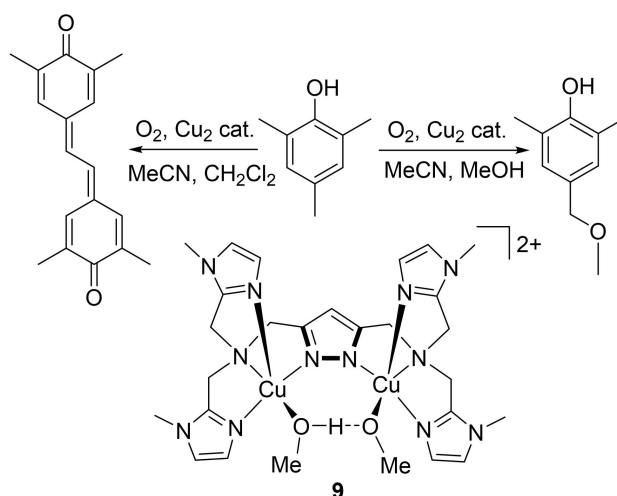
Scheme 5. Oxidative C–C coupling by bimetallic copper(II) complex.[31]

Scheme 6. Various cooperative actions of dinuclear iridium complexes.

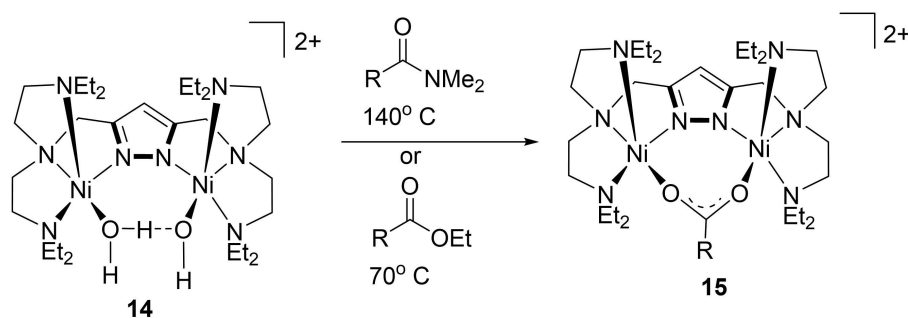## 2.2. Transformation of C—O and C—N bonds

Meyer and co-workers have reported the dinuclear nickel(II) complex **14** based on pyrazolate building block having a resting state in which the metal binds hydroxide as a H_3O_2 unit.[35] The complex is comprised of similar active metal sites as in the urease metalloenzyme with a Ni⋯Ni separation of 4.452 Å and allows for the transformations of small molecules at the bimetallic nickel site in a cooperative fashion. Therefore, the reaction of the dinuclear complex with unactivated amides or esters results in the hydrolysis of the substrates and leads to the formation of carboxylato-bridged complexes of type **15** (Scheme 7).

Cooperativity is also observed in the hydroformylation reaction catalyzed by dinuclear rhodium(I) complexes bearing phosphine donor ligands.[36] It is worth mentioning that the billion kilograms of aldehydes and alcohols are being produced each year by the world's largest industrial processes using the hydroformylation reaction.[37] The process involves the reaction of alkene together with hydrogen and carbon monoxide to yield either linear or branched aldehydes.

Two different dinuclear rhodium(I) complexes with conformational flexibility have been prepared with both *rac*-et,ph-P$_4$ and *meso*-et,ph-P$_4$ ligands (Figure 3).[38] Both dinuclear complexes show superior activity compared to the industry

dominating mononuclear rhodium triphenylphosphine (Rh/PPh$_3$) catalysts. Interestingly, the dinuclear complex with *rac*-phosphine donor ligand shows greater activity compared to the complex with the *meso*-phosphine donor ligand. To be precise, the *rac*-phosphine donor complex shows ~40 times faster reaction rate and has a higher linear to branch aldehyde regioselectivity when compared with the commercially available catalysts (Rh/PPh$_3$). Bimetallic complexes and cluster complexes showing less hydroformylation activity compared to the commercial Rh/PPh$_3$ catalysts have also been demonstrated in literature.[36] The dinuclear complex *rac*-**16** contains no Rh—Rh bond and the two rhodium centers are separated by a distance of 5.505 Å.[39] The close proximity of the two rhodium centers is responsible for the observed cooperative catalysis with dinuclear rhodium complexes *rac/meso*-**16**. This conclusion was further confirmed by comparing the activity of this complex with two other similar complexes **17** and **18**. In both complexes, the two rhodium centers are separated further apart by utilizing 1,3-propylene or rigid *p*-xylene spacers. Both complexes show poor activity, which is comparable to their mononuclear counterparts. This evidence again supports the bimetallic cooperativity in complexes having shorter metal-metal distances.

The ability of zinc(II)-containing catalysts to promote the hydrolytic cleavage of ester bonds has been studied for

Scheme 7. Hydrolysis of unactivated amides and esters by dinuclear nickel(II) complex.

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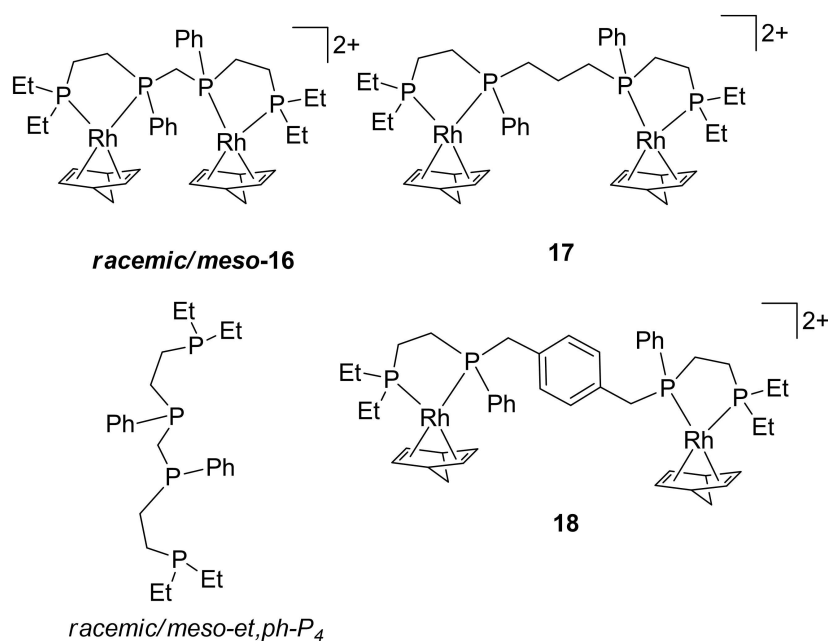European Chemical
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Figure 3. Dinuclear rhodium(I) complexes for hydroformylation reaction.

decades. However, improvement of the catalysts to accelerate hydrolysis of special phosphate esters has drawn much attention.[40] A promising approach to augment the efficiency of either the catalysts or the hydrolytic agents is the use of polymetallic systems. One of the early examples of synthetic bimetallic catalysts for the mentioned purpose was demonstrated by Breslow in 1995.[41] In these bimetallic catalysts each zinc(II) center is coordinated to a tridentate macrocyclic ligand and which are connected to each other by different spacer units (Figure 4). The reactivity of a specific type of complex can be controlled by varying these spacer units. When using a flexible alkyl linker, the reactivity of the catalyst remains the same as the mononuclear zinc(II) complexes. However, employing a rigid 4,4′-biphenyl spacer leads to an decreased reactivity of the bimetallic catalyst compared to the monometallic counterpart (Figure 4).[41]

The influence of the ligand scaffold on cooperative reactivity has also been investigated.[42,43] Bencini, Bianchi, Paoletti and co-workers synthesized dinuclear zinc(II) complex bearing a macrocyclic [30]aneN₆O₄-ligand.[44] This dinuclear zinc
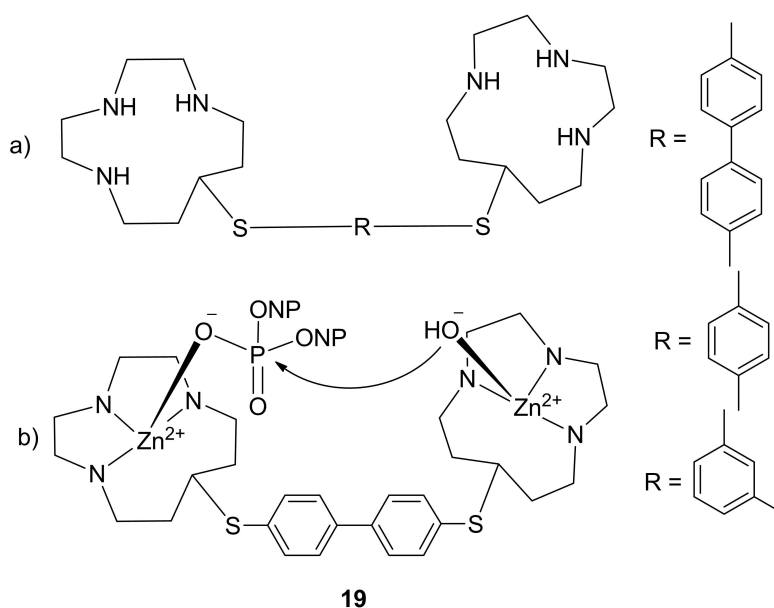

Figure 4. a) Structure of ligand scaffold; b) The proposed mechanism of the bimetallic catalysis.

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(II) complex **21** is ~10 times more active compared to the corresponding mononuclear complex (Figure 5). Although in both complexes (**19** and **21**) the substrate binds to both zinc(II) ions, in the latter the two zinc(II) centers stay in close proximity, leading to augmented cooperative activity compared to complex **19**. In contrast to **19**, both metals in complex **21** form the reactive hydroxo complex and the resulting dihydroxo species, which is also responsible for the substantial increase in reactivity compare to the bimetallic monohydroxo complex **19**. The monohydroxo complex is less reactive as it has a great tendency to undergo the unreactive μ-hydroxo bridge formation.[42,43] A large number of reports demonstrating cooperative catalysis using bimetallic zinc(II) complexes based on different ligand scaffold and spacer units.[45]

Zinc complexes have also been employed in enzyme-like catalytic transesterification reactions. The tetranuclear cluster $Zn_4(OCOCF_3)_6O$ (**22**) was able to transform methylesters with a variety of alcohols with high chemoselectivity,[46,47] as well as the conversion to oxazolines (Scheme 8).[48] The addition of a base, such as DMAP, drastically improved catalytic activity. Investigations into the mechanism showed that the catalytically active species seem to be dinuclear and trinuclear zinc complexes, while equivalent mononuclear species showed virtually no activity.[47] For manganese and cobalt, two structurally similar dinuclear systems were synthesized and employed
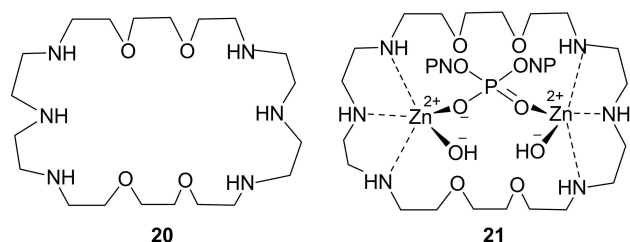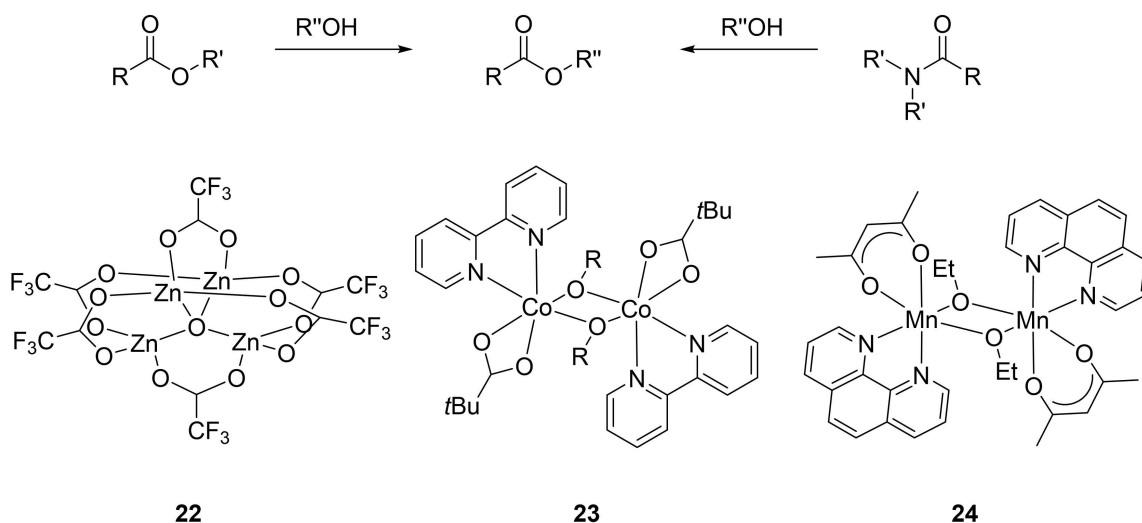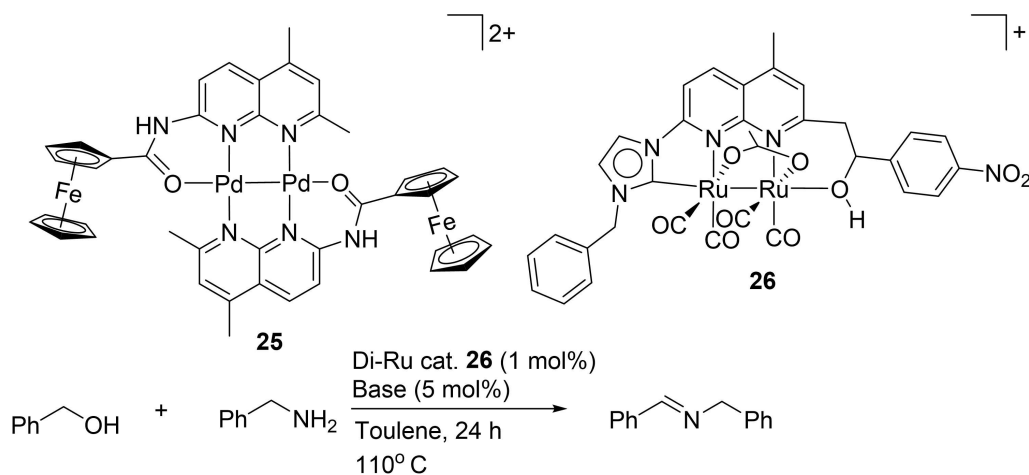
in the transesterification of amides and esters, respectively.[49] These complexes feature two octahedral coordinated metals chelated by a bidentate N,N-ligand and a carboxylato- or acetylacetonato moiety, as well as two bridging alkoxides. Similar to the zinc complex, the catalytic activity of comparable mononuclear complexes was remarkably lower than that of those bimetallic systems.

One forward step towards the highly challenging design of suitable ligands to pursue enhanced bimetallic catalysis has been taken by Bera and co-workers,[50] who have investigated the catalytic activity of a dinuclear palladium(II) complexes having a direct Pd–Pd bond. An amide-linked naphthyridine-ferrocene hybrid building block was used to accommodate both palladium atoms in close proximity within the same molecule (Scheme 9). The dinuclear palladium(II) complex appeared as an excellent catalyst for various organic transformations such as phosphine-free Suzuki cross-coupling and Heck-coupling reactions. The distance between two palladium centers in the dinuclear palladium complex measures 2.395 Å.[51] A bimetallic cooperative mechanism on the same di-palladium platform operating with substrate addition and product elimination has been proposed to explain the enhanced catalytic activity of complex **25**. Dinuclear ruthenium complexes of type **26** bearing NHC-functionalized 1,8-naphthyridine ligand have also been investigated by the same research group.[50,52] These dinuclear ruthenium complexes show both metal-ligand and with metal-metal cooperation in the formation reaction of imine from respective alcohols via dehydrogenative coupling (Scheme 9).

Cooperative activity of complexes is not only restricted to bimetallic systems. Polynuclear complexes with a precise ligand design are also known in literature, showing synergistic mechanism during catalysis. The tetranuclear ruthenium-oxo-hydroxo-hydride complex **27** (Scheme 10) shows tremendous activity in nitrile hydration reactions.[53] The enhanced activity is due to the effective cooperative action of four metal centers and the mechanism is also supported by Hill inhibition kinetics

Figure 5. Structure of macrocyclic ligand scaffold[30] aneN6O4 and the proposed mechanism of the bimetallic catalysis.

Scheme 8. Multimetallic complexes for transesterification catalysis.

Scheme 9. Dinuclear palladium(II) and ruthenium complexes in catalysis.
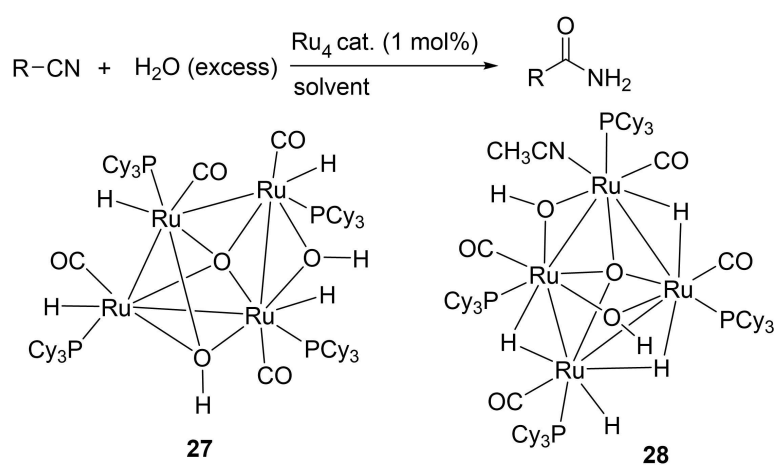
Scheme 10. Tetranuclear ruthenium complexes in cooperative nitrile hydration reactions.

for the hydration reaction of benzonitrile.[53] Interestingly, the reaction of acetonitrile with the tetrameric ruthenium complex at 0 °C yields the mono acetonitrile coordinated tetranuclear ruthenium complex **28**, which is even more active than the tetranuclear ruthenium complex **27** for the same catalytic hydration reaction. It is believed that the relaxed core geometry of the acetonitrile-coordinated tetranuclear ruthenium complex promotes the substrate binding to the other ruthenium centers in a cooperative manner. The Ru–Ru distances in complex **28** fall in the range 2.70–2.87 Å.
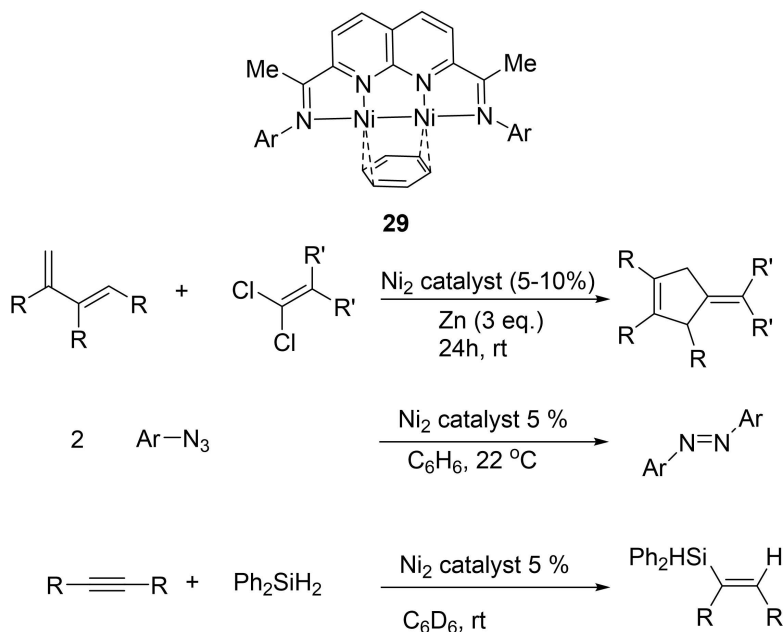
2.3. Transformation of carbon-carbon multiple bonds

Uyeda and co-workers successfully synthesized a dinuclear Ni-complex based on a naphthyridine-diimine framework.[54] The complex features two Ni-atoms with a relatively short metal-metal distance of 2.496 Å, and it has been shown that it is capable of an impressive amount of cooperative activation reactions, as well as catalysis (Scheme 11).[55,56] In the cyclo-
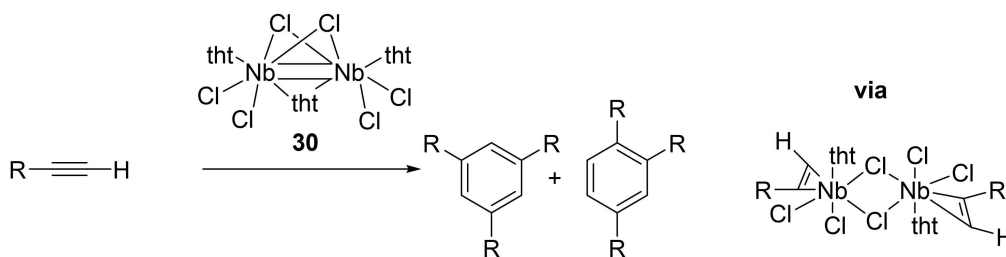
trimerization of alkynes, efficient transformation via a pathway that is not accessible by its monometallic counterparts was observed,[56] which elegantly highlights the scope of cooperative catalysis.

A number of bimetallic early d-block complexes featuring metal-metal multiple bonds have been found to catalyze the cyclotrimerization of alkynes. An early example is a series of tantalum and niobium chloride complexes bearing organic sulfur or selenium ligands.[57] These catalysts are more selective than their monometallic counterparts, as they exhibit a preference for the 1,3,5-substituted product. While the mechanism is not fully understood, preliminary reactions of niobium catalyst **30** with two equivalents of alkyne gave rise to a complex in which both metal atoms underwent cyclometallation with one alkyne. This suggests that the following reactions of alkyne occur independently on both atoms, to furnish the trimerization products (Scheme 12).

In contrast to the niobium catalysts, in the bimetallic chromium and molybdenum systems featuring metal-metal quintuple bonds, alkynes are activated along this bond,

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Scheme 11. Dinuclear Ni-catalyst and selected catalytic reactions.

Scheme 12. Cyclotrimerization with a dinuclear niobium catalyst.

allowing for high regioselectivity.[58] The corresponding [2+2] and [2+2+2] intermediates could be identified, showing that both metals cooperatively activate the triple bonds (Scheme 13).
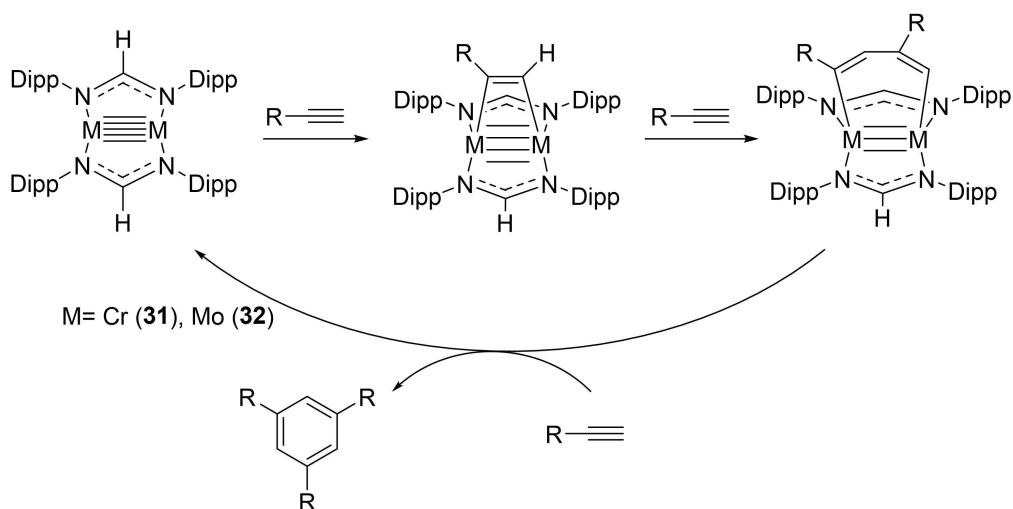
Complexes containing Mo—Mo quadruple bonds have further been utilized in the activation of haloalkanes. Mashima and co-workers demonstrated that this reactivity allows for catalytic hydrodehalogenation, addition and polymerization reactions.[59] Experimental as well as quantum chemical studies[60] show that the quadruple bond undergoes one-electron reductive abstraction of the halide allowing for subsequent radical pathways.

While the molybdenum and chromium complexes furnish the 1,3,5-substituted cyclotrimerization products, cobalt and nickel complexes have been found to give rise to the 1,2,4-substituted products with high selectivity (Scheme 14).[56,61] Detailed considerations of the mechanism have been discussed in another review[15]; it can be summarized that the activation of the triple bond does not occur in a similar symmetric fashion along both metals as in the group 6 complexes.[56,62] The first equivalent of alkyne coordinates to both metals perpendicular
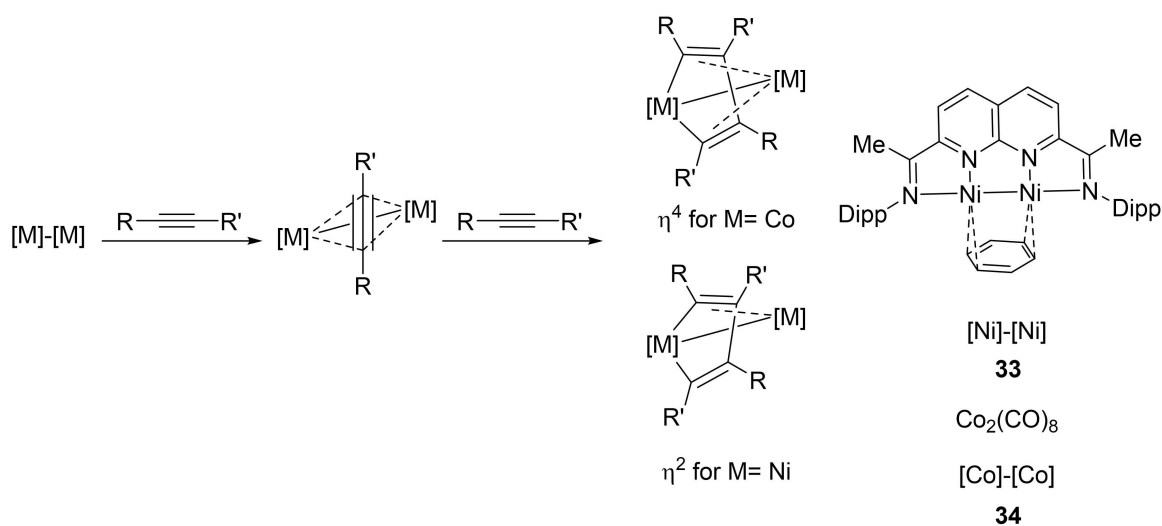
to the metal-metal bond (Scheme 14). A second equivalent then reacts to give a cyclometallated complex, in which one metal is part of the five-membered ring and the other is coordinated by the π-system. The third equivalent then furnishes the cyclotrimerization product and the catalyst is regenerated.

Compared to mononuclear complexes, the Ni₂ system performs far better and with higher regioselectivity. This again demonstrates that cooperative activation can lead to improved catalytic activity. When compared to the Nb, Mo and Cr systems, it also shows that no generalization of catalytic systems in "seemingly" similar transformations can be made and a variety of different reaction pathways are possible.
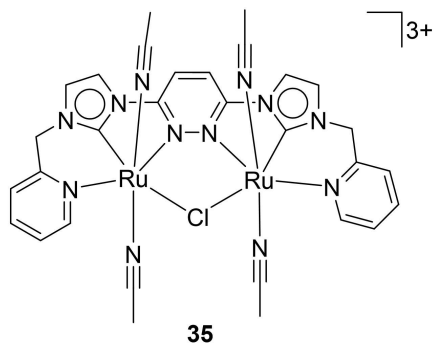
Further transformation reactions of alkenes by a dinuclear ruthenium(II) complex **35** comprised of a bis-NHC ligand on 3,6-disubstituted pyridazine platform have also been reported in literature.[63] The complex has been prepared by the deprotonation of the corresponding bis-imidazolium salt, followed by the addition of [Ru(p-cymene)(Cl)₂]₂. The dinuclear complex **35** exhibits excellent catalytic activity in the alkene oxidation reaction depicted in Scheme 15, which can be ascribed to

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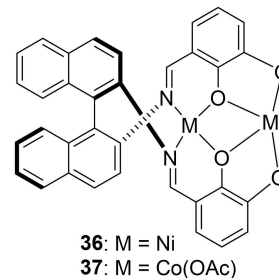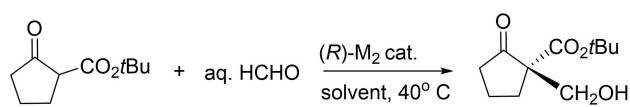**Chemistry Europe**
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Scheme 13. Cyclotrimerization with dinuclear Cr and Mo catalysts.

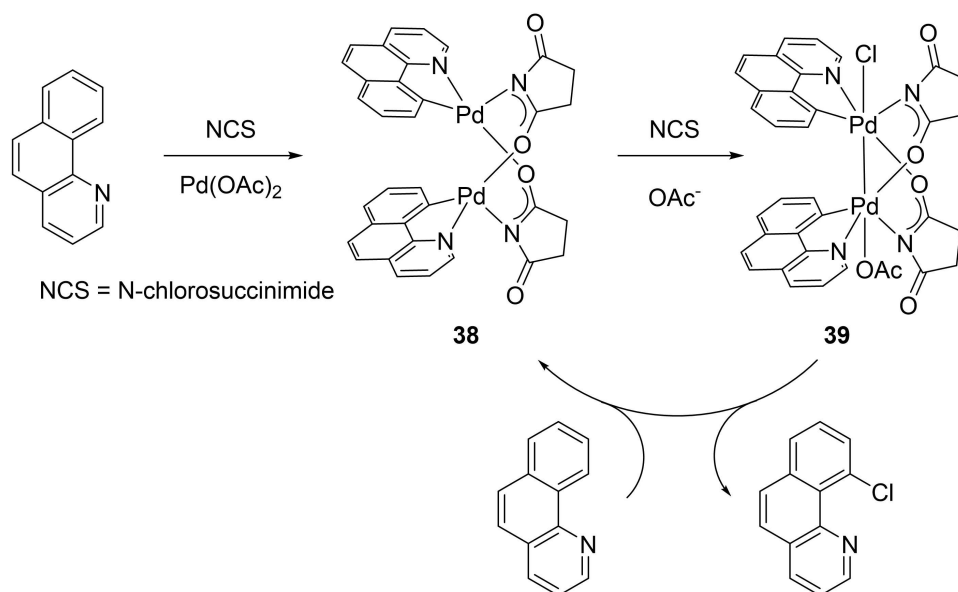**Scheme 14.** Cyclotrimerization catalyzed by Ni and Co complexes.
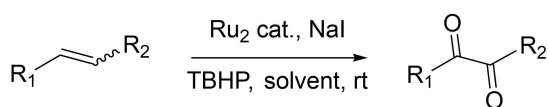
Scheme 15. Oxidation of alkenes by a dinuclear Ru(II) complex.

Scheme 16. Bimetallic complexes for cooperative asymmetric aldol condensation reaction.

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NCS = N-chlorosuccinimide

38   **39**

Scheme 17. Dinuclear Pd-catalyzed C-H transformation.

Ru⋯Ru cooperation during the catalysis. The Ru⋯Ru distance in the dinuclear ruthenium complex was measured to be 3.785 Å.

2.4. Cross-coupling reactions and transformation of C-H bonds

Shibasaki and co-workers have presented a number of dinuclear Schiff-base complexes as catalysts for various organic transformations. Some of the examples are shown in Scheme 16 with the dinuclear nickel(II) and cobalt(III) complexes (**36** and **37**) catalyzing an asymmetric aldol reaction between β-keto ester and formaldehyde.[64] The reactions show excellent yields owing to the proposed cooperative mechanism where both substrates are coordinated with the dinuclear catalyst (each substrate coordinated to one of the metal centers) through the carbonyl moieties. Many other dinuclear Schiff-base complexes have also been developed afterwards not only for the cooperative catalysis but also to catalyze the reactions with less active substrates.[65,66]

In 2010, Ritter and co-workers reported a palladium mediated C—H functionalization, catalysed by dinuclear complex **38**, which forms in the reaction mixture by self-assembly (Scheme 17).[67] The Pd⋯Pd distance in the dinuclear complex **38** was measured to be 2.8628 Å. When investigating the mechanisms of Pd catalysis, the literature oftentimes discusses Pd(II/IV) cycles. In this case, oxidation occurs on both Pd atoms affording a Pd$_2$(II/III) cycle. This study represents a powerful example of cooperative catalysis and shows that previously assumed monomeric reactions might actually undergo different reaction pathways.

Examples have already been shown in this review that dinuclear ruthenium(II) complexes bearing one NHC-coordinated ruthenium depicts enhanced catalytic activity

(Scheme 15). Following the same strategy of holding two metal centers in a shorter distance, Chen and co-workers prepared dinuclear nickel(II) complexes **40** and **41** with bis(NHC) ligands, showing expected enhanced catalytic activity in C—C cross coupling reactions due to bimetallic synergetic effects (Figure 6).[68] It is worth mentioning that the Ni⋯Ni distances (3.255–3.216 Å) in both dinuclear complexes (**40** and **41**) are shorter than the sum of their van der Waals radii (3.3 Å) of nickel(II). Therefore, the electronic interaction among two nickel(II) centers is expected to play a significant role in the observed cooperative catalysis. Surprisingly, the similar dinuclear palladium complexes bearing pyridazine-functionalized NHC ligand failed to show the expected enhanced catalytic activity. These complexes showed good catalytic activity for C—C coupling reactions with variety of aryl chlorides and aryl bromides.[69]

2.5. Polymerization reactions

Convincing evidence of bimetallic complexes having augmented catalytic activity has been made by Grubbs *et al.* Complex **42** shows significantly higher activity (approx.
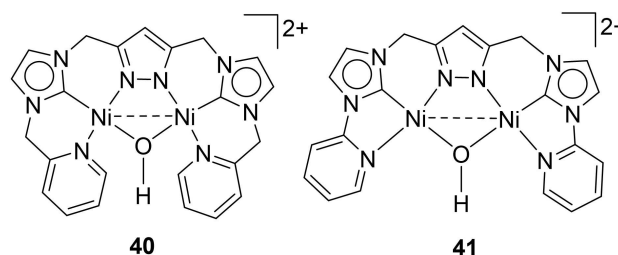

40   **41**

Figure 6. Dinuclear nickel(II) complexes showing enhanced catalytic activity.

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20 times) compared to the corresponding mononuclear complex [(Cl)$_2$(PCy$_3$)$_2$Ru=CHCHC(Ph)$_2$] in ring-opening and ring-closing olefin metathesis reactions (Scheme 18).[70,71] The hetero-bimetallic analogues of these dinuclear complexes, however, show an even more dramatic increase (up to 80 times) in activity, which is discussed later in this review.

The enhanced reactivity of the aforementioned bimetallic complexes towards olefin metathesis can also be explained on the basis of the associative mechanism. The ancillary metal center in the bimetallic complex might be acting as hemilabile chelating group and renders the dissociation of tricyclohexylphosphine during the metathesis reaction.[71]

Ring opening polymerization (ROP) catalysed by dinuclear complexes are well known in literature and have been extensively discussed in another review.[72] Nonetheless, we want to exemplify some complexes showing enhanced reactivity due to cooperative behavior. Wang and co-workers generated dinuclear aluminum complexes bearing amino bis(phenolate) ligand **43** (Figure 7).[73] The bimetallic complexes show higher activity compared to their mononuclear analogues in the ring opening polymerization (ROP) reactions, suggesting cooperation between metal centers. It is suspected, that one aluminum atom serves as the Lewis acid, while the alkoxy group bound to the second metal center attacks the incoming carbonyl moiety of the lactide substrate. A related dinuclear aluminum complex **44** possessing imino bis(phenolate) ligand was reported by Carpentier, Kirillov, and co-workers (Figure 7).[74] This ligand scaffold is more rigid and possesses a higher rotational barrier around C$_{Ar}$–C$_{Ar}$ bond than those
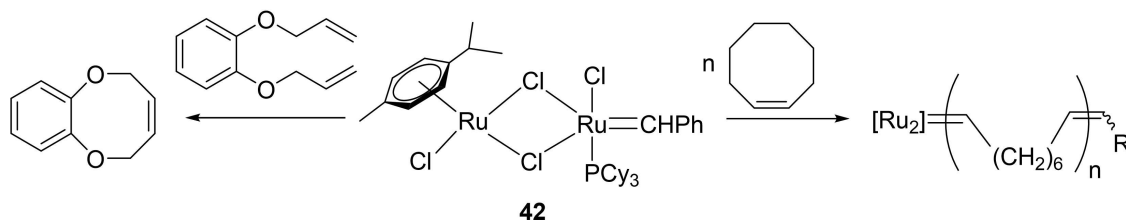
mentioned in amino bis(phenolate) aluminum alkyl complexes. The catalytic activity of this complex in ROP was also higher than the analogous mononuclear complex.

3. Cooperative effects in homo-multimetallic complexes with long metal-metal distances

Although it is well accepted that the close proximity of two metal centers (3.5–6 Å)[24] leads to enhanced cooperativity, cooperation between the metal centers has also been observed in multimetallic complexes with large metal-metal separations. A significant enhancement in the reaction rate has been achieved for dihydroalkoxylation of alkyne diol with bimetallic iridium(I) and rhodium(I) complexes (**45** and **46**); (Scheme 19).[75] In these complexes, each metal center is coordinated with two carbonyl donors and with two pyrazolyl donor moieties. A series of complexes based upon the different spacer units have been synthesized for the comparative study in catalysis. The catalytic activity was found to be highest for the complexes comprising of an anthracene spacer unit when compared with the 1,3- and 1,4-substituted phenylene spacer units.

Mirkin and co-workers have synthesized allosteric supramolecular metallosalen catalyst by connecting two Cr(III)-salen units via phosphine and thioether bonds to two rhodium (I) centers (Scheme 20).[76]

The supramolecular assembled Cr(III)-salen catalyst **47** shows ~20 fold increase in reaction rate compared to the

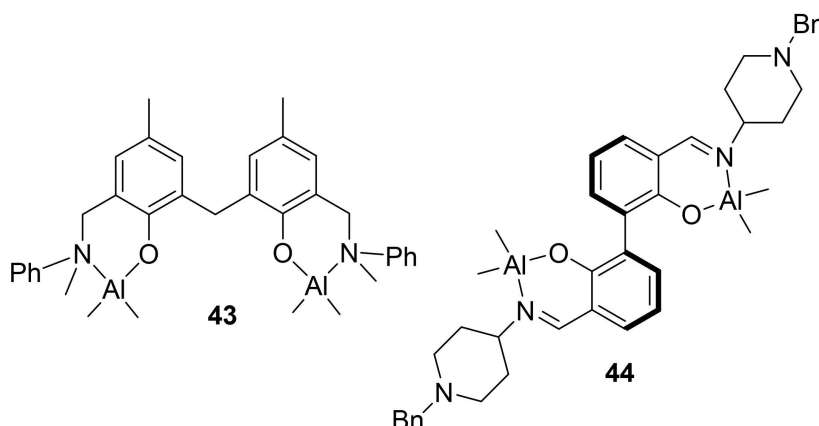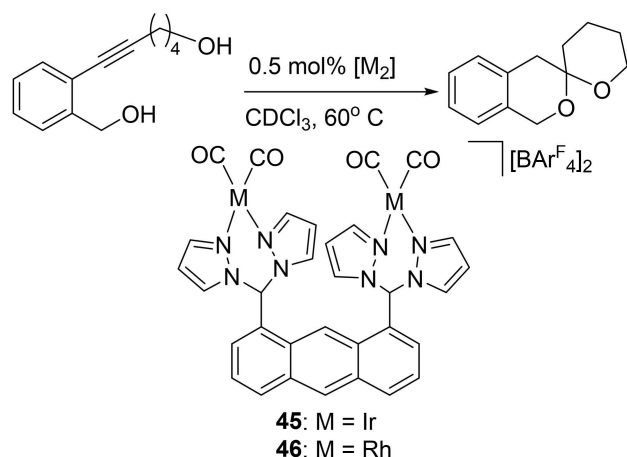**Scheme 18.** Dinuclear ruthenium complexes and their application in olefin metathesis reactions.

Figure 7. Examples of dinuclear aluminum complexes showing cooperativity in the ROP of lactides.

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Scheme 19. Dihydroalkoxylation of alkyne diol using dinuclear Rh(I) and Ir(I) catalysts.

than one metal enhances the catalytic activity of the dinuclear complex instead of having a large Pd⋯Pd separation (∼13.9 Å). More pronounced effects in the catalytic activities of these complexes have been observed in the Suzuki-Miyaura cross coupling reactions, and the dinuclear complexes appeared to be more active compared to their mononuclear counter parts (Scheme 21).[80] A plausible explanation for the enhanced activity of the dinuclear complexes is assumed to be either due to the reflection of the higher local concentration of the metal in the catalytic cycle or to the presence of non-covalent interactions between substrate and catalyst through the conjugated π system.

The same research group has also prepared the trinuclear palladium(II) complexes (**50** and **51**) bearing tris-NHC ligands. In both complexes, each palladium center is coordinated with one NHC donor, one chloride and one η³-allyl ligand. Albeit of the large Pd⋯Pd separation, both complexes show good to excellent activity in α-arylation of propiophenone with aryl bromides (Scheme 22). In all the cases, the trinuclear complexes delivered better yield compared to the similar mononuclear palladium complex.[81]

Sarkar and co-workers have also presented dinuclear iridium (III) complexes bearing either triazole or cyclometallated NHC ligands showing enhanced catalytic activity compared to the similar mononuclear counterparts in the transfer hydrogenation reaction (Scheme 23). Two newly formed iridacycles in the dinuclear iridium(III) complex **52** and **53** are almost coplanar with the central phenyl ring. This planarity is presumed to conduct the electrochemical communication between two iridium centers and finally results the cooperativity during the catalysis.[82] Complex **52** comprising of cyclometallated bis-NHC ligand appeared as more active compare to the complex **53**. In both complexes, the Ir⋯Ir separation is almost 7 Å. A similar trinuclear iridium(III) complex **54**, comprising of 1,3,5-triphenyl-benzene derived triply cyclometallated tris-MIC ligand, has also been tested for the same catalytic transfer hydrogenation reaction. The triply cyclometallated complex **54** shows less activity compare to the doubly cyclometallated complex **52**,
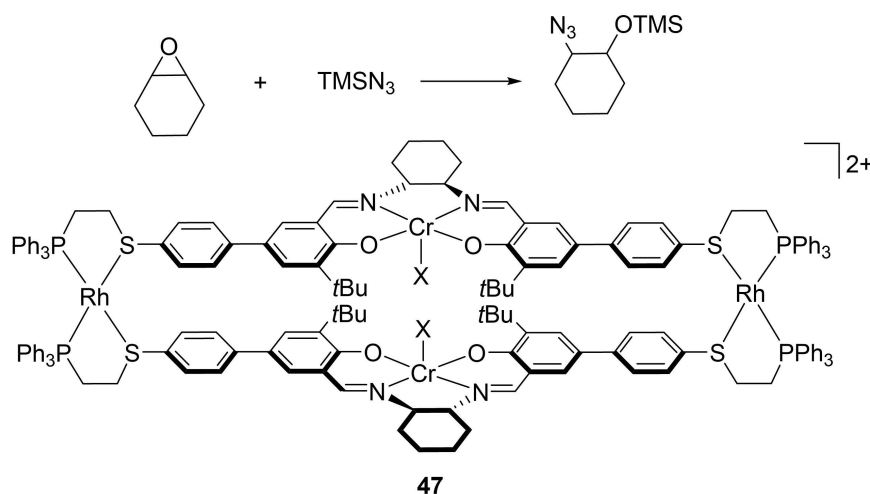
monomeric system in the Cr-catalyzed ring opening reaction of cyclohexene oxide with azide.[76] These catalytic results are also consistent with the cooperativity observed by Jacobsen and co-workers with a oligomeric Co(III)-based catalyst.[77] Cooperativity in multimetallic salen complexes has also been observed in immobilized metallosalen systems on dendrimers containing long-chain polymers. For instance, Jacobsen and Breinbauer developed catalysts comprised of dendrimeric Co(III)-salen units, which show superior activity in hydrolytic kinetic resolution (HKR).[66,78] Although it is well accepted that the metal centers should stay in close proximity to show the enhanced cooperative catalysis, a significant cooperative effects have also been observed with large metal-metal distances in many others macromolecular multimetallic structures known as dendrimer effect.[79]

Peris and co-workers have demonstrated pyracene-linked bis-imidazolylidene-coordinated dinuclear palladium(II) complexes **48** and **49**. In both complexes, the presence of more
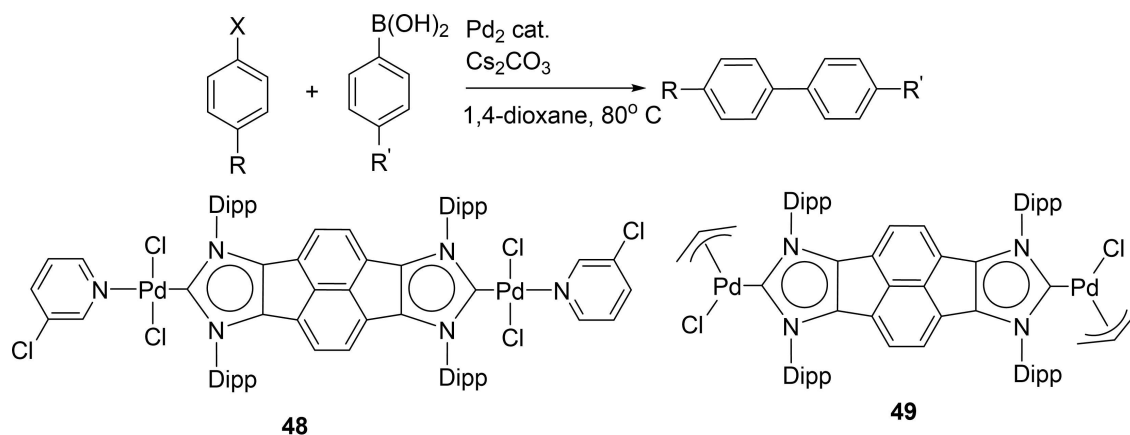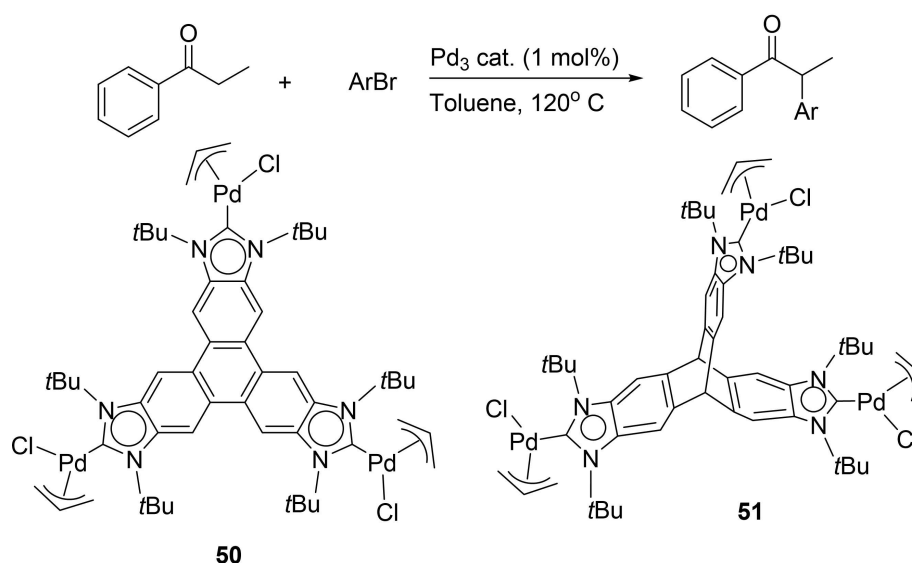

Scheme 20. Supramolecular dinuclear chromium(III)-salen complex for cooperative catalysis.

Scheme 21. Dinuclear palladium(II) NHC complexes in Suzuki-Miyaura cross coupling reactions.

Scheme 22. Trinuclear palladium(II) NHC complexes for α-arylation reaction.

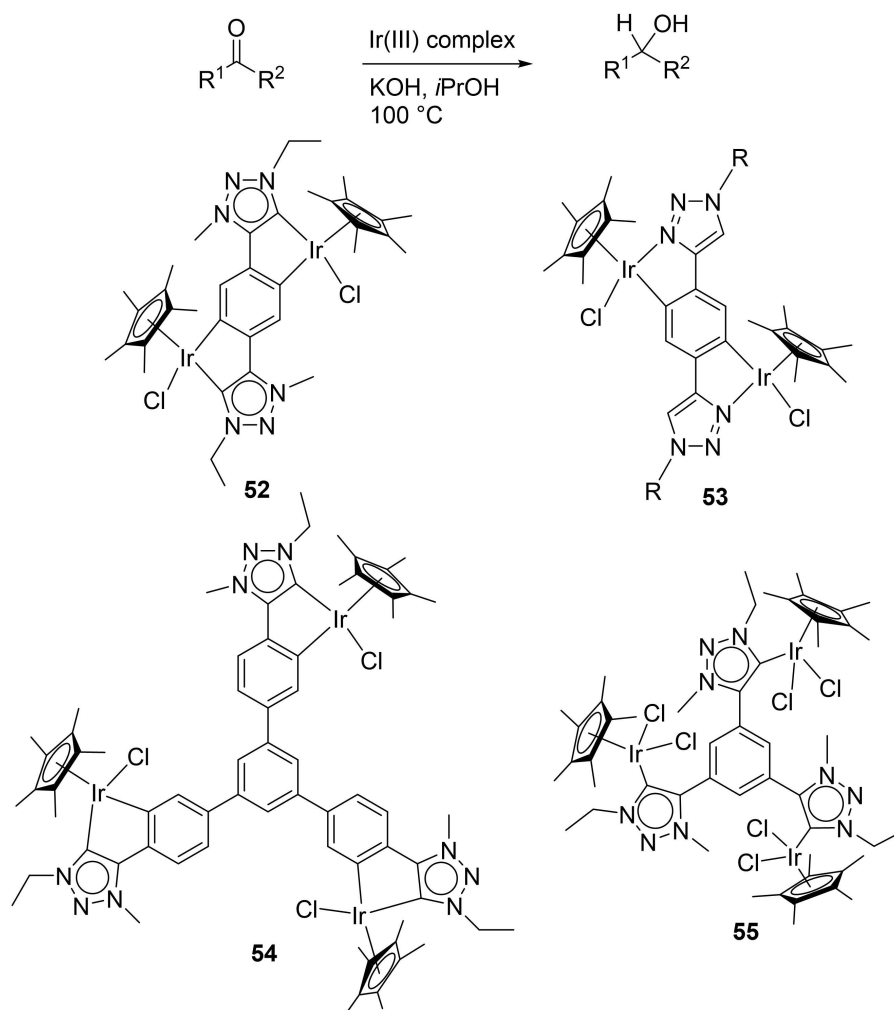however, appeared as more active precatalyst than the cyclo-metallated mononuclear counterpart.[83]

The corresponding trinuclear non-cyclometallated iridium (III) complex **55** bearing tris-aNHC ligand featuring a 1,3,5-substitution pattern of the central phenylene ring has also been synthesized by the same research group. The trinuclear complex (average Ir⋯Ir separation: 8.36 Å) delivers conversions in the transfer hydrogenation reactions, which are almost two times more than the cyclometallated mononuclear counterpart.[84] The catalysis results are in agreement with the dependence of cooperativity with metal-metal separation in the complexes.

The 1,3,5-triphenylbenzene derived tris-MIC ligand platform has also been used for the preparation of a trinuclear palladium PEPPSI (pyridine-enhanced precatalyst preparation stabilization and initiation) type complex **56**. The trinuclear palladium(II) complex **56** displays possible signs of cooperative effects for the homogeneous intermolecular α-arylation reactions

(Scheme 24)[83] and gave much higher yield of α-arylation products when compared with the equivalent yields obtained by using the corresponding mononuclear complex.

The Pd⋯Pd separation in this complex measures 14.07 Å, however, the observed intermolecular π⋯π interactions between two central aryl rings might bring the palladium centers in close proximity to show the observed cooperativity.

Cooperative catalysis with the octanuclear samarium complex **57** bearing large metal-metal separation has also been documented for N₂ activation reaction (Figure 8).[85] In the activation process, four divalent samarium centers are acting in a cooperative fashion and each samarium atom is donating one electron towards the four electron N₂ reduction process.[85] Different multimetallic complexes have also been demonstrated in literature for cooperative activation of N₂.[86]

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Scheme 23. Multinuclear iridium(III) complexes in transfer hydrogenation reactions.

4. Cooperative effects in hetero-multimetallic complexes

Heterometallic catalysts possessing more than one catalytically active metal center on a single ligand frame, potentially facilitate complicated catalytic transformations by combining different catalytic reactions into a single-pot tandem process. The ligand design is a very logical approach for the synthesis of heterobimetallic complexes. Examples are demonstrated in literature where these complexes show augmented catalytic activity compared to the combined action of their mononuclear counterparts.
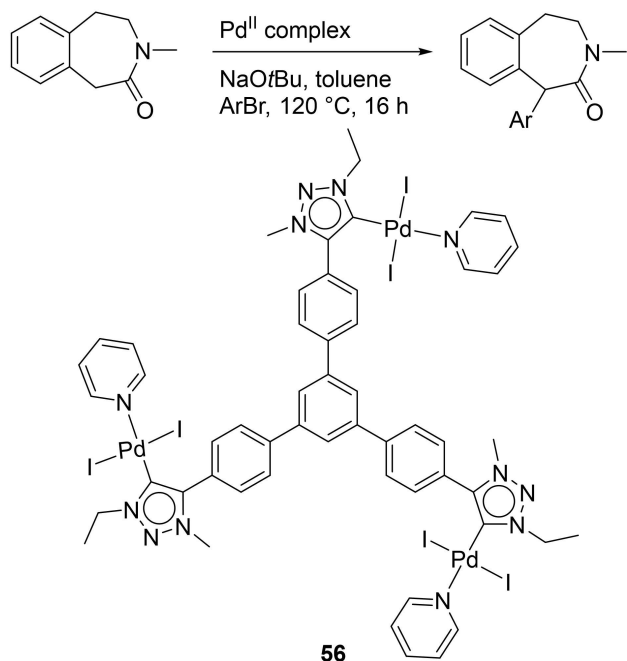
4.1. Cooperativity in early and mid transition metal systems

Thomas and co-workers developed a series of dinuclear Co/Zr complexes featuring significant metal-metal interactions. These compounds exhibit unexpected reactivity that is not observed in their monomeric counterparts. In the Kumada coupling, a better performance than for comparable monomeric cobalt complexes was observed (Scheme 25). Furthermore, alkylchlorides could be used as a coupling partner, which is usually not possible for Co-catalyzed cross-couplings.[87] Computational studies revealed that the Co–Zr interaction allows for the reduction to the two-electron-reduced active species. The reductive elimination step is also facilitated by an intramolecular phosphine-dissociation pathway due to the electron withdrawing capacity of the Zr atom.[88]

A structurally similar complex was able to catalyze the hydrosilylation of ketones (Scheme 26). In this example, the Zr atom seems to serve as the reactive site undergoing a ketyl-radical pathway, while the Co center serves to stabilize the active Zr(III) site.[89] These two examples show the effect of electronic communication in multimetallic systems, allowing for unusual reaction pathways of both metal centers.

Recently, the same group published the semihydrogenation of alkynes, utilizing another Zr/Co complex. The system contains a formal Zr–Co triple bond and is able to cooperatively activate dihydrogen. Mechanisms of the subsequent hydrogenation are not yet fully understood, and at present exper-

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Scheme 24. Trinuclear palladium(II) complex for α-arylation reactions.

Figure 9. Heterobimetallic complexes showing very large cooperative effect in ethylene polymerization.

imental data suggests two simultaneous pathways (Scheme 26).[90]

Recently, Marks, Delferro and co-workers have demonstrated heterobimetallic Ti[IV]/Cr[III] complexes showing very large cooperative effects in the ethylene polymerization reactions (Figure 9).[91]

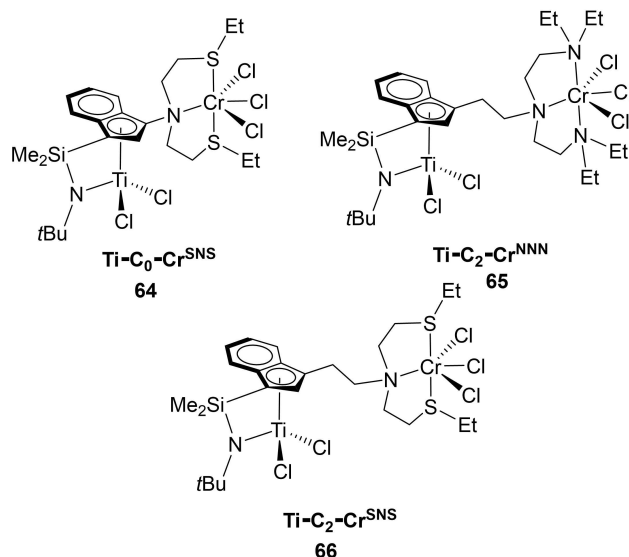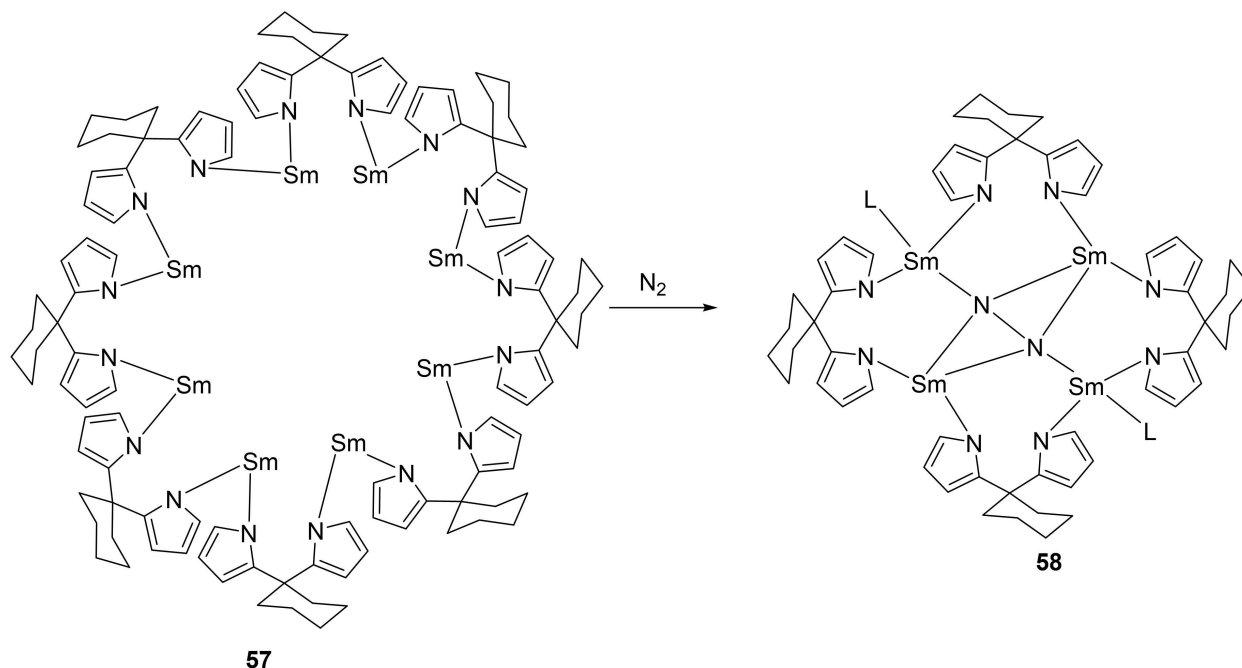These heterobimetallic complexes proved to be more active compared to a mixture of Ti[IV] and Cr[III] tandem catalyst. Interestingly, it has also been found that the activity of the heterobimetallic polymerization catalysts diminished with increasing the Ti···Cr spatial separation (Ti···Cr distances: 4.67 Å for Ti–C$_0$–Cr^{SNS} (**64**) and 6.34 Å for Ti–C$_2$–Cr^{SNS} (**66**)). Therefore, complex **64** yields polyethylenes with greater activity and branch density than the heterobimetallic complexes Ti-C$_2$-Cr^{SNS} and Ti-C$_6$-Cr^{SNS} under identical reaction conditions. The close

Figure 8. Multinuclear Sm[II] complex for cooperative N$_2$ activation.

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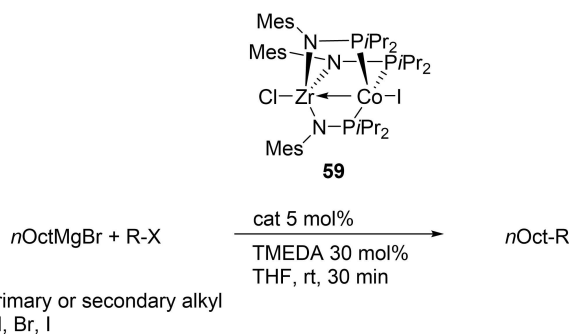
Scheme 25. Cooperative cross-coupling with a dinuclear Zr/Co complex.

Ti···Cr separation along with weak C—H···Ti and C—H···S interactions have a tremendous impact on enchainment and chain transfer rates, which has also been supported by DFT calculations.
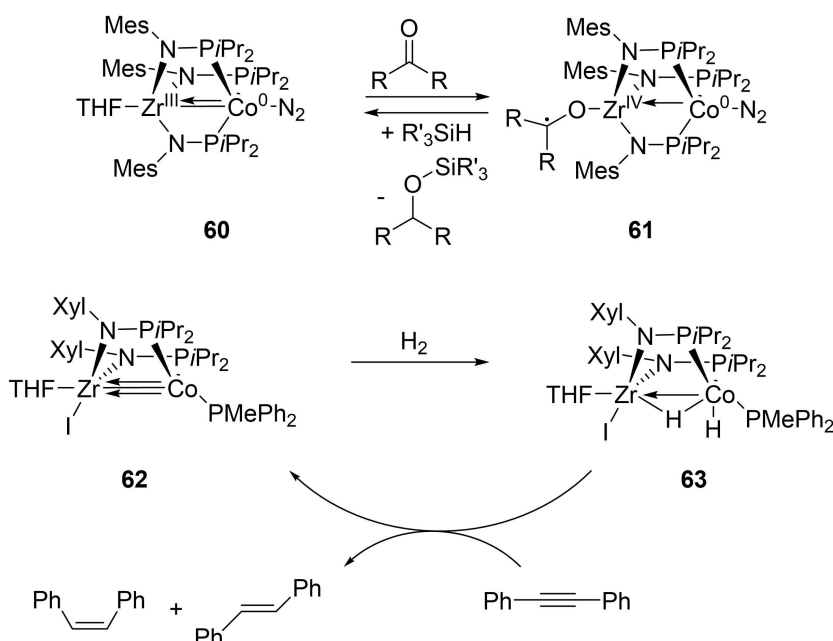
Williams and co-workers reported a series of heterobimetallic Co^{III}/M^{I} (M = group I metals) complexes bearing macrocyclic ligands (Scheme 27). These complexes show high efficiency and outstanding yields of PPC (polypropylene carbonate) polyols in the ring-opening copolymerization reaction of CO_2 and propylene oxide.[92] The Co···K separation measures 3.698 Å, which fall in the range to show metal-metal cooperation in ring-opening intermediate and transition state.[93] Further examples of cooperativity in transition metal/alkali metal systems have recently been reported by Garden and co-workers.[94]

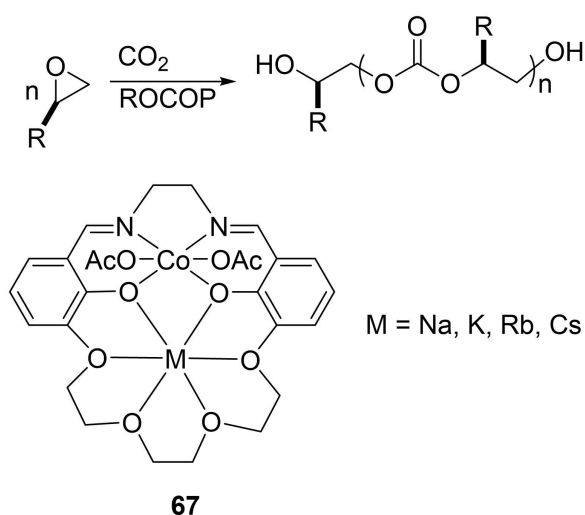## 4.2. Cooperativity in mid and late transition metal systems

As halide-bridged heterobimetallic complexes are both thermodynamically and kinetically unstable, these complexes show advantages in catalytic applications owing to their intrinsic reactivity.[28] Although several examples of the aforementioned complexes are demonstrated in literature, synthetically useful complexes to show cooperative effects are still rare. The heterobimetallic Rh^{III}/Ru^{II} complex showed exceptional activity over the monometallic counterpart in the oxidation of secondary alcohols (Scheme 28).[95]

It has already been discussed that the dinuclear ruthenium (II) NHC complex shows enhanced catalytic activity towards olefin metathesis reaction (Scheme 18). However, Herrmann and co-workers found that the related heterobimetallic Rh(III)/Ru(II) NHC complex shows dramatically enhanced activity in the ROMP of 1,5-cyclooctadiene to yield polyoctadienamer (Scheme 29). This heterobimetallic complex **69** is known to be one of the most active catalyst precursors developed for olefin metathesis reactions. It is also believed that the rhodium(III) center has a drastic interaction with the ruthenium(II) center during catalysis.[96]

The heterotrimetallic catalyst $PdCl_2(PPh_3)_2$—$Co_2(CO)_8$ (**70**, Pd/Co atomic ratio: 1/1) shows high activity in the hydroformylation reaction of di-substituted alkynes. The catalyst also shows synergistic effects during catalysis and leads to the formation of the unsaturated aldehyde with 49% yield after 24 h, whereas $PdCl_2(PPh_3)_2$ or metal carbonyls result in low yield. An excellent yield of the unsaturated aldehyde (95%) was obtained by a modified heterotrimetallic $PdCl_2(PCy_3)_2$—$Co_2(CO)_8$ catalyst under the same reaction conditions (Scheme 30).[97] Nickel/magnesium bimetallic cooperation has also been demonstrated in literature for various cross-coupling reactions.[98]

Scheme 26. Catalytic Hydrosilylation and Hydrogenation with Zr/Co complexes.

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Scheme 27. Heterobimetallic catalyst for ring opening polymerization.
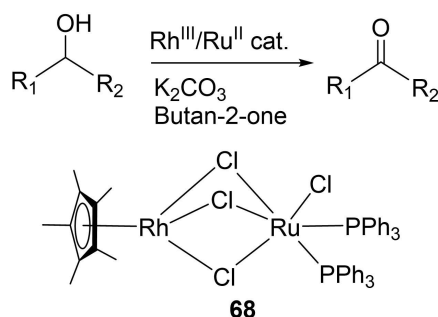
Scheme 28. Catalytic oxidation of alcohols by heterobimetallic Rh(III)/Ru(II) complex.

Scheme 29. ROMP of 1,5-cyclooctadiene by heterobimetallic Rh^{III}/Ru^{II} NHC complex.

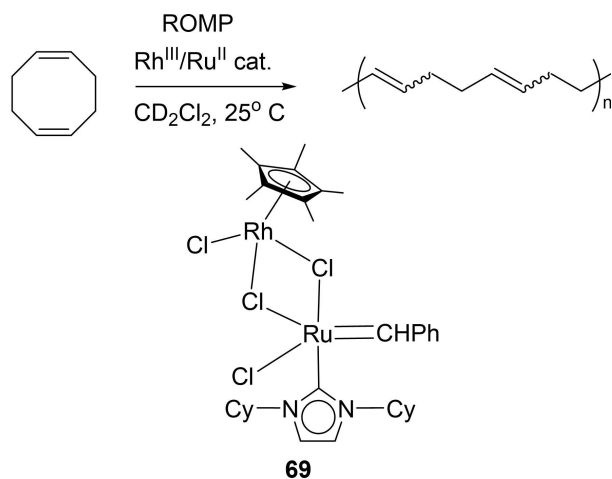A well-defined molecular heterotrimetallic Pd$_2$(II)/Pt(II) catalyst **71** was also found to be highly active for the widespread palladium(II)-catalyzed Heck-type C—C coupling reactions

(Scheme 31).[99] The complex showed superior activity compared with the similar type mononuclear palladium(II) complex in the formation of stilbene from styrene and iodobenzene by Heck reaction.[91]

A complex containing bis-palladacycles with tosylate as the anion, which can be generated in situ from the corresponding complex **72**, catalyzes the C—C coupling reaction between α-phenyl-substituted cyanoacetate and methyl vinyl ketone with excellent yields (Scheme 32).[100,101] The Pd···Pd distances in these complexes fall in the range of 3.15 to 5.27 Å.
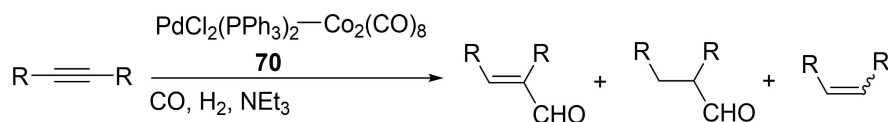
It has been proposed that both metal centers act in a cooperative fashion to activate the electrophile and nucleophile. The coordination of the nitrile group to the palladium(II) center (**73**) facilitates the enolization reaction and the enone group is concurrently activated by another palladium(II) center present in the bimetallic active-precatalyst (Scheme 33). The bimetallic cooperative mechanism operating in this reaction has also been confirmed from the absolute configuration of the reaction product.[100,101]

Similar heterotrimetallic complexes Ru(II)/Pd$_2$(II) and Fe(II)/Pd(II)/Pt(II) have also been successfully synthesized, and used for the different cooperative organic transformations.[102] Peters and co-workers have also synthesized heterobimetallic Ni(II)/Pd(II) complexes using salen bis-NHC hybrid type ligands using a stepwise synthetic protocol. The heterobimetallic complexes showed moderate activity in the 1,4 addition reaction of oxindole and 2-nitrostyrene, however, the activities are greater compared to the homodimetallic palladium complexes (Scheme 34).[103] The intermetallic distances in the complexes are in the range 3.057–6.169 Å.
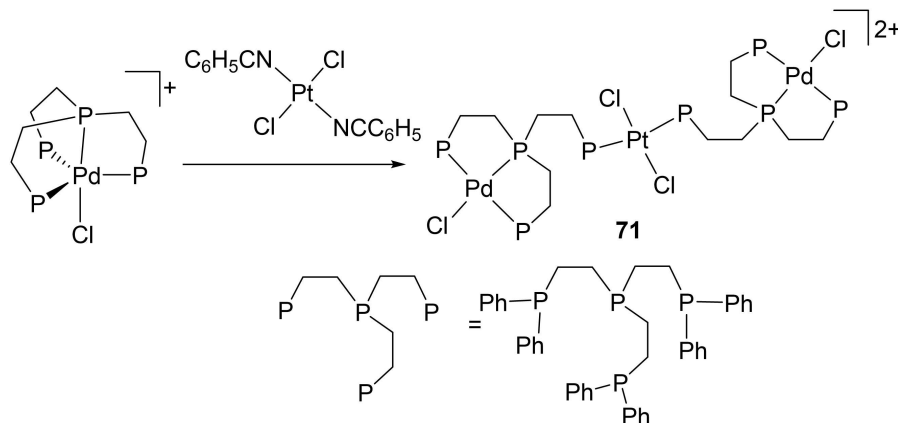
Peris and co-workers have prepared varieties of heterobimetallic complexes depicted in Figure 10. In all the complexes, both metals are active in a wide range of organic transformations. Therefore, the combination of both metals on same ligand platform makes the catalysts active towards various tandem organic transformations performed in a single reaction pot. In addition, these complexes afforded significantly higher yields of final products compared to the yields obtained from mixture of homodimetallic complexes used in same catalytic ratio under the same reaction conditions.[104,105] Therefore, these results provide a key piece of evidence of catalytic cooperativity operating between two different metal centers. The metal-metal separations in these heterobimetallic complexes measure around 6 Å for complexes bearing 1,2,4-triazolyl-3,5-diylidene ligand, and around 6.7 Å in the complexes bearing Y-shaped tris-NHC ligand.

The heterobimetallic Pd(II)/Ir(III) complexes **78** and **79** showed excellent activity in the tandem Suzuki-Miyaura/transfer hydrogenation reactions in a single reaction pot and the catalyst also afforded an improved yield of the biphenyl alcohol **83** when compared with the mixture of similar dinuclear complexes (Scheme 35).[105]

The heterobimetallic Ir(III)/Pt(II) complex **84** has been found to be highly active in the preparation of functionalized indole ring by the reaction of amino alcohol with alkynyl alcohols through multistep synthetic procedure.[106] The iridium(III) center is responsible for the oxidative cyclization of amino alcohol to

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Scheme 30. Heterotrimetallic complex for synergistic hydroformylation reaction.
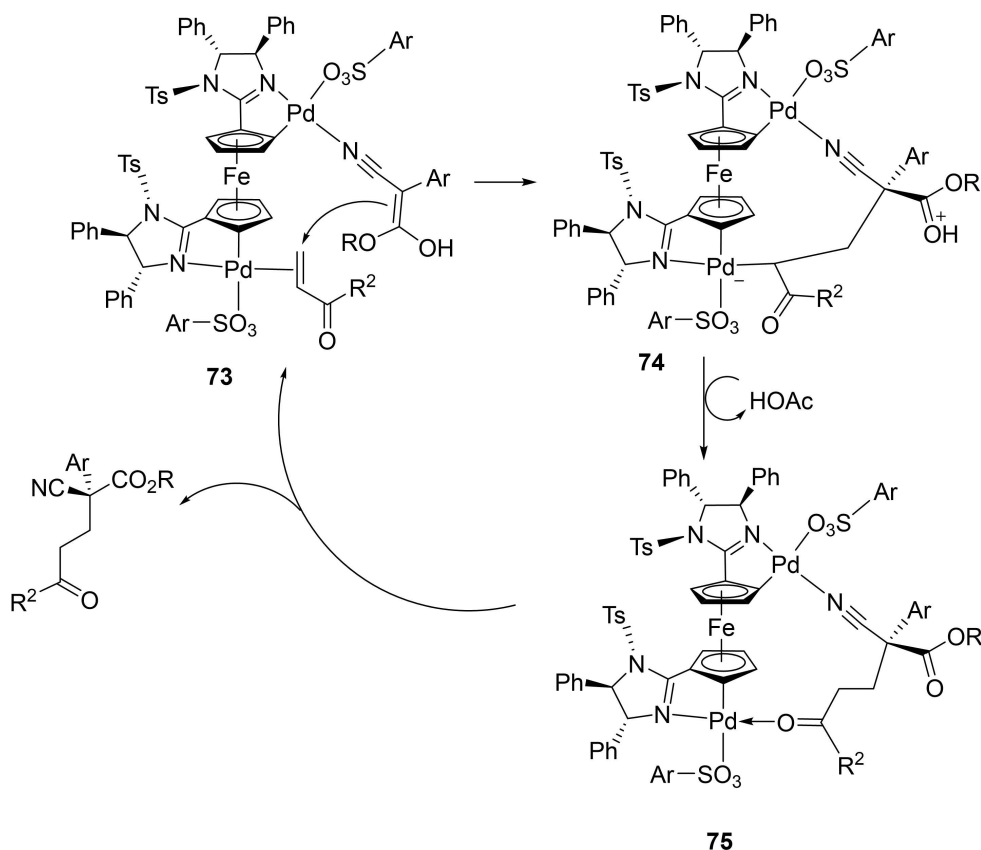

Scheme 31. Heterotrimetallic Pd$_2$(II)/Pt(II) catalyst.
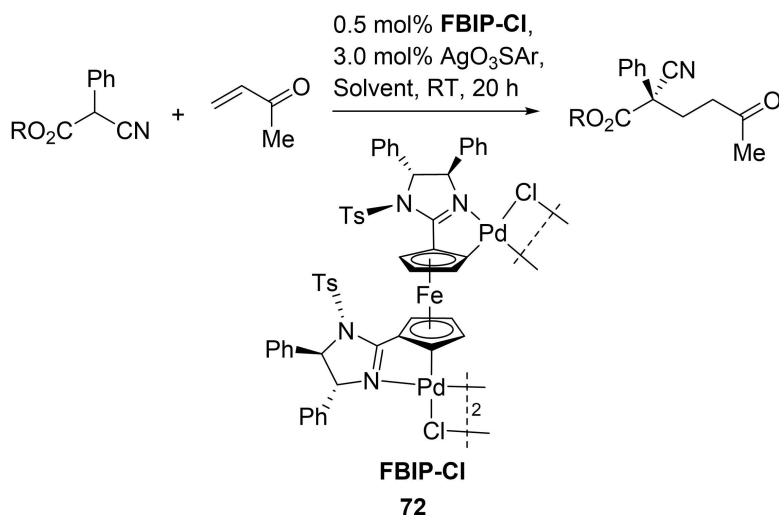
Scheme 32. Multinuclear Pd^{II} complex for cooperative C–C coupling reaction.

yield indole, which further reacts with alkynyl alcohols in the presence of platinum(II) catalyst to result the final cyclized C–C coupling product **85** (Scheme 36).

Carbon-fluorine bonds, which are documented[107] as most passive organic functionality, have also been activated using heterobimetallic complexes under mild reaction conditions. A heterobimetallic complex bearing a ruthenium(II) and a cyclometallated palladium(II) has been employed for the catalytic dehalogenation of aryl halides and the dehalogenated products have been obtained with excellent yields.[108] The heterobimetallic Ru(II)/Pd(II) catalyst **86** also appears to be a better catalyst compared to the combined action of the corresponding homo-

dinuclear complexes, and therefore, shows cooperative interaction of two different metal centers in the catalytic cycle (Scheme 37). A wide range of other bifunctional organic transformations have been successfully carried out with good to excellent yields using these heterobimetallic complexes with a combined action of both metal centers. The interaction between two hetero metal atoms is also supported by cyclic voltammetry studies. Both homodinuclear ruthenium(II) and heterobimetallic Ru(II)/Ir(III) (**80**, Figure 10) complexes show electronic coupling in the cyclic voltammetry studies.[109]

The synthesis of different types of heterobimetallic complexes, which could act as potential catalysts in cooperative

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Scheme 33. Catalytic cycle for the cooperative C–C coupling reactions.
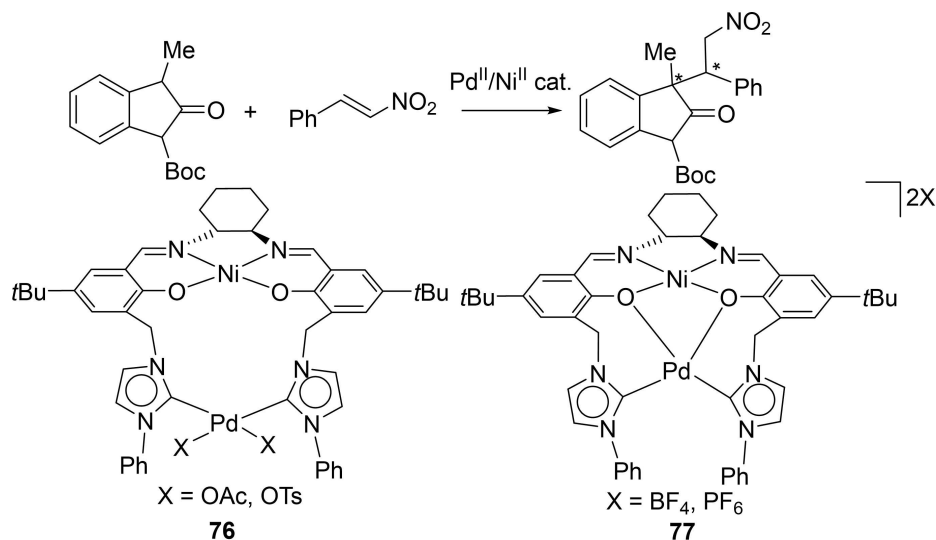
Scheme 34. Synthesis of oxindole spirocycle by heterobimetallic complexes.

tandem catalysis have also been demonstrated in literature. Some of the potential candidates are depicted in Figure 11 (metal-metal separation: 7.240 Å in **88**). The heterobimetallic complex **91** (metal-metal separation: 6.14 Å) bearing bis-NHC donor ligand shows much higher yields in tandem Suzuki-Miyaura coupling/transfer hydrogenation reactions when com-

pared to the equimolar mixture of their mononuclear Pd(II) and Ir(III) counterparts. Interestingly, the heterobimetallic complexes **87** and **88** have been synthesized in one-pot depending on the regioselective preferences of two different metal centers (Pd(II) and Ir(III)).[110]

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Figure 10. Heterobimetallic complexes for cooperative catalysis.

Scheme 35. Tandem Suzuki-Miyaura/transfer hydrogenation reaction catalyzed by Pd(II)/Ir(III) complex.

Scheme 36. Heterobimetallic Ir(III)/Pt(II) complex for functionalized indole preparation.

Scheme 37. Heterobimetallic Ru(II)/Pd(II) complex for cooperative tandem catalysis.

Very recently, Ghosh and co-workers have demonstrated heterotrimetallic Cu$_2$/Mn complex **92** showing cooperative catalysis in the biomimetic oxidase activities[111]. The heterotrimetallic complexes comprise of doubly condensed tetradentate Schiff base ligands derived from 1,3-propanediamine, o-hydroxyacetophenone and salicylaldehyde. The labile coordination of the H$_2$O to the Mn(II) center in complex **92** facilitates its catalytic activity (Scheme 38). This is one of the first examples showing mechanistic insight of biomimetic oxidase reactions with well-defined molecular heterotrimetallic complex.[111]

Scheme 38. Heterotrimetallic complex showing cooperative oxidase activity.

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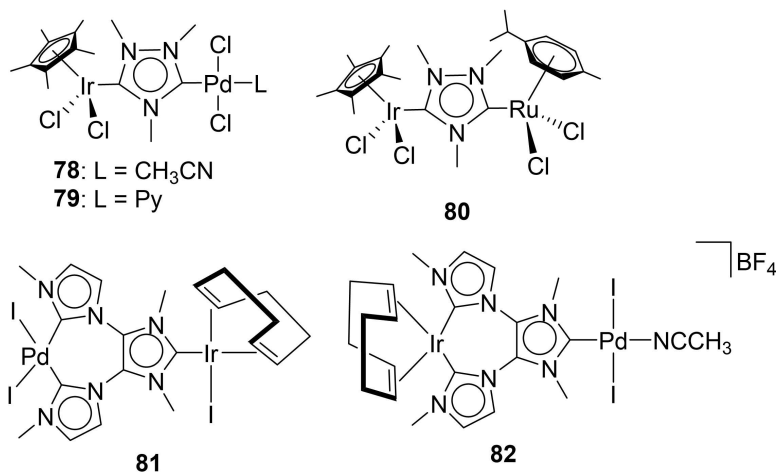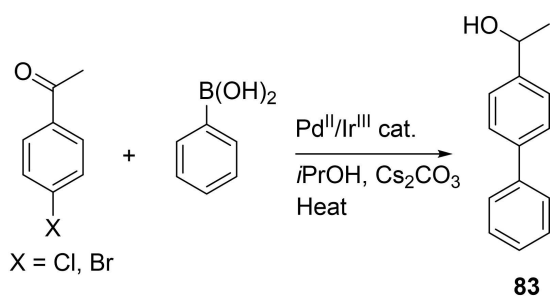European Chemical
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Figure 11. Potential hetero-bimetallic and hetero-trimetallic complexes for cooperative catalysis.

87: M = Rh
88: M = Ir

89

90

91

5. Cooperativity in metallocene-based multimetallic systems

Since its discovery in 1951, ferrocene has become an ubiquitous building block in chemistry. A variety of substitution reactions on ferrocene allow for access of rigid and robust bidentate ligands and allow for introduction of chiral information by utilizing its planar chirality. Especially bidentate phosphines such as 1,1'-bis(diphenylphosphino)ferrocene (dppf) have found widespread applic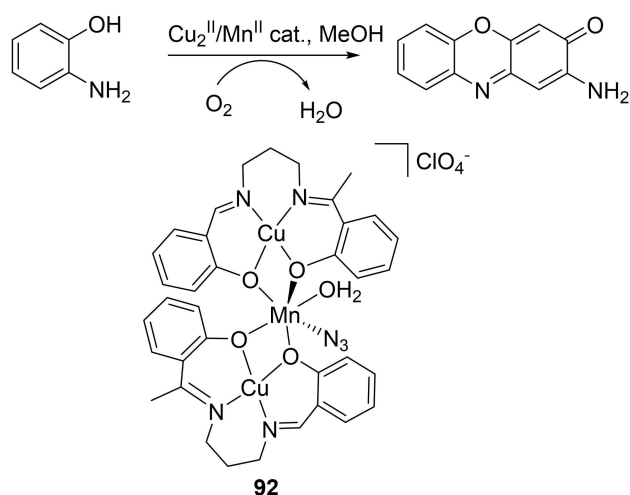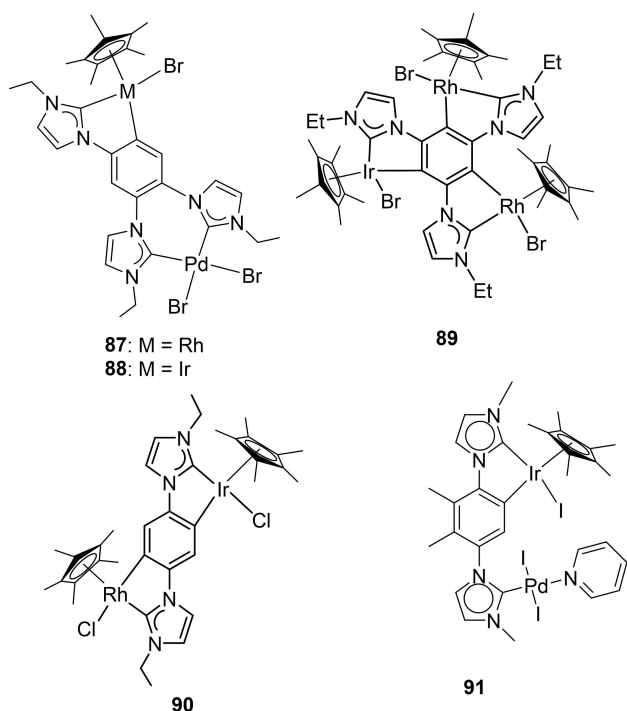ation as ligands for catalysis with late transition metals.[112] While these properties are certainly the main interest in the usage of ferrocene-based systems in catalysis, its electronic properties should not be neglected. Ferrocene and its derived ligands can oftentimes easily be oxidized predesignating this class of compounds for applica-

tions in the emerging field of redox-switchable catalysis.[113,114] Furthermore, observations of ferrocene acting as a non-innocent ligand have been made.

As already mentioned, ferrocene-based systems, in which donor moieties are fused directly to both Cp-rings, have become popular ligands and find a variety of applications. For example, [Pd(dppf)Cl$_2$] and similar complexes are commercially available and are used as catalysts in cross-coupling reactions.

The ferrocene moiety is generally used as a stable backbone with a desirable bite angle, allowing for chelation of a catalytically active metal center. However, examples for "unusual" structures with direct Fe–M bonds have also been known for a long time.[115] The $\kappa^2 D$-coordination mode (D=donor atom) in these complexes is extended with the ferrocenyl-moiety now acting as a κ^3-ligand (Figure 12). Although compounds with such Fe–M interactions are not uncommon and could be imagined as intermediate species in catalytic cycles, surprisingly little research has been done in this area of chemistry considering the ubiquitous application of bidentate ferrocene ligands in transformation reactions.

These complexes are usually accessible from the parent tetracoordinated complex by anion exchange with a non-coordinating anion or by reaction of the ferrocene ligand with a suitable weakly chelated metal precursor.[116]

It has also been shown that Pd(II) complexes of bidentate ferrocene ligands cannot always simply be formulated as the κ^2-tetracoordinated species. As such, [(dtbpf)PdI$_2$] (dtbpf=[1,1'-bis(di-*tert*-butylphosphino)ferrocene] actually has a structure of [(dtbpf)PdI][I] (**95**).[117,118] Similar observations have been made for [(dtbpf)PdBr$_2$] in chloroform solution[118] (**94**, Figure 13). For [(dtbpf)Pd(C$_6$H$_4$–4–CN)X] (X=Br, O–C$_6$H$_4$–4–OMe, O–C$_6$H$_3$–3,5–(*t*-Bu)$_2$) it was shown that in nonpolar solvents the complexes exist as κ^2-tetracoordinated species, partial reversible dissociation occurs in polar solvents like THF and chloro-

D= PR$_2$, S, SR, NR
M= Ni, Pd, Pt
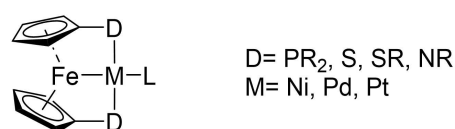
Figure 12. Schematic representation of the κ^3-binding mode.

93

κ^2- coordination

94

κ^3- coordination
(in chloroform)

95
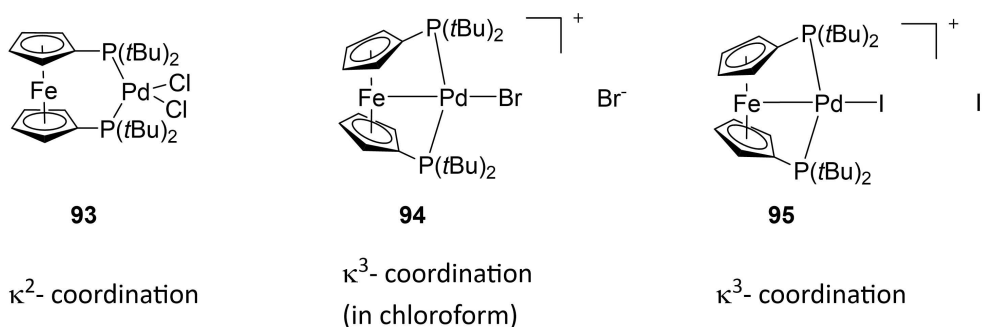
κ^3- coordination

Figure 13. Coordination modes in dtbpf complexes of different Pd salts.

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form to give the corresponding [(dtbpf)Pd(C₆H₄—4—CN)][X] compounds.[119]

The activity of κ^3-Pd compounds in catalysis has been investigated in the fields of methoxycarbonylation of styrene[120] and ethene[121], copolymerization of carbon monoxide with ethene[122], as well as α-arylation of ketones[118,123]. When [(dtbpf)Pd(PPh₃)]²⁺ was used in the methoxycarbonylation of styrene it showed shorter reaction times than its related complexes [(dtbpf)PdCl₂] and [(dtbpf)Pd(MeCN)₂]²⁺, which might hint at an influence of the κ^3-coordination mode on subsequent reactivity. A reverse trend was observed by Colacot *et al.* who reported that [(dtbpf)PdCl₂] (**93**) and [(dtbpf)PdBr₂] (**94**) made for efficient catalysts in α-arylation of ketones, while [(dtbpff)PdI₂], which actually adopts the ionic form [(dtbpf)PdI][I] (**95**), showed no reactivity[123]. Investigations in this direction by Diaconescu and co-workers similarly revealed a trend of decrease in reactivity for the heavier halides. Furthermore, when **93** was reacted with potassium tetrakis(pentafluorophenyl)borate (TFAB), the complex [κ^3-(dtbpf)PdCl][TFAB] was produced. This complex performed far worse than straight [(dtbpf)PdCl₂] suggesting that κ^3-(dtbpf)-coordination modes are unlikely resting states in this transformation[118]. These examples show that further investigations into this unusual binding mode might give interesting results and help in future designs of more reactive ferrocene-based phosphine ligands. It should be noted that, while these bidentate ferrocene ligands have yet to be used in redox-switchable catalysis (RSC), investigations in this direction are currently being made.[124]

One significant observation is the ability of ferrocene for electronic communication with coordinated metals. This type of cooperativity has been demonstrated by Rheingold *et al.* who showed a solvent dependent charge redistribution in a Rh(I) system supported by a ferrocenyl-functionalized ligand (Scheme 39).[125] Twofold oxidation of **96** in dichloromethane leads to the corresponding oxidized complex **97**, which slowly decomposes. However, if acetonitrile is added or if the oxidation is carried out in pure acetonitrile, the octahedral Rh(III) compound **98** is formed. Interestingly, when the ligand
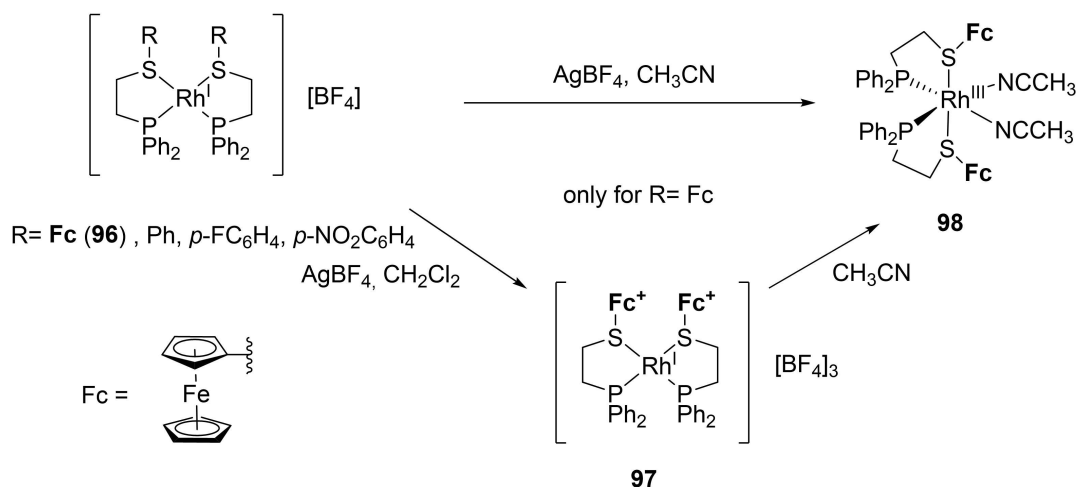
was substituted with moieties of different electron withdrawing capabilities, no oxidation and uptake of acetonitrile could be observed, which underlines the importance of the ferrocenium entity for this reaction to take place.

The use of ferrocene as an electron relay has been further demonstrated with a ferrocenyl phosphine-NHC ligand coordinating a Rh(I) center (Scheme 40).[126,127] Twofold oxidation of **99** gives a Rh(III) complex, which undergoes intramolecular C—H activation on the ferrocenyl moiety. Cyclic voltammetry experiments show that ferrocene is oxidized before rhodium. The monocationic Fe(III) complex **100** can also be first prepared by oxidation with AgBF₄ in dichloromethane.[126] Even though the oxidation potential of Ag(I) in acetonitrile is reduced below the oxidation potential of the ferrocene moiety, due to the irreversibility of the process, further oxidation in this solvent is possible.

While these examples in systems **96** and **99** do not fall in the category of cooperative catalysis, it nonetheless shows the capability of a ferrocene moiety to act as an electron-relay to support unusual transformation reactions.

One example of the importance of electronic communication and effects in metallic complexes was impressively demonstrated in the ruthenium complex [Cp*(dppf)RuH] (**102**, Scheme 41).[128,129] The system shows two reversible oxidations assignable to the Ru(III/II) and Ru(IV/III) redox couples. When the dppf-moiety is replaced by two Ph₂MeP ligands, one reversible oxidation is observed only for the Ru(III/II) couple. Most importantly, this system is capable of catalyzing the splitting of dihydrogen into two electrons and two protons in the presence of a one-electron acceptor (Scheme 41). By analogy to hydrogenases, this complex is the first example of a homogenous catalyst capable of such reactivity. While detailed studies have not been conducted, the ferrocenyl moiety seems indispensable for this reaction, which suggests the importance of electronic cooperativity in this system.[128,130]

Ferrocene-based systems are also employed in dinitrogen fixation and activation.[131,132] Cyclic voltammetry investigations on the PNP-pincer system **103** revealed that the free ligand is

Scheme 39. Oxidation of a ferrocene/Rh(I) to a ferrocene/Rh(III) complex.

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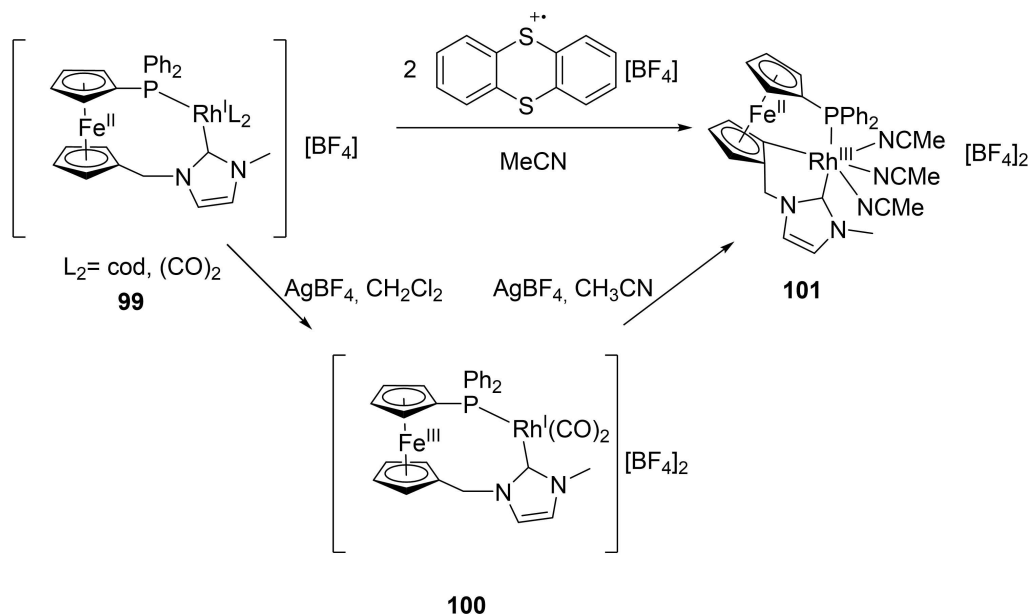
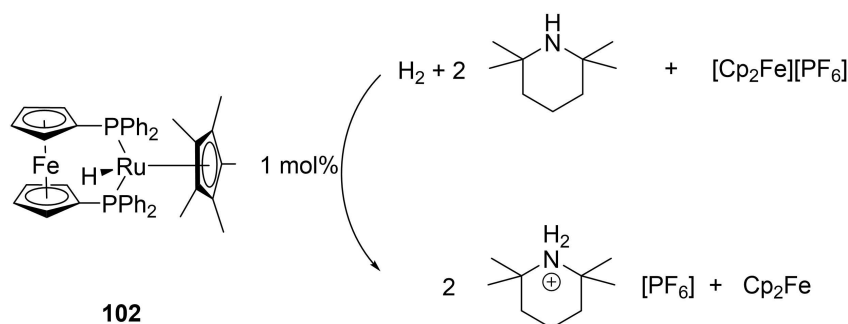**Scheme 40.** Oxidation with subsequent C–H activation of a ferrocene-Rh complex.

Scheme 41. Catalytic splitting of dihydrogen.

oxidized at a potential of $+0.10$ V vs. Fc/Fc$^+$, while the unfunctionalized Mo(III) complex is detected at $+0.14$ V. Coordination of MoCl$_3$ to the free ferrocenyl ligand shifts the redox potential of the iron atom to $+0.42$ V, while the Mo(III/IV) couple is detected at $+0.10$ V, which indicates strong communication between the two metal centers. Introduction of a bridge between the ferrocene unit and the coordination site decreases the redox potential of the iron atom, which is indicative of reduced electronic communication. When ferrocene was substituted for ruthenocene, only a reversible oxidation for the Mo fragment is detected. Utilization of these complexes in the catalytic transformation of dinitrogen showed a clear trend between electronic communication and activity of the complex (Scheme 42). As such, the unlinked ferrocene complex gave the best results, while the ruthenocene-based complex gave much poorer yields in comparison.[131]

Arduengo and coworkers synthesized a metallocene-fused imidazol-2-ylidene **105** on the basis of ruthenocene (Figure 14).[133] The palladium complexes of these show electronic influence between the two metals, as cyclic voltammetry shows
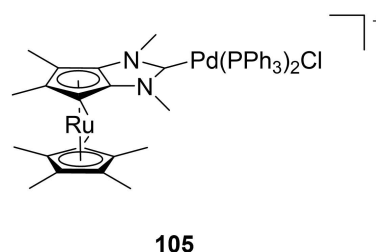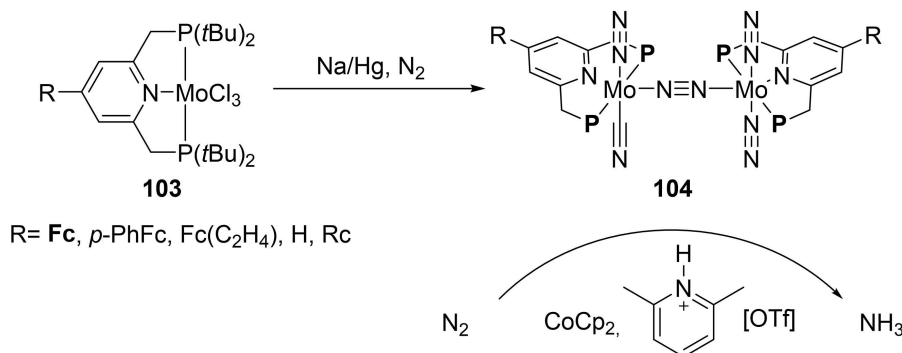

**Figure 14.** Ruthenocene/Pd complex for Suzuki coupling.

reversible oxidation only for the Pd complex but not for the hydrochloride precursor.[134] Furthermore, good catalytic activity for the Suzuki-coupling was observed in aqueous media.

Scheme 42. Catalytic transformation of dinitrogen to ammonia with a Fc/Mo complex.

6. Redox-switchable catalysis

Redox-switchable catalysis (RSC) aims at changing the catalytic behavior of an active complex. Addition of an oxidant or reductant to the reaction mixture leads to a change of the oxidation state, which changes parameters such as activity or substrate selectivity. Electronic communication between the metals, either through the ligand framework or through space is thus a necessary requirement for this kind of reactivity. Switching of the redox state of one metal also changes the communication, which leads to different behavior and reactivity. Most research in the area of RSC has been conducted in the area of polymerization reactions. The first demonstration of redox-switchable catalysis in this field was done by Gregson *et al.*, who used a ferrocene-functionalized salen-type ligand coordinated to titanium (Scheme 43).[135] While no on/off switch was obtained, the reduced catalyst performed markedly better
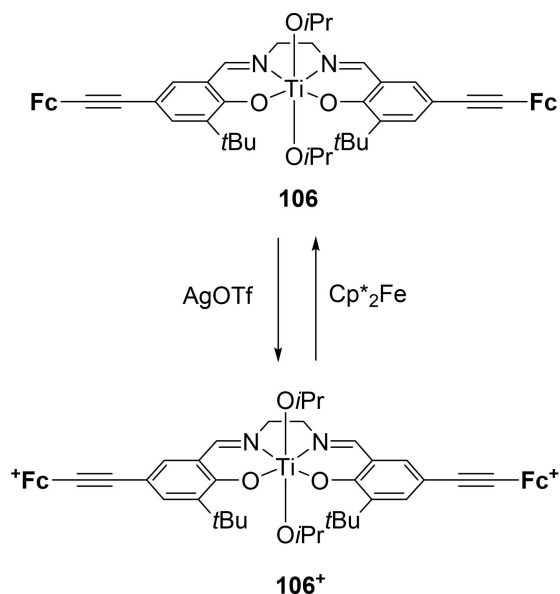
than the oxidized and *in situ* switching without loss of activity was possible.

Further investigations into this research area led to the development of a series of symmetrically substituted tetradentate 1,1'-ferrocene ligands that incorporate early transition or group 13 metals (Figure 15).[136,137–140]

While detailed examinations of these catalysts have already been summarized in another review,[114] in regards to cooperativity it should be noted that oxidation generally influences the reactivity of the catalyst. An interesting example for this is the usage of a Y(III) and an In(III) catalyst, which bear the same ligand in polymerization of trimethylene carbonate.[137] While oxidation led to a decrease in activity of the Y(III) catalyst, the reverse is true for the In(III) catalyst showing that the effects and interactions of the oxidation of the iron atom depend heavily on the coordinated metal. In the case of In(III), quantum chemical calculations suggest a bond elongation allowing for easier substrate coordination.[141] A remarkable achievement is the usage of redox-active polymerization catalysts to generate triblock polymers by means of switching the catalyst *in situ* multiple times (Scheme 44).[138–140] Oxidation of the complex leads to a change in selectivity towards the monomers, essentially switching off the activity for one substrate, while switching it on for another.

Besides ROP, redox-switchable ferrocene-systems have also been applied in olefin polymerization.[142] First research in this area was done by Plenio and co-workers in 2013, who developed a series of Hoveyda-type catalyst (**108**) in which the Fischer carbene moiety was functionalized with a ferrocene unit
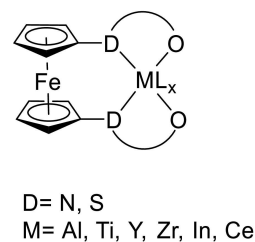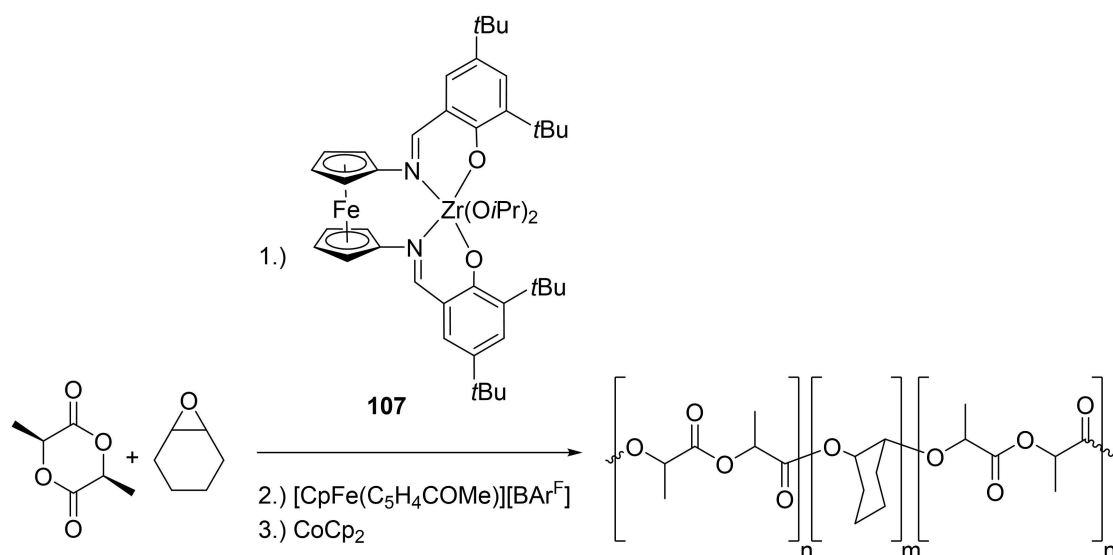

Scheme 43. Redox-switching of a Fc/Ti system.

D= N, S
M= Al, Ti, Y, Zr, In, Ce

Figure 15. General structure of tetradentate ferrocene complexes.

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Scheme 44. Redox-switchable copolymerization for triblock polymers.

(Figure 16).[143] Investigations in redox studies revealed that the oxidized species performed better than the reduced one in the polymerization of *cis*-cyclooctene. Interestingly, in the same year, the Bielawski group developed a Hoveyda-type catalyst in which the NHC moiety was functionalized with ferrocene (**109**).[144] This complex showed the inverse behavior and in the polymerization of 1,4-cyclooctadiene and the reduced species

Figure 16. Redox-switchable complexes for polymerization of cyclooctene.
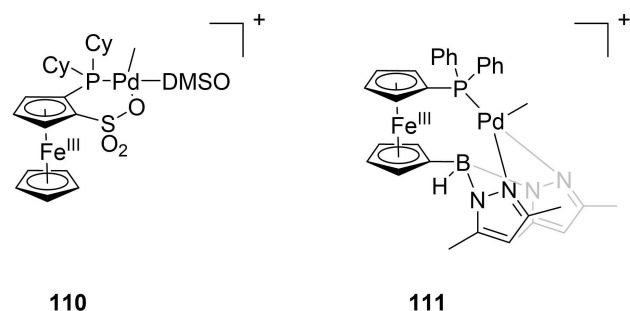
Figure 17. Catalysts for the polymerization of norbornene.

was found to be more active than the oxidized one. The effect in the former (**108**) is attributed to lowered electron density on the coordinated nitrogen atom in the trans position to the NHC moiety, as well as an increased positive charge on ruthenium[143], while in the latter (**109**) the activity change is assumed to originate from the lowered donor capacity of the NHC ligand.[144] Similar observations have been made in the cyclization of alkenes.[145]
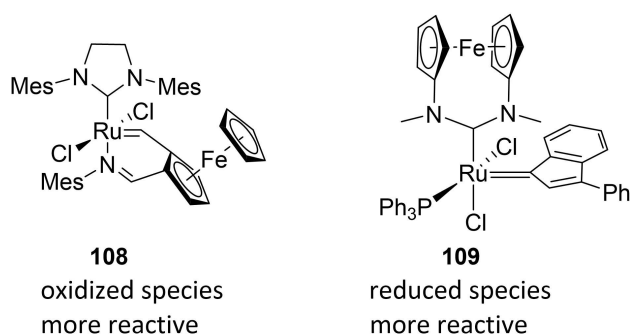
Further examples for cooperativity in catalysis were demonstrated in a series of Pd complexes for olefin polymerization. In 2015, Chen and co-workers used ferrocene phosphine-sulfonate ligands (**110**) to probe the influence of oxidation on catalytic performance (Figure 17).[146] Interestingly, activity in the polymerization of ethylene was lower when the oxidized complex was used, even though it has been observed that a decrease of electron density on the Pd center in sulfonate complexes leads to the contrary result.[147] Further investigations showed that these results can be explained by the electron-poorer Pd atom being more reactive, resulting in β-H chain transfer and thus deactivating the catalyst. When the complexes were probed for the polymerization of norbornene, the oxidized species indeed performed better than their reduced counterparts.[146] Similar observations have been made by Diaconescu and co-workers, who used a palladium complex based on a ferrocene heteroscorpionate ligand (**111**).[148] In these systems, only the oxidized species was capable of polymerization, which could be switched off *in situ* by addition of a reductant. However, these results were explained by an increase of the hemilability of the phosphine moiety allowing for better coordination of norbornene.

In 2017, Chen and co-workers were able to show the ability of controlling topology in polyethylenes by means of redox-control.[149] Oxidation of the catalyst (**112**) decreased its activity due to an increased stability of the palladium olefin coordination complex (Figure 18). This, however, increases chain-transfer reactions, which leads to a change in topology and polydispersity.

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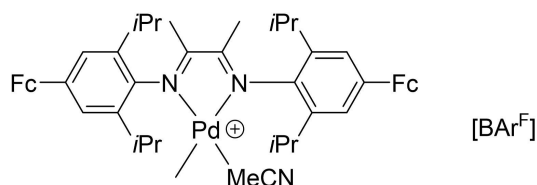
112

BArF= Tetrakis(3,5-bis(trifluoromethyl)phenyl)borate)

Figure 18. Pd catalyst for polymerization of ethenylenes.

While more research in this field could lead to even better responding catalysts, it can clearly be seen, that a wide range of aims for RSC have already been achieved.

Polymerization catalysts have certainly been the main focus of RSC, a variety of systems capable of other transformations have been studied in recent years. In the seminal work, Wrighton and co-workers described the first example for a redox-switchable catalyst.[150] In its reduced state, the cobaltocene-based rhodium complex **113** catalyzes the hydrogenation of cyclohexene, which is switched off almost completely by oxidation to **113**$^+$. However, the reverse was observed for the activity in hydrosilylation reactions. While the monocationic species is almost inactive, oxidation leads to strong increase in catalytic performance (Scheme 45).

The effects of oxidation in Fc/Rh systems was also demonstrated by directly attaching ferrocene moieties to a η^6-coordinated phenyl-Rh(I) fragment (Scheme 46).[151] The system undergoes self-exchange between the two phenyl moieties. Due to the electron-withdrawing capability of the Rh(I) atom, the first oxidation takes placed on the ferrocene unit, that is further apart from the coordinated metal. Although the rate of
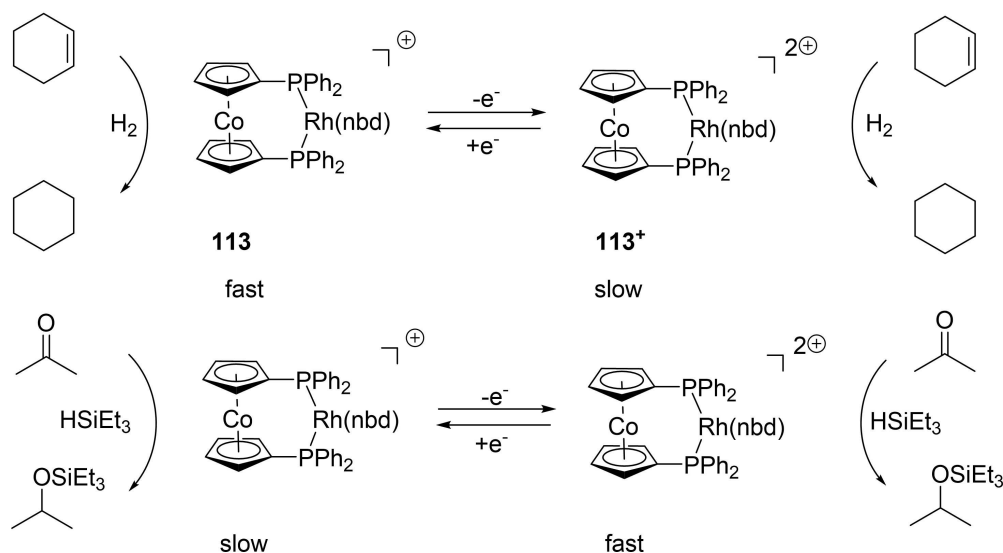
Scheme 45. Redox-switchable hydrogenation and hydrosilylation catalysis with a dppc-ligated Rh complex.
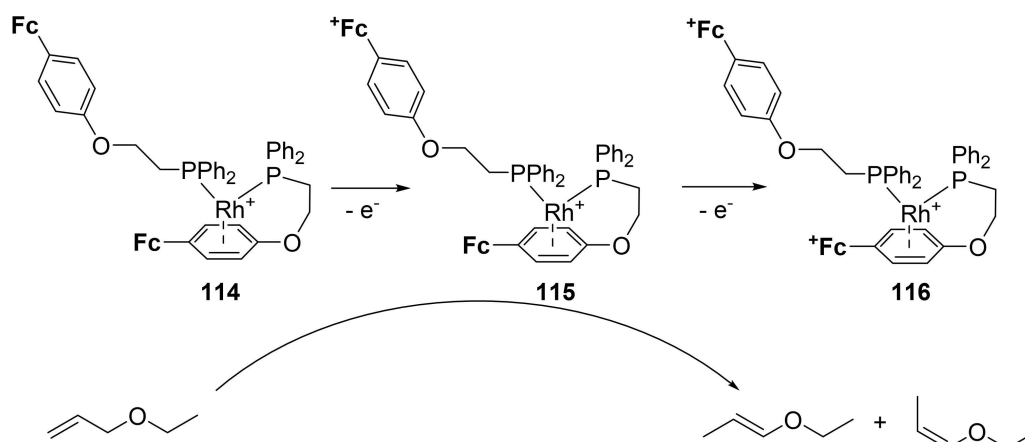
Scheme 46. Catalytic isomerization of allylethers.

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self-exchange is not heavily influenced by this, oxidation of both ferrocene-moieties leads to a strong increase. This is further demonstrated by catalytic isomerization of allylethers. For the reactivity, liberation of the coordination site on the Rh(I) atom occupied by the η^6-arene is crucial. The doubly oxidized complex **116** thus reacts between two and three times faster than the unoxidized **114** and mono oxidized **115** complexes.

Ferrocene-based complexes of transition metals are able to catalyze hydroamination reactions, as has been demonstrated by several groups. A variety of Au(I) systems based on phosphine or carbene ligands have been developed (Figure 19).[152,153,154] Hydroamination reactions carried out with these catalysts suggest that the main influence on reaction speed upon oxidation of the iron center stems from a decrease/increase in the donating/accepting capabilities of the ligand. As such, all systems investigated so far show an increase in catalytic activity upon addition of an oxidant. While the substrates used to probe the activity of **117** and **119** do not allow a direct comparison, measurements of the Tolman electronic parameter (TEP)[155] support the aforementioned argument. For **119**⁺, an increase in TEP of roughly $2\ cm^{-1}$ is observed and the change in activity is rather small (increase of up to 10%). Oxidation of **117** on the other hand, leads to an increase in TEP of roughly $7\ cm^{-1}$ and catalytic activities increase by up to a factor of six.

Complex **117** has also been used in a variety of cyclization reactions where in similar fashion the oxidized complex performed far better than the reduced one.[153,156] For complex **119**, even though the aforementioned change in TEP is small, on and off switching was accomplished in the reaction of terminal alkynes with 2,4-dimethylfuran, in which only the oxidized species showed any reactivity.[154] Very high activities were observed in the redox-induced hydroamination of alkynes by employing a redox-active gold(I) complex **118** featuring an electron-deficient, terphenyl-substituted phosphonite-based ligand. The hydroamination proceeds roughly two-fold faster with the *in-situ* oxidized catalysts than with its reduced form.[152a]

A recently developed zirconium(IV) complex based on an OSSO-functionalized tetradentate ferrocene ligand (**120**) showed a change in selectivity between oxidized and reduced species.[157] While the reduced molecule catalyzes intramolecular addition of primary aminoalkenes, the oxidized does so for secondary aminoalkenes (Figure 20). EPR and Mössbauer studies

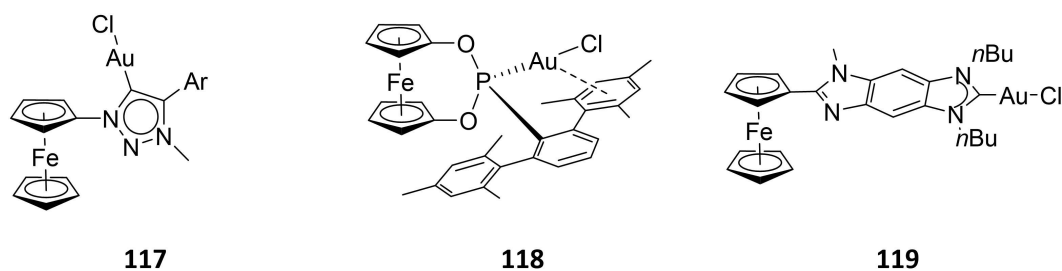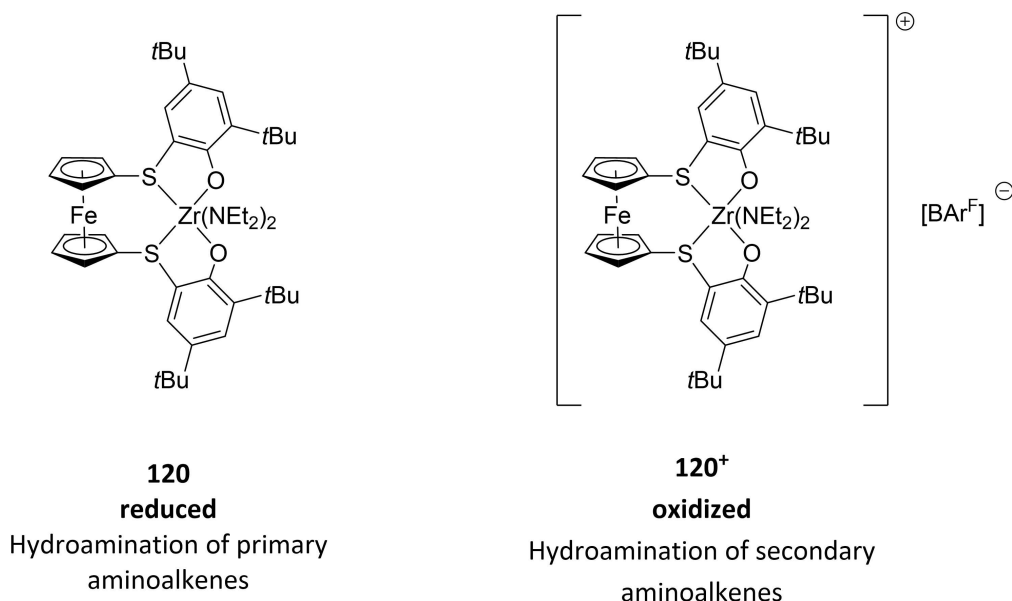**Figure 19.** Complexes for redox-switchable hydroamination catalysis.

120
reduced
Hydroamination of primary aminoalkenes

120⁺
oxidized
Hydroamination of secondary aminoalkenes

Figure 20. Zr complexes for redox-switchable hydroamination.

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suggest that the positive charge in this system is not centered on the iron atom, which remains in oxidation state +II but rather hint at an organic radical.

Rather unexpected reaction patterns have also been observed. Heinze and co-workers synthesized a ferrocene-based Fischer carbene coordinated to a gold(I) unit (**121**, Scheme 47).[158] Upon reaction with Magic Blue, the expected oxidation on the iron(II) center takes place. However, over time, reorganization from the iron(III)/gold(I) complex towards an iron(II)/gold(II) complex **123**, supported by the [SbCl$_6$]$^-$ counter anion, takes place and reaches equilibrium after ~5 h at room temperature (Scheme 47).

While gold(II) compounds are known[159], insights in their reactivity remain scarce. Investigations into the reactivity of **121** in the cyclization reaction of N(2-propyn-1-yl)benzamide to the oxazoline show no conversion. However, upon addition of Magic Blue and an induction period of 2.5 h, a sharp increase in activity is observed, which suggests that **123** rather than **122** is the catalytically active species.

Redox switchable catalysts have also been applied in transfer hydrogenations.[160] For both systems, **124** and **125** (Figure 21), activity is reduced upon addition of an oxidant. The influence is much more pronounced for **124** where catalysis is basically switched off by oxidation, while **125** generally remains active with a decrease in reactivity.

In hydrosilylation catalysis, [1]phosphaferrocenophanes were investigated. The synthesis and characterization of several metal complexes of a redox-switchable, mesityl(Mes)-substituted [1]phosphaferrocenophane, FcPMes, have been reported by Breher and co-workers.[161] Cyclic voltammetry studies on several bimetallic complexes, in conjunction with DFT calculations, provided indications for a good electronic communica-

tion between the metal atoms. In order to confirm that the ferrocenophane unit might be able to electrochemically influence the reactivity of the coordinated transition metal, the rhodium complex **126** was employed as redox-switchable catalyst in the hydrosilylation of terminal alkynes. All reactions were greatly accelerated with *in situ* generated **126**$^+$ as a catalyst as compared to **126** (Scheme 48). Even more importantly, a markedly different selectivity was observed. Both factors were attributed to different mechanisms operating for **126** and **126**$^+$ (alternative Chalk-Harrod and Chalk-Harrod mechanism, respectively).[162] DFT calculations revealed relatively large differences for the activation barriers for **126** and **126**$^+$ in the reductive elimination step of the classical Chalk-Harrod mechanism. Thus, the key to the understanding is a cooperative "oxidatively induced reductive elimination" step, which facilitates both a higher activity and a markedly different selectivity.[161]

RSC hydroalkoxylation has also been described.[163] The activity of the cobalt complex can reversibly be switched off and on again *in situ*.

The influence of the oxidation of ferrocene has also been investigated in Suzuki-Miyaura[164] and Buchwald-Hartwig-coupling[165] reactions. In case of the Suzuki-Miyaura-coupling, a PCP-type pincer ligand was used (Scheme 49). Interestingly, reaction of **127** with Me$_3$SiSO$_3$CF$_3$ in acetone did not lead to exchange with the chloride anion but led to the oxidized complex **127**$^+$. The oxidized species performed much better than the neutral one, with up to four times as much turnover. The effect was more pronounced when multiphasic systems were employed.

For the Buchwald-Hartwig-coupling, a series of monodentate ferrocenylphosphines was investigated by Breher *et al.*
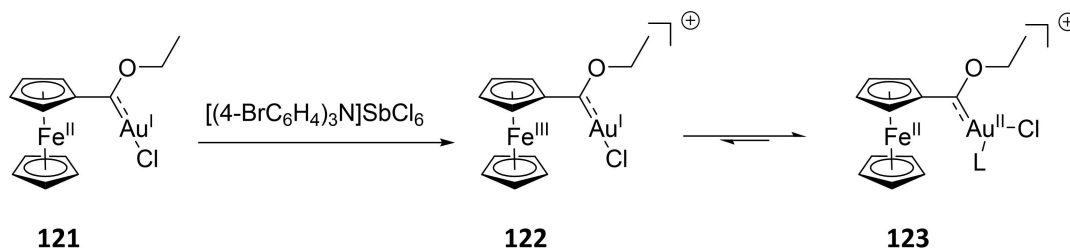
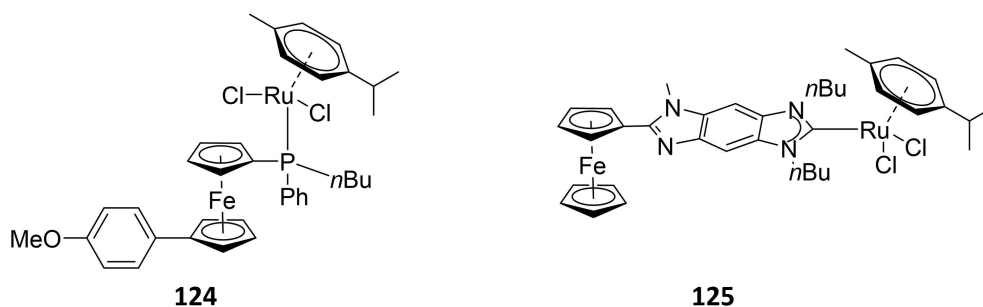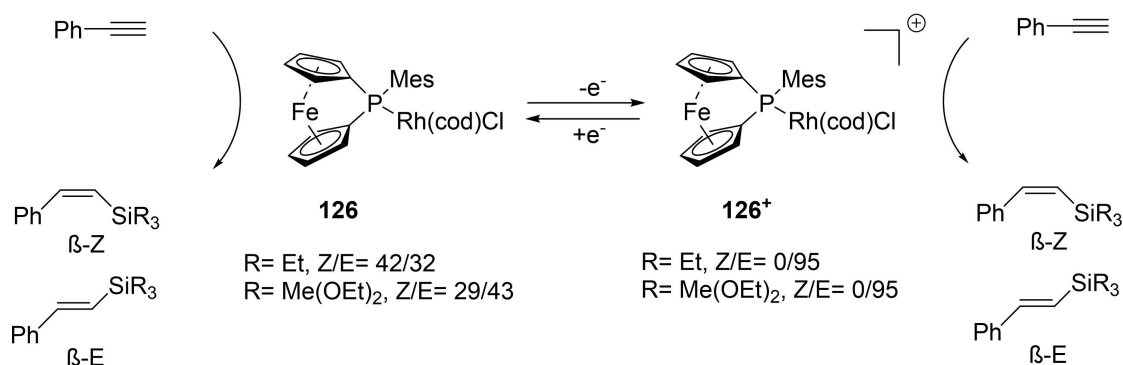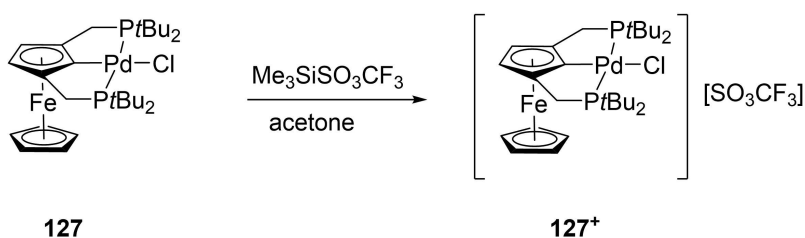**Scheme 47.** Formation of a Au(II) complex by oxidation of a Fc/Au(I) complex.

Figure 21. Catalysts for redox-switchable transfer hydrogenation reactions.

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Scheme 48. Redox-switchable catalysis with different product distribution for switched catalysts.

Scheme 49. Oxidation of a Fc/Pd complex.

Oxidations were carried out *in situ* with diacetyl ferrocenium tetrafluoroborate. Surprisingly, no clear trend between activity and oxidation state could be observe, as for some substrates the oxidized species showed to be the more efficient catalyst, while the reverse was true for other substrates. It is speculated that for the substrates, in which the reduced complex was more active, the rate determining step is not the reductive elimination but rather the oxidative addition, which is less favorable in the electron-poorer ferrocenium complexes.

Last but not least, it should also be noted that influence of the oxidation of the ferrocene moiety on catalytic performance does not necessarily have to be the result of cooperative effects. Given the right solvent system, switching off the catalysis can also be achieved by precipitation of the catalyst due to decrease of solubility of the oxidized species. Such phase tags have been demonstrated to work in Grubbs-Hoveyda-type catalysts.[166]

7. Conclusions and future perspectives

Clear examples of cooperative catalysis involving multimetallic complexes have been presented in this work. Cooperative catalysis makes organic transformations easier and more convenient. The close proximity of metal centers is one only of the essential criteria for observing cooperativity in multimetallic systems. It is interesting that several examples of multimetallic complexes with larger metal-metal separations have also been displayed augmented catalytic activities. This fact can likely be explained by the electronic influence of one metal center on the other. The beauty of ligand design is often reflected in metal-metal cooperativity in both homo- and hetero-bimetallic systems. The hetero-bimetallic complexes have been used for tandem catalytic applications for a wide range of organic transformations. In addition, these complexes also often display superior catalytic outcomes when compared with the mixture of their homometallic counterparts, owing to the cooperation of the metal centers during the catalysis. A lot of effort has been invested for developing multimetallic systems that would perform a wide range of organic transformations in more efficient ways. However, detailed mechanistic investigations are needed to understand the exact operation of metal-metal cooperation in multimetallic systems during catalysis.

Apart from examples of catalytic cooperativity in complexes with smaller metal-metal distances, many examples are also known in which electronic communication is responsible for cooperative effects. While cooperativity can be observed in systems in which a substrate is simultaneously activated by two metal centers, electronic cooperation can probably also play a key role in such transformation reactions. Redox-switchability in metallocene complexes, for example, demonstrates this clearly, as it can alter the activity of a complex, even though the active center does not formally change its oxidation state. Effects like partial charge redistribution can lead to changes in energy of activation barriers, leading to enhanced reactivity. Substantial progress has been made in the emerging field of redox-switchable catalysis in recent years showcasing its potential for possible applications. While quantum chemical calculations help in better explaining reactivity, further investigations are needed for understanding the underlying effects. Additionally,

incorporation of multiple triggers, such as proton-sensitive or UV-switchable sites could be envisioned, allowing for fine-tuning of the reactivity on a catalytic site.[167]

Acknowledgements

Conflict of Interest

The authors declare no conflict of interest.

Keywords: cooperative catalysis · homo-multimetallic complexes · hetero-multimetallic complexes · metal-metal interactions · redox-switchable catalysis

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