**Review Article**

Heterobimetallic Complexes as Promising Catalysts

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Abstract

Bimetallic complexes have gained a distinguished position in the materials science and catalysis due to their unique spectroscopic properties and reactivities. Amongst bimetallic, heterobimetallic complexes have attracted great interest in the recent decade due to their unusual catalytic activities which is assigned to the cooperation of different metal sites. Cooperative effects in multimetallic complexes have been observed in many homogeneous catalytic transformations. The use of heterobimetallic catalysis emerges as a new strategy to increase efficiency and selectivity with development of novel functional materials showing specific catalytic properties. This review emphasis on recent contributions of heterobimetallic complexes in the developing field of catalysis as they offer an opportunity to study cooperative interaction between metal ions depending on the preferred stereo chemical disposition of metal and the bonds formed in coordination. However, it is hoped that the examples expressed herein will stimulate some reflection on future possibilities in this exciting area of inorganic chemistry.
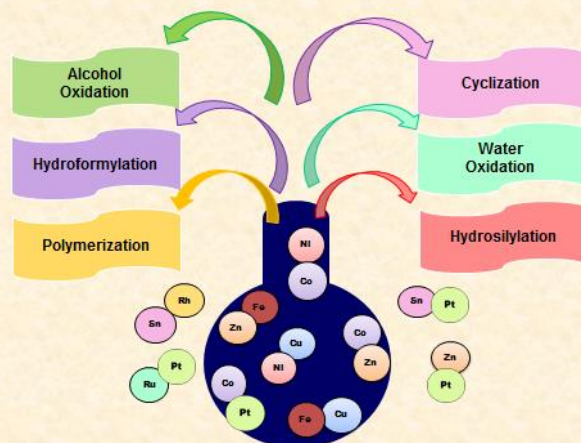
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Introduction

In current years, much attention has been devoted to the study of heteronuclear metal-containing compounds [1–5]. The reasons for exploring materials containing disparate metal centers are widespread, but common to many of them are applications in activating substrates arising from the bifunctionality of the differing metal atoms. Mononuclear metal complexes have historically received much attention (along with homodinuclear complexes, to some extent), but the exhilaration regarding heterodinuclear compounds springs from reactivity hitherto unseen in their mono- or homodinuclear counterparts; in other words, compounds containing two different metal centers exhibit synergistic reactivity that is different from that observed for compounds containing only one type of metal [6].

Binuclear and polynuclear transition metal complexes have been subject of thorough investigation because of their application on the study of mixed metal interactions, magnetic exchange, catalysis and binuclear metal reactivity [7]. The presence of two metals in the same molecule largely affects both the physical properties and the reactivity of the complexes. Recent publications largely highlight key advances on bimetallic complexes and on their chemically addressable applications in challenging areas like biology, medicine, catalysis, nanoscience, redox and photoactive materials, *etc*. This explosive expansion is mainly due to the unique ability of the metals that not only possess much of the interesting reactivity and spectroscopy within the periodic table, but they also engage in some of the most diverse binding modes and geometries [8] that allow the fine tuning of their chemical reactivity in terms of both kinetics (rate of ligand exchange) and thermodynamics (strengths of metal-ligand, redox potentials, etc.)[9]. Cooperative interaction between different metal ions in hetero-polynuclear complexes [10] constitutes an active area of research of cooperative interaction between metal ions in polynuclear complexes [11]. They might prove helpful in

investigating the mutual influence of two metal centers on the electronic, magnetic and redox properties of such systems [12]. Multidendate ligands possessing more than one co-ordination environment serve as an important means of synthesizing hetero metal compounds. They can selectively bind one metal ion to one site and different metal ions to another.

Heterobimetallic complexes feature two different metals held in close proximity, either through a ligand scaffold or a direct metal–metal bond, which allows them to interact or work together to facilitate catalysis. The disparity between the electronic properties of the two metals, such as in early/late heterobimetallic complexes, can impart unique metal reactivity due to electron-sharing. This pairing of two electronically different metals creates a dative interaction between an electron deficient, Lewis-acidic early transition metal and an electron rich, Lewis-basic late transition metal and drastically alters the reactivity of the original metals [13]. The new properties introduced by the presence of a second metal allow for each metal center to behave differently than its monometallic analogue and thereby achieve unprecedented reactivity. In addition, modifications to the structure of the supporting ligands at either of the metal centers serve as a strategy for improving selectivity while maintaining reactivity with the metal- metal interaction.

In the past two decades, cooperative multimetallic catalysis has attracted wide attention of the catalysis community as it is rightly said that **"Chemistry without catalysis, would be a sword without a handle, a light without brilliance, a bell without sound".** In terms of efficiency, selectivity and mechanistic intrigue, cooperative multimetallic catalysis offers multitudinous opportunities to the practitioners in the community. There exist many challenges in the design of new heterobimetallic complexes and exploiting their catalytic potential. This review focuses on the development of heterobimetallic complexes with emphasis on their application in field of catalysis.

Exploitation of Heterobimetallics as Catalysts

One of the fascinating aspects in the history of organometallic complexes to be employed as catalysts with its countless successful applications in the organic synthesis is the structural variety of complexes which are to be used as a catalyst. Many catalysts have been developed based on different ideas and concepts of mechanistic effect. However, in spite of the abundance of such catalysts which have been successfully applied in catalysis, not a handful of them possess multifunctional abilities catalyzing different type of reactions.

Recently, multimetallic catalysis has received much attention, since it offers reactivity and/or selectivity patterns different from those shown by monometallic systems. The metal centers in a multimetallic catalyst act synergistically during substrate activation and coupling steps in the catalytic cycle, leading to enhanced catalytic activity and selectivity [14]. In a multimetallic catalyst, the metal centers may be grafted within a single motif, or may be added as separate molecular units, the former case is referred as 'intramolecular multimetallic catalysis', and the latter as 'intermolecular multimetallic catalysis'. In the intramolecular version, two or more metals are linked together by a metal–metal bond (as type 1, **Figure 1**) or via a ligand (as type 2, **Figure 1**) and these metals participate in substrate activation directly or indirectly [15]
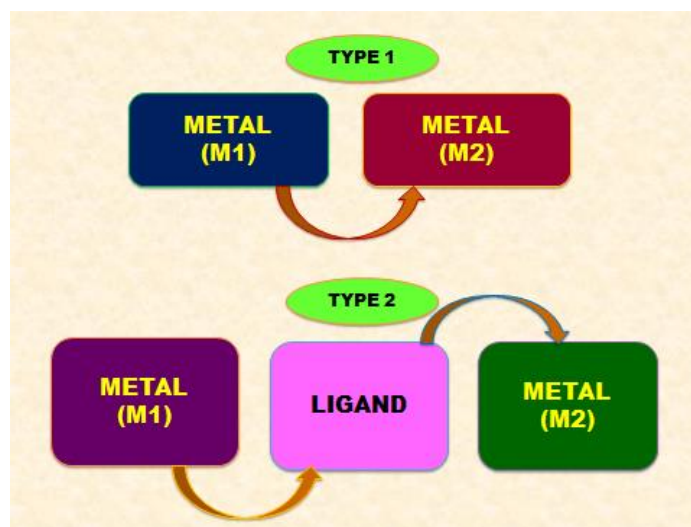

Figure 1 Schematic representation of intramolecular multimetallic catalysts

Catalysis Employing TM-Sn Motif

Multimetallic catalysis has witnessed rapidly increasing developments during the past few decades. Innumerable chemical reactions are facilitated by catalysts. The study of heterobimetallic catalysis dates back to the early 1800s. Faraday was one of the first scientist to examine the ability of platinum to facilitate oxidation reactions. Many other catalytic processes were subsequently developed that facilitated hydrogenation, dehydrogenation, isomerization and polymerization reactions. These catalytic reactions all played a key role in the development of the industrial revolution [16]. Intramolecular multimetallic catalysts, those having a metal–metal bond between a transition metal (TM) and a tin atom are very promising due to their ability in mediating a wide variety of organic transformations. Utilization of such multimetallic catalysts is a challenging and evolving area in the field of homogeneous catalysis. The tin atom in stannylenes (SnR_2) uses two of its p-electrons in covalent bonding with the R group. The other two electrons constitute a lone pair, the latter can be used to form an adduct with soft Lewis acids as well as transition metals (TM). Stannylenes also have low-lying empty p- and d-orbitals, which can participate in hybridization with the orbitals of tin, and generate empty orbitals, the latter being suitable for complex formation with Lewis bases. Therefore stannylene can act both as a Lewis base and a Lewis acid. Indeed, the trichlorostannyl anion $[SnCl_3]^-$ is a better Lewis base than $SnCl_2$ and can also act as an excellent ligand towards transition metals [17]. As stannylenes possess one unshared lone pair of electrons and vacant d-orbitals, the trichlorostannyl species can be considered as a potential σ-donor and π-acceptor ligand for transition metals. Coordination of tin to a transition metal removes electron density from the tin atom and lowers the energy of its empty orbitals. The increasing electron deficiency at the tin center indeed enhances its π back-bonding interaction with the transition metal.[20 R]

Catalysis across a 'TM–Sn' motif is an emerging area in the broader domain of multimetallic catalysis. The TM–Sn catalyzed reactions include Friedel–Crafts alkylation, carbonylation, polymerization, cyclization, olefin metathesis, Heck coupling, hydroarylation Michael addition and tandem coupling [18] (**Table 1**).

Table 1 List of various reactions catalyzed by TM-Sn motif

Metallic Couple	Catalyzed Organic Transformation
Platinum-Tin	Hydroformylation of olefins Cyclization reactions
Palladium-Tin	Cyclocarbonylation of monoterpenes Suzuki coupling Heck type arylation
Molybednum-Tin	Alkylation with acetate
Iridium-Tin	Alkylation with alcohol and ether Dehydrogenation of acyclic alcohols
Ruthenium-Tin	Olefin metathesis
Cobalt-Tin	Hydrolysis of cyclic carbonates Double carbonylation reaction Isomerization of terminal epoxides Ring opening of epoxides with alcohols
Tungsten-Tin	Hydroarylation of hydrocarbons
Rhodium-Tin	Michael addition

Catalytic N-N Bond Cleavage

Heterobimetallic complexes have recently gained much attention for the unique ability of metal– metal communication to alter the electronic properties of the catalytically active metal and influence catalysis. This influence is often achieved by having two electronically disparate metals held in close proximity to each other,

allowing the orbitals of each metal to interact. Although many studies have been conducted with regards to the structure of and bonding in heterobimetallic complexes, there is still a general lack of understanding of how formation of a dative metal-metal interaction can impact catalysis [19]. Thomas et al. reported that the treatment of the tris(phosphinoamide) titanium precursor $ClTi(XylNP^iPr_2)_3$ (1) with CoI_2 leads to the heterobimetallic complex (η^2-$^iPr_2PNXyl)Ti(XylNP^iPr_2)_2(\mu$- Cl)CoI (2). One-electron reduction of 2 affords (η^2-$^iPr_2PNXyl)$- $Ti(XylNP^iPr_2)_2CoI$ (3), which can be reduced by another electron under dinitrogen to generate the reduced diamagnetic complex $(THF)Ti(XylNP^iPr_2)_3CoN_2$ (4).
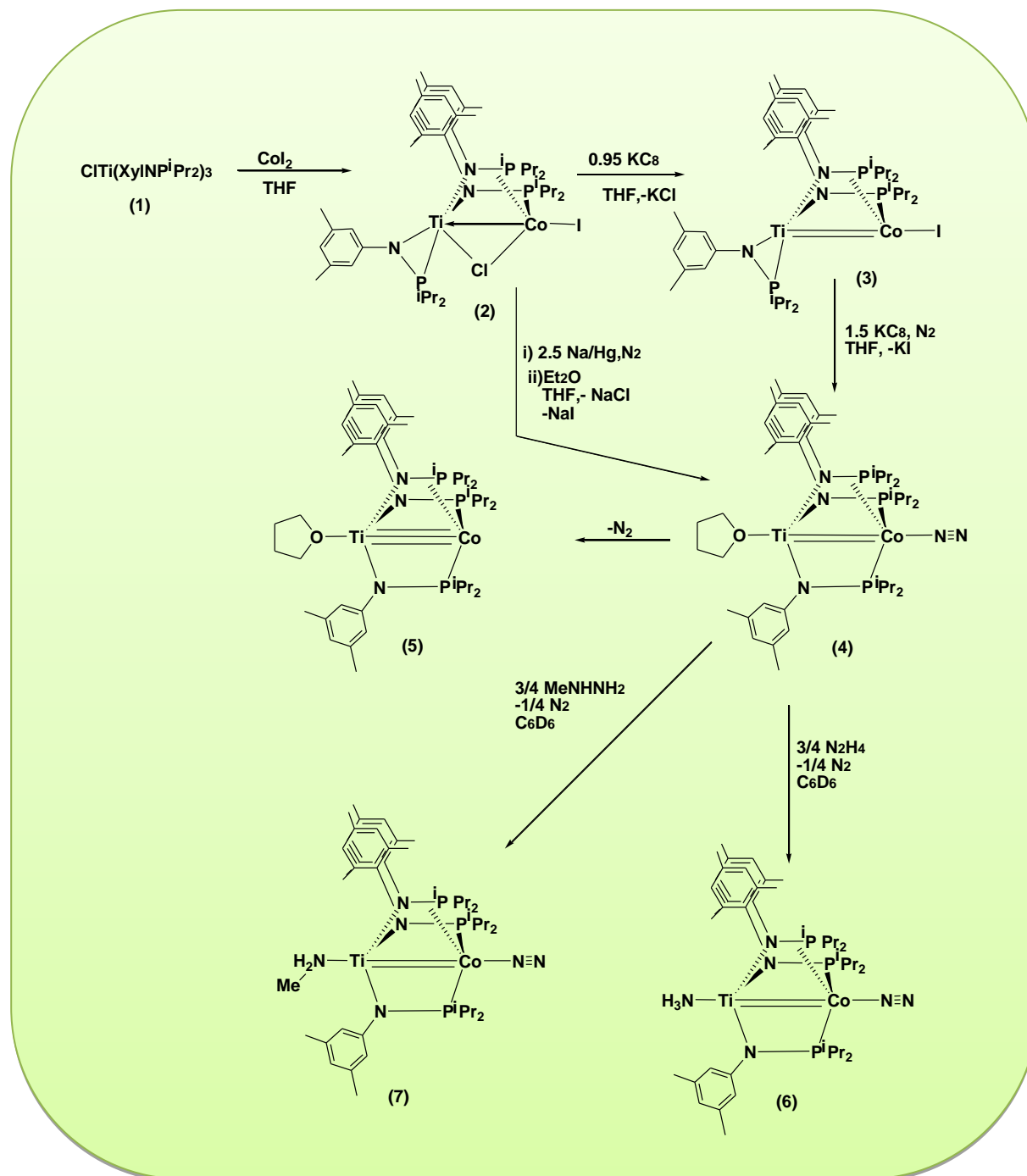

Figure 2 Synthesis of heterobimetallic complexes incolved in catalytic N-N bond cleavage

The removal of the dinitrogen ligand from 4 under vacuum affords (THF)Ti- $(XylNP^iPr_2)_3Co$ (5), which features a Ti−Co triple bond. Treatment of 4 with hydrazine or methyl hydrazine results in N−N bond cleavage and affords the new diamagnetic complexes $(L)Ti(XylNP^iPr_2)_3CoN_2$ (L = NH_3 (6), $MeNH_2$ (7))(**Figure 2**). Both the metals Ti and Co play an important role in the reaction mechanism and, more importantly are a more reactive pair than Zr and Co in the tris(phosphinoamide) heterobimetallic scaffold. Complexes 4, 5, and 6 have been shown to catalyze the disproportionation of hydrazine into ammonia (**Table 2**) and dinitrogen gas through a mechanism involving a diazene intermediate [20].
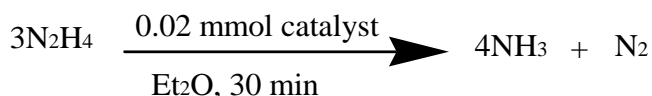
$$3N_2H_4 \xrightarrow[\text{Et}_2\text{O, 30 min}]{\text{0.02 mmol catalyst}} 4NH_3 + N_2$$

Table 2 Catalytic Disproportionation of Hydrazine by Heterobimetallic Ti/Co complexes 4-6

Entry	Catalyst	N_2H_4 (equ.)	NH_3 Yield[a] (m mol)	NH_3 Yield (equ.) [theoretical]	Turnover
1	4	1	0.026	1.3[1.3]	1.0
2	4	5	0.13	6.6[6.7]	5.0
3	4	10	0.26	13[13]	10
4	4	20	0.42	21[27]	16
5	4	50	0.47	22[67]	18
6	5[b]	20	0.38	19[27]	14
7	6	20	0.46	23[27]	17

[a]Determined by colorimetry. [b]Reaction was carried out in an argon filled glovebox

Ethanol Conversion Employing Heterobimetallic Zeolite

The expansion of biomass derived ethanol industry and concurrent development of distribution channels during the last 20 years have created interest in ethanol conversion to industrial chemicals. The commercialization of ethylene derived from bioethanol represents a successful deployment of a renewable industrial chemical [21]. The addition of biomass derived ethanol to gasoline in the transportation sector is an important step in the utilization of renewable energy. Ethanol conversion to hydrocarbons employing zeolites as catalysts dates back to 1970s [22]. Since then, a large number of reports have appeared in literature on ethanol conversion to hydrocarbons [23-30]. The reaction temperature for ethanol transformation is generally > 350 °C and the pressure ranges from ambient to several atmospheres [30-38]. The product stream is generally high in C_2 hydrocarbons (e.g., ethylene and ethane), which are not valuable for liquid fuel production or commodity chemical production. The mechanism of ethanol conversion is still being debated. A simple mechanism with ethanol dehydration to ethylene or diethyl ether as the first step and subsequent upgrading to C_{3+} hydrocarbons was proposed in 1978 by Derouane *et al.* and reaffirmed in 2006 by Inaba *et al.*. Narula et al. have recently reported a versatile heterobimetallic catalyst, InV-ZSM-5, that completely converts ethanol to hydrocarbons in 250–450 °C range and atmospheric pressure without added hydrogen. The heterometallic zeolites, MM'-ZSM-5, are a new class of zeolites where the interaction between M and M' plays an important role [39]. The InV-ZSM-5 catalyst exhibits superior performance compared to monometallic catalysts, In-ZSM-5 or V-ZSM-5 as determined by low C_2 yield and high durability. All these catalysts are robust to water content in ethanol (5–95%) and volatile impurities in fermentation stream. Thus, this method of direct conversion of ethanol offers a pathway to produce suitable hydrocarbon blend-stock that may be blended at a refinery to produce fuels such as gasoline, diesel, JP-8, and jet fuel, or produce commodity chemicals such as BTX [40].

Photochemical Water Oxidation using Heterobimetallic Complexes as Catalysts

Solar energy is converted into chemical energy on a massive scale by natural photosynthesis in plants, green algae, and cyanobacteria. One attractive alternative for a renewable energy source on a global scale is solar energy conversion in the form of artificial photosynthesis. The main aim of artificial photosynthesis is to mimic the light induced photosynthetic reactions and to create systems capable of decomposing water to O_2 and H_2 using light energy [41]. An artificial photosynthesis system consists of three main components: a photosensitizer, a proton reduction catalyst and a water oxidation catalyst. Separate examples of all three components are known, but the development of water oxidation catalysts is generally seen as a bottle-neck for a complete artificial photosynthesis system [42].In this

regard, Pavliuk et al. investigated heterometallic Mn/V compounds and their ability to catalyze photochemical water oxidation. A novel synthetic route has been proposed for the preparation of Mn/V complexes in a one-pot reaction, following the "direct synthesis" approach, using water as a solvent. Two Mn/V compounds, $(NH_4)_2[Mn_2(HGly)(H_2O)_{10}][V_{10}O_{28}] \cdot (HGly) \cdot 2H_2O$ (8) and $(NH_4)_2[Mn(\beta-HAla)(H_2O)_5]_2[V_{10}O_{28}] \cdot 2H_2O$ (9) have been synthesized and characterized by single crystal X-ray analysis, FTIR and EPR spectroscopy. For complexes 8 and 9 photochemical water oxidation has been investigated in a system using $Ru(bpy)_3^{2+}$ as a photosensitizer [43]. Magnetic measurements showed the presence of an antiferromagnetically coupled Mn dimer for complex 8 in the solid state. Electrochemical measurements showed that the oxidative potential of the two complexes is high enough for further application as catalysts in water splitting. Catalytic water oxidation activity studies of 8 and 9 were performed using the standard $Ru(bpy)_3^{2+}$ / visible light / persulfate combination and resulted in a maximum TON ~1 mol O_2 per mol Mn. A synergetic effect between Mn and V centres was proposed to explain the increased activity. Based on the *ex situ* EPR data of samples taken under catalytic conditions, vanadium was suggested to not be involved in redox processes whilst Mn(II) was oxidized by photogenerated Ru(III). The obtained complexes are promising catalysts for water oxidation.

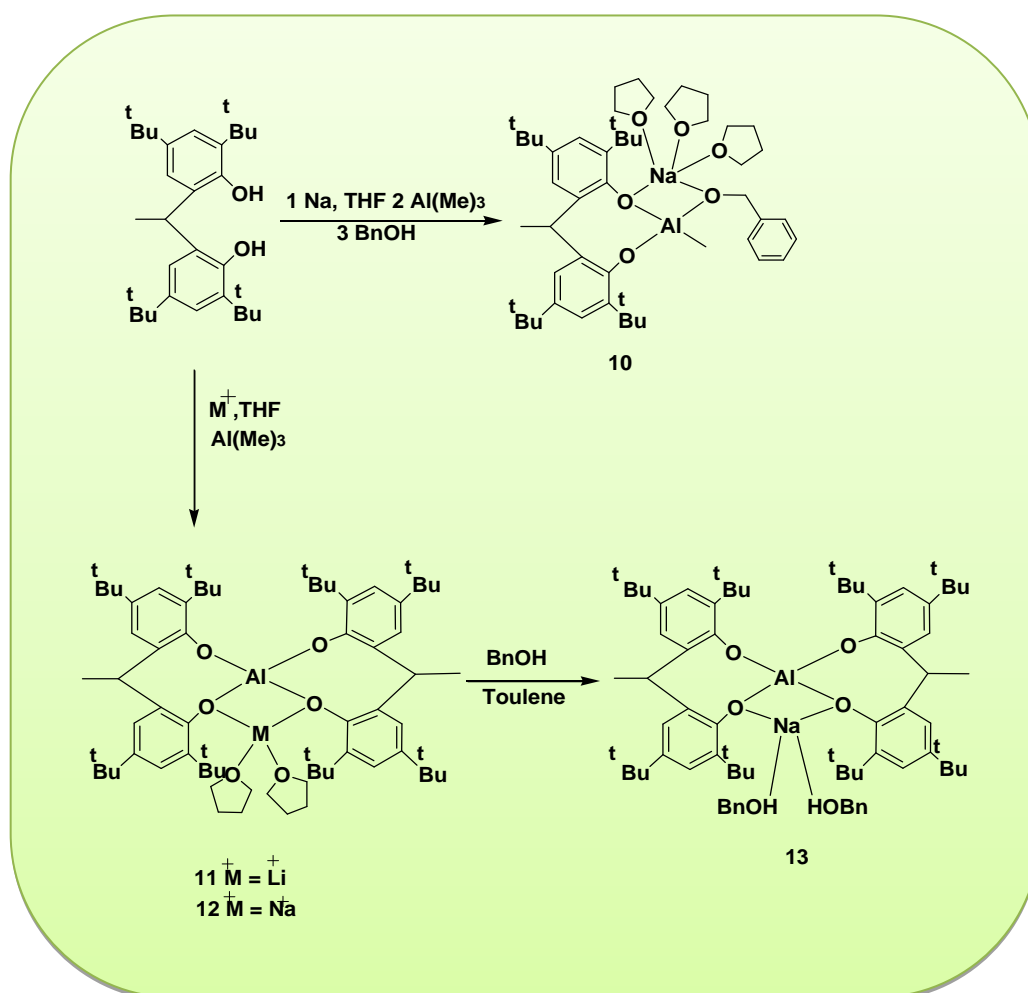*Heterobimetallics as Efficient Catalysts for Ring Opening Polymerization*

Figure 3 Synthetic route for heterobimetallic complexes with application in the polymerization of ε–caprolactum

Biodegradability, biocompatibility, and permeable properties of aliphatic polyesters, such as poly(ε-caprolactone) (PCL) [44], poly (lactide) (PLA) [45] and poly(trimethylenecarbonate)(PTMC) [46] and their copolymers show their potential applications in the medical field as biodegradable surgical sutures or as a delivery medium for controlled

release of drugs [47]. Therefore, there has been increasing interest in the development of efficient catalytic systems for the preparation of PCL, PLA and PTMC. The major polymerization method used to synthesize these polymers has been the ring-opening polymerization (ROP) of ε-caprolactone (ε-CL). Though several effective initiators that initiate ROP of CL have been reported [48], the cytotoxicity and difficulties in removal of the catalyst from the resulting polymer have limited their utilization. Pan et al. reported the reaction of 2,2′-ethylidenebis(4,6-di-tert-butylphenol)(EDBP-H$_2$) with sodium, Al(Me)$_3$ and BnOH with a molar of ratio of 1:1:1:1 in THF which gives hetero-bimetallic complex of [(EDBP)Al(CH$_3$)(μ$_2$-OBn)Na(THF)$_3$](10) in 85% yield [49]. In order to investigate the different anion effects on the ROP of ε-caprolactone, complexes [(EDBP)$_2$Al][(Li)(THF)$_2$] (11) and [(EDBP)$_2$Al][(Na)(THF)$_2$] (12) were prepared in an analogous manner to that of complex 10 in 63% and 71% yields respectively. Further reaction of compound 12 with excess BnOH in toluene produces compound 13 in 78% yields (**Figure 3**).Results show that the heterobimetallic complex 10 is an efficient catalyst for the ring-opening polymerization of ε-caprolactone.

Another biodegradable polymer polylactide (PLA) has a broad range of applications, due to its excellent mechanical and physical properties and its biocompatible and biorenewable nature. Ring-opening polymerization (ROP) of lactide is the most convenient method to prepare PLA with high molecular weight and low polydispersity [50]. For this process, a large number of metal-based initiators have been described, including Sn, Al, or rare-earth-metal derivatives [51]. Because of PLA's use as a biomaterial for pharmaceutical and medical applications [52] the development of new catalyst/initiators with nontoxic metals is an interesting goal for synthetic chemists. A wide variety of initiators with biocompatible metals such as Li, Na, K, Mg, Ca, and Zn have been synthesized[53] frequently stabilized with salen or hemisalen ligands [54]. The homometallic azo complexes of lithium [Li$_2${(η^2-O(C$_{10}$H$_6$)N=N(C$_6$H$_5$)}$_2$]$_n$ (14) and magnesium [Mg{(η^2- O(C$_{10}$H$_6$)N=N(C$_6$H$_5$)}$_2$]$_n$ (15) and the heterometallic lithium–magnesium derivative [Li$_2$Mg$_2${(η^2-O(C$_{10}$H$_6$)N=N(C$_6$H$_5$)}$_6$] (16) have been synthesized by Gallegos and co-workers (**Figure 4**).
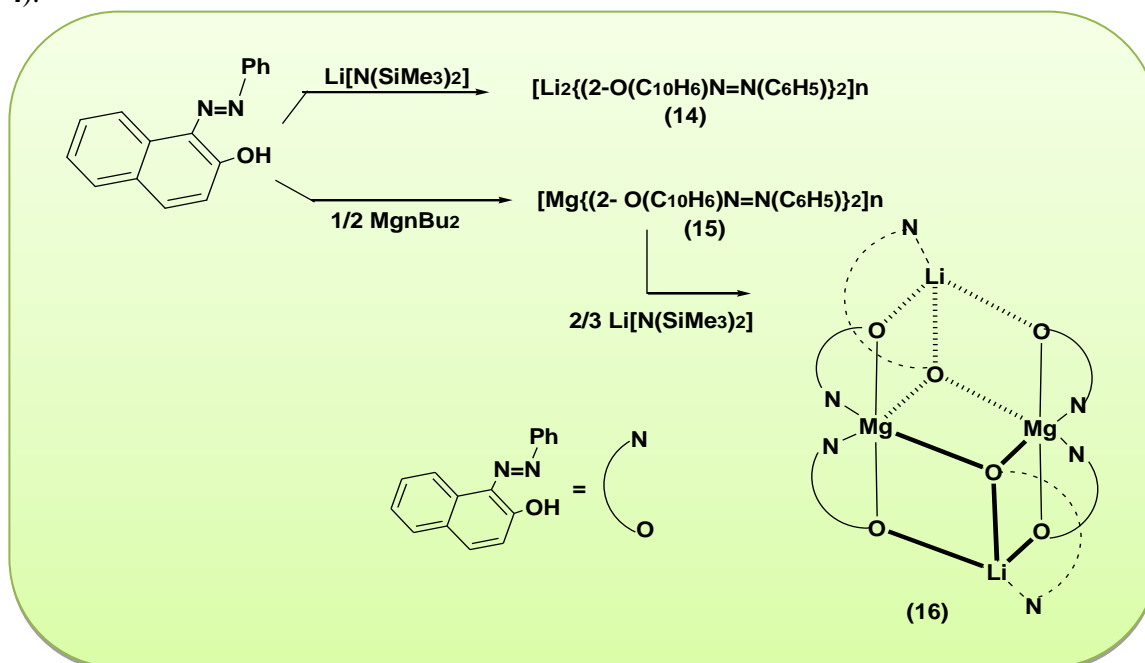

Figure 4 Synthesis of Heterobimetallic Lithium-Magnesium complex

The heterometallic complex exhibits a novel structure described as two truncated cubes that share a Mg$_2$O$_2$ ring as one of the cube sides. These complexes have been studied in the polymerization of L- and rac-lactide in the presence of benzyl alcohol. The influence of the selected solvent seems not to be significant, and similar polymerization behavior is observed for each metal derivative, with only a slight decrease in the polymerization rate observed for THF. The L-lactide and rac-lactide polymerizations show that lithium derivative 14 is much more active than

magnesium complex 15, which only reaches high conversions at 70 °C. Nevertheless, the heterometallic complex 16 shows an activity intermediate between complexes 14 and 15, reaching high conversions at 25 °C [55].

Electrochemical Oxidation of Alcohol wth Heterobimetallic Complexes

Homogeneous catalysis with well-defined heterobimetallic systems has been a topic of interest due in part to the potential to explore the cooperative interaction of the two metals as well as the possibility for each metal center to perform a separate and distinctive task [56-63]. Recent efforts toward the development of electrooxidation catalysts for direct methanol fuel cells have included the incorporation of a second metal to improve the performance of Pt anodes. In addition to the commonly utilized Pt/Ru systems [64-70] other electrode materials including PtSn [71-73] PtRe [73] PtRuOs [74] and PtRuOsIr [75] have been investigated. Binary Pt/Ru alloys are among the most active, exhibiting lower overpotentials and less surface poisoning than pure Pt anodes. The heterobimetallic complexes $CpRu(PPh_3)(\mu\text{-}Cl)(\mu\text{-}dppm)PdCl_2$ (17) [dppm= bis(diphenylphosphino) methane], $CpRu(PPh_3)Cl(\mu\text{-}dppm)AuCl$ (18), and $CpRu(PPh_3)(\mu\text{-}Cl)(\mu\text{-}dppm)PtCl_2$ (19) were synthesized by Lisa and co-workers via the reaction of $CpRu(PPh_3)Cl(\eta^1\text{-}dppm)$ with $Pd(COD)Cl_2$, $AuPPh_3Cl$, and $Pt(COD)Cl_2$, respectively (**Figure 5**).
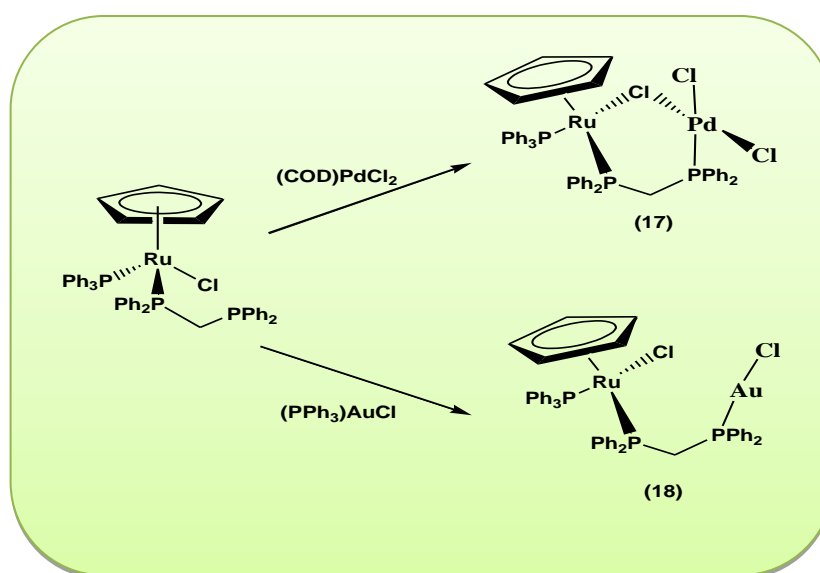

Figure 5 Synthesis of heterobimetallic complexes of Ruthenium with Platinum and Gold

Compounds 17 and 18 were characterized by X-ray crystallography. Electrochemical oxidation of CH_3OH in the presence of 17, 18, or 19 leads to considerable enhancement of the oxidative currents and formation of the organic products $CH_2(OCH_3)_2$ and $HCOOCH_3$. Addition of water increases both the current and the proportion of the more highly oxidized product, $HCOOCH_3$. Current efficiencies obtained with heterobinuclear complexes 17-19 were significantly higher than those obtained using the model compound $CpRuCl(\eta^2\text{-}dppm)$ as catalyst [76].

In the past decade catalysis with iron complexes has attracted significant attention, due to their low price and ready availability [77-83]. Taking this into consideration, Lisa and co-workers prepared carbonyl-containing Ru and Fe heterobimetallic complexes and tested them as electrocatalysts for the oxidation of methanol and ethanol. GC analysis of the electrolyte solution during bulk electrolysis indicated that $CpRu(CO)(\mu\text{-}I)(\mu\text{-}dppm)PtI_2$ (20), $CpFe(CO)(\mu\text{-}I)(\mu\text{-}dppm)$- PtI_2 (21), and $CpRu(CO)(\mu\text{-}I)(\mu\text{-}dppm)PdI_2$ (22) were catalysts for the electrooxidation of methanol and ethanol, while $CpFe(CO)(\mu\text{-}I)(\mu\text{-}dppm)$- PdI_2 (23), $CpRu(CO)I(\mu\text{-}dppm)AuI$ (24), and $CpFe(CO)I(\mu\text{-}dppm)AuI$ (25) did not function as catalysts (**Figure 6**). The oxidation of methanol resulted in two- and four-electron oxidation to formaldehyde and formic acid, respectively, followed by condensation with unreacted methanol to yield dimethoxymethane and methyl formate as the observed products [84]. The oxidation of ethanol afforded 1,1'-diethoxyethane as a result of two-electron oxidation to acetaldehyde and condensation with excess ethanol. FTIR analysis of the headspace gases during the electrochemical oxidation of methanol indicated formation of CO_2 while Isotopic labeling experiments demonstrated that the CO_2 resulted from oxidation of the CO ligand instead of complete oxidation of CH_3OH.
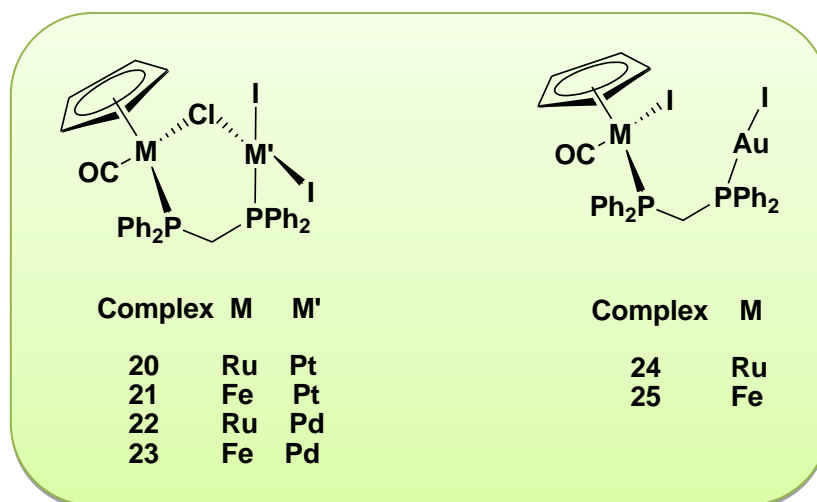
Figure 6 Heterobimetallic complexes involved in electrochemical oxidation of alcohol

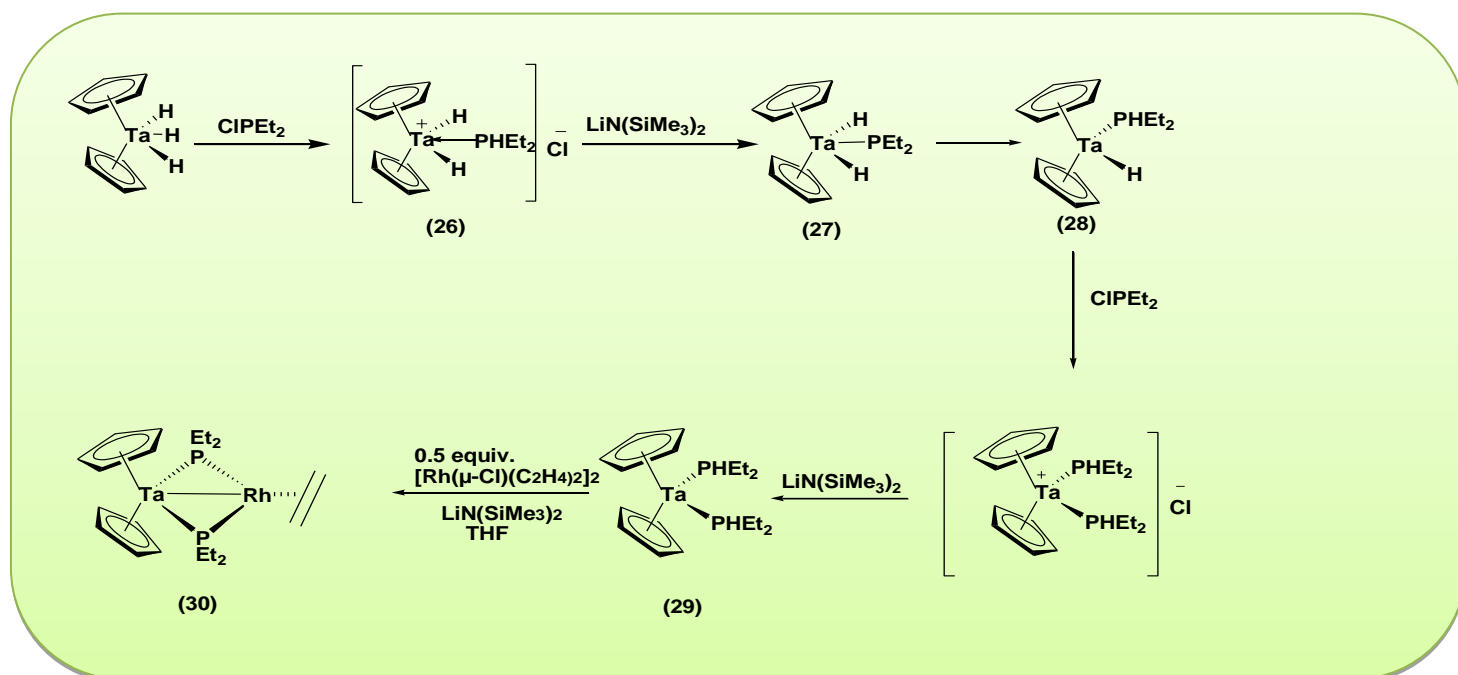*Catalytic Hydrosilylation of Acetophenone*

Figure 7 Synthesis of heterobimetallics involved in hydrosilylation of acetophenone

Phosphine complexes of the late transition metals play a prominent role in molecular catalysis. Phosphine ligands bind strongly to metals and their electronic and steric properties can be easily adjusted by varying the substituents at phosphorus atom [85]. Another approach to a rational design of phosphine-based catalysts is based on the substitution at the phosphorus atom by an electron releasing organometallic group. Such a metalaphosphine ligand, L_nM–PR_2 possessing a highly polarized $M^{\delta+}$–$P^{\delta-}$ bond might be envisioned to be a better ligand to a catalytically active late transition metal [86]. Application of this idea to the Suzuki– Miyaura reaction catalysed by phosphido-bridged Re/Pd and Ru/Pd complexes has been previously reported by Gladysz [87]. The ability of rhodium phosphine complexes to catalyze hydrosilylation reactions is well established [88]. These reactions are usually mediated by Rh(I) complexes and proceed, after the Si–H oxidative addition, *via* intermediate formation of Rh(III) species [89]. In an effort to develop more effective catalyst for hydrosilylation, Nikonov et al. reported that the bimetallic complex featuring a

formally Rh(0) centre and an easily oxidizable Ta–Rh bond could facilitate the Si–H oxidative addition and presumably possess a superior catalytic activity. Deprotonation of the cationic complex $[Cp_2Ta(H_2)(PEt_2)]^+$ (26) initially affords the dihydrido phosphide $Cp_2Ta(H_2)(PEt_2)$ (27) which slowly re-arrangers into the hydride-phosphine derivative $Cp_2Ta(H)(PHEt_2)$ (28). The latter compound was used to prepare the phosphido-phosphine complex $Cp_2Ta(PEt_2)(PHEt_2)$ (29) which was then employed as a metalaphosphine ligand to the rhodium/olefin fragment $Rh(\eta^2\text{-}C_2H_4)$ in the preparation of the bimetallic species $Cp_2Ta(\mu\text{-}PPh_2)_2Rh(\eta^2\text{-}C_2H_4)$ (30) (**Figure 7**).

The latter complex was found to catalyze the hydrosilylation of acetophenone by $PhMeSiH_2$, but more sluggishly than the previously studied complexes $Cp_2Nb(=NBu^t)(\mu\text{-}PPh_2)Rh(Cl)(COD)$ and $[(\mu\text{-}Cl)RhCOD]_2$ [90].

Hemilabile ligands play a prominent role in modern catalysis [91]. They usually feature a soft center (usually based on C, S, or P), which ensures strong binding to the metal, and a hard center (O or N based), which can bind loosely to a vacant metal site, thus creating a masked form of an unsaturated complex. It is suggested that the attachment of hard and soft ligands such as imido and phosphido to an early transition metal would give rise to a new type of "spectator" metalloligand [92] that could be used as a hemilabile ligand to a catalytically active late transition metal. Herein again Nikonov et al. reported the application of this concept to the preparation of imido phosphido niobocene $Cp_2Nb(=NBu^t)\text{-}(PPh_2)$ (31) and the synthesis of some Nb/Rh heterobimetallics derived therefrom. Application of the new Nb/Rh ELHB (early-late heterobimetallics) to catalytic hydrosilylation of acetophenone and benzaldehyde is also reported. The new imido phosphido complex $Cp_2Nb(=NBu^t)(PPh_2)$ (31) serves as a metallophosphine ligand to rhodium olefin fragments $\{ClRhL_2\}$, affording phosphido-bridged bimetallic complexes. The outcome of the reaction depends on the nature of the olefin L. With L=ethylene, the main product is an unusual Cp/Cl exchange complex, $Cp(Cl)Nb(\mu\text{-}NBu^t)\text{-}(\mu\text{-}PPh_2)RhCp$ (32), featuring a bridging imido group in addition to bridging phosphido group. When L_2 is the chelating diolefin COD, the reaction of 1 with 0.5 equiv of $[(\mu\text{-}Cl)RhCOD]_2$ proceeds as a simple phosphide addition to furnish the bimetallic product $Cp_2Nb(=NBu^t)(\mu\text{-}PPh_2)Rh(Cl)(COD)$ (33)(**Figure 8**).
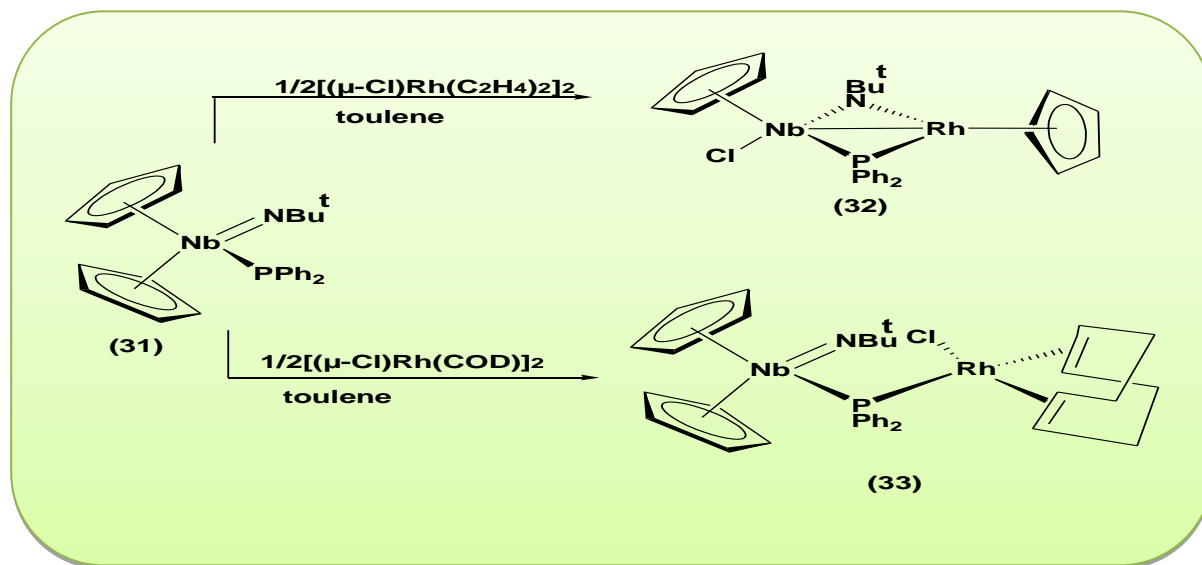

Figure 8 Synthesis of heterobimetallic complexes of Niobium and Rhodium

Both 32 and 33 were found to be active precatalysts for hydrosilylation of acetophenone and benzaldehyde. The neutral complex 33 exhibits enhanced reactivity in comparison with the cationic derivative $[Cp_2\text{-}Nb(NBu^t)(PPh_2)Rh(COD)]^+$, presumably because the latter has the imido ligand too tightly coordinating to the Rh center [93].

Heterobimetallics as Catalysts for Polymerization of Olefins
Olefin polymerization by transition metal complex catalysts has been one of the most attractive research fields since the discovery of Ziegler-Natta catalysts [94]. Even a few decades after its first discovery, this field continues to attract

considerable attention in both academic and industrial communities. In the typical polymerization process, the transition metal complexes are activated by different types of cocatalysts to form cationic species, which are proposed to catalyze the polymerization process [95]. Aluminum reagents such as alkyl aluminum and methylaluminoxane (MAO) play an important role as cocatalysts [96] and these Al complexes are also involved in the catalysis by forming heterobimetallic complexes or counteranions with titanium complexes [97]. These bimetallic complexes exhibit high activity in the catalysis and produce polymers with different microstructures. The activation of metal complexes is usually associated with a decrease in complex stability due to the electronic deficiency of the metal center, but this can be prevented by modification of ligands with several donor atoms that can coordinate when necessary [98]. Hetero-bimetallic Ti-Al complexes containing tris(aryloxo)amine ligands of type [TiR′{(μ_2-O-2,4-$R_2C_6H_2$-6-CH_2)(O-2,4-$R_2C_6H_2$-6-CH_2)$_2$N}][R′$_2$Al(μ_2-O^{i}Pr)] [(36a,b and 37a;R=Me (36), ^{t}Bu (37); R′=Me(a), Et(b)] have been prepared by Nomura et al. via reacting Ti(O^{i}Pr)[(O-2,4-$R_2C_6H_2$-6-CH_2)$_3$N] [R=Me (36), ^{t}Bu (37)] with 1.0 equiv of AlR′$_3$ in toluene (**Figure 9**).
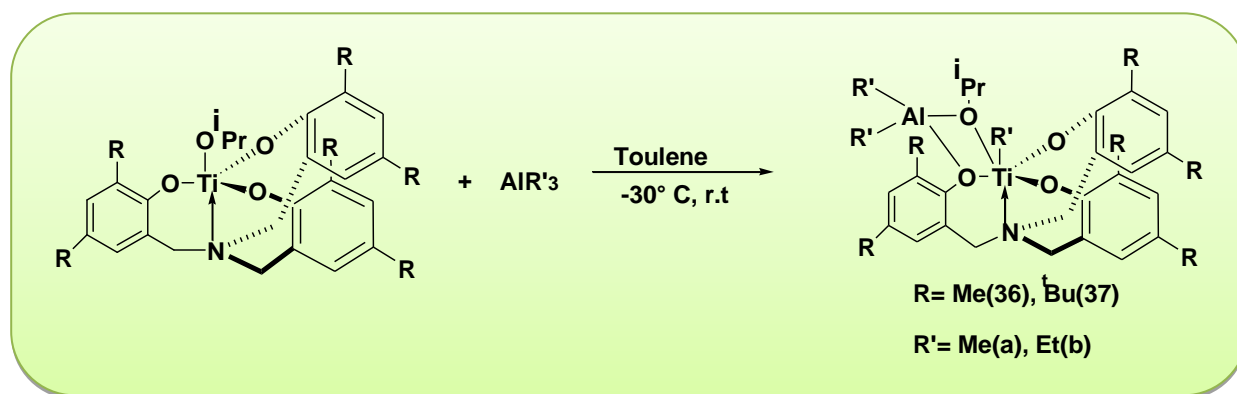

Figure 9 Synthesis of heterobimetallics involved in polymerization of olefins

Crystallographic analyses of 36a,b and 37a reveal that these complexes have a distorted octahedral geometry around Ti and a distorted tetrahedral geometry around Al. Complexes 36a,b and 37a exhibited moderate catalytic activities for ethylene polymerization in toluene in the presence of methylaluminoxane (MAO) at 80-120°C, and 35a showed higher activity than 36a,b. The tert-butyl analogue (37a) itself polymerizes ethylene without cocatalysts to afford high molecularweight polymer with a uniform distribution, clearly suggesting a hypothesis that cleavage of Ti-O bonds would generate the catalytically active cationic species in this catalysis [99].

Early-late heterobimetallic complexes have been extensively investigated with Group 4 metallocenes as attractive components for these complexes because of their high reactivity as olefin polymerization catalysts [100]. Although a number of such heterobimetallic complexes have been prepared, surprisingly few cases report their utilization as polymerization catalysts [101]. It is, in many cases, probably because the reactive sites of metallocenes are used to construct the bimetallic structures and the olefins may not be allowed to interact with the metal center. Although such complexes show catalytic activity in a few cases, it is simply because they dissociate into monometallic components in catalytic systems. In view of catalysis, a bimetallic structure should be designed so that late transition metals do not block the reaction sites of the group 4 metallocenes. Novel heterobimetallic complexes that consist of zirconium and rhodium, LRh (η^2- CH_2=CH)$_2$Si (η^5-C_5H_2-2,4-Me_2)$_2ZrCl_2$ (38a L = η^5-C_9H_7, 38b L = η^5-C_5H_5, 38c L = η^5-C_5Me_5), were synthesized by Yamaguchi et al. and 38b was structurally characterized (**Figure 10**).

The complexes have a "$C2$-symmetric" *ansa*-zirconocene part and the rhodium metal on the bridge part. The complexes 38a-c in combination with methylaluminoxane catalyzed highly isospecific polymerization of R-olefins. Their catalytic activities were higher than that of the parent zirconocene complex, and the obtained polymer had a larger molecular weight [102].
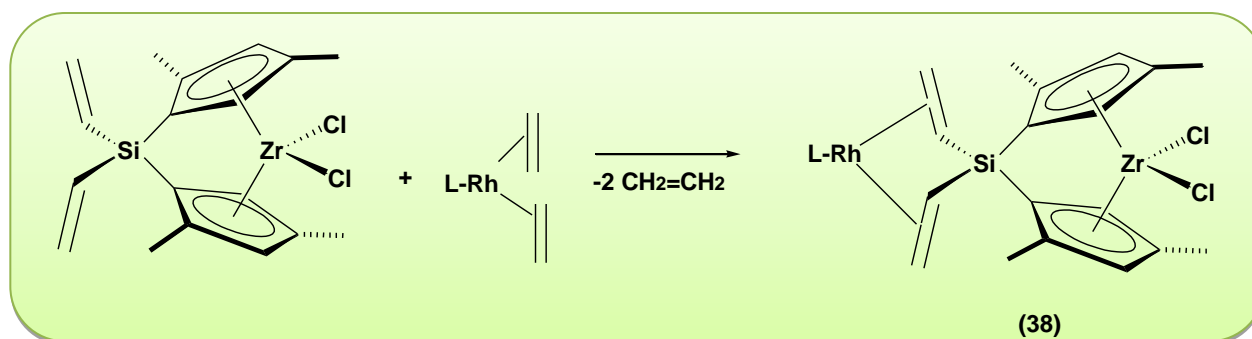
Figure 10 Synthesis of heterobimetallic complexes of Zirconium and Rhodium
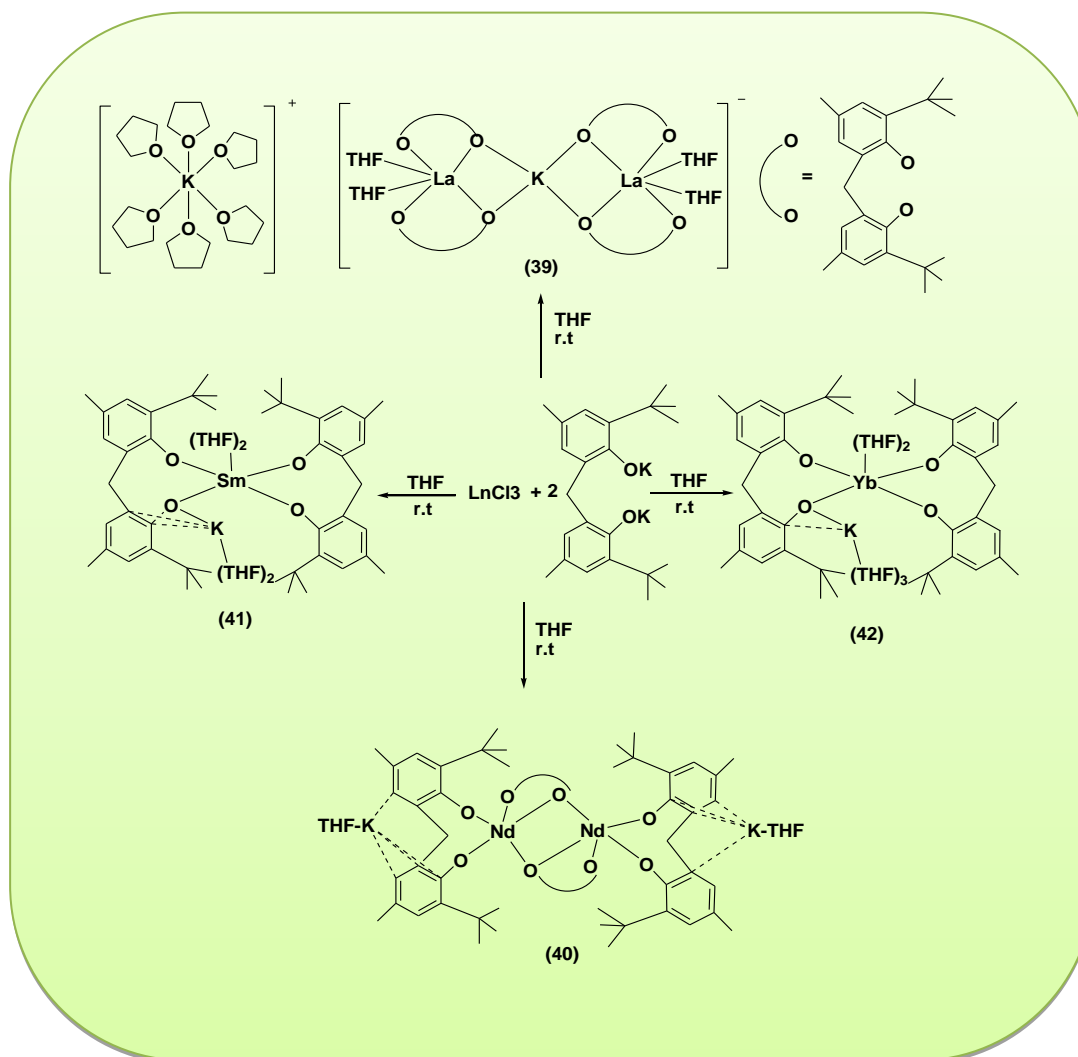
Catalytic Amidation of Aldehydes

Figure 11 Synthesis of lanthanide-alkali heterobimetallic complexes

Heterobimetallic complexes of a lanthanide metal and an alkali metal have been well known for a long time, but their catalytic behavior has not been explored intensively, because most of these complexes were reported as unexpected ligand redistributed products during the syntheses of organolanthanide complexes [103]. However, it has been found that some heterobimetallic lanthanide-alkali metal complexes showed interesting activity in catalytic transformations.

For example, the heterobimetallic lanthanide-alkali metal complexes based on BINOL were versatile catalysts in a wide range of asymmetric reactions, which have never been possible using monometallic lanthanide catalysts [104]. Our recent results revealed also that heterobimetallic lanthanide-alkali metal complexes are more efficient catalysts in organic synthesis and ring-opening polymerization of cyclic esters than the monometallic ones [105]. Four heterobimetallic lanthanide-potassium complexes stabilized by the carbon-bridged bis(phenolate) ligand MBMP^{2-} (MBMP = 2,2'-methylene bis(6-*tert*-butyl-4-methylphenolate)),[{(MBMP)$_2$La(THF)$_2$}$_2$K][K(THF)$_6$] (39), [(MBMP)Nd(μ-MBMP)K(THF)]$_2$ (40), [(THF)$_2$Sm-(MBMP)$_2$K(THF)$_2$] (41), and [(THF)$_2$Yb(MBMP)$_2$K(THF)$_3$] (42), were synthesized by Xu et al. and their structural features were provided (**Figure 11**). It was found that the ionic radii of lanthanide metals have a profound effect on the structures of the heterobimetallic complexes. Complexes 39 to 42 are efficient catalysts for amidation reactions of aldehydes with amines to produce amides in good to excellent yields under mild conditions [106].
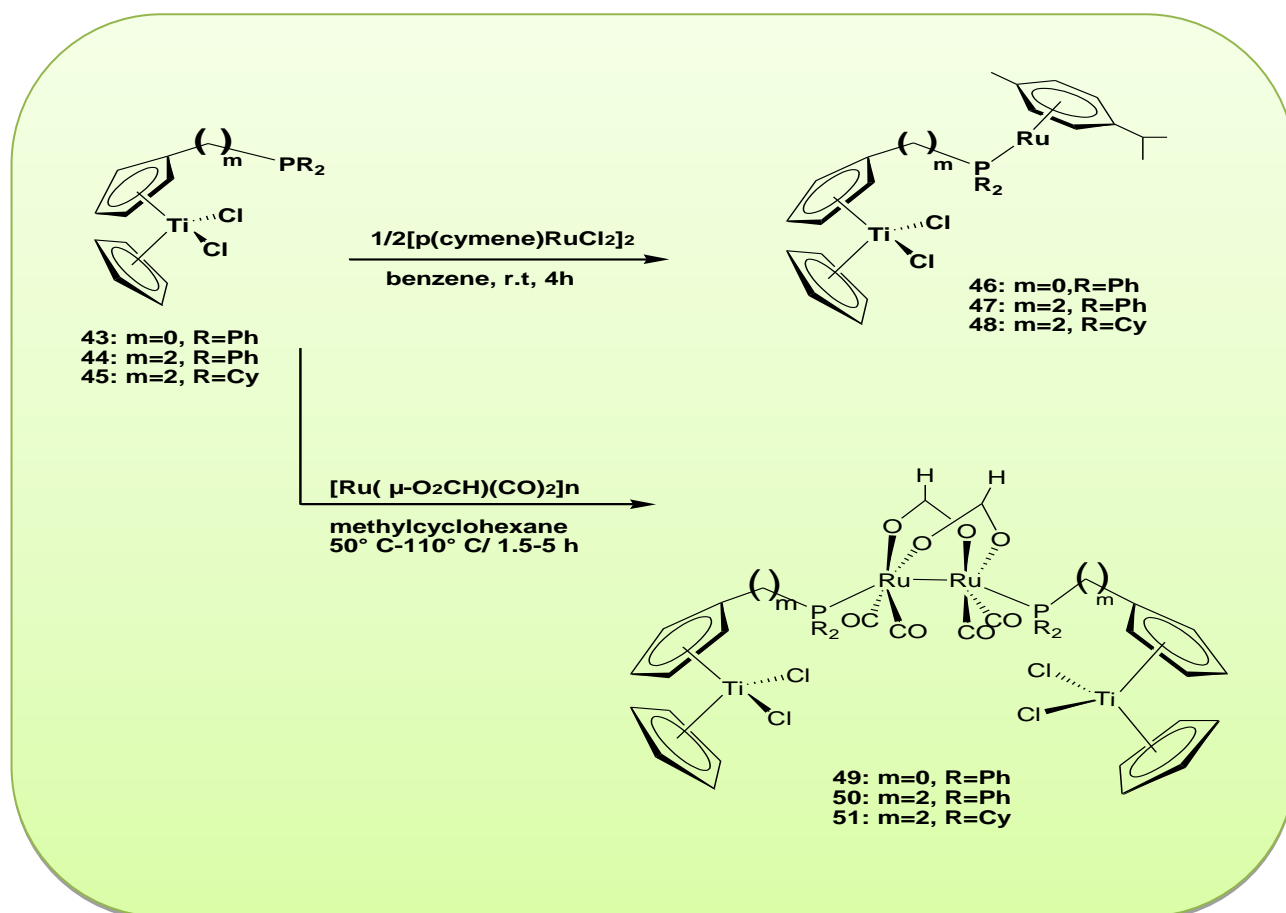
Catalytic Synthesis of Enol Esters

Figure 12 Synthesis of heterobimetallic complex of Titanium and Ruthenium

The preparation and the study of early-late heterobimetallic complexes constitute a particularly active research area in organometallic chemistry owing to their potential application as catalysts [107], materials [108], or as biomimetic models [109]. Moise and co-workers studied bimetallic complexes built from an arene ruthenium and a titanocene dichloride fragment [110]. Both moieties are able to catalyze a wide variety of reactions [111] and therefore their combination constitutes a new material with powerful catalytic ability. They reported the synthesis of bimetallic complexes (46-48) through the complexation of the titanocene monophosphanes (43-/45) with the binuclear complex [(p-cymene)RuCl$_2$]$_2$. Preliminary assessment of the performance of these complexes in ring closing metathesis revealed an excellent Ti-/Ru precatalyst and described a new application of these bimetallic systems as catalysts for the synthesis of enol formate. Indeed the monometallic (arene)RuCl$_2$(PR$_3$) complexes are known to catalyse the

Markovnikov addition of carboxylic acids to terminal alkynes resulting in the formation of enol esters [112]. Good insight of the influence of the titanocene fragment on its late metal neighbour were thus obtained by comparing the performance of the bimetallic complexes 46-/48 in the addition of formic acid to 1-hexyne with the activity of their monometallic analog. These preliminary results led to synthesize and characterize a series of new tetrametallic complexes $Ru_2(\mu\text{-}O_2CH)_2(CO)_4[(\eta^5\text{-}C_5H_5)(\mu\text{-}\eta^5:\eta^1\text{-}C_5H_4(CH_2)_mPR_2)TiCl_2]_2$ (49-51) (**Figure 12**). Their catalytic potential has also been evaluated [113].

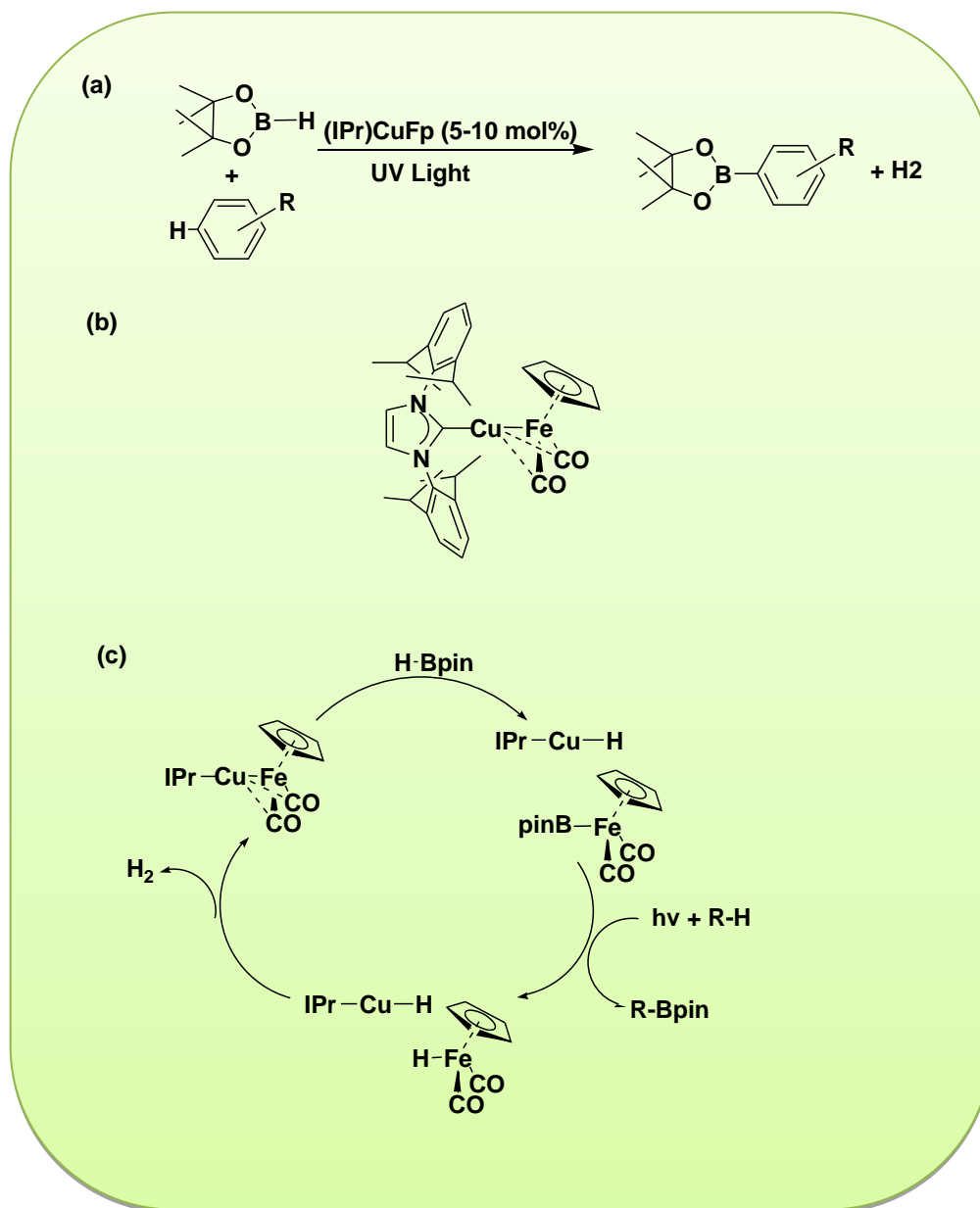*Heterobimetallic Catalyst for C-H Borylation*

Figure 13 a) C-H borylation catalyzed by Cu-Fe cooperativity; b) the optimum catalyst, (IPr)CuFp; c) proposed heterobimetallic mechanism for C-H borylation. Catalytic conditions: 450-W Hg are lamp, ambient temperature, neat arene

The quest for improved sustainability and the potential for discovering new modes of reactivity and/or selectivity drive developments in catalysis from earth-abundant elements [114]. A common theme in this field is the development of nontraditional methods that accomplish fundamental reaction steps such as oxidative addition (OA) and reductive elimination (RE). While such steps are typically the provenance of singlesite noble metals such as Rh, Ir, Pd, and Pt, OA and RE steps have been mediated using catalysts involving earth-abundant elements that exploit innovative strategies including frustrated Lewis acid−base cooperativity [115], distorted coordination geometries [116], strong ligand fields [117], noninnocent ligand residues and bimetallic cooperativity [118]. A Cu-Fe heterobimetallic catalyst was reported recently by Keith et al. for C-H borylation [119], which previously required noble metal catalysts, often based on Ir. The bimetallic system relies on cooperativity between an electrophile Cu site and a nucleophilic Fe site and requires the equimolar presence of both metal sites. Metal-metal cooperativity has been acknowledged as a source of reaction rate acceleration or selectivity amplification in certain scenarios, but it is rare for a homogeneous catalyst to require metal-metal cooperativity. This cooperativity presumably enables the Cu-Fe pairing to mimic the behavior of single-site Ir systems. Such metal-metal cooperativity also has implications for bioinorganic and heterogeneous catalysis, respectively, where cooperative bond-breaking and bond-forming events mediated by adjacent metal sites are well accepted but difficult to characterize [120]. The proposed mechanism (**Figure 13**) for the heterobimetallic C-H borylation reaction includes bimetallic analogues of the oxidative addition (OA) and reductive elimination (RE) reactions typically associated with single-site noble metals, *i.e.* B-H bimetallic oxidative addition (BOA) and H-H bimetallic reductive elimination (BRE). The feasibility of these bimetallic reaction pathways in a catalytic scenario indicates that other transformations traditionally proceeding through OA/RE cycling at single-site precious metal catalysts can instead be carried out with earth abundant bimetallic reaction centers [121].
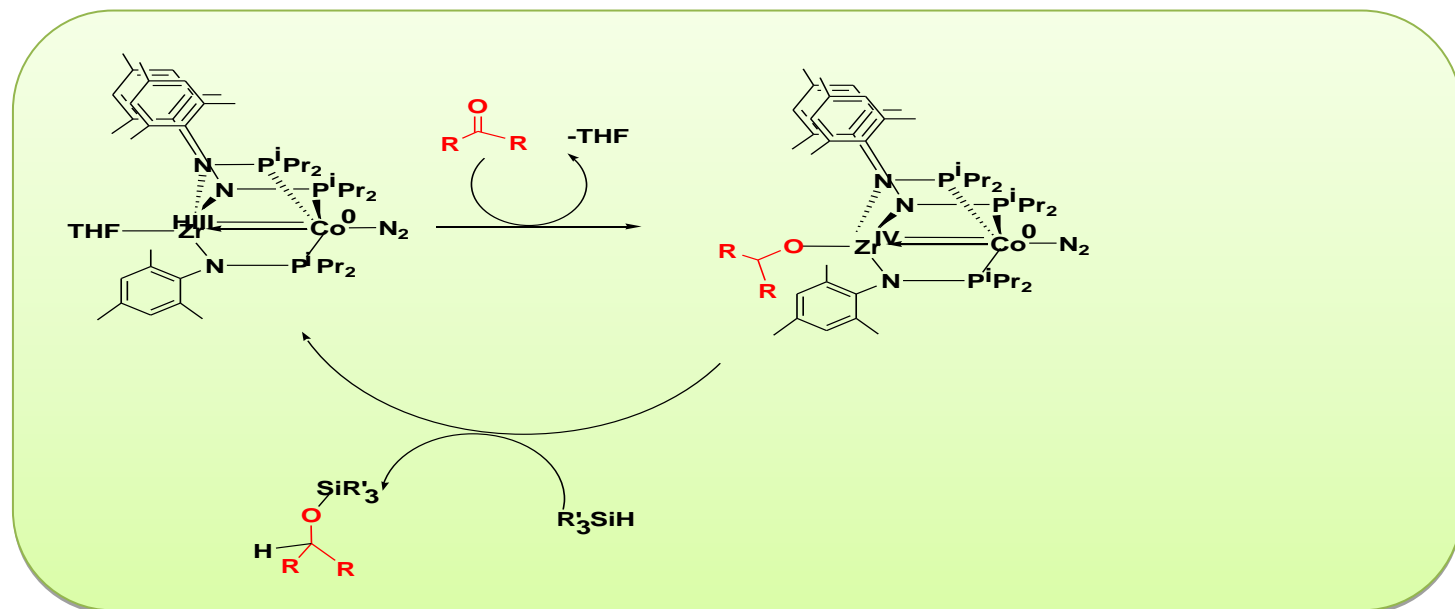
Catalytic Hydrosilylation of Ketones

Figure 14 The working of tris (phosphinoamide)-linked heterobimetallic Co/Zr complex (THF)Zr(MesNP^{i}Pr$_2$)$_3$CoN$_2$ (52) as a catalyst for the hydrosilylation of ketones

Hydrosilylation is a fundamental organometallic transformation for the reduction of alkenes, carbonyl, and imine functionalities. The most common ketone hydrosilylation catalysts feature noble metals, such as Rh [122] and Ir [123] however, hydrosilylation is now well-precedented for a variety of first-row transition metals, including titanium, zinc, copper, nickel, and iron. A recent theme emerging in catalytic methodology is the use of bimetallic metal complexes to catalyze organic transformations [124]. While studies of homobimetallic catalysts are now quite common, comparatively little attention has been placed on early/late heterobimetallic catalysts [125] particularly given the vast literature on the synthesis of early/late heterobimetallic complexes. Several researchers have investigated ketone

hydrosilylation reactions catalyzed by early/late heterobimetallic complexes. Nikonov and coworkers screened several heterobimetallic Nb−Rh complexes for the catalytic hydrosilylation of acetophenone and benzaldehyde, but little mechanistic insight was provided and catalytic activities were similar to those observed with monometallic Rh complexes. Similarly, Comte and Le Gendre et al. reported that ketone hydrosilylation with a heterobimetallic Ti−Rh complex proceeds more rapidly than with similar monometallic Rh or Ti complexes [126]. Notably, these heterobimetallic examples of ketone hydrosilylation catalysts utilize metals that are both known to be catalytically competent as monometallic species. A more interesting target, however, is a heterobimetallic system that promotes reactivity that is inaccessible with a monometallic analogue. The tris(phosphinoamide)-linked heterobimetallic Co/Zr complex $(THF)Zr(MesNP^iPr_2)_3CoN_2$ (52) has been investigated as a catalyst for the hydrosilylation of ketones with $PhSiH_3$ by Zhou and co-workers (**Figure 14**).

Catalytic activity superior to monometallic Co or Zr analogues has been observed, demonstrating the importance of cooperative reactivity between Co and Zr. Upon examining stoichiometric reactions, complex 52 was found to be unreactive toward $PhSiH_3$, implying that the mechanism diverges from the typical Chalk−Harrod-type hydrosilylation pathway. In contrast, 52 reacts readily with ketones, and in the case of benzophenone, a radical coupling product $[(Ph_2CO)Zr(MesNP^iPr_2)_3CoN_2]_2$ (53) was isolated, implying the intermediacy of a Zr-bound ketyl radical fragment. A radical-based hydrosilylation mechanism is proposed involving hydrogen atom transfer from $PhSiH_3$ to the Zr-bound ketyl-radical [127].

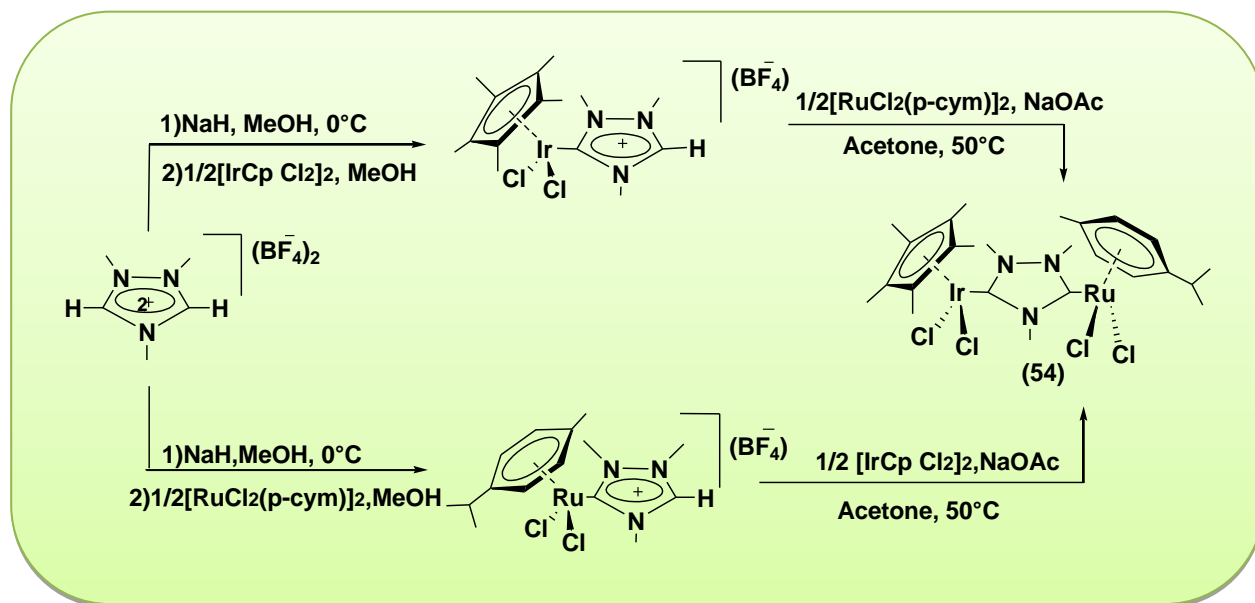### Catalytic Behavior of Heterobimetallic Iridium-Ruthenium Assemblies

Figure 15 Synthesis of heterobimetallic Ir (III) - Ru (II) complex

Synthesis by means of catalytic processes is one of the most rapidly evolving research areas in chemistry. Natural catalysts are known to be far more efficient than those developed by chemists. While the mechanism of action of enzymes often benefits from the mutual cooperation provided by two or more metals, man-made catalysts rarely exploit this approach. In the past few years, many sophisticated metal-based multicatalyst systems have been reported and reviewed [128]. In most of the cases, the action of the one-pot cocatalyst refers to (i) two catalysts that carry out sequential organic transformations (each step carried out by one catalyst) or (ii) cooperative catalytic actions on substrates by suitable catalysts occurring in a substrate-selective manner, followed by the coupling of the resulting activated substrates [129]. In order to avoid the use of two different catalysts, the preparation of dinuclear complexes containing two metals in close proximity has become the subject of extensive investigations in order to design efficient bimetallic catalysts [130]. During the past few years an efficient method for the preparation of homo- and heterobimetallic complexes bound to a 1,2,4- triazolyl-3,5-diylidene has been reported [131]. The preparation of such types of heterobimetallic complexes has allowed the study of several catalyzed tandem reactions in which each of the

metal fragments facilitates a mechanistically different cycle [132] and, more importantly, allowed to find clear experimental evidence for catalytic cooperativity between the metals comprised in the bimetallic unit [133]. Sabater et al. reported that high yield of a (p-cymene)- Ru II(triazolium-ylidene) complex allows the synthesis of an heterobimetallic Ir(III)−Ru(II) complex(54) with a triazole-diylidene bridge (**Figure 15**). A full electrochemical study of the heterobimetallic complex has been performed, and the results have been compared with those for the related homobimetallic triazolediylidene bridged complexes of ruthenium and iridium, where a weak metal−metal interaction has been detected. The Ir−Ru complex and some other related (p-cymene)Ru(NHC) complexes have been tested in a new tandem process, implying the chelation-assisted arylation of arylpyridines with 1-(4- halophenyl)ethanol. The arylation is accompanied by the transformation of the alcohol into a ketone, in the presence of acetone, through an Oppenauer oxidation process [134].

Catalytic Activity of Heterobimetallic Rare Earth-Zinc Ethyl BINOLate Analogues of Shibasaki's Catalysts

The heterobimetallic complexes $[M_3(THF)_n]$ -[(BINOLate)$_3$RE] (REMB, RE = La−Lu, Y; M = Li, Na, K; BINOLate = 1,1′-bi-2-naphtholate), developed by Shibasaki and co-workers, have proven to be highly enantioselective in a broad range of mechanistically diverse reactions [135]. These multifunctional catalysts contain two unique Lewis acid components (RE^{III} and M$^+$) and Bronsted-basic BINOLate oxygens within close proximity of each other. This characteristic facilitates intramolecular cooperativity in reactivity and is proposed to be responsible for the high levels of selectivity in comparison with monometallic Lewis acid catalysts [136]. The REMB framework is easily tuned by variation of the central and peripheral metal ions' ionic radii, offering an array of accessible catalysts from a single enantioenriched ligand (BINOL). Despite their utility in asymmetric catalysis, there have been few reports incorporating other metal ions into the heterobimetallic system. One approach toward this goal is to substitute metals with different oxidation states for the central 3+ metal ion. Walsh and co-workers reported the first example of substitution of the peripheral metal cations in Shibasaki's catalysts with the introduction of Zn^{2+}, resulting in the synthesis and characterization of rare earth−zinc ethyl heterobimetallic complexes, (EtZn)$_3$(THF)$_2$(BINOLate)$_3$RE^{III}(THF) (RE = La, Pr, Eu) (55) (**Figure 16**). They have determined that (EtZn)$_3$(THF)$_2$(BINOLate)$_3$RE-(THF) complexes are isostructural with their lithium analogues and have demonstrated their catalytic activity in enantioselective ethyl addition to benzaldehyde [137].
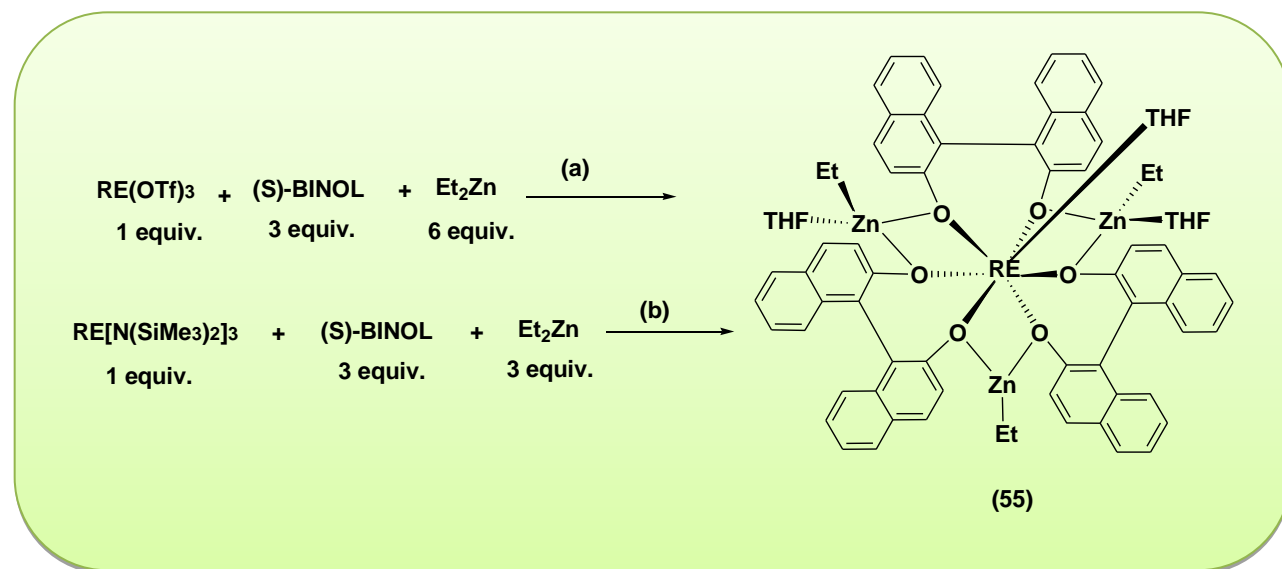

Figure 16 Synthesis of heterobimetallic complex (EtZn)$_3$(THF)$_2$(BINOLate)$_3$RE(THF)

Catalytic Activity of Heterobimetallics containing N-Heterocyclic Carbene

The heterobimetallic structures are hoped to exhibit unusual catalytic activity due to cooperative reactivity of the two different metals [138]. N-Heterocyclic carbenes (NHCs) have been receiving increasing attention as strong donating ancillary ligands for organometallic chemistry and homogeneous catalyis [139]. Donor functionalized NHC ligands contain multiple donor atoms with different electronic and steric properties offering opportunities for the construction

of bi- and polynuclear organometallic complexes [140]. Chen et al. synthesized mono- and polynuclear complexes containing 3-(1,10-phenanthrolin-2-yl)-1-(pyridin-2-ylmethyl)- imidazolylidene (L), [NiL$_2$](PF$_6$)$_2$ (56), [CoL$_2$](PF$_6$)$_3$ (57), [PtLCl](PF$_6$) (58), [PdAgL$_2$](PF$_6$)$_3$ (59), [PdCuL$_2$](PF$_6$)$_3$ (60), [Pd$_2$L$_2$Cl$_2$](PF$_6$)$_2$ (61), and [Pd$_3$L$_2$Cl$_4$](PF$_6$)$_2$ (62) which were fully characterized by NMR, ESI-MS spectroscopy, and X-ray crystallography (**Figure 17**).
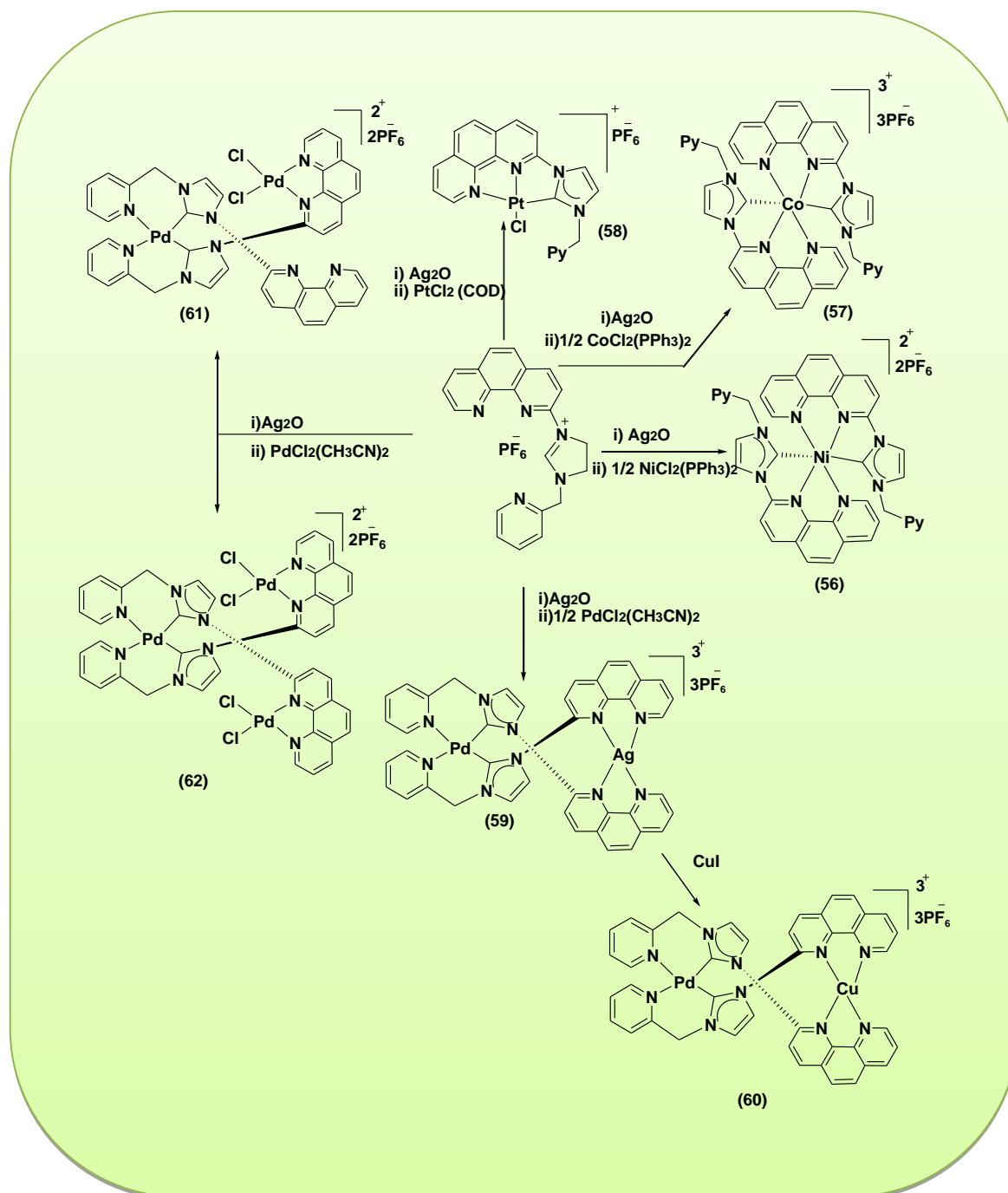

Figure 17 Synthesis of NHC complexes

In complexes 56-58, the ligand binds to metals in a pincer NNC fashion with the pyridine group uncoordinated. Complexes 59 and 60 are isostructural to each other in which the palladium ions are surrounded by two pyridines and two imidazolylidenes and Ag(I) or Cu(I) is coordinated by two 1,10-phenanthroline moieties. In the trinuclear

palladium complex 62, one palladium ion has an identical coordination mode as in 59 and 60, and the other two palladium ions are bonded to the 1,10-phenanthroline. Among all these complexes, complex 60 exhibits excellent catalytic activity for the tandem click/Sonogashira reaction of 1-(bromomethyl)-4-iodobenzene, NaN_3, and ethynylbenzene in which three C–N bonds and one C–C bond are formed in a single flask [141].

Catalytic Activity of Heterobimetallics with Dianionic Pentalene as Bridging Ligand

Organometallic chemistry of bimetallic systems has become an area of great interest and many of these complexes have been shown to possess unique properties, such as charge transfer, conductivity, and nonlinear optical behavior [142]. On the other hand, the applications to stoichiometric and catalytic reactions appear very attractive because bimetallic complexes may have higher reaction rates and could lead to transformations that do not occur on mononuclear species [143]. One of the most interesting types of ligands to study in binuclear organometallic complexes consists of fused aromatic rings. These ligands may connect two or more organometallic centers (which may have different oxidation states) and allow interaction between them [144]. A common assumption is that cooperative interaction between the two metal centers might cause significant increase in the reaction rates. Burgos and co-workers reported the synthesis of the ruthenium(II) pentalenyl complex $[Cp^*Ru(\eta^5-C_8H_7)]$ [145] which reacts, in tetrahydrofuran solution at -80 °C, with a stoichiometric amount of n-butyllithium in hexane and leads to the uncharacterized intermediate lithium compound $[Cp^*Ru(\eta^5-C_8H_6)Li]$ (63), which in turn reacts with $[\{Rh(\mu-Cl)(\eta^4-COD)\}_2]$ to give the heterobimetallic 34-electron complex $[Cp^*Ru(\mu-C_8H_6)Rh(\eta^4-COD)]$ (64) and is characterized spectroscopically and structurally (**Figure 18**). The structure of this compound exhibits the two metal centers bonded in an anti-disposition to the pentalenyl ligand. The displacement of the coordinated COD by carbon monoxide is studied. This bimetallic complex shows a high activity and selectivity for the dehydrogenative silylation of styrene [146].
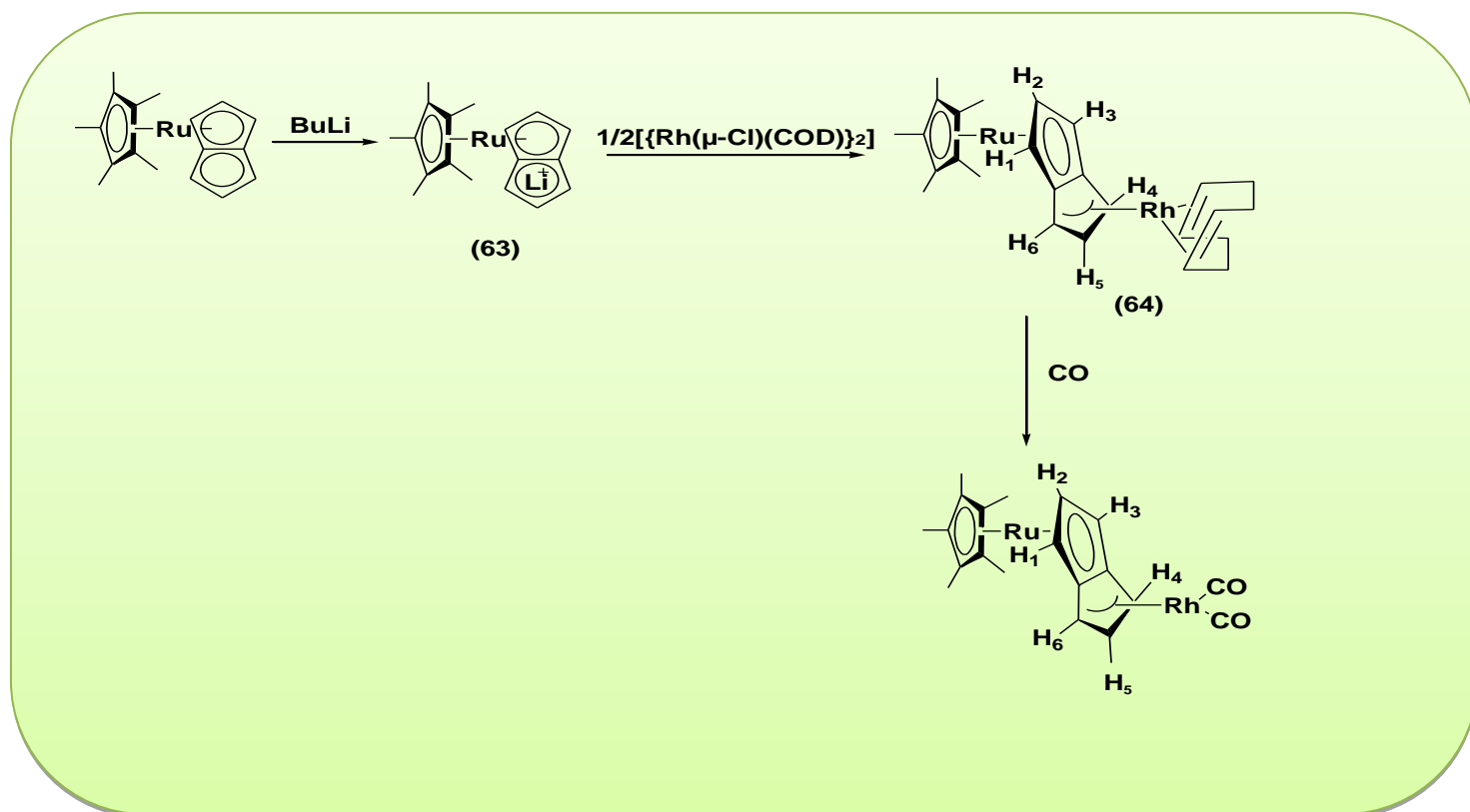

Figure 18 Synthesis of heterobimetallic complex $[Cp^*Ru(\mu-\eta^5,\eta^3-C_8H_6) Rh (\eta^4-COD)]$

Conclusion

In the past two decades, multimetallic catalysis has attracted wide attention of the catalysis community. An enormous range of heterobimetallic complexes has been developed that are found to catalyze reactions such as hydrogenation, isomerization, polymerization etc. These areas represent many important subfields of heterobimetallic catalysis. Even today there is limited understanding of the ''synergy'' observed between the components of bimetallic catalysts. This needs further in situ spectroscopic investigations and advanced characterization of the bimetallic catalysts to gain a deeper understanding. This information is vital in developing better catalysts or in overcoming the disadvantages of the current catalysts. The future of this arena lies in gaining a better understanding of the fundamental transformations arising at heterobimetallic centers and evaluating the independent roles of each metal.

Acknowledgements

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