Status of Organometallics and Catalysis Research in India: N–Heterocyclic Carbene (NHC) Ligands for Organometallic Catalysis

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(Received on 03 March 2019; Revised on 25 May 2019; Accepted on 05 June 2019)

The core activities in the field of organometallic chemistry and catalysis research in India are summarized in this article. It aims to portray the depth and diversity of the chemistry led by different research groups across the country. Selected works on the chemistry of metal–NHC compounds are highlighted.

Keywords: Organometallics; Catalysis; N-heterocyclic Carbenes (NHC); Metal-catalyzed Transformations

Background

Organometallics is the chemistry of metal-carbon bonds. The widespread interest on organometallic compounds stems largely from their intriguing structure-bonding relationships and vast applications in organic transformations. Organometallic chemistry plays a prominent role for the synthesis of fine chemicals, natural products, pharmaceuticals, agricultural products polymers and other useful materials. In recent years, sustainable processes and products are developed utilizing new generation metal-based catalytic systems. The relevance of organometallic catalysis is evident in renewable energy research. The 2005 (Casey, 2005; Chauvin, 2006) and 2010 (Nagendrappa and Kumar, 2011; Croft, 2010) Nobel prizes in chemistry are the recognition of the immense and continued impact of organometallics in chemical synthesis. The aim of this article is to present a bird’s-eye view of contemporary organometallic chemistry and catalysis research in India. A comprehensive coverage is impractical within the scope of this article. Rather, it highlights the core activities of different research groups, followed by a focused and short description of the chemistry of metal–N-heterocyclic carbene (M–NHC) compounds – a self-serving choice. Efforts are made to cover significant activities that fit within the broader definition of organometallics. Any inadvertent omission, as it may well be, is regretted.

Metal Salts in Catalysis

There have been sustained activities on the direct use of metal salts as catalysts for a wide range of organic transformation reactions. Chandrasekaran group (IISc) explored the chemistry of MoS$_4^{2-}$ and WSe$_4^{2-}$ as versatile sulfur and selenium transfer reagents, respectively, to access functionalized disulfides, diselenides, selenoamides, selenoureas, and cyclicselenide derivatives (Sureshkumar et al., 2012; Suresh et al., 2005; Devarajulu et al., 2010; Devarajulu et al., 2007a; Devarajulu et al., 2007b). At IITK, Iqbal group research focused on developing synthetic methodologies involving cobalt-catalyzed functional group transformations for applications in synthetic chemistry (Iqbal et al., 1994; Bhatia et al., 1993; Punniyamurthy et al., 1993; Iqbal et al., 1991). Periasamy group (UH) demonstrated carbynolation of organic compounds using metal carbonyls (Beesu and Periasamy, 2011; Beesu and Periasamy, 2012; Periasamy et al., 2008). Fe(CO)$_5$ was employed for the carbynolation of alkynes to obtain cyclobutenediones and anhydrides (Periasamy et al., 2004). In addition, they developed new synthetic methodology involving TiCl$_4$/R$_3$N reagent systems

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(Periasamy, 2002; Bharathi and Periasamy, 1999; Bharathi and Periasamy, 2000; Periasamy et al., 2010; Karunakar and Periasamy, 2006). Kotha group (IITB) exploited various ruthenium catalyzed metathesis reactions as key steps to access ring annulated products (Kotha and Gunta, 2017; Kotha et al., 2015; Kotha et al., 2011; Kotha and Chavan, 2010; Kotha and Khedkhar, 2009; Kotha et al., 2009). Further, they exploited Suzuki–Miyaura cross-coupling strategy to access diverse polycyclic aromatics (Kotha and Ghosh, 2004; Kotha and Mandal, 2006; Kotha and Mandal, 2009; Kotha et al., 2007; Kotha et al., 2002). M. Lakshmi Kantam from IICT has exploited metal nanoparticles on different solid supports for a wide variety of organic transformations (Layek et al., 2012; Chakravarti et al., 2011; Kantam et al., 2013; Arundhathi et al., 2013; Kantam et al., 2009). Ranu group (IACS) used metal nanoparticles as catalysts for a variety of organic transformation reactions, in particular, Pd and Fe nanoparticles for direct C–H functionalization (Saha et al., 2010; Panja et al., 2017; Chatterjee et al., 2014; Kundu, et al., 2013) and reduction reactions (Panja et al., 2017; Dey et al., 2012; Saha and Ranu, 2008).

Organometallic Chemistry

These activities had a thick organic chemistry flavor. Other research groups have pursued classical organometallic chemistry research that includes the synthesis of organometallic compounds, their reactivity studies and potential use in catalysis. S S Krishnamurthy (IISc) group designed and developed an array of P-N and P-N-P based ligands. Palladium-allyl, ruthenium-hydride and carbonyl cluster compounds supported by those ligands were synthesized and exploited in catalytic coupling and transfer hydrogenation reactions (Reddy et al., 1992; Maji et al., 2011; Mandal et al., 2003; Venkatakrishnan, et al., 2006; Venkatakrishnan, et al., 2007; Mandal et al., 2006). Chandrasekhar group (IITK) studied the organometallic chemistry of main group elements (Chandrasekhar et al., 2009a; Chandrasekhar et al., 2009b). Significant advances were made in the chemistry of organostannoxane and organotelluroxane compounds. Carboxylates, phosphate and sulphonates supported organotin molecular assemblies were synthesized and structurally characterized (Chandrasekhar et al., 2007; Chandrasekhar et al., 2005). Organostannoxane supported palladium nanoparticles were employed for the efficient cross-coupling reactions (Heck and Suzuki) (Chandrasekhar et al., 2009; Chandrasekhar et al., 2011). Bhaduri at Reliance Industries studied platinum and ruthenium carbonyl cluster complexes and exploited inorganic-oxides supported metal carbonyl catalysts for hydrogenation reactions (Bhaduri et al., 1998; Bhaduri et al., 1983; Basu et al., 1986; Bhaduri et al., 2001; Paul et al., 2003). They also developed technologies for the industrial scale manufacture of polypropylene utilizing supported or modified Ziegler-Natta type of catalysts (Gnanakumar et al., 2011; Bhaduri et al., 2006; Thushara et al., 2012). Singh group (IITB) works on the organoselenium and organotellurium compounds (Manjare et al., 2012; Kumar et al., 1990; Panda et al., 1990). The coordination behavior of these compounds with Pd(II) has been studied (Chakraborty et al., 2011a; Chakraborty et al., 2011b) and the catalytic utility of these complexes are evaluated for cross-coupling reactions (Ghavale et al., 2015; Chakraborty et al., 2011a). Samuelson (IISc) group examines anti-cancer activities of half-sandwich metal complexes with heterocyclic ancillary ligands (Mitra et al., 2012; Mitra et al., 2014). Besides metal-catalyzed transformation reactions, (Dinda et al., 2010; Kumar et al., 2011) his group undertakes electronic structure calculations to gain insight on bonding and energetics of organometallic compounds (Bera et al., 1999; Dindar et al., 2012). E D Jemmis (UH/IISc/IISER-TVM) (Jemmis et al., 2002; Jemmis et al., 2003; Kiran et al., 2002; Roy et al., 2014; Mondal et al., 2018) and R B Sunoj (IITB) (Jindal et al., 2014; Reddi et al., 2019; Kumarasamy et al., 2017; Bhaskararao and Sunoj, 2015) offer theoretical perspectives on the structures, bonding and reactivities of organometallic compounds. Mathur (IITB) explored the cluster chemistry involving chalcogen-bridged mixed-metal carbonyl clusters (Datta et al., 1994; Mathur et al., 1994; Mathur et al., 2000; Mathur et al., 2000; Mathur et al., 2002; Klose et al., 2003) and their acetylenic derivatives (Mathur et al., 1995; Mathur et al., 1993; Mathur et al., 1996; Mathur et al., 1995). Gupta group (IITK) examined the structure-property relationship of organo-cobalt and vitamin B12 model compounds (Gupta et al., 2011; Dutta et al., 2011; Bhuyan et al., 2008; Mandal and Gupta, 2007). The reactivity of the Co-C bond was examined by the reactions of organocobaloximes with...
molecular oxygen and Br₂ (Kumar and Gupta, 2011; Mandal et al., 2007; Kumar et al., 2011; Dutta et al., 2012). Elias (IITD) has developed cobalt and iron sandwich compounds bearing tetraphenyl-cyclobutadiene and cyclopentadiene derivatives (Kumar et al., 2016). Several donor groups are attached on the Cp ring and their metal complexes are synthesized (Hazra et al., 2017; Singh et al., 2016). Palladacycles constructed by chemical modification of the Cp ring were utilized for organic transformation reactions (Singh et al., 2015; Singh and Elias, 2011; Singh et al., 2014). His group earlier pursued organometallic reactions on moieties derived from cyclophosphazene cores (Elias et al., 2011; Kumar et al., 2014; Kumar et al., 2008; Keshav et al., 2010; Kumar et al., 2011). Lahiri (IITB) has employed well known Ru based catalysts for alcohol dehydrogenation, amide synthesis from primary and secondary amines and epoxidation reactions (Ray et al., 2018; Ray et al., 2014; Chowdhury et al., 2011). Iron salts are also used for oxidation and nitrosation of terminal alkenes (Chowdhury et al., 2012a; Chowdhury et al., 2012b; Ray et al., 2013). Jagirdar group (IISc) is engaged in examining heterocyclic X-H bond activation at highly electrophilic metal center (Nagaraja et al., 2007; Mala et al., 2017; Mala et al., 2018; Ramaraj et al., 2016). Their work has provided valuable insight on the H-atom exchange process between the η²-H₂ and hydride ligands on the metal. His group has also developed a protocol for the synthesis of metal and bimetal alloy nanoparticles employing amine-boranes with appropriate metal salts. The use of amine-borane serves dual purposes – to reduce the metal ions to its elemental form and the generated BNHx polymer acts as stabilizing agent. Dissolution of the capping polymer in water afforded mesoporous metal nanosponges which are conveniently used for a variety of reduction reactions under mild conditions (Kalindini et al., 2011; Sanyal and Jagirdar, 2012; Kalindini and Jagirdar, 2012; Ghosh and Jagirdar, 2018). Roy group (IICT/IITKGP/IIT BHU) developed heterobimetallic chemistry for catalytic organic transformations (Das et al., 2015; Roy and Roy, 2010; Das et al., 2012). Notably, transition metal–tin (TM-Sn) systems are devised for allylation, propargylation, allenylation, selenylation, benzylolation reactions (Choudhury et al., 2005; Podder et al., 2007a; Podder et al., 2007b; Kundi and Roy, 2007). A. K. Singh group (IITD) has exploited Pd, Ru, Ir compounds with organochalcogen ligands for cross-coupling, oxidation and transfer hydrogenation reactions (Bhaskar et al., 2018; Prakash et al., 2013; Dubey et al., 2018; Saleem et al., 2013). Pandey at BHU uses half-sandwich Ru arene complexes for a variety of purposes (Kumar et al., 2014; Singh et al., 2014). Singh expands the similar chemistry at IITI (Dwivedi et al., 2018; Awasthi et al., 2018). Ghosh at IITM has combined organometallic fragments with borane constructs (De et al., 2018; Anju et al., 2014; Saha et al., 2017). Anantharaman (IITK) studies metal-NHC compounds and their catalytic activity towards cross-coupling reactions (Karthik et al., 2014; Bhat et al., 2019; Karthik et al., 2013).

Organometallic Catalysis

Rao (IITK) explores palladium catalyzed cross-coupling reactions for organic synthesis. Stable triarylbi(bismuths are effectively used as aryl transfer reagents under palladium-catalyzed conditions for a wide variety of C-C bond forming reactions (Shimada and Rao, 2012; Rao et al., 2010a; Rao et al., 2010b; Rao et al., 2008). Sekar (IITM) group research emphasizes on metal nanocatalysts (Savitha et al., 2016a; Savitha et al., 2016b; Surya et al., 2016; Ganapathy et al., 2014; Sharma et al., 2017). Further, they have studied metal-catalyzed reduction of ß-keto amides and their functionalization (Mamillapalli and Sekar, 2015a; Mamillapalli and Sekar, 2014; Mamillapalli and Sekar, 2015b; Kotha et al., 2014; Muthukumar and Sekar, 2017; Muthukumar et al., 2018). Punniyamurthi (IITG) focuses on the transition-metal catalyzed stereoselective carbon-carbon and carbon-heteroatom bond formation (Talukdar et al., 2019; Banerjee et al., 2019; Satheesh et al., 2018; Mahesh et al., 2017; Mahesh et al., 2016; Sengoden et al., 2017; Sengoden and Punniyamurthi, 2013). Hotha (IISER Pune) group employs gold catalysts for the synthesis of glycosides and furanosides respectively (Hotha and Kashyap, 2006; Kayastha and Hotha, 2012; Thadke et al., 2013; Vidadala et al., 2011; Sureshkumar and Hotha, 2008). The metal-catalyzed C-H bond activation and functionalization is an important area of research in chemical synthesis. Several groups are independently leading this activity- notable names are Maiti (Achar et al., 2018; Maji et al., 2018; Deb et al., 2017), Jeganmohan (Ramesh and Jeganmohan, 2017; Reddy and Jeganmohan, 2017; Manikandan et al., 2016),
Anbarasan (Reddy et al., 2017; Yadagiri et al., 2016; Yadagiri and Anbarasan, 2015), Sundararaju (Kalsi et al., 2018; Barsu et al., 2017; Sen et al., 2016), and Baidya (Mandal et al., 2017; Dana et al., 2018a; Dana et al., 2018b).

Chattopadhyay group (CBMR, Lucknow) engineered new catalytic systems integrating noncovalent interactions on transition metal complexes to generate novel concepts and hypotheses in C–H activation chemistry. Moreover, they have developed series of new denitrogenative annulation strategies employing organometallic complexes for the construction of diverse nitrogen heterocycles (Bisht et al., 2018; Smith III et al., 2018; Bisht and Chattopadhyay, 2016; Hoque et al., 2017). Gunanathan (NISER) group studies ruthenium catalyzed deuteration of organic compounds using D₂O to labelled products (Chatterjee et al., 2016; Krishnakumar and Gunanathan, 2018; Chatterjee and Gunanathan, 2016; Chatterjee and Gunanathan, 2015; Thiyagarajan and Gunanathan, 2019). Balaraman group (IISER-Tirupati) efforts lie in the domain of catalytic hydrogenation and dehydrogenation reactions (Midya et al., 2015; Sahoo et al., 2017; Sahoo et al., 2018; Jaiswal et al., 2017; Nandakumar et al., 2015). Chikkali group (CSIR-NCL) uses metal catalysts bearing phosphorus ligands featuring supramolecular binding property for hydrophosphination, hydrogenation, hydroformylation, polymerization reactions (Koshti et al., 2014; Koshti et al., 2015; Pandey and Chikkali, 2015; Pandey et al., 2018; Mote et al., 2017). Biplab group (IISERKolkata) is developing new synthetic methodology using manganese to construct new C-C bonds by alcohols activation (Barman et al., 2018a; Maji and Barman, 2017; Barman et al., 2018b; Jana et al., 2018). Kundu (IITK) group has exploited alcohol as an alkylation agent to construct new C-C and C-N bonds for organic synthesis (Shee et al., 2018; Paul et al., 2018; Maji et al., 2018; Chakrabarti et al., 2017).

Heterogeneous Catalysis

Although most activities in organometallic catalysis are confined under homogenous conditions, there is a vibrant community who work on heterogeneous catalysis. Prof. B M Choudary from IICT, Hyderabad is the pioneer utilizing layered double-hydroxides, copper apatite, nanocrystalline MgO, OsO₄ incorporated in resins, for a range of reactions such as C–H activation, N-arylation of heterocycles, Claisen-Schmidt condensation, asymmetric epoxidation and dihydroxylation of olefins (Choudary et al., 2005; Choudary et al., 2004; Choudary et al., 2002; Choudary et al., 2001). P. Selvam from IITM has synthesized several heterogeneous catalysts based on mesoporous silica (MCM-41) and their aluminate derivatives. These catalysts are evaluated for selective oxidation, hydrogenation, wet air oxidation of aniline, reductive cleavage of azo compounds (Selvam et al., 2011; Mohapatra et al., 2002; Gomes et al., 2005; Sonavane et al., 2003). S B Umbarkar from NCL, Pune exploited in situ generated molybdenum oxo-peroxo complexes as recyclable catalysts for oxidation reactions (Biradar et al., 2008; Chaudhure et al., 2012; Nguyen et al., 2012; Chandra et al., 2013). In recent time, V. Polshettiwar group from TIFR, Mumbai developed dendritic fibrous nano-silica (DFNS) based nanocatalysts, such as TaH supported on silica, single atoms and nanoparticles of metal supported on amine and polycyclic functionalized DFNS, for various range of catalytic transformations and CO₂ capture-conversions (Bayal et al., 2017; Polshettiwar et al., 2011; Polshettiwar et al., 2009; Polshettiwar et al., 2010; Singh and Polshettiwar, 2009).

Books on Organometallic Chemistry

The continued tradition of organometallic chemistry is reflected in the numbers of books written by Indian authors. Prof. R C Mehrotra offered an introductory account of organometallic chemistry (Mehrotra, 2000). V Chandrasekhar has authored a book on Inorganic and Organometallic polymers (Chandrasekhar, 2005). Anil Elias and B D Gupta (Gupta and Elias, 2010; 2013) have written a modern book on organometalics that has become an essential handbook for students and teachers as well. Anil Elias has recently introduced a well-researched book on the chemistry of the p-block elements (Elias, 2018). S. Bhaduri and D. Mukesh have written a book on homogeneous catalysis with particular emphasis on industrial applications (Bhaduri and Mukesh, 2014).

Metal–N-heterocyclic Carbene Complexes

Arduengo reported the first stable NHC (1,3-diadamantylimidazole-2-ylidene) in 1991 (Scheme I). Initially NHCs were viewed as neutral 2-e donor
alternatives to phosphines and the synthesis to metal-NHC compounds was considered difficult than their phosphine counterparts. However, NHCs soon found numerous applications, and prominently in organometallic catalysis. Several synthetic protocols are developed over the years to access metal–NHC compounds. It is now well recognized that NHCs offer several advantages over phosphines. The NHC features a directional sp$^2$-type lone pair compared to non-directional σ-type orbital for phosphine. The extent of π-back-bonding is lower in metal-NHC than in metal-phosphine complexes. These factors contribute to the stability of the metal-NHC compounds imposing higher electron density on the metal center. It has direct implications on their performances in catalytic processes. The Pd–NHC catalysts are in general more active and offer better turnover values for cross-coupling reactions than related phosphine-based catalysts. The evolution of Grubbs olefin metathesis catalysts is another example of the superiority of NHC ligands over phosphines.

The phosphine ligands played an important role in the early development of organometallic chemistry and catalysis. The footprint of Indian chemists in that era had been rather limited. In recent times, metal-catalyzed reactions involving metal–NHC compounds are the major topics of catalysis research and Indian chemists are making a sizable contribution to this field. We focus on research from selected groups engaged in exploring the chemistry of metal–NHC compounds.

**Selected Works on the M–NHC Chemistry in India**

Sarkar group at NCL Pune worked on the chemistry of metal-carbene complexes. A variety of reactions involving Fischer carbene complexes were studied including alkylation (Amin and Sarkar, 1995) and annihilation, (Mathur et al., 1998) regioselective 1,3-dipolar addition of organic azides (Chakraborty et al., 2010) and rearrangement to ketone (Nandi et al., 1992). Thermal rearrangement of aryl(allyloxy)carbene complexes of Cr and W afforded the corresponding ketones (Scheme 2). The rearrangement is general and applicable for aryl(allyloxy)carbene complexes as well. It was demonstrated that electronic tuning on the carbene carbon dictates the reactivity of the complexes. (Sathe et al., 1996)

Sarkar exploited suitably modified Fischer carbene complexes for the reduction of Au salts and stabilization of nanoparticles (Samanta et al., 2006). Hydrophilic Fischer carbene complexes are used as organometallic bio-markers (Samanta et al., 2005). A ferrocene-analog of Grubbs catalyst was developed which show efficient RCM reactions (Scheme 3) (Maishal and Sarkar, 2002).

Ghosh at IITB initiated the chemistry of NHC based metal complexes, (Ramasamy and Ghosh, 2016; John and Ghosh 2010) focusing on exploring the potential of these compounds in biomedical applications, with a particular emphasis on developing Pd–NHC complexes for anticancer studies (Scheme 4a), (Kumar et al., 2017; Ray et al., 2007a; Kumar et al., 2018) and also in catalytic applications. On the homogeneous catalysis front, Ghosh’s group have demonstrated the utility of these complexes for simple Pd-mediated C–C cross-coupling reactions like the Suzuki, (Ray et al., 2007b) Sonogashira (Scheme 4b)
Ghosh’s group has successfully developed the more challenging bifunctional catalysis on NHC ligand platforms using nickel complexes for the chiral (Rao et al., 2015) and achiral (Samantaray et al., 2009; Ray et al., 2009) variants of the base-free Michael addition reactions (Scheme 4e). Further, his group also reported Fe-NHC complexes for asymmetric Michael addition reactions (Prakasham et al., 2018). They pursued applications of these complexes in industrially important and environmentally relevant atom-economic reactions like the hydroamination of activated olefins (Scheme 4d) (Kumar et al., 2017; Dash et al., 2010a) and the hydroamination of alkynes (Scheme 4e) (Katari et al., 2012; Dash et al., 2010b). Ghosh successfully performed silylation reactions in the form of hydrosilylation of carbonyl compounds using iron complexes (Scheme 4f) (Kumar et al., 2014) and reported the catalytic utility of inert coinage metals like silver and gold in polymerization reactions for producing environmentally benign polylactide polymers using Ring Opening Polymerization of L-lactides (Scheme 4g) (Samantaray et al., 2006; Ray et al., 2006). In the domain of asymmetric catalysis, Ghosh’s group has reported rhodium and iridium based precatalysts for the transfer hydrogenation of ketones (Scheme 4h) (Ramasamy et al., 2017). Overall, Ghosh’s group work represents the expansion of the application space, both biomedical and catalytic, of NHC based metal complexes using variation in carbene ligands and their well-defined metal complexes along with obtaining detailed mechanistic insights for further improvements of the property of interest.

Mandal at IISER Kolkata developed the chemistry of mesoionic carbene (MIC) which is also known as abnormal N-heterocyclic carbene (aNHC) where C2-position of imidazole ring is blocked with a phenyl group. By virtue of its strong nucleophilic nature (Thakur et al., 2016; Sau et al., 2016; Sau et al., 2019; Hota et al., 2018), a variety of transition metal complexes were prepared (Scheme 5). For example, Mandal and co-workers prepared halobridged C–H activated palladium dimers (Scheme 5(a)) (Hota et al., 2015; Hota et al., 2017), which are active catalysts for the Suzuki–Miyaura cross-coupling of a number

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**Scheme 4:** Catalysts developed in Ghosh laboratory and catalytic activities
of aryl chlorides at room temperature with low catalyst loading (up to 0.005 mol%) (Sau et al., 2012; Sreejyothi et al., 2018; Ahmed et al., 2017). Importantly, complex (a) remained active for 10 successive catalytic runs without any loss of its activity, confirming the robustness of the Pd-aNHC bond. More recently, complex (a) was reported as an active catalyst for dehydrogenative cross-coupling using a variety of heteroarenes such as benzothiazole, benzoxazole, 2-formyl thiophene, furfural and N-methyl benzimidazole. Cu(I)-MIC complex (Scheme 5b) was applied for cycloaddition of azides and alkynes at very low catalyst loadings and a wide range of triazoles in good to excellent yields were obtained (Scheme 5) (Sau et al., 2013). The MIC based iron (0) catalyst (Scheme 5c) was used for selective hydroisilylation of various aldimines and ketimines for the synthesis of corresponding amines (Bhunia et al., 2016). An aryl C-H activated nickel(II) cyclooctenyl complex (Scheme 5d) was also isolated (Vijaykumar et al., 2017). Complex (5d) catalyzes hydroheteroarylation of various olefins through C-H bond activation, offering a highly atom-economical method for the synthesis of 1,1- or 1,2-diarylalkanes. Besides transition metal chemistry, Mandal and co-workers also prepared main-group metal complexes (5e), (5f) and (5g) (Scheme 5). (MIC)K(I) complex was utilized for the polymerization of rac-lactide in toluene at room temperature showing 96% conversion within 2.5 h (Bhunia et al., 2017). (MIC)Al(III) complex (Scheme 5f) and (MIC)Zn(II) complex (Scheme 5g) also act as catalysts for the ring opening polymerization of various cyclic esters (Sen et al., 2013).

Choudhury group (IISERB) has revealed an unprecedented chemistry of Rh-NHC backbone for the synthesis of highly conjugated, cationic and annulated organic molecules (Ghorai and Choudhury, 2014; Ghorai and Choudhury, 2015; Thenarukandiyil and Choudhury, 2015; Ghorai et al., 2016; Thenarukandiyil et al., 2016a; Thenarukandiyil et al., 2016b; Dutta et al., 2019). The rhodium(III) catalyzed C-H bond activation of aromatic, heteroaromatic and vinylc motifs was achieved by utilizing a novel conjugative action of NHC ligand as directing group followed by insertion of internal alkynes and subsequent annulation of various imidazolium salts (Scheme 6a-c). They also reported a series of iridium(III)-NHC complexes with varying ring size for hydride-transfer reaction (Semwal et al., 2014; Semwal et al., 2017). Based on the bite angle and yaw angle of these complexes, their electronic properties were studied for the efficient hydride donor

**Mandal’s work**

![Scheme 5: Catalysts developed in Mandal laboratory](image-url)
ability to unsaturated organic molecules (Scheme 6d). Along this line, recently they developed a NHC-based iridium catalyst featuring a hybrid anionic amido-type supporting ligand for CO$_2$-conversion chemistry (Scheme 6e) (Semwal et al., 2018; Kumar et al., 2019). Further, they have introduced smartly designed benzimidazole-pyridinylidene-based NHC hybrid ligand constructed Ir and Ru complexes as a new class of ‘molecular switch’ to demonstrate stimulus-switchable hydrogenation/dehydrogenation catalysis for reversible hydrogen storage and delivery processes (Scheme 6f) (Semwal and Choudhury, 2016; Semwal and Choudhury, 2017). The same group has reported a series of Pd-mono and bis-imidazolylidene-NHC (Scheme 6g) and Ru-NHC-based complexes (Scheme 6h) for oxidative C-H functionalization (acetoxylation and halogenation) of arenes and oxidative scission of alkenes and alkynes to the corresponding carbonyl compounds, respectively (Desai et al., 2015; Gupta et al., 2016; Gupta and Choudhury, 2016).

Bera group designs and develops organometallic catalysts for the conversion of earth-abundant molecules to useful chemical feedstock. Employing ‘bifunctional’ metal-ligand cooperation strategy, new bond activation mechanism has been devised. Utilizing water as a reagent, nitrile hydrations (Scheme 7a-b), (Daw et al., 2012; Singh et al., 2017) olefin oxygenation (Scheme 7c) (Ghatak et al., 2015) and direct conversion of alcohol to carboxylic acid (Scheme 7d) (Sarbajna et al., 2017) have been demonstrated in his laboratory. Recent research in Bera group is geared towards the development of sustainable processes and products. Alternate catalytic method is established that avoids the use of hazardous ozone generator for the selective conversion of olefins to aldehydes (Scheme 7e) (Daw et al., 2014). Alcohols are catalytically dehydrogenated followed by dehydrogenative coupling on a dimetal platform (Scheme 7f) (Saha et al., 2014). Employing bifunctional activation strategy, amines are doubly dehydrogenated to nitriles providing two molecules of dihydrogen under acceptorless and oxidant-free conditions (Scheme 7g) (Dutta et al., 2018). This recent result raises the prospect of amines as Liquid Organic Hydrogen Carrier (LOHC). New strategies are being developed for catalyst systems that would hydrogenate the dehydrogenated product nitrile back to amine using abundant biomass. Double dehydrogenation of amine under moderate conditions with an output of two molecules of hydrogen gas and off-site refueling utilizing biomass is an important step towards the goal of establishing hydrogen economy.

**Choudhury’s Work**

![Scheme 6: Catalysts developed in Choudhury laboratory](image)
Bera’s work

Jana group at TIFR, Hyderabad demonstrated that NHC can reversibly coordinate to the \( p \)-block compound, diphosphene Ter\(^{Mes} \)P=PTer\(^{Mes} \), at room temperature (Scheme 8) (Dhara et al., 2018).

The same group further reported the abnormal addition of NHC\(^{Dip} \) to a conjugate acid of CAAC which leads to the adduct formation (Scheme 9) (Mandal et al., 2018). Mechanistic studies revealed that it proceeds through \textit{in situ} formation of an imidazolium cation and \( N \)-iPr substituted CAAC, followed by oxidative addition.

Concluding Remarks

It has been a challenge to capture the essence of India’s organometallic chemistry and catalysis research in this concise article. The efforts have been to convey the diversity and the depth of the chemistry. Hopefully this article would allow one to assess the Indian contribution in organometallic chemistry and catalysis field. Last few years have witnessed a dramatic development in organometallic research, transitioning from classical studies on organometallic compounds to catalyst design and development for challenging molecular transformations. The infusion of young talents has made the field highly vibrant and competitive. A critical mass is reached. The future of organometallic chemistry research in India looks bright today.

Acknowledgements

I thank colleagues, far too many to mention individually, for their insights and comments on this...
article. The contributions of the organometallic research community who laid the foundation, on which the present generation continues to build up, are gratefully acknowledged. The generous support by the DAE, India for our research is much appreciated. JKB thanks the SERB, DST India for the J C Bose fellowship. C.R. thanks IITK for a post-doctoral fellowship. P.P. thanks CSIR for a fellowship.

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