METAL COMPLEXES AND NANOPARTICLES TAILORED WITH ORGANOCHALCOGEN LIGAND/DOPING WITH PHOSPHORUS: DESIGNING AND APPLICATIONS

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by

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Submitted

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CERTIFICATE

This is to certify that the thesis entitled, **"METAL COMPLEXES AND NANOPARTICLES TAILORED WITH ORGANOCHALCOGEN LIGAND/DOPING WITH PHOSPHORUS: DESIGNING AND APPLICATIONS"** being submitted by **Mr. ALPESH KUMAR SHARMA** to the Indian Institute of Technology Delhi for the award of the degree of **Doctor of Philosophy** in Chemistry, is a record of bonafide research work carried out by him. Mr. Alpesh Kumar Sharma has worked under my guidance and supervision. He has fulfilled the requirements for the submission of this thesis, which to my knowledge has reached the requisite standard.

The results contained in this dissertation have not been submitted, in part or in full, to any other university or institute for award of any degree or diploma.

Date:

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ABSTRACT

The present thesis is focused on metal complexes of bidentate and tridentate organochalcogen ligands including hybrid ones and metal based NPs as catalysts. The Pd(II), Ru(II) and Ir(III) are the selected metal ions. Metal complexes of organophosphine have been used as a single source precursor (SSP) for synthesis of metal phosphide NPs. Magnetite NPs were layered with sulfated Schiff base (SB) and Ru(OH)x or tetraethyl orthosilicate (TEOS), SePh and Pd(0) to generate nanocomposite. The newly designed NPs and complexes have been investigated as catalyst for Suzuki-Miyaura coupling (SMC), C-O coupling, synthesis of disubstituted benzimidazole derivatives, aerobic oxidation of alcohols, Oppenauer-type oxidation of alcohols, transfer hydrogenation (TH) reaction of carbonyl compounds, amide synthesis and hydrogen evolution reaction.

Unsymmetrical bidentate benzimidazole based chalcogen ligands, 1-benzyl-3-phenylchalcogenylmethyl-1,3-dihydrobenzoimidazole-2-chalcogenone (**L1**-**L4**) when treated with $[(\eta^6\text{-}C_6H_6)RuCl(\mu\text{-}Cl)]_2$ in methanol followed by NH_4PF_6 resulted in $[(\eta^6\text{-}C_6H_6)Ru(\mathbf{L1}\text{-}\mathbf{L4})Cl][PF_6]$ (**1**-**4**). Ru has pseudo-octahedral half sandwich "piano-stool" geometry in all the four complexes. Pd(II) complexes $[(Pd(\mathbf{L})Cl_2]$ (**5**-**8**) synthesized by reacting **L1**-**L4** with $Pd(CH_3CN)_2Cl_2$ in acetonitrile have distorted square planar geometry around Pd. The **1**-**4** have been explored for TH of carbonyl compounds using various sources of hydrogen. Catalytic process is more efficient with **3** followed by **1** ≈ **4** and **2**, (0.01-0.5 mol%) in 2-propanol and glycerol (found most suitable solvent). DFT calculations support experimental results. The **5**-**8** have been used to catalyze SMC with 0.01 mol% loading of the catalyst.

The ligands (**L** = **L1**-**L4**) when treated with $[(\eta^5\text{-}Cp^*)IrCl(\mu\text{-}Cl)]_2$, followed by NH_4PF_6, resulted in $[(\eta^5\text{-}Cp^*)Ir(\mathbf{L})Cl][PF_6]$ (**9**-**12**). Single crystal X-ray diffraction

revealed “piano-stool” geometry around Ir. One pot synthesis of disubstituted benzimidazole derivatives was carried out from *o*-phenylenediamnie and aromatic alcohols with excellent to good yield using 0.1 mol% loading of **9-12** as catalyst. The **9-12** were also found promising for aerobic oxidation of aromatic alcohols and Oppenauer-type oxidation of alcohols to aldehydes when their loading was 0.1 and 0.01 mol% respectively.

Schiff base ligands (**L5:** sulfated and **L6:** selenated) having ferrocene core on treatment with Na_2PdCl_4 in the presence of NaOAc formed cyclopalladated complexes [Pd(**L5/L6**-H)Cl] (**13**/**14**). The **13** on reacting with one equivalent of PPh_3 gave [Pd(**L5**-H)PPh_3Cl] (**15)**, formed *via* cleavage of Pd-S bond**.** Single crystal X-ray diffraction revealed nearly square planar geometry of Pd in all the complexes. The catalytic activity of **13-15** for C-O coupling and SMC at 0.5 and 0.01 mol% catalyst loading respectively was found promising. The catalytic process was somewhat more efficient with **14** (Pd bonded with **L6**), than **15,** followed by **13.**

The silica magnetite NPs have been reacted with phenylselenylchloride under N_2 atmosphere and $PdCl_2$ successively in aqueous medium to prepare composite NPs Fe_3O_4@SiO_2@SePh@Pd(0). The magnetite layered with sulfated Schiff base (SB) reacted with $RuCl_3.xH_2O$ in water resulting Fe_3O_4@SB@Ru(OH)x. The magnetically retrievable Ru catalyst was explored for one pot synthesis of primary amides from aldehydes and nitriles in water (yield upto 96%) and TH of carbonyl compounds with glycerol in aqueous medium (yield upto 96%) using 1 mol% of catalyst. Reusability of catalyst was more than 7 reaction cycles for all catalytic reactions. Pd anchored magnetic NPs were found efficient as catalyst for *O*-arylation of phenols (yield up to 93%) and SMC (yield up to 94%) in water with 0.1 mol% loading for ArBr and

0.75% for ArCl. Heterogeneity of the catalytic process was authenticated from hot filtration test and ICP-AES analysis.

Palladium phosphides nanophases ($Pd_3P_{0.95}$) and Co_2P nanorods prepared by thermolysis of $[M(PPh_3)_2Cl_2]$ complexes (M = Pd, Co). $[Pd(PPh_3)_2Cl_2]$ in trioctylphosphine (TOP) and oleylamine (OA):octadecane (ODE) (1:1) resulted in $Pd_3P_{0.95}$ QD and $Pd_3P_{0.95}$ NPs respectively at 280 ^{0}C. $^{31}P\{^1H\}$ NMR experiments revealed phosphorus present in $Pd_3P_{0.95}$ QDs comes from TOP whereas in $Pd_3P_{0.95}$ NPs from triphenylphosphine. $Pd_3P_{0.95}$ QDs have been found efficient catalyst for the interconversion of amides and nitriles (yield up to 92% in 4 h) and hydration of nitriles at 90 °C (yield up to 94% in 4 h). The reusability of $Pd_3P_{0.95}$ QDs for both the reactions was up to 4 times. Co_2P nanorods were grafted on graphene oxide, resulting GO-Co_2P composite which showed good catalytic efficiency for hydrogen evolution reaction (HER) in 0.5 M aqueous H_2SO_4 as overpotentials required to drive cathodic current densities of 20 and 100 mA/cm^2 were 80 and 154 mV respectively and durability of the catalyst was supported by chronopotentiometric stability test at an applied current density of 100 mA/cm^2 for 70 h.

शोध प्रबंध-सार

वर्तमान शोध प्रबंध ओर्गनोचालकोजनयुक्त हाइब्रिड बाईडेंटेड और ट्राईडेंटेड मेटल काम्प्लेक्स और मेटल नैनो पार्टिकल्स पर केंद्रित है। पैलेडियम (II), रुथेनियम (II) और इरीडियम (III) चयनित धातु आयन हैं। मेटल फास्फाइड नैनो पार्टिकल्स के संश्लेषण के लिए ऑर्गोनोफोसफ़िन के मेटल कॉम्प्लेक्स को एकल स्रोत अग्रदूत के रूप में उपयोग किया गया है। मैग्नेटिक नैनो कम्पोजिट बनाने के लिए मैग्नेटाइट नैनो पार्टिकल्स को सल्फेटेड शिफ बेस (एसबी) और रुथेनियम हइड्रोक्साइड या टेट्राइथाइल ऑर्थोसिलिकेट, फिनाइल सेलेनिल और पैलेडियम (0) के साथ स्तरित किया गया। सुज़ुकी-मीयुरा कपलिंग (एसएमसी), C-O कपलिंग, डाईसब्स्टिटूटेड बेन्ज़िमिडाजोल डेरिवेटिव के संश्लेषण, अल्कोहल के एरोबिक ऑक्सीकरण, अल्कोहल के ओपनोर-प्रकार के ऑक्सीकरण, कार्बोनिल यौगिकों के ट्रांसफर हाइड्रोजनीकरण, एमाइड संश्लेषण और हाइड्रोजन ईवोलुशन अभिक्रिया करने के लिए नव-डिजाइन नैनो पार्टिकल्स और कॉम्प्लेक्स की जांच की गई है।

अनसीमेट्रिकल बाईडेंटेड बेंज़िमिडाजोल आधारित चालकोजनयुक्त लिगेंड, 1-बेंज़िल-3-फिनाइल चालकोजनिलमिथाइल-1,3-डाइहाइडोबेंजोइमिडाजोल-2-चालकोजिनोन (**L1-L4**) की अभिक्रिया [(η^6-C_6H_6) $RuCl(\mu\text{-}Cl)]_2$ से कराने के पश्चात NH_4PF_6 के साथ कराने पर [(η^6-C_6H_6)Ru(**L1-L4**)Cl][PF_6] (**1-4**) प्राप्त हुआ। रुथेनियम सभी चार कॉम्प्लेक्सेज़ में स्यूडो ऑक्टाहेड्रल हॉफ सैंडविच "पियानो-स्टूल" ज्यामिति रखता है। पैलेडियम (II) कॉम्प्लेक्सेस [(Pd(**L**)Cl_2] (**5-8**) जो कि **L1-L4** की अभिक्रिया $Pd(CH_3CN)_2Cl_2$ के साथ एसिटोनाइट्राइल में कराने पर प्राप्त हुआ, पैलेडियम के चारों ओर नियरली स्क्वेयर प्लैनर ज्यामिति रखता है । कॉम्प्लेक्सेज़ **1-4,** कार्बोनिल कंपाउंड के विभिन्न स्रोतों का उपयोग करते हुए ट्रांसफर हाइड्रोजिनेशन के लिए प्रयुक्त हुए । 2-प्रोपेनॉल और ग्लिसरॉल में, (0.01-0.5 मोल%) (सर्वाधिक् उपयुक्त परीलक्षित विलायक) उत्प्रेरक प्रक्रिया **3** > **1** ≈ **4** > **2** क्रम का पालन करती है । DFT गणना प्रायोगिक परिणामों का समर्थन करते हैं। उत्प्रेरक के 0.01 मोल% के साथ एसएमसी उत्प्रेरित करने के लिए **5-8** का उपयोग किया गया।

लिगेंड (**L1-L4**) की अभिक्रिया [(η^5-Cp*)$IrCl(\mu\text{-}Cl)]_2$ से कराने के पश्चात NH_4PF_6 के साथ कराने पर [(η^5-Cp*)Ir(**L**)Cl][PF_6] (**9-12**) प्राप्त हुआ। इरीडियम के चारों ओर "पियानो-स्टूल" ज्यामिति सिंगल क्रिस्टल एक्स-रे डिफ्रैक्शन द्वारा प्रमाणित हुई । ऑर्थोफिनाइलडाई एमीन और एरोमेटिक अल्कोहल से डाईसब्स्टिटूटेड बेन्ज़िमिडाजोल डेरिवेटिव का संश्लेषण,

9-12 (0.1 मोल%) द्वारा किया गया । **9-12**, (0.1 और 0.01 मोल%) एरोमेटिक एल्कोहल के एरोबिक और एल्कोहल के ओपनोर प्रकार के ऑक्सीकरण के परिणाम स्वरुप उत्पादित एल्डिहाइड के लिए उपयुक्त परीलक्षित हुआ ।

फेरोसिन कोर युक्त शिफ बेस लिगैंड (**L5:** सल्फेटेड और **L6:** सेलेनटेड) ने NaOAc की उपस्थिति में साइक्लोपेलेडेट कॉम्प्लेक्स [Pd(**L5/L6**-H)Cl] (**13**/**14**) उत्पाद बनाया। काम्प्लेक्स **13** ने एक समतुल्य PPh_3 के साथ अभिक्रिया करने पर Pd-S बंध विभाजन द्वारा [Pd(**L5**-H)PPh_3Cl] (**15**) उत्पादित किया। सिंगल क्रिस्टल एक्स-रे डिफ्रैक्शन ने पैलेडियम के चारों ओर नियरली स्क्वेयर प्लैनर ज्यामिति प्रतिपादित की। C-O कपलिंग और एसएमसी के लिए उत्प्रेरक क्षमता क्रमशः 0.5 और 0.01 मोल% पर परीलक्षित हुई। कॉम्प्लेक्स **14** का उत्प्रेरण सामर्थ्य **15** और **13** की तुलना में (**L6** के साथ बंधित Pd) अधिक परीलक्षित हुआ ।

सिलिका मैग्नेटाइट नैनो पार्टिकल्स की नाइट्रोजन की उपस्थिति फिनाइलसेलेनिलक्लोराइड और जलीय माध्यम में क्रमिक रूप से $PdCl_2$ से अभिक्रिया करने पर Fe_3O_4@SiO_2@ SePh@ Pd(0) प्राप्त हुआ । सल्फेटेड शिफ बेस (SB) के साथ स्तरित मैग्नेटाइट की $RuCl_3.xH_2O$ के साथ पानी में अभिक्रिया के परिणामस्वरूप Fe_3O_4@SB@Ru(OH)x उत्पादित हुआ। चुंबकीय पुनर्जनीय रुथेनियम उत्प्रेरक, एल्डिहाइड और नाइट्राइल (96% उत्पादकता) के जलीय माध्यम में एक पात्रीय प्राथमिक एमाइड संश्लेषण के लिए और ग्लिसरॉल के साथ कार्बोनिल यौगिकों के जलीय माध्यम में ट्रांसफर हाइड्रोजनीकरण (उत्पादकता 96%) के लिए 1 मोल% के साथ प्रयुक्त हुआ। सभी उत्प्रेरक के लिए प्रयोज्यता 7 उत्प्रेरण अभिक्रिया से अधिक परीलक्षित हुई । पैलेडियम युक्त चुंबकीय नैनो पार्टिकल्स को ऑर्थो-एरायलेशन (93% उत्पादकता) और एसएमसी (94% उत्पादकता) के लिए उत्प्रेरक के रूप में समर्थ पाया गया, जिसमें प्रयुक्त मात्रा ArBr के लिए 0.1 मोल% और ArCl के लिए 0.75% है। उत्प्रेरक प्रक्रिया की हेटेरोजेनेसिटी हॉट फिल्ट्रेशन परीक्षण और आईसीपी-एईएस विश्लेषण से प्रमाणित की गई।

पैलेडियम फॉस्फोइड नैनोफेजेज ($Pd_3Pd_{0.95}$) और Co_2P नैनो रोड्स [$M(PPh_3)_2Cl_2$] (M = Pd, Co) के ताप-अपघटन द्वारा तैयार किए गए हैं। [$Pd(PPh_3)_2Cl_2$] 280 ^{0}C पर ट्राई ओक्टिलफोस्फीन और ओलाइलैमिन: ओक्टाडेकन (1: 1) विलायक में करने पर क्रमशः $Pd_3Pd_{0.95}$ क्वांटम डॉट और $Pd_3Pd_{0.95}$ नैनो पार्टिकल्स प्राप्त होते है। $^{31}P\{^1H\}$ NMR से सत्यापित हुआ कि $Pd_3Pd_{0.95}$ क्वांटम डॉट में उपस्थित फॉस्फोरस ट्राई ओक्टिलफोस्फीन से, जबकि $Pd_3Pd_{0.95}$ नैनो पार्टिकल्स में उपस्थित फॉस्फोरस ट्रिपिनोल्फॉफ़्फ़ीन से स्थानांतरित हैं।

$Pd_3Pd_{0.95}$ क्वांटम डॉट एमाइड और नाइट्राइल के अंतर रूपांतरण (4 घंटे में 92%) और 90 ^0C (4 घंटे में 94%) पर नाइट्राइल के हाईड्रेशन के लिए उपयुक्त पाए गए हैं। दोनों उत्प्रेरक क्रियाओं के लिए $Pd_3Pd_{0.95}$ क्वांटम डॉट की पुन: प्रयोज्यता 4 उत्प्रेरण अभिक्रिया चक्र तक पाई गई । Co_2P नैनोरोड्स को ग्रेफीन ऑक्साइड पर स्थापित किया गया, जिसके परिणामस्वरूप निर्मित GO-Co_2P कंपोजिट ने हाइड्रोजन ईवोलुशन अभिक्रिया के लिए 0.5 M जलीय H_2SO_4 में अच्छी उत्प्रेरक दक्षता दिखायी, क्योंकि 20 और 100 mA/cm^2 के कैथोडिक विद्युत् धारा घनत्व के लिए आवश्यक अधिविभव क्रमशः 80 और 154 mV पाए गए और उत्प्रेरक की स्थायित्व क्रोनोपोटेन्सीओमीट्रिक स्थिरता परीक्षण द्वारा समर्थित किया गया जो 100 mA/cm^2 विद्युत् धारा घनत्व पर 70 घंटे के लिए निष्पादित हुआ ।

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GLOSSARY OF SYMBOLS AND ABBREVIATIONS

%	percent
δ	chemical shift
ν	frequency
Å	angstrom
Ar	Aryl
µL	microlitre
°C	degree centigrade
br	broad signal
n-Bu	*n*-butyl
C_q	quaternary carbon
C−C	carbon−carbon
cm	centimeter
$CHCl_3$	chloroform
CH_3CN	acetonitrile
d	doublet
DCM	dichloromethane
DMA	dimethylacetamide
DMF	dimethylformamide
DMSO	dimethyl sulfoxide
e.g.	for example
g	gram
h	hour
HR	high resolution
Hz	hertz
i.e.	that is
kV	kilovolt
m	multiplet
m/z	mass/charge
MHz	megahertz
M^+	molecular ion
M	molar

mmol	millimole
mol	mole
mL	milliliter
m.p.	melting point
NMP	*N*-methyl-2-pyrrolidone
NMR	nuclear magnetic resonance
Ph	phenyl
n-Pr	*n*-propyl
SMC	Suzuki-Miyaura Coupling
t	triplet
THF	tetrahydrofuron
TLC	thin layer chromatography
TMS	tetrametylsilane
XRD	x-ray diffraction