METAL COMPLEXES OF CHALCOGENATED LIGANDS AND RELATED NANOPARTICLES: DESIGNING AND CATALYTIC APPLICATIONS

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by

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CERTIFICATE

This is to certify that the thesis entitled, **"METAL COMPLEXES OF CHALCOGENATED LIGANDS AND RELATED NANOPARTICLES: DESIGNING AND CATALYTIC APPLICATIONS"** being submitted by **Ms. RENU BHASKAR** 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. Ms. Renu Bhaskar 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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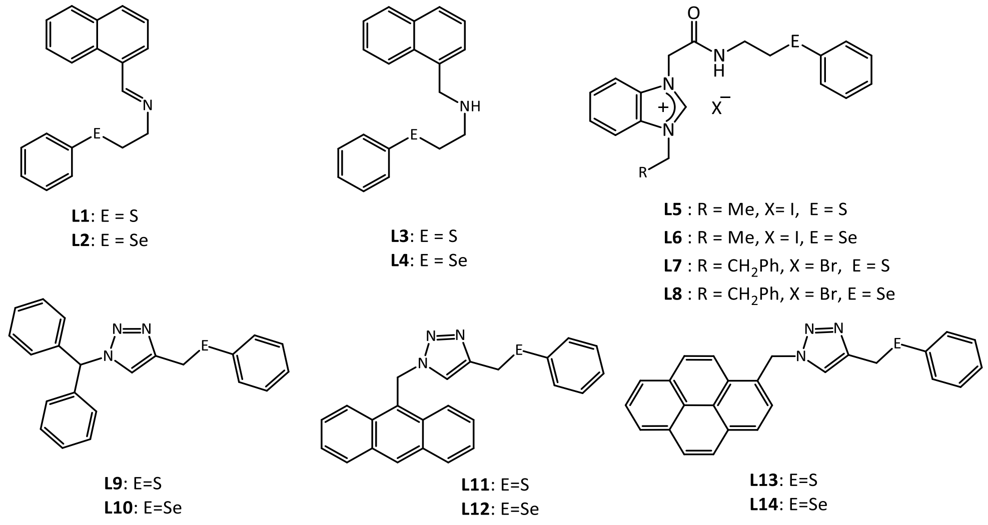
ABSTRACT

The thesis is focused on designing and catalytic applications of chalcogen stabilized nanoparticles (NPs) and metal complexes of hybrid organochalcogen ligands. The ligands shown in Chart 1 were designed and their coordination chemistry with Pd(II) and Ru(II) was explored. Pd NPs were stabilized on functionalized graphene oxide (GO) with the help of selenated amine. The newly designed NPs and complexes were investigated as catalyst for Suzuki-Miyaura coupling (SMC), Sonogashira coupling, regioselective C-H activation of imidazoles, transfer hydrogenation (TH) reaction of carbonyl compounds and or amide synthesis.



L1: E = S
L2: E = Se

L3: E = S
L4: E = Se

L5 : R = Me, X= I, E = S
L6 : R = Me, X = I, E = Se
L7 : R = CH_2Ph, X = Br, E = S
L8 : R = CH_2Ph, X = Br, E = Se

L9: E=S
L10: E=Se

L11: E=S
L12: E=Se

L13: E=S
L14: E=Se

Chart 1

The treatment of graphene oxide with $ClCH_2COOH$, thionyl chloride and 2-(phenylselenyl)ethylamine successively resulted in functionalization of its surface with chelating (Se, N) donor sites. The graphene oxide grafted with selenated ethylamine (GO-Se) on treatment with Na_2PdCl_4 and NaOH gave GO-Se anchored with Pd(0) nano-particles (NPs) (GO-Se-Pd)) of size ~1-3 nm decorated uniformly. The X-ray diffraction (powder), FT-IR, XPS, Raman spectroscopy, thermogravimetric analysis (TGA), electron microscopic techniques (SEM and HR-TEM) authenticated the GO-Se-Pd. The catalyst GO-Se-Pd was efficient in TH of carbonyl compounds with catalyst loading equivalent to

0.25 mol% of Pd resulting alcohols in good to nearly quantitative yield. Further the catalyst is recyclable upto six reaction cycles. Even in the sixth run the conversion was ~96% with negligible leaching as revealed by flame AAS analysis of GO-Se-Pd after sixth reaction cycle. Hot filtration experiment suggested heterogeneous nature of catalysis.

Schiff base ligands (**L1**: sulfated and **L2**: selenated) having naphthalene core on treatment with Li_2PdCl_4 in the presence of NaOAc gave cyclopalladated complexes [Pd(**L1/L2-**H)Cl] (**1**/**2**). The reduction of **L1** and **L2** with sodium borohydride gives ligands **L3**/**L4**. The reaction of **L3**/**L4** at room temperature similar to those of **L1/L2** resulted in complex [Pd(**L3/L4**)Cl_2] (**3**/**4)** in which the ligand coordinates in a bidentate (N, E) mode. The reduced Schiff bases failed to show pincer mode of coordination. Ligands (**L1-L4**) and their complexes (**1-4)** were authenticated with HR-MS, ^{1}H, $^{13}C\{^{1}H\}$ and $^{77}Se\{^{1}H\}$ NMR spectra. The crystal structures of **L1** and **1-4** established by X-Ray crystallography reveal nearly square planar geometry around Pd in each complex. The catalytic activity of **1-4** for SMC and Cu and amine free Sonogashira coupling at 0.01 and 0.05 mol% catalyst loading respectively under aerobic conditions was found promising. The **1**/**2** was found more efficient catalyst than **3**/**4**. Palladium containing NPs were isolated during both coupling reactions and HR-TEM revealed their size as ~2-7 nm. The SEM-EDX indicated the presence of organochalcogen ligands or their fragments in them. They independently catalyze both reactions and therefore catalytic role of these NPs formed *in situ* during the use of molecular complexes **1-4** as a catalyst, can be envisaged undoubtedly.

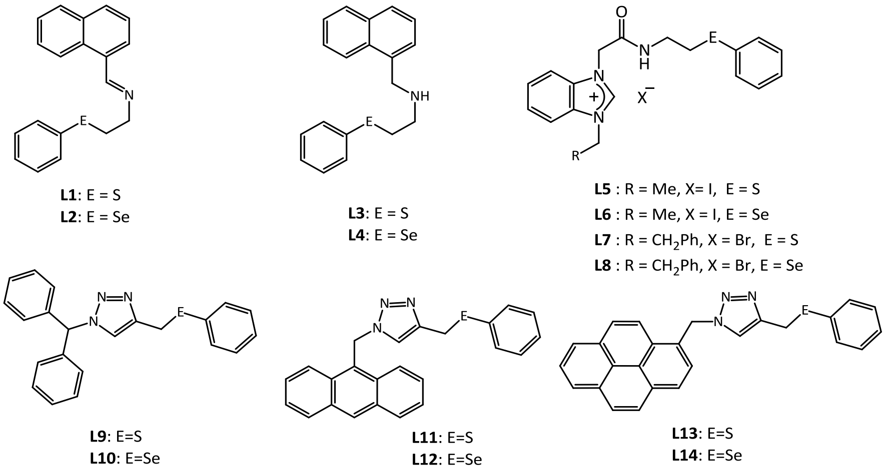
The synthesis of chalcogenated acetamide-functionalized 1*H*- benzimidazolium salts (**L5**−**L8**), precursor to (C, N^-, S/Se) ligands and their *N*-heterocyclic carbene (NHC) complexes [Pd(**L**−H_2X)Cl] (**5-8**; **L= L5-L8**) was carried out by silver carbene transfer reaction. The **L5**−**L8** and **5**−**8** were characterized by elemental analyses, HR-MS, ^{1}H,

$^{13}C\{^1H\}$ and $^{77}Se\{^1H\}$ NMR spectroscopy. The crystal structures of **L6** and **5−7** established by X-Ray crystallography, reveal geometry of palladium as nearly square planar and alignment of NHC rings as nearly perpendicular to the coordination plane of Pd. Complexes **5−8** were found efficient for regioselective C-5 arylation of imidazoles under aerobic conditions with loading of 0.5 to 1 mol%. The complexes of selenium containing ligands were found more efficient as catalysts than their sulfur counterparts. The **5−8** are recyclable for six times for regioselective arylation of imidazole with very little decrease in efficiency. Few arylated products of imidazole were identified with X-ray diffraction on their single crystals.

The bidentate 1-benzhydryl-4-((phenylthio/seleno)methyl)-1*H*-1,2,3-triazole (**L9/L10**), 1-(anthracen-9ylmethyl)-4-((phenylthio/seleno)methyl)-1*H*-1,2,3-triazole (**L11**/**L12**) and 4-((phenylthio/seleno)methyl)-1-(pyren-1-ylmethyl)-1*H*-1,2,3-triazole (**L13**/**L14)** ligands synthesized by 'Click' reaction, react with $[\{(\eta^6\text{-benzene})RuCl(\mu\text{-}Cl)\}_2]$ (followed by reaction with NH_4PF_6), at room temperature resulted in complexes $[(\eta^6\text{-}C_6H_6)Ru(\mathbf{L})Cl]PF_6$ (**9-14**) (**L** = **L9**-**L14**) respectively. The crystal structures of **9−13** established by X-Ray crystallography, reveal a pseudo-octahedral "piano-stool" disposition of donor atoms around Ru. The catalytic activity of **9-14** (optimum loading 0.1−0.5 mol% of Ru) was explored for TH of aldehydes/ketones and one pot synthesis of primary amides from aldehydes (yield up to 98%). The **10/12/14** having selenium ligands were found more efficient than their S analog **(9/11/13**) for both TH and amide synthesis. Reusability of these catalysts was more than 6 reaction cycles for both the catalytic reactions.

शोध प्रबंध-सार

वर्तमान शोध प्रबंध चेलकोजन स्थिरीकृत नैनोकणों और हाइब्रिड ऑर्गोडाल्कोजन लिगैंड्स के धातु परिसरों के डिजाइन और उत्प्रेरक अनुप्रयोगों पर केंद्रित है। चार्ट 1 में दिखाए गए लिगैंड्स को डिजाइन किया गया था और पैलेडियम (II) और रुथेनियम (II) के साथ उनके समन्वय रसायन शास्त्र का पता लगाया गया था। पैलेडियम नैनोकण को सेलेनेटेड अमीन की मदद से कार्यात्मक ग्रेफेन ऑक्साइड पर स्थिर किया गया था। नए डिजाइन किए गए नैनोकण और कॉम्प्लेक्स की समीक्षा सुजुकी-मियौरा कपलिंग, सोनोगशिरा कपलिंग, इमिडाज़ोल के रेजीओसेलेक्टीव सी-एच सक्रियण, कार्बोनील यौगिकों के ट्रांसफर हाइड्रोजनीकरण प्रतिक्रिया को हस्तांतरित करने या संश्लेषित करने के लिए उत्प्रेरक के रूप में की गई थी।



चार्ट 1

$ClCH_2COOH$, थियोनिल क्लोराइड और 2-(फेनिलसेलेनिल) एथिलामाइन के साथ ग्रैफेन ऑक्साइड की अभिक्रिया इसके सतह के चेलाटिंग (Se, N) दाता साइटों के कार्यान्वयन के परिणामस्वरूप हुआ। Na_2PdCl_4 और NaOH के साथ उपचार पर सेलेनेटेड एथिलामाइन (GO-Se) के साथ तैयार किए गए ग्रैफेन ऑक्साइड को Pd (0) नैनो-कण (आकार ~ 1-3 nm) के साथ GO-Se- मंडित किया गया (GO-Se-Pd)। एक्स-रे विवर्तन (पाउडर), एफटी-आईआर, एक्सपीएस, रमन स्पेक्ट्रोस्कोपी, थर्मोग्रामिमेट्रिक विश्लेषण (टीजीए), इलेक्ट्रॉन माइक्रोस्कोपिक तकनीक (एसईएम और एचआर-टीईएम) ने GO-Se-Pd प्रमाणित किया। ट्रांसफर हाइड्रोजनीकरण के लिए पैलेडियम 0.25 मोल% के साथ प्रयुक्त हुआ । इसके अलावा उत्प्रेरक छह उत्प्रेरण अभिक्रिया चक्र तक पुन: प्रयोज्य है । छठे अभिक्रिया चक्र में भी रूपांतरण GO-Se-Pd के एएएस विश्लेषण द्वारा प्रकट नगण्य लीचिंग के साथ ~ 96% था। गर्म निस्पंदन प्रयोग ने उत्प्रेरण की विषम प्रकृति का सुझाव दिया।

नेफ्थालेन कोर के शिफ बेस लिगैंड्स (L1: सल्फेटेड और L2: सेलेनेटेड) की NaOAc की उपस्थिति में Li_2PdCl_4 के साथ अभिक्रिया पर साइक्लोप्लाएटेड कॉम्प्लेक्स [Pd(**L1**/**L2**-H)Cl] (**1**/**2**) प्राप्त हुआ । सोडियम बोरोहाइड्राइड के साथ **L1** और **L2** का अपचयन लिगैंड्स **L3**/**L4** देता है। **L1** और **L2** के समान **L3**/**L4** की प्रतिक्रिया कमरे के तापमान पर कॉम्प्लेक्स [Pd(**L3**/**L4**)Cl_2] (**3**/**4**) की प्राप्ति हुई जिसमें लिगैंड एक द्विदांतु (N, E) मोड में संयोजित है। अपचयित शिफ बेस पिंसर मोड दिखाने में विफल रहे। **L1**/**L2** और उनके कॉम्प्लेक्स (**1**-**4**) HR-MS, ^1H, $^{13}C\{^1H\}$ और $^{77}Se\{^1H\}$ NMR स्पेक्ट्रा के साथ प्रमाणित किए गए थे। एक्स-रे क्रिस्टलोग्राफी द्वारा स्थापित **L1** और **1**-**4** की क्रिस्टल संरचनाएं प्रत्येक कॉम्प्लेक्स में Pd के आसपास लगभग स्क्वायर प्लेनर ज्यामिति प्रकट करती हैं। SMC और Cu और अमीन मुक्त सोनोगशिरा के लिए **1**-**4** की उत्प्रेरक क्रिया क्रमशः 0.01 और 0.05 मिलीग्राम% उत्प्रेरक लोडिंग पर एरोबिक स्थितियों में सफल रही । **1**/**2**, **3**/**4** की तुलना में अधिक कुशल उत्प्रेरक पाया गया था। NPs युक्त पैलेडियम दोनों युग्मन प्रतिक्रियाओं के दौरान पृथक किये और आकार HTEM से ~ 2-7 nm पाया । SEM-EDX ने ऑर्गोडाल्कोजन लिगैंड्स या उनके टुकड़ों की उपस्थिति का संकेत दिया। वे स्वतंत्र रूप से दोनों प्रतिक्रियाओं को उत्प्रेरित करते हैं और इसलिए उत्प्रेरक के रूप में कॉम्प्लेक्स **1**-**4** के उपयोग के दौरान बने NPs की उत्प्रेरक भूमिका निस्संदेह पर विचार की जा सकती है।

चॉकोजेनेटेड एसीटामाइड- फंक्शनलिज़्ड 1 H-बेंज़ीमिडाज़ोलियम साल्ट (**L5**-**L8**) का संश्लेषण जो की (C, N^-, S/Se) लिगैंड्स और उनके N-हेटरोक्साइकल कार्बीन (NHC) कॉम्प्लेक्स [Pd(**L**−H_2X)Cl] (**5**-**8**; **L**= **L5**-**L8**) का अग्रदूत है, सिल्वर कार्बीन स्थानांतरण प्रतिक्रिया द्वारा किया गया था। **L5**-**L8** और **5**-**8** को HR-MS, ^1H, $^{13}C\{^1H\}$ और $^{77}Se\{^1H\}$ NMR स्पेक्ट्रोस्कोपी द्वारा विश्लेषित किया । एक्स-रे क्रिस्टलोग्राफी द्वारा स्थापित एल **L6** और **5**-**7** की क्रिस्टल संरचनाएं, पैलेडियम की ज्यामिति को लगभग स्क्वायर प्लेनर और NHC के छल्ले के संरेखण के रूप में प्रकट करती हैं जो Pd के समन्वय प्लेन के लगभग लंबवत है। कॉम्प्लेक्स **5**-**8** को 0.5 से 1 मोल% लोड करने के साथ एरोबिक स्थितियों के तहत इमिडाज़ोल के रेजीओसेलेक्टीव C-5 एराईलेशन के लिए कुशल पाया गया था। लिगैंड युक्त सेलेनियम के कॉम्प्लेक्स को उनके सल्फर समकक्षों की तुलना में उत्प्रेरक के रूप में अधिक कुशल पाया गया था। **5**-**8** दक्षता में बहुत कम कमी के साथ इमिडाज़ोल के रेजीओसेलेक्टीव एराईलेशन के लिए छह बार पुन: प्रयोज्य हैं। इमिडाज़ोल के कुछ एराईलेशन उत्पादों को उनके एकल क्रिस्टल पर एक्स-रे विवर्तन के साथ पहचाना गया था।

द्विपक्षीय 1-बेंजाइड्रिल -4 - ((फेनिलथियो / सेलेनो) मिथाइल) -1 एच-1,2,3-ट्राज़ोल (**L9/L10**), 1-(एंथ्रेसेन-9ylmethyl) -4 - ((फेनिलथियो / सेलेनो) मिथाइल) -1 एच-1,2,3-ट्राज़ोल (**L11/L12**) और 4 - ((फेनिलथियो / सेलेनो) मिथाइल) -1- (पायरेन -1-यल्मेथिल) -1 एच -12,3-ट्राज़ोल (**L13/L14)** 'क्लिक' प्रतिक्रिया द्वारा संश्लेषित लिगैंड, $[\{(\eta 6\text{-benzene})RuCl(\mu\text{-}Cl\}_2$ के साथ कमरे के तापमान पर प्रतिक्रिया करने पर (NH_4PF_6 के साथ प्रतिक्रिया के बाद), क्रमशः $[(\eta^6\text{-}C_6H_6)Ru(\mathbf{L})Cl]PF_6$ (**9-14**) (**L** = **L9**-**L14**) कॉम्प्लेक्स प्राप्त हुए । एक्स-रे क्रिस्टलोग्राफी द्वारा स्थापित **9-13** की क्रिस्टल संरचनाएं, Ru के चारों ओर दाता परमाणुओं के छद्म-ऑक्टाहेड्रल "पियानो-स्टूल" स्वभाव को प्रकट करती हैं। **9-14** की उत्प्रेरक गतिविधि (Ru के लोडिंग 0.1-0.5 मोल%) को एल्डिहाइड/कीटोन के TH और एल्डेहाइडस (98% प्राप्ति) से प्राथमिक अमाइड के संश्लेषण के लिए खोजा गया था। 10/12/14 सेलेनियम लिगैंड्स को उनके सल्फर एनालॉग (**9**/**11**/**13**) से TH और एमाइड संश्लेषण दोनों के लिए अधिक कुशल पाया गया था। उत्प्रेरक प्रतिक्रियाओं के लिए इन उत्प्रेरकों की पुन: प्रयोज्यता 6 उत्प्रेरण चक्र से अधिक थी।

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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−C	carbon−carbon
cm	centimeter
CH_2Cl_2	dichloromethane
$CHCl_3$	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
HC	Heck coupling
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