ORGANOCHALCOGEN TAILORED NANOPARTICLES AND METAL COMPLEXES IN CATALYSIS OF ORGANIC REACTIONS

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by

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Submitted

in fulfillment of the requirements of the degree of

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DEDICATED

TO

MY PARENTS

CERTIFICATE

This is to certify that the thesis entitled, **"Organochalcogen Tailored Nanoparticles and Metal Complexes in Catalysis of Organic Reactions"** being submitted by **Mr. HEMANT JOSHI** 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. Hemant Joshi 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.

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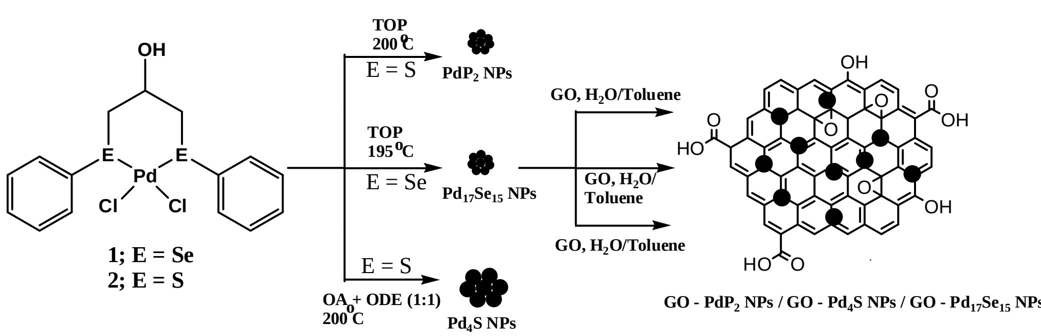
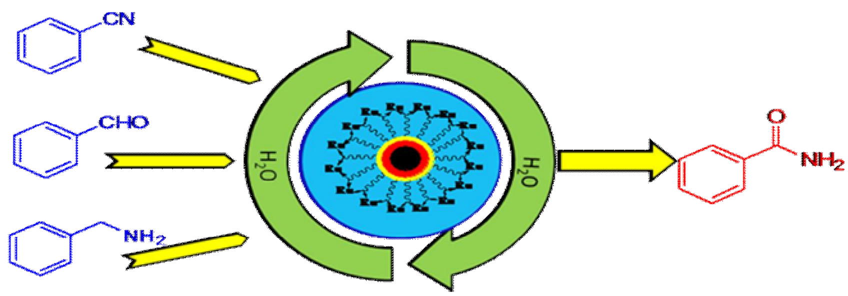
ABSTRACT

The present thesis is focused on chalcogen based nanoparticles (NPs) and organochalcogen ligands including the ones based on NHCs. The coordination chemistry of the ligands with Pd(II) and Ag(I) has been explored. The complexes have been found suitable as a single source precursor (SSP) for synthesis of various nanoparticles. Magnetite NPs were layered with silica, SePh and Ru(OH)x to generate composite NPs. The newly designed NPs and complexes have been investigated for catalytic organic reactions such as C–C, C–O coupling, amide synthesis and three-component coupling reaction of alkyne, aldehyde and amine.

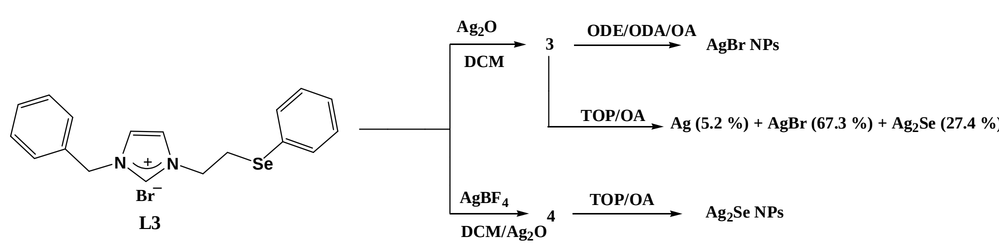
Synthesis of $Pd_{17}Se_{15}$, Pd_4S and PdP_2 NPs have been carried by using complexes **1** and **2** as SSP. The $Pd_{17}Se_{15}$ NPs grafted on graphene oxide (GO), GO–$Pd_{17}Se_{15}$ NPs show high catalytic activity for C–O coupling at room temperature (Pd loading 1 mol%; yield up to 94%). Further the catalyst is recyclable upto next four reaction cycles. GO–PdP_2 and GO–Pd_4S NPs have been tested for Suzuki Miyaura coupling reaction. The GO–PdP_2 NPs have been found more efficient catalyst in comparison to GO–Pd_4S NPs. The size of NPs and their distribution on GO appear to be key factors affecting the catalytic efficiency of the composite NPs.



The silica coated nanostructured magnetite has been reacted with phenylselenylchloride under N_2 atmosphere and $RuCl_3.xH_2O$ successively in aqueous medium to prepare $Fe_3O_4@SiO_2@SePh@Ru(OH)_x$ nanoparticles(NPs). These magnetically retrievable NPs have been found efficient catalyst for one pot conversion of aldehydes, nitriles and benzyl amine to primary amides in water. For aldehydes and nitriles yields of primary amides are up to 93%. The recyclability of these NPs is more than 7-times for synthesis from benzonitrile. In a gram scale conversion reaction of benzonitrile the catalyst shows ~86% yield of desired product.



The synthesis and characterization of selenium containing imidazolium salt, (**L3**), which is precursor to (Se, C_{NHC}) ligand, and their *N*-heterocyclic carbene (NHC) complexes $[Ag_2(\mathbf{L})_2Br_2]$ and $[Ag(\mathbf{L}\text{-}HBr)_2]BF_4$ (**3** and **4**) have been carried out. The unique feature of bonding in complex **3** is that the pre-carbene site remains intact and Ag(I) is coordinated only with Se. Synthesis of silver bromide and silver selenide NPs from **3** and **4** (single source precursors) by thermolysis have been achieved. The complexes **3**, **4**, AgBr and Ag_2Se NPs have been found efficient as catalysts for three-component coupling reaction of alkyne, aldehyde, and amine. The achieved isolated yields in A^3 coupling were up to 95% in 6 h. The catalytic performance for A^3 coupling reaction follow the order **4** > Ag_2Se > AgBr > **3.**



Activation of Suzuki coupling by palladacycles and palladium complexes designed using same Schiff base ligand has been found to differ in efficiency and in pathways. Palladacycles are more efficient, as their 0.001 mol% loading gives good conversion (Yield > 90%) in several cases. Higher loading than this is required for Pd-complexes to get a similar yield. The activation with palladacycles involves a role of nanosized Pd containing species generated in situ during catalysis, whereas with Pd(II) complexes no such particle is formed and probably Pd(0) remains protected by sulfur of thienyl group. The PPh_3 / Hg poisoning, and two phase tests indicate nature of catalytic process for both palladacycles and palladium complexes as largely homogeneous, probably via leaching of Pd(0) species from NPs in case of palladacycles.

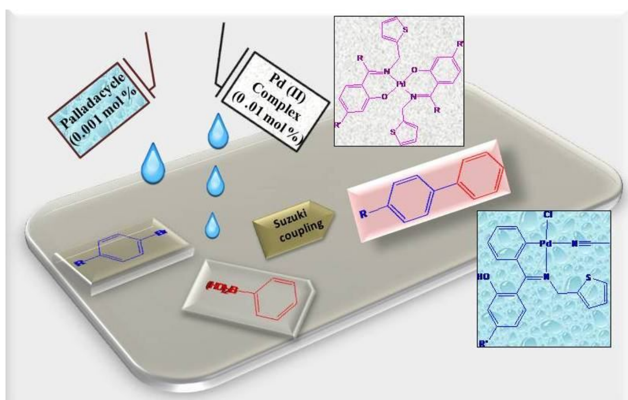


Table of Contents

Sl. No.	Contents	Page No.
1	Certificate	i
2	Acknowledgements	ii
3	Abstract	iv
4	Table of Contents	vii
5	List of Figures	xii
6	List of Tables	xiv
7	Glossary of Symbols and Abbreviations	xv

Chapter 1 Introduction

Sl. No.	Contents	Page No.
1.1	Wet-Chemical Processes for Transition Metal Chalcogenide Synthesis	2
1.2	Organochalcogen Ligands in Designing SSP for Metal Chalcogenides	2
1.3	Metal Complexes of Organochalcogen Ligands as SSP	6
1.4	Applications of Metal Chalcogenide NPs	10
1.5	Graphene Oxide as Support for Metal Chalcogenide NPs	12
1.6	Fe_3O_4 as Support for Magnetically Retrievable Catalysis	14
1.7	Catalytic Amide Synthesis	20
1.8	Carbon Oxygen Coupling Reaction	22
1.9	Suzuki Miyaura Coupling Reaction	26
1.10	Catalytic Three-Component Coupling Reaction	28
1.11	Objectives and Scope of the Present Work	29
1.12	References	32

Chapter 2 Materials and Methods

Sl. No.	Contents	Page No.
2.1	Chemicals and Reagents	49
2.2	Synthesis of Precursors	49
2.2.1	Graphene Oxide	49

2.2.2	1-(2-Chloro-ethyl)-1*H*-imidazole	50
2.2.3	Immobilization of 4-Bromobenzoic Acid on Silica	50
2.2.4	Bis(acetonitrile)dichloropalladium(II)	51
2.3	Characterization Techniques	51
2.3.1	Elemental Analysis	51
2.3.2	Melting Point Determination	51
2.3.3	Nuclear Magnetic Resonance Spectroscopy	51
2.3.4	Mass spectrometery	52
2.3.5	Single Crystal X-ray Diffraction Studies	52
2.3.6	Powder X-ray Diffraction (PXRD)	52
2.3.7	Atomic Absorption Spectroscopy	53
2.3.8	Scanning Electron Microscopy (SEM-EDX)	53
2.3.9	Transmission Electron Microscopy (TEM)	53
2.3.10	Thermogravimetric Analysis	53
2.3.11	Infra-red Spectra	53
2.4	References	54

Chapter 3 Graphene Oxide Grafted Palladium Chalcogenide/Phosphide Nanoparticles and Their Catalytic Applications

Sl. No.	Contents	Page No.
3.1	Introduction	55
3.2	Experimental Section	57
3.2.1	Synthesis of 1, 3-Bis(phenylselenyl)propan-2-ol	57
3.2.2	Synthesis of 1, 3-Bis(phenylsulfanyl)propan-2-ol	58
3.2.3	Procedure for Synthesis of [Pd(L1/L2)Cl_2]	59
3.2.4	Synthesis of Palladium Chalcogenide/Phosphide NPs via.SSPs	59
3.2.5	Synthesis of Palladium Chalcogenide/Phosphide Nanoparticles Grafted on Graphene Oxide	60
3.2.6	General Procedure for the C-O Coupling Reaction of Aryl Halides with Phenol Catalyzed with GO-$Pd_{17}Se_{15}$ NPs	60
3.2.7	General Procedure for Suzuki-Miyaura Coupling of Aryl Bromides Catalyzed with GO-PdP_2 and GO-Pd_4S NPs	61

3.2.8	Hot Filtration Experiment	61
3.2.9	Two–Phase Test	62
3.3	Results and Discussion	62
3.3.1	NMR Spectra	63
3.3.2	Crystal Structures of Complexes **1** and **2**	64
3.3.3	Characterization of the NPs and Nanocomposites with GO	69
3.3.4	Catalytic Applications	75
3.4	Conclusions	86
3.5	References	88

Chapter 4 Selenated Magnetite Nanoparticles Layered with Ruthenium Hydroxide and their Catalytic Applications

Sl. No.	Contents	Page No.
4.1	Introduction	96
4.2	Experimental Section	97
4.2.1	Synthesis of magnetic NPs of Fe_3O_4	97
4.2.2	Synthesis of Fe_3O_4@SiO_2 NPs	98
4.2.3	Synthesis of Fe_3O_4@SiO_2@SePh NPs	98
4.2.4	Synthesis of Fe_3O_4@SiO_2@SePh@ $Ru(OH)_x$ NPs	98
4.2.5	Hydration of nitriles	99
4.2.6	Synthesis of amides from aldehydes	99
4.2.7	Synthesis of amides from amines	99
4.2.8	Recyclability	100
4.2.9	Hot filtration experiment	100
4.3	Results and Discussion	100
4.3.1	Characterization of the Nanoparticles	101
4.3.2	Catalytic Applications	105
4.3.3	Recyclability	110
4.4	Conclusions	113
4.5	References	114

Chapter 5 Silver(I) Complexes of Selenated *N*-Heterocyclic Carbenes, AgBr and Ag_2Se Nanoparticles: Synthesis and their Catalytic Applications

Sl. No.	Contents	Page No.
5.1	Introduction	118
5.2	Experimental Section	120
5.2.1	Synthesis of 1−(2−(Phenylseleno)ethyl)−1*H*−Imidazole	120
5.2.2	Synthesis of 3-Benzyl-1-(2-Phenylselanyl-ethyl)-3*H*-Imidazolium Bromide	121
5.2.3	Synthesis of Ag(I) Complex **3**	121
5.2.4	Synthesis of Ag(I) Complex **4**	122
5.2.5	Synthesis of Silver Bromide Nano-Particles	123
5.2.6	Synthesis of Silver Selenide Nano-Particles	123
5.2.7	General Procedure for Catalytic Three-Component Coupling Reaction of Aldehyde, Amine and Alkyne	123
5.3	Results and Discussion	123
5.3.1	NMR and Mass Spectra	124
5.3.2	Crystal Structure of Complex **3**	126
5.3.3	Characterization of Nanoparticles	129
5.3.4	Catalytic Three-Component Coupling Reactions	135
5.4	Conclusions	139
5.5	References	142

Chapter 6 Palladacycle and Palladium(II) Complexes of Schiff Bases Derived from 2-thiophene methylamine and their Catalytic Application

Sl. No.	Contents	Page No.
6.1	Introduction	147
6.2	Experimental Section	149
6.2.1	Synthesis of Schiff Base Ligands **L4**, **L5**, and **L6**	149
6.2.2	Synthesis of Palladacycle Complexes **5** and **7**	150
6.2.3	Synthesis of Pd(II) Complexes **6**, **8**, and **9**	151
6.2.4	General Procedure for Suzuki-Miyaura Coupling Reaction	153
6.2.5	Hg Poisoning Test	153
6.2.6	PPh_3 Poisoning Test	153

6.2.7 Two-Phase Test 153
6.2.8 Isolation of NPs Generated from Complexes **5** and **7** 154
6.2.9 Procedure for Suzuki Reaction Catalyzed with NPs Obtained from **5** and **7** 154
6.3 Results and Discussion 155
6.3.1 Crystal Structures 157
6.3.2 Applications in Suzuki–Miyaura Coupling Reactions 166
6.4 Conclusions 173
6.5 References 175

Bio Data 178

Supporting Information in CD

List of Figures

Figure No.	Description	Page No.
Figure 3.1	Molecular structure of complex **1**	64
Figure 3.2	Molecular structure of complex **2**	65
Figure 3.3	Molecular packing framework of complex **1**	68
Figure 3.4	Molecular packing framework of complex **1**	69
Figure 3.5	PXRD patterns of (a) $Pd_{17}Se_{15}$ (b) GO-$Pd_{17}Se_{15}$ (c) PdP_2 (d) GO-PdP_2 (e) Pd_4S and (f) GO-Pd_4S NPs.	71
Figure 3.6	TEM images of graphene oxide	72
Figure 3.7	TEM images of $Pd_{17}Se_{15}$ and GO-$Pd_{17}Se_{15}$ NPs	72
Figure 3.8	TEM images of PdP_2 and GO-PdP_2 NPs	72
Figure 3.9	TEM images of Pd_4S and GO-Pd_4S NPs	72
Figure 3.10	TGA of SSP **1**	73
Figure 3.11	TGA of SSP **2**	73
Figure 3.12	IR of $Pd_{17}Se_{15}$ NPs	74
Figure 3.13	IR of PdP_2 NPs	75
Figure 3.14	IR of Pd_4S NPs	75
Figure 3.15	Proposed mechanism of C−O coupling reaction	80
Figure 4.1	PXRD of (a) Fe_3O_4 (b) Fe_3O_4@SiO_2 (c) Fe_3O_4@SiO_2@SePh (d) Fe_3O_4@SiO_2@SePh@$Ru(OH)_x$ NPs	103
Figure 4.2	TEM images of Fe_3O_4 NPs	104
Figure 4.3	TEM images of (a) Fe_3O_4@SiO_2 (b) Fe_3O_4@SiO_2@SePh NPs	104
Figure 4.4	TEM images of Fe_3O_4@SiO_2@SePh@Ru(OH)x NPs	104
Figure 4.5	Size distribution curve of (a) Fe_3O_4 (b) Fe_3O_4@SiO_2@SePh@Ru(OH)x NPs	105
Figure 4.6	Proposed mechanism for amide synthesis	113
Figure 5.1	Molecular structure of complex **3**	126
Figure 5.2	Molecular packing framework of complex **3**	129
Figure 5.3	PXRD patterns of AgBr NPs	131
Figure 5.4	PXRD pattern of Ag_2Se NPs	131

Figure 5.5	TEM images of AgBr NPs	132
Figure 5.6	TEM image of Ag_2Se NPs	132
Figure 5.7	Size distribution curves of (a) AgBr and (b) Ag_2Se NPs	133
Figure 5.8	IR spectra of AgBr NPs	134
Figure 5.9	IR spectra of Ag_2Se NPs	134
Figure 5.10	UV-visible spectra of AgBr NPs	135
Figure 5.11	UV-visible spectra of Ag_2Se NPs	135
Figure 6.1	Molecular structure of complex **5**	158
Figure 6.2	Molecular structure of complex **6**	158
Figure 6.3	Molecular structure of complex **8**	159
Figure 6.4	Molecular structure of complex **9**	159
Figure 6.5	Inter-molecular interactions in complex **5**	163
Figure 6.6	Inter-molecular interactions in complex **6**	164
Figure 6.7	Inter-molecular interactions in complex **8**	164
Figure 6.8	Inter-molecular interactions in complex **9**	165
Figure 6.9	HR-TEM micrographs of NPs (a) **5** and (b) **7**	170
Figure 6.10	Size distribution curve of NPs isolated from (a) **5** and (b) **7**	170
Figure 6.11	TGA of complex **5**	173
Figure 6.12	TGA of complex **7**	173

List of Tables

Table No.	Description	Page No.
Table 3.1	Crystal data and structural refinements for complexes **1**and **2**	66
Table 3.2	Bond lengths [Å] and bond angles [^{o}] for complexes **1** and **2**	67
Table 3.3	Distances [Å] of non-covalent interactions for complexes **1** and **2**	68
Table 3.4	Screening of base and solvents for *o*-arylation of 4-bromobenzaldehyde with phenol[a]	77
Table 3.5	C−O coupling reactions of aryl/heteroaryl halide	78
Table 3.6	Recycling experiment with GO−$Pd_{17}Se_{15}$ NPs	79
Table 3.7	Effect of different Pd Loading on reaction with GO-PdP_2	82
Table 3.8	Suzuki Miyaura coupling reaction catalyzed by GO-PdP_2 and GO-Pd_4S	83
Table 3.9	Recycling of GO-PdP_2 NPs	83
Table 4.1	Optimization of reaction conditions	106
Table 4.2	One pot Synthesis of amides from aldehydes	108
Table 4.3	Hydration of nitriles	109
Table 4.4	Recycling experiments	110
Table 5.1	Crystal data and structural refinement for complex **3**	127
Table 5.2	Bond lengths [Å] and bond angles [^{o}] for complex **3**	128
Table 5.3	Distances [Å] of non-covalent interactions for complex **3**	128
Table 5.4	Three-component coupling reactions catalyzed with **3** and **4**	137
Table 5.5	Three-component coupling reactions catalyzed with AgBr and Ag_2Se	138
Table 6.1	Crystal data and structural refinements for complexes **5** and **6**	160
Table 6.2	Crystal data and structural refinements for complexes **8** and **9**	161
Table 6.3	Bond lengths [Å] and bond angles [^{o}] for complexes **5, 6, 8** and **9**	162
Table 6.4	Distances [Å] of non-covalent interactions for complexes **5,** and **6**	165
Table 6.5	Distances [Å] of non-covalent interactions for complexes **8,** and **9**	165
Table 6.6	Suzuki–Miyaura coupling reaction catalyzed by using **5** and **7**	167
Table 6.7	Suzuki–Miyaura coupling reaction catalyzed by using **6, 8** and **9**	168
Table 6.8	Suzuki−Miyaura coupling reactions catalyzed by isolated NPs	169

GLOSSARY OF SYMBOLS AND ABBREVIATIONS

%	percent
δ	chemical shift
v	frequency
Å	angstrom
°C	degree centigrade
bs	broad singlet
C−C	carbon−carbon
C−O	Carbon−Oxygen
cm	centimeter
CH_2Cl_2	dichloromethane
$CHCl_3$	chloroform
CH_3CN	acetonitrile
d	doublet
DMF	dimethylformamide
DMSO	dimethyl sulfoxide
EDX	energy dispersive X-ray analysis
e.g.	for example
g	gram
GO	graphene oxide
h	hour
HR-MS	high resolution mass spectra
Hz	hertz
m	multiplet
m/z	mass/charge
MHz	megahertz
M^+	molecular ion
M	molar
mmol	millimole
mL	milliliter
m.p.	melting point
NHC	N-heterocycle carbene
nm	nanometer

NP	nano-particle
NMR	nuclear magnetic resonance
OA	oleic acid
ODE	1-octadecene
ORTEP	oak ridge thermal ellipsoid plot
Pd	palladium
Ph	phenyl
pzs	bis[2-(3,5-dimethyl-1-pyrazolyl)ether] sulfide
q	quartet
S	sulphur
Se	selenium
SEM	scanning electron microscopy
SSP	single source precursor
t	triplet
THF	tetrahydrofuron
TEM	transmission electron microscopy
TLC	thin layer chromatography
TMS	tetrametylsilane
TOP	tri-*n*-octylphosphine
XRD	X-ray diffraction