

**CHALCOGENATED N-HETEROCYCLES BASED
LIGANDS IN CATALYTIC ACTIVATION AND
NANOPARTICLES SYNTHESIS**

KAMAL NAYAN SHARMA



**DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY DELHI
JANUARY 2015**

© Indian Institute of Technology Delhi (IITD), New Delhi, 2015

**CHALCOGENATED N-HETEROCYCLES BASED
LIGANDS IN CATALYTIC ACTIVATION AND
NANOPARTICLES SYNTHESIS**

by

KAMAL NAYAN SHARMA

Department of Chemistry

Submitted

in fulfillment of the requirements of the degree of

Doctor of Philosophy

to the



Indian Institute of Technology Delhi

January 2015

CERTIFICATE

This is to certify that the thesis entitled, “**CHALCOGENATED N-HETEROCYCLES BASED LIGANDS IN CATALYTIC ACTIVATION AND NANOPARTICLES SYNTHESIS**” being submitted by **Mr. KAMAL NAYAN 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. Kamal Nayan 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:

Dr. AJAI K. SINGH
Professor
Department of Chemistry
Indian Institute of Technology,
Delhi
New Delhi-110 016

ACKNOWLEDGEMENTS

This thesis arose in part out of years of research that has been done since I joined Prof. Singh's group. By the time, I have worked with a great number of people whose contribution in assorted ways to the research and the making of the thesis deserved special mention. It is a pleasure to convey my gratitude to them all in my humble acknowledgment.

First and foremost, I have great pleasure in expressing my deep and sincere gratitude to my supervisor Professor Ajai Kumar Singh. His wide knowledge and logical way of thinking have been of great value for me. He has extended his magnanimous moral support and helped me to find directions through all the crucial and trying phases of my work. No words of acknowledgement would be adequate to fully express my gratitude to him. I am extremely lucky to have a supervisor who cared so much about my work and responded to my queries promptly. His understanding, unflinching encouragement, inspiration, advice, appreciation and guidance have made the thesis to take present shape.

I sincerely thanks to the Head, Department of Chemistry for providing necessary research facilities. I acknowledge the help extended by all faculty members during my stay here, especially to Dr. Nidhi Jain and Dr. S. Nagendran. I would like to thank my SRC committee members Prof. S. N. Naik, Prof. D. Bandyopadhyay and Prof. P. S. Pandey. I had the privilege of learning from them in IIT Delhi. I thank all technical staff members for their help rendered during this work.

Many thanks to my group members Dr. Pradhumn Singh, Dr. Dipanwita Das, Dr. G. K. Rao, Dr. Om Prakash, Fariha Saleem, Satyendra Kumar, Mahabir Pratap Singh, Pooja Dubey, Renu Bhaskar, Sonu Gupta, Dr. Arun Kumar, Dr. V. V. Singh, Dr. U. Kumar, Dr. Poornima Singh and Dr. Neetu Singh for their cooperation and help.

I gratefully acknowledge the immense assistance, persistent encouragement received from my friends Hemant Joshi, Alpesh K. Sharma (my lab-mates), Mukesh Tiwari, Aditya Joshi, Dheeraj Kumar, Pradeep Muwal and Dharendra Yadav. Without you guys (especially Hemant), I definitely could not have done this. I would like to express my gratitude for the love, affection and support received from my teachers Dr. A. K. Barjatya, Dr. R. K. Sharma, Dr. Jitendra Sharma, Mr. R. S. Sekhawat, Mr. R. D. Sani, Mr. G. R. Meena, Mr. Tej R. Sharma and Mr. Karan S. Rajawat.

I would like to express my heartfelt thanks to I. I. T. Delhi for offering me an ideal environment in which I felt free and could concentrate on my research.

The financial support from Council of Scientific and Industrial Research, New Delhi, India is gratefully acknowledged.

Thesis is dedicated to my grandfathers Late Shri Rameshwar Prasad Sharma, Late Shri Ramadhar Sharma and Late Shri Ramcharan Sharma. They always taught me how to be persevered and prepared to face challenges with discipline, faith and humility. I always feel their presence that urges me to strive to achieve my goals in life.

My family members deserve special attention for their support and persistent confidence in me. I am extraordinarily fortunate to have the blessings of my grandmother Late Smt. Keshar Devi. My mother, Smt. Sumitra Devi always blessed me with the shower of caring and love. I don't have words to express my gratitude to my father, Shri Laxmi Narayan Sharma, who is my first "Guru" (teacher). He has put high moral values inside me and makes me strong enough to face any obstacle in life. The constant support, encouragement and affection of my uncles Dr. Badri P. Sharma, Mr. Kedar L. Sharma and my in-laws Mr. Om K. Sahariya and Mrs. Sharda Sahariya are also acknowledged. My brother Mr. Jagdish P. Sharma and his wife Mrs. Guddi Sharma, my sisters Maya, Neetu and Savitri and their husbands Mr. Satish Sharma, Mr. Pankaj Chaturvedi and Mr. Manish Sharma who have been my pillar of strength throughout my study and makes the impossible to possible for me that I am able to see this day. My brother-in-law Naveen Sahariya and sister-in-law Prerna Sahariya need a special mention for their deep affection.

I express my love to Yashu, Priyanshu, Madhav, Yanu, Daksh, Devansh, Bhavisya, Kinshu, Mayank and Saransh. Words fail me to express my appreciation to my wife Jagrati whose love, dedication, priceless support, blessed care and persistent confidence in me, has taken the load off my shoulder. I owe her for being unselfishly let her intelligence, passions and ambitions collide with mine.

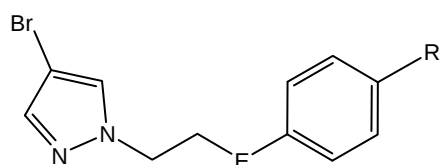
Last but not the least I thank almighty Lord Vishnu.

Kamal Nayan Sharma

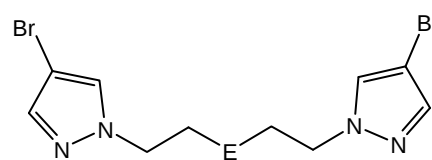
ABSTRACT

Metal complexes of chalcogenated N-heterocycles and NHCs and their application in catalysis and metal chalcogenide nanoparticles synthesis are focus of the thesis.

Synthesis and characterization of chalcogenated pyrazole based neutral bidentate (**L1–L3**) and tridentate (**L4–L6**) ligands and their Pd(II) complexes [Pd(**L1–L3**)Cl₂] (**1–3**) and [Pd(**L4–L6**)Cl].BF₄ (**4–6**) have been carried out. ¹H, ¹³C{¹H}, ⁷⁷Se{¹H} and ¹²⁵Te{¹H} NMR, IR and HR-MS have been used to characterize them. Single crystal structures of **1–6** have revealed square planar geometry of Pd.



L1: E = S, R = H; **L2:** E = Se, R = H;
L3: E = Te, R = OCH₃



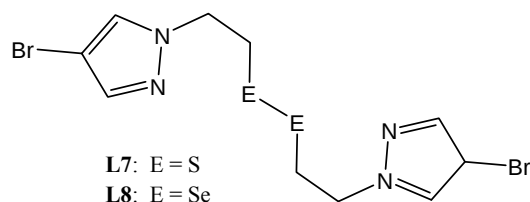
L4: E = S; **L5:** E = Se; **L6:** E = Te

Thermally stable, moisture and air insensitive complexes **1**, **2**, **4** and **5** have been found efficient catalysts (0.01 mol%) for Suzuki-Miyaura coupling reactions (Yield up to 96% in 2 h). Nanoparticles (NPs) composed of Pd and S or Se with high % of Pd (size ~3–19 nm), were formed in the beginning of these reactions. These NPs generated *in situ* from complexes **1**, **2**, **4** and **5** have been isolated and characterized with HR-TEM and SEM-EDX. The real catalysts appear to be these NPs and Pd(II) complexes **1**, **2**, **4** and **5**, most probably are the pre-catalysts.

Single source precursor (SSP) routes for the synthesis of Pd₄Se, PdSe and PdTe NPs have been developed by thermolysis of **2**, **3**, **5** and **6** at substantially lower temperature 200–250 °C. The PdP₂ NPs were formed when attempts were made to prepare nano-sized phases of palladium-sulfide by thermolysis of **1** and **4** in TOP. The

tellurium containing complexes **3** and **6** on thermolysis in TOP have given cubic PdTe nanorods whereas in OA/ODE (1 : 1) hexagonal PdTe NPs. HRTEM, SEM, SEM-EDX and powder XRD authenticate these nanostructures.

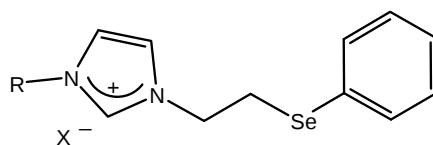
Pyrazolated disulfide and diselenide (**L7** and **L8**) and Pd(II) chalcogenolates $[\text{PdCl}(\text{E}^\text{N})]_2$ (**7** and **8**) and $[\text{Pd}(\text{CH}_3\text{CN})(\text{E}^\text{N})]_2 \cdot 2\text{BF}_4$ (**9** and **10**) [$\text{E}^\text{N} = 2\text{-(4-bromo-pyrazol-1-yl)ethan}$ chalcogenolate; $\text{E} = \text{S/Se}$] have been designed and characterized with ^1H , $^{13}\text{C}\{^1\text{H}\}$ and $^{77}\text{Se}\{^1\text{H}\}$ NMR, IR and HR-MS. Single crystal structures of **8–10** have been determined with X-ray diffraction.



Single source precursor routes for the synthesis of palladium-chalcogenide NPs have been developed by thermolysis of **7–10** in 1:1 mixture of OA and ODE. $\text{Pd}_{17}\text{Se}_{15}$ NPs were formed by the thermolysis of both the Pd(II) selenolates (**8** and **10**), whereas Pd_4S NPs and a mixture of Pd_{16}S_7 (~68%) and PdS (~32%) NPs were obtained from Pd(II) thiolates **7** and **9**, respectively under same reaction conditions. HRTEM, SEM-EDX and powder XRD have authenticated these NPs.

Synthesis and characterization of selenium containing imidazolium salts, (**L9–L11**) (differing in the chain length of alkyl substituent of N), which are precursors to (Se, C_{NHC}) ligands and Pd(II)-NHC complexes $[\text{Pd}(\text{L}-\text{HX})\text{Cl}_2]$ (**11–13**) [$\text{L} = \text{L9–L11}$, $\text{X} = \text{I/Br}$] have been carried out. Single crystal structures of square planar Pd(II) complexes **11** and **12** have been established with X-ray diffraction. The complexes **11–13** (stable under ambient conditions) have been explored as catalyst (0.01 mol%) for Suzuki-Miyaura C–C coupling reactions and nature of real catalytic species generated *in situ* from molecular complexes established. Amongst **11–13**, the

complex **13** has a pendent longest alkyl chain as a substituent on N. The length of pendent alkyl chain appears to affect catalytic activity of complex.



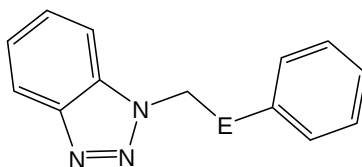
L9: R = CH₃; X = I

L10: R = CH₂-(CH₂)₆-CH₃; X = Br

L11: R = CH₂-(CH₂)₁₆-CH₃; X = Br

The catalytic efficiency of **13** was found to be highest whereas **11** showed significantly lower efficiency than that of **13**. As electronic properties of donor atoms remain unaffected with chain length, the variation in catalytic activities of **11–13** has been ascribed to the properties of NPs formed in the course of catalytic reactions. These NPs (~2–5 nm) were isolated and characterized by HRTEM, TEM–EDX and SEM–EDX. The NPs from **13** are much more uniformly dispersed than those formed from **11**. This appears to be cause of difference in catalytic activities of **11** and **13**.

Synthesis and characterization of benzotriazole based ligands (**L12** and **L13**), and their polymeric silver(I) complexes [$\{\text{Ag}(\mu\text{-L})\text{NO}_3\}_n$] (**14** and **15**) have been made. The ligands and complexes have been characterized with ¹H, ¹³C{¹H} and ⁷⁷Se{¹H} NMR and IR spectroscopy and X-ray diffraction (on single crystals of **14** and **15**).



L12: E = S, **L13**: E = Se

The complexes **14** and **15** (stable under ambient conditions) have been found efficient catalysts (2.0 mol%) for three-component coupling reaction between aldehyde, alkyne and amine (Yield were upto 94% in 6 h at 60 °C).

TABLE OF CONTENTS

<i>Certificate</i>	i
<i>Acknowledgements</i>	ii
<i>Abstract</i>	iv
<i>Table of Contents</i>	vii
<i>List of Figures</i>	xii
<i>List of Tables</i>	xv
<i>Glossary of Symbols and Abbreviations</i>	xvii
 Chapter 1 Introduction	
1.1 N-HETEROCYCLES BASED ORGANOCHALCOGEN LIGANDS	3
1.1.1 Metal Complexes of Pyrazole, Imidazole and Triazole Based Organosulfur Ligands	4
1.1.2 Metal Complexes of Pyrazole, Imidazole and Triazole Based Organoselenium/tellurium Ligands	9
1.2 CATALYTIC APPLICATIONS	11
1.2.1 Catalysis of C–C Coupling Reactions	11
1.2.2 Catalysis of Three-Component Coupling Reaction	17
1.3 METAL CHALCOGENIDE NANOPARTICLES SYNTHESIS	17
1.4 OBJECTIVES AND SCOPES OF THE PRESENT WORK	23
1.5 REFERENCES	25
 Chapter 2 Materials and Methods	
2.1 CHEMICALS AND REAGENTS	43
2.2 SYNTHESIS OF PRECURSORS	43
2.2.1 4-Methoxyphenyltellurium Trichloride	43
2.2.2 Bis(4-methoxyphenyl)ditelluride	44
2.2.3 1-(2-Chloro-ethyl)-1 <i>H</i> -imidazole	44
2.2.4 1-(2-Phenylselanyl-ethyl)-1 <i>H</i> -imidazole	45
2.2.5 Bis(acetonitrile)dichloropalladium(II)	45
2.2.6 Immobilization of 4-Bromobenzoic Acid on Silica	45
2.3 CHARACTERIZATION TECHNIQUES	46

2.3.1	Elemental Analysis	46
2.3.2	Melting Point Determination	46
2.3.3	Nuclear Magnetic Resonance Spectroscopy	46
2.3.4	Infra-red Spectra	46
2.3.5	High Resolution Mass Spectra	46
2.3.6	Single Crystal X-ray Diffraction Studies	47
2.3.7	Powder X-ray Diffraction	47
2.3.8	Thermogravimetric Analysis	47
2.3.9	Atomic Absorption Spectroscopy	47
2.3.10	Scanning Electron Microscopy	48
2.3.11	Transmission Electron Microscopy	48
2.4	REFERENCES	49

Chapter 3 Palladium(II) Complexes of Pyrazolated Chalcogenoethers and their Applications

3.1	INTRODUCTION	50
3.2	EXPERIMENTAL SECTION	52
3.2.1	Synthesis of 4-Bromo-1-(2-chloro-ethyl)-1H-pyrazole (A)	52
3.2.2	Synthesis of 4-Bromo-1-(2-phenylsulfanyl-ethyl)-1H-pyrazole (L1)	52
3.2.3	Synthesis of 4-Bromo-1-(2-phenylselanyl-ethyl)-1H-pyrazole (L2)	53
3.2.4	Synthesis of 4-Bromo-1-[2-(4-methoxy-phenyltellanyl)-ethyl]-1H-pyrazole (L3)	54
3.2.5	Synthesis of Bis[2-(4-bromo-pyrazol-1-yl)-ethyl]chalcogenides (L4–L6)	54
3.2.6	Procedure for Synthesis of [Pd(L1–L3)Cl ₂] (1–3)	56
3.2.7	General Procedure for Synthesis of [Pd(L4–L6)Cl].BF ₄ (4–6)	58
3.2.8	General Procedure for Suzuki-Miyaura Coupling of Aryl Bromides Catalyzed with 1 , 2 , 4 and 5	59
3.2.9	Isolation of NPs Generated from 1 , 2 , 4 and 5 During Suzuki-Miyaura Coupling Reactions	60

3.2.10	Hg Poisoning Test	60
3.2.11	PPh ₃ Poisoning Test	60
3.2.12	Single Source Precursor Synthesis of Palladium-chalcogenide/phosphide Nanostructures	60
(a)	Synthesis of Pd ₄ Se, PdSe nanoparticles and PdTe nanorods	60
(b)	Synthesis of PdTe hexagonal nanoparticles	61
(c)	Synthesis of PdP ₂ nanoparticles	61
3.3	RESULTS AND DISCUSSION	61
3.3.1	NMR and IR Spectra	63
3.3.2	Crystal Structures of 1–6	64
3.3.3	Catalytic Applications of 1 , 2 , 4 and 5 in Suzuki-Miyaura Coupling	78
3.3.4	Palladium Chalcogenide NPs Generated in situ in Catalysis	80
3.3.5	Synthesis of Pd ₄ Se, PdSe and PdTe NPs and PdTe Nanorods <i>via</i> Single Source Precursors	82
3.4	CONCLUSIONS	90
3.5	REFERENCES	92

Chapter 4 Palladium(II) Thio/Selenolates Formed by Cleavage of Pyrazole Based Disulfide/selenide and their Applications

4.1	INTRODUCTION	97
4.2	EXPERIMENTAL SECTION	98
4.2.1	Synthesis of Bis[2-(4-bromo-pyrazol-1-yl)-ethyl] Disulfide (L7)	98
4.2.2	Synthesis of Bis[2-(4-bromo-pyrazol-1-yl)-ethyl] Diselenide (L8)	99
4.2.3	Synthesis of [PdCl(μ -S [†] N)] ₂ (7)	99
4.2.4	Synthesis of [PdCl(μ -S [†] N)] ₂ (8)	100
4.2.5	Synthesis of [Pd(CH ₃ CN)(μ -S [†] N)] ₂ .2BF ₄ (9)	101
4.2.6	Synthesis of [Pd(CH ₃ CN)(μ -Se [†] N)] ₂ .2BF ₄ (10)	101
4.2.7	Synthesis of Palladium-Sulfide/Selenide Nanoparticles	102
(a)	Synthesis of palladium-sulfide nanoparticles	102
(b)	Synthesis of palladium-selenide nanoparticles	102

4.3	RESULTS AND DISCUSSION	102
4.3.1	NMR Spectra	104
4.3.2	Crystal Structures	106
4.3.3	Single Source Precursors of Palladium-Sulfide/Selenide Nanoparticles	113
4.4	CONCLUSIONS	117
4.5	REFERENCES	118

Chapter 5 Palladium(II) Complexes of Selenated N-Heterocyclic Carbenes and their Catalytic Applications in Suzuki-Miyaura Coupling Reaction

5.1	INTRODUCTION	121
5.2	EXPERIMENTAL SECTION	123
5.2.1	Synthesis of 1-Methyl-3-(2-ethyl-1-selenophenyl)-3 <i>H</i> -imidazolium Iodide (L9)	123
5.2.2	Synthesis of 1-Octyl-3-(2-ethyl-1-selenophenyl)-3 <i>H</i> -imidazolium Bromide (L10)	123
5.2.3	Synthesis of 1-Octadecyl-3-(2-ethyl-1-selenophenyl)-3 <i>H</i> -imidazolium Bromide (L11)	124
5.2.4	Procedure for Synthesis of [Pd(Se, C _{NHC})Cl ₂] (11–13)	125
5.2.5	Procedure for the Suzuki-Miyaura Reaction Catalyzed with 11–13	127
5.2.6	Hg Poisoning Test	127
5.2.7	PPh ₃ Poisoning Test	127
5.2.8	Two Phase Test	127
5.2.9	Isolation of <i>in situ</i> Generated NPs from Complexes 11–13 During Suzuki-Miyaura Coupling	128
5.2.10	Procedure for Suzuki-Miyaura Coupling Catalyzed by NPs Obtained from 11 and 13	128
5.3	RESULTS AND DISCUSSION	129
5.3.1	NMR and Mass Spectra	130
5.3.2	Crystal Structures	131
5.3.3	Application in Suzuki-Miyaura Reaction Catalyzed with 11–13	137

5.4	CONCLUSIONS	145
5.5	REFERENCES	147

Chapter 6 Polymeric Silver(I) Complexes of Chalcogenated Benzotriazoles and their Catalytic Applications

6.1	INTRODUCTION	151
6.2	EXPERIMENTAL SECTION	152
6.2.1	Synthesis of 1-Phenylsulfanylmethyl-1 <i>H</i> -benzotriazole (L12)	152
6.2.2	Synthesis of 1-Phenylselanylmethyl-1 <i>H</i> -benzotriazole (L13)	153
6.2.3	Synthesis of Polymeric Complex [Ag(μ - L12)(NO ₃)] _n (14)	154
6.2.4	Synthesis of Polymeric Complex [Ag(μ - L13)(NO ₃)] _n (15)	154
6.2.5	General Procedure for Catalytic Three-Component Coupling Reaction of Aldehyde, Amine and Alkyne	155
6.3	RESULTS AND DISCUSSION	155
6.3.1	NMR Spectra	156
6.3.2	Crystal Structure of 14 and 15	157
6.6.3	Catalytic Applications of 14 and 15 in Three-Component Coupling Reactions of Aldehyde, Amine and Alkyne	164
6.4	CONCLUSIONS	169
6.5	REFERENCES	170
	Bio-data	175

Annexure I Supporting Information in CD
