METAL COMPLEXES OF CHALCOGENATED BULKY LIGANDS AND *N*-HETEROCYCLIC CARBENES: SYNTHESIS AND CATALYTIC APPLICATIONS

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SEPTEMBER 2018

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by

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Submitted

in fulfillment of the requirements of the degree of Doctor of Philosophy

to the

INDIAN INSTITUTE OF TECHNOLOGY DELHI

SEPTEMBER 2018

CERTIFICATE

This is to certify that the thesis entitled, **"METAL COMPLEXES OF CHALCOGENATED BULKY LIGANDS AND *N*-HETEROCYCLIC CARBENES: SYNTHESIS AND CATALYTIC APPLICATIONS"** being submitted by **Ms. POOJA DUBEY** 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 her. Ms. Pooja Dubey has worked under my guidance and supervision. She 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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ACKNOWLEDGEMENTS

I have great pleasure in expressing my deep and sincere gratitude to my mentor and supervisor Prof. Ajai K. Singh. His vast knowledge imparted by his experience about life and research has always been as light in the darkness. He has extended her 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, encouragement, inspiration, advice, appreciation, and guidance have made the thesis.

Besides my supervisor, I would like to thank my SRC committee: Prof. Ravi Shanker, Dr. Rajiv K Srivastava, and Dr. S. Nagendran for their insightful comments and brilliant suggestions which encouraged me to broaden my research from different perspectives.

My sincere thanks are to the Head, Department of Chemistry, Prof. Ravi Shanker and Ex. Head, Prof. A. Ramanan for providing necessary research facilities. I acknowledge the help extended by all faculty members and all the technical staff members for their help rendered during this work. I would like to express my gratitude to all the teachers who taught me throughout. I also take the privilege to thank all technical staff members (especially Mr. Keshav Choudhary) for their help offered during my Ph.D.

I express my gratefulness to I. I. T. Delhi for offering me an ideal work environment where I was free to work without time constraints and could concentrate on my research. I also acknowledge the financial assistance received from "UGC" which has made my Ph.D. work possible over here.

I could not be thankful enough to God who made me capable to achieve my goal and showered millions of blessings at every step of my life.

I would like to take this opportunity to offer my sincere regards to my ever supportive parents Mr. Dayashanker Dubey and Mrs. Kamla Dubey. Today this thesis is fruitful because I have nurtured with moral support, love, encouragement, and discipline from my parents throughout my life. I thank both of my brothers, Deovrat Dubey and Praveen Dubey for their love and support. Thanks to my grandparents for being a shower of blessings to me. I thank my bhabhi and my loving niece (lado) as she was always a reason for my smile in the moments of distress.

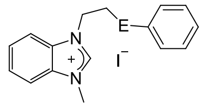
It gives me gratification to express my sincere thanks to all my lab mates who have directly or indirectly contributed to the present research work. Their words of motivation, affection, suggestions, celebrations over the happy moments and their presence through all the thick and thin times are remarkable. Their support was like a fragrance in the garden of my lab life. But this part of acknowledgement is unfinished without mentioning their names. I extend my thankfulness to Dr. Arun Kumar, Dr. G. K. Rao, Dr. V. V. Singh, Dr. U. Kumar, Dr. Poornima Singh, Dr. Om Prakash, Dr. Kamal Nayan Sharma, Dr. Fariha Saleem, Dr. Hemant Joshi, Dr. Manoj Yadav, Dr. Satyendra Kumar, Dr. Mahabir Pratap Singh, Dr. Alpesh Kumar Sharma and Renu Bhaskar. I also want to thank Dr. Amanpreet Kaur, Dr. Ashish Pandey, Rituraj Mishra, Dharmendra Singh, for extending their help in my research.

The greatest gift of life is in form of friends who never leave our hands and their support is worth mentioning here. I recognize the enormous cooperation and encouragement received from my friends Vineeta Garg, Dr. Deepika Tyagi, Kalpana Singh, Suman, Neha Gupta, Dr. Shalinee Prasad, Aabha Pandey, Sameer Prasad, Pawan Vats, Dr. Chanderpratap Singh. Finally, I would like to give special token of thanks to Sonu Gupta (lab mate) for all his support in days of sunshine and shade. His critical suggestions, motivation and care refined my research and pushed me forward towards accomplishment of this thesis. Last but not the least, I thank to all those whom I have not mentioned here personally but were around. It would have not been possible without you all.

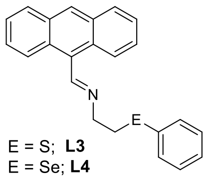
Pooja Dubey

ABSTRACT

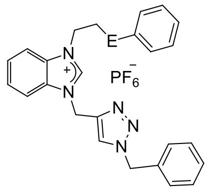
The present thesis is focused on metal complexes of bidentate and tridentate organochalcogen ligands including hybrid ones **L1**–**L8** is explored. Their ligation with Pd(II), Ru(II), Ir(III) and Rh(III).



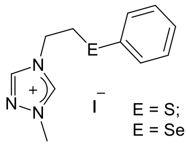
E = S; **L1** E = Se; **L2**



E = S; **L3**
E = Se; **L4**



E = S; **L5**
E = Se; **L6**



E = S; **L7**
E = Se; **L8**

The newly designed complexes have been investigated as catalyst for nitrile-amide interconversion, Sonogashira coupling, transfer hydrogenation (TH) reaction of carbonyl compounds, *N*-alkylation of amines with benzyl alcohols.

The trinuclear Pd(II) complexes $[Pd_3(\mathbf{L1}\text{-}HI)_2(CH_3CN)Cl_6]$ (**1**) and $[Pd_3(\mathbf{L2}\text{-}HI)_2(CH_3CN)Cl_6]$ (**2**) were synthesized from 3-methyl-1-(2-(phenylthio/seleno)ethyl)-1H-benzo[d]imidazol-3-ium iodide (**L1**/**L2**), by reacting it with Ag_2O in dichloromethane followed by treatment with $[Pd(CH_3CN)_2Cl_2]$ in acetonitrile (metal to ligand ratio 3:2). The single crystal structures (determined with X-ray diffraction) of **1** and **2** have been solved and reveal square planar geometry for Pd. The **1-2** have been explored for selective nitrile-amide interconversion and Sonogashira coupling reactions. A catalyst loading of 0.5–2.0 mol% is optimum for nitrile-amide interconversion, while for Sonogashira coupling a loading of 1.0–2.0 mol% of Pd is essential. The catalytic efficiency of complex **1**, is somewhat higher relative to complex **2**. The Pd(II) and Pd(0) species derive interconversion and Sonogashira coupling respectively.

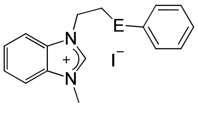
The Schiff bases having anthracene core $[\mathrm{PhS(CH_2)_2C{=}N\text{-}9\text{-}C_{14}H_9}]$(**L3**) / $[\mathrm{PhSe(CH_2)_2C{=}N\text{-}9\text{-}C_{14}H_9}]$ (**L4**) synthesized by condensation of 2-(phenylsulphanyl)ethylamine/2-(phenylselenyl)ethylamine with anthracene-9-carbaldehyde reaction on treatment with sodium tetrachloropalladate(II) and $[\{(\eta^6\text{-benzene})\mathrm{RuCl}(\mu\text{-Cl})\}_2]$ (followed by reaction with $\mathrm{NH_4PF_6}$), at room temperature result in cyclopalladated [Pd(**L**–H)Cl] (**3** and **4**) and $[(\eta^6\text{-}\mathrm{C_6H_6})\mathrm{Ru}($**L**$)\mathrm{Cl}]\mathrm{PF_6}$ (**5** and **6**) (**L** = **L3** or **L4**) complexes respectively. Single crystal structures of **3**−**6** were solved. The geometry of Pd in **3** and **4** is distorted square planar while in case of **5** and **6** there is a pseudo-octahedral “piano-stool” type disposition of donor atoms around Ru. The catalytic activity of complexes **3** and **4** (optimum loading 0.05-0.2 mol% of Pd) was explored for TH. The **3** and **4** was found somewhat more efficient for aldehydes than ketones. For catalysis of base-free *N*-alkylation of aniline with benzyl alcohol both **5** and **6** were explored. Their optimum loading as catalyst was found to be 0.5 mol % of Ru. The **4**/**6** having selenium ligand is more efficient than **3**/**5** (S analog) for both TH and base-free *N*-alkylation of aniline.

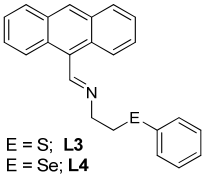
The ligand (**L** = **L3**/**L4**) when treated with $[(\eta^5\text{-Cp*})\mathrm{RhCl}(\mu\text{-Cl})]_2$ and $[(\eta^5\text{-Cp*})\mathrm{IrCl}(\mu\text{-Cl})]_2$, and $\mathrm{CH_3COONa}$ at 50 °C followed by $\mathrm{NH_4PF_6}$ gives rhodacycles $[(\eta^5\text{-Cp*})\mathrm{Rh}($**L-H**$)][\mathrm{PF_6}]$ and iridacycles, $[(\eta^5\text{-Cp*})\mathrm{Ir}($**L-H**$)][\mathrm{PF_6}]$ (**7** and **11: L=L1; 8** and **12: L=L2**). The same reaction in the absence of $\mathrm{CH_3COONa}$ gives complexes $[(\eta^5\text{-Cp*})\mathrm{Rh}($**L**$)\ \mathrm{Cl}][\mathrm{PF_6}]$ and $[(\eta^5\text{-Cp*})\mathrm{Ir}($**L**$)\mathrm{Cl}][\mathrm{PF_6}]$ (**9**, **10**, **13** and **14**) in which **L** = **L3** (**9** and **13**)/**L4**(**10** and **14**) ligates in a bidentate mode. Single crystal X-ray diffraction studies revealed “piano-stool” geometry around Rh and Ir. These complexes **7-14** have been explored as a catalyst in base-free transfer hydrogenation of carbonyl compounds using 2-propanol as hydrogen source with excellent to good yield using 0.1-0.5 mol% loading of **7-14** as a catalyst. The real catalytic species proposed in the case of rhoda/iridacycles result due to loss of Cp* ring. The **7-14** were also found promising for *N*-alkylation of aniline with benzyl alcohol under base free condition when their loading was 0.5 mol%. The catalytic processes are more efficient with Rh complexes than the corresponding Ir analogue. Both the reactions involves the formation of metal hydride species.

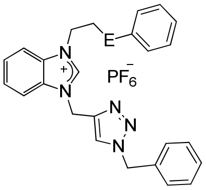
3-(1-Benzyl-1H-1,2,3-triazol-4-yl)methyl)-1-(2-(phenylthio/selanyl)ethyl)-1H-benzo[d]imidazol-3-ium hexafluorophosphate (**L5**/**L6**) precursor of sulfated/selenated *N*-heterocyclic carbene were synthesized via a 'copper-catalyzed click reaction' and 4-methyl-1-(2-(phenylthio/selanyl)ethyl)-1H-1,2,4-triazol-4-ium iodide (**L7**/**L8**), precursor of sulfated/selenated *N*-heterocyclic carbene, were synthesized by reaction of triazole with 1,2-dichloroethane followed by treatment with PhS/SeNa and MeI. The reaction of **L5**/**L6** and **L7**/**L8** with Ag_2O followed by transmetallation with $[Pd(CH_3CN)_2Cl_2]$, resulted in palladium(II) complexes, [Pd(**L5**/**L6**-H)Cl] $[PF_6]$ (**15-16**) and [Pd(**L5**/**L6**-HI)$(Cl)_2$] (**17-18**). The geometry around Pd in **17** and **18** is distorted square planar. The catalytic activity of **15-18** for *N*-alkylation of aniline with benzyl alcohol in an inert atmosphere and Cu and amine free Sonogashira C-C coupling under aerobic condition at 0.5 and 0.02-0.1 mol% catalyst loading respectively was found promising. The catalytic process was somewhat more efficient with **15** (Pd bonded with **L5**), than **16,** followed by **17** and **18**.

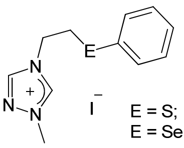
शोध प्रबंध-सार

वर्तमान शोध प्रबंध बाईडेंटेड और ट्राइडेंटेट ऑर्गोनोचालकोजन लिगेंड्स के मेटल कॉम्प्लेक्सेज़ पर केंद्रित है जिसमें हाइब्रिड वाले **L1-L8** का पता लगाया गया है। पैलेडियम (II), रुथेनियम (II), इरीडियम (III) और रोडियम (III) के साथ उनका लायगेशन।


E = S; **L1** E = Se; **L2**


E = S; **L3**
E = Se; **L4**


E = S; **L5**
E = Se; **L6**


E = S; **L7**
E = Se; **L8**

नए डिजाइन किए गए कॉम्प्लेक्सेज़ की जांच नाइट्रिल-एमाइड इंटरकवर्जन, सोनोगशिरा कपलिंग, कार्बोनील यौगिकों की ट्रांसफर हाइड्रोजनीकरण, बेंजाइल अल्कोहल के साथ अमाइन के एन-अल्काइलेशन के लिए उत्प्रेरक के रूप में की गई है।

ट्राइन्यूक्लियर पैलेडियम (II) कॉम्प्लेक्सेज़ [Pd_3(**L1**-HI)$_2$(CH_3CN)Cl_6] (1) और [Pd_3(**L2**-HI)$_2$(CH_3CN)Cl_6] (2), 3-मेथिल-1-(2-(फिनाइलथायो/सेलेनो)एथिल)-1एच-बेंजो[डी]इमिडाज़ोल-3-आईम आयोडाइड (**L1**/**L2**), से संश्लेषित किया गया, इसे डाइक्लोरोमेथेन में Ag_2O के साथ अभिक्रिया कराने के पश्चात [$Pd(CH_3CN)_2Cl_2$] के साथ एसीटोनिट्रियल में कराने पर प्राप्त हुआ (मेटल से लिगैंड अनुपात 3: 2)।

सिंगल क्रिस्टल संरचनाओं (एक्स-रे डिफ्रैक्शन के साथ निर्धारित) **1** और **2** का हल किया गया है और जौ पैलेडियम की स्क्वायर पलैनर ज्यामिति प्रतिपादित करता है। **1-2** को चुनिंदा नाइट्रिल-एमाइड इंटरकवर्जन और सोनोगशिरा कपलिंग अभिक्रियाओं के लिए प्रयुक्त हुए। 0.5-2.0 मोल% की उत्प्रेरक लोडिंग नाइट्रिल-एमाइड इंटरकवर्जन के लिए इष्टतम है, जबकि सोनोगशिरा कपलिंग के लिए पैलेडियम के 1.0-2.0 मोल% की लोडिंग आवश्यक है। कॉम्प्लेक्स **1** की उत्प्रेरण सामर्थ्य कॉम्प्लेक्स **2** के तुलना में अधिक परीलक्षित है। पैलेडियम (II) और पैलेडियम (0) स्पीशीज़् डिराइव क्रमशः इंटरकोनवर्जन और सोनोगशिरा कपलिंग।

एंथ्रेसीन कोर युक्त शिफ बेस $[PhS(CH_2)_2C{=}N\text{-}9\text{-}C_{14}H_9]$ (**L3**)/$[PhSe(CH_2)_2C{=}N\text{-}9\text{-}C_{14}H_9]$ (**L4**), 2- (फिनाइल-सल्फैनियल/सेलेनियल) एथिलअमाइन और एंथ्रेसीन-9-कार्बाल्डेहाइड के संघनन द्वारा संश्लेषित किया गया, इसे सोडियम टेट्राक्लोरोपालाडेट (II) और $[\{(\eta^6\text{-benzene})RuCl(\mu\text{-}Cl)\}_2]$ के साथ, कमरे के तापमान पर अभिक्रिया कराने बाद क्रमश: साइक्लोपेलेडेट $[Pd(\mathbf{L}\text{-}H)Cl]$ (**3** and **4**) और $[(\eta^6\text{-}C_6H_6)Ru(\mathbf{L})Cl]PF_6$ (NH_4PF_6 के साथ अभिक्रिया कराने के बाद) (**5** and **6**) (**L** = **L3** or **L4**) कॉम्प्लेक्स परिणामस्वरुप प्राप्त हुआ। **3-6** की सिंगल क्रिस्टल संरचनाओं को हल किया गया था। **3** और **4** में पैलेडियम (II) की ज्यामिति विकृत स्क्वायर पलैनर है जबकि **5** और **6** में रुथेनियम के चारों ओर स्यूडोऑक्टाड्रल "पियानो-स्टूल" ज्यामिति है। कॉम्प्लेक्स **3** और **4** की उत्प्रेरक क्षमता (Pd के इष्टतम लोडिंग 0.05-0.2 मोल%) टीएच के लिए प्रयुक्त हुए। **3** और **4** की उत्प्रेरक क्षमता कीटोन की तुलना में अल्डेहाइड के लिए अधिक पाया गया था। बेंजाइल अल्कोहल के साथ एनिलइन की बेस-फ्री एन-अल्काइलेशन के उत्प्रेरण के लिए दोनों **5** और **6** प्रयुक्त हुए। उत्प्रेरक के रूप में Ru की 0.5 मोल% लोडिंग को इष्टतम पाया गया था। सेलेनियम युक्त लिगैंड **4/6**, टीएच और बेस-फ्री एन-अल्काइलेशन दोनों के लिए **3/5** (सलफर एनालॉग) से अधिक कुशल है।

लिगेंड (**L** = **L3**/**L4**) की अभिक्रिया जब $[(\eta^5\text{-}Cp*)RhCl(\mu\text{-}Cl)]_2$ और $[(\eta^5\text{-}Cp*)IrCl(\mu\text{-}Cl)]_2$, और CH_3COONa से 50 °C पर कराने के पश्चात NH_4PF_6 के साथ कराने पर रोडासाइक्ल $[(\eta^5\text{-}Cp*)Rh(\mathbf{L\text{-}H})][PF_6]$ और इरिडासाइक्ल $[(\eta^5\text{-}Cp*)Ir(\mathbf{L\text{-}H})][PF_6]$ (**7** और **11: L = L3; 8** और **12: L = L4**) प्राप्त हुआ। यही अभिक्रिया CH_3COONa की अनुपस्थिति में कॉम्प्लेक्स $[(\eta^5\text{-}Cp*)Rh(\mathbf{L})\ Cl][PF_6]$ और $[(\eta^5\text{-}Cp*)Ir(\mathbf{L})Cl][PF_6]$ (**9**, **10**, **13** और **14**) जिसमे **L** = **L3** (**9** और **13**)/**L4**(**10** और **14**) बाईडेंटेड मोड में लायगेटस है। सिंगल क्रिस्टल एक्स-रे डिफ्रेक्शन ने रोडियम और इरीडियम के चारों ओर "पियानो-स्टूल" ज्यामिति प्रतिपादित किया। इन कॉम्प्लेक्स **7-14** को उत्प्रेरक के रूप में 0.1-0.5 मोल% लोडिंग का उपयोग करके हाइड्रोजन स्रोत के रूप में 2-प्रोपेनॉल का उपयोग करके उत्कृष्ट से अच्छी उपज के साथ कार्बोनील यौगिकों के बेस-फ्री ट्रांसफर हाइड्रोजनीकरण के लिए प्रयुक्त हुए। वास्तविक प्रस्तावित उत्प्रेरक स्पीशीज़ रोडासाइकल/इरीडासाइकल के मामले में Cp∗ रिंग के नुकसान के कारण परिणामस्वरूप बनता है। **7-14** को बेंजाइल अल्कोहल के साथ एनीलीऩ के बेस फ्री एन-एल्काइलेशऩ के लिए प्रयुक्त हुए जब उनकी लोडिंग 0.5 मोल% थी। रोडियम कॉम्प्लेक्स की उत्प्रेरण सामर्थ्य इरीडियम एनालॉग के तुलना में अधिक परीलक्षित है।

दोनों अभिक्रियाओं में मेटल हाइड्राइड स्पीशीज़् का गठन शामिल है। 3-(1-बेंजिल-1एच-1,2,3-ट्रायज़ोल-4-वाईएल)मिथाइल)-1-(2-(फेनिलथायो/सेलेनिल)एथिल)-1एच-बेंजो[डी]इमिडाज़ोल-3-आईम हेक्साफ्लोरोफॉस्फेट (**L5**/**L6**) सल्फेटेड/सेलेनेटेड एन-हेटरोक्साइकल कार्बिन के प्रीकर्सर को 'कापर-उत्प्रेरित क्लिक अभिक्रिया के माध्यम से संश्लेषित किया गया और 4-मेथिल-1-(2-(फेनिलथायो/सेलेनिल)एथिल)-1एच-1,2,4-ट्रायज़ोल-4-आईम आयोडाइड (**L7**/**L8**), सल्फेटेड/सेलेनेटेड एन-हेटरोक्साइक्लिक कार्बिन के प्रीकर्सर, को ट्रायज़ोल की 1,2-डाइक्लोरोथेन के साथ अभिक्रिया कराने के पश्चात PhS/SeNa और मीथाय़ल आयोडाइड के साथ अभिक्रिया द्वारा संश्लेषित किया गया था। Ag_2O के साथ **L5**/**L6** और **L7**/**L8** की अभिक्रिया ट्रांसमेटेलेशन द्वारा कराने के पश्चात $[Pd(CH_3CN)_2Cl_2]$ के साथ कराने पर, जिसके परिणामस्वरूप पैलेडियम (II) कॉम्प्लेक्सेज़, [Pd(**L5**/**L6**-H)Cl] $[PF_6]$ (**15**-**16**) and [Pd(**L5**/**L6**-HI)$(Cl)_2$] (**17**-**18**) प्राप्त हुआ। **17** और **18** में पैलेडियम के चारों ओर विकृत स्क्वायर पलैनर ज्यामिति है।

15-17 की उत्प्रेरक क्षमता एक निष्क्रिय वातावरण में बेंजाइल अल्कोहल के साथ एनीलीऩ के एन-अल्काइलेशन और एरोबिक स्थिति में कापर और अमीन मुक्त सोनोगशिरा सी-सी कपलिंग के लिए उत्प्रेरक लोडिंग क्रमशः 0.5 और 0.02-0.1 मोल% पर परीलक्षित हुई। **15** (**L5** के साथ बंधित Pd) की उत्प्रेरण सामर्थ्य **16**, **17** और **18** के तुलना में अधिक परीलक्षित है।

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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
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
Pd	palladium
Ph	phenyl
n-Pr	*n*-propyl
S	sulfur
Se	selenium
SMC	Suzuki-Miyaura Coupling
t	triplet
THF	tetrahydrofuran
TLC	thin layer chromatography
TMS	tetrametylsilane
XRD	x-ray diffraction