

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

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INDIAN INSTITUTE OF TECHNOLOGY DELHI  
SEPTEMBER 2018**

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SYNTHESIS AND CATALYTIC APPLICATIONS**

by

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Submitted

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

to the



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## 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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The Schiff bases having anthracene core [PhS(CH<sub>2</sub>)<sub>2</sub>C=N-9-C<sub>14</sub>H<sub>9</sub>](**L3**) / [PhSe(CH<sub>2</sub>)<sub>2</sub>C=N-9-C<sub>14</sub>H<sub>9</sub>] (**L4**) synthesized by condensation of 2-(phenylsulphanyl)ethylamine/2-(phenylselenyl)ethylamine with anthracene-9-carbaldehyde reaction on treatment with sodium tetrachloropalladate(II) and [ $\{(\eta^6\text{-benzene})\text{RuCl}(\mu\text{-Cl})\}_2$ ] (followed by reaction with NH<sub>4</sub>PF<sub>6</sub>), at room temperature result in cyclopalladated [Pd(**L-H**)Cl] (**3** and **4**) and [ $(\eta^6\text{-C}_6\text{H}_6)\text{Ru}(\text{L})\text{Cl}$ ][PF<sub>6</sub>] (**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 [ $(\eta^5\text{-Cp}^*)\text{RhCl}(\mu\text{-Cl})\}_2$ ] and [ $(\eta^5\text{-Cp}^*)\text{IrCl}(\mu\text{-Cl})\}_2$ ], and CH<sub>3</sub>COONa at 50 °C followed by NH<sub>4</sub>PF<sub>6</sub> gives rhodacycles [ $(\eta^5\text{-Cp}^*)\text{Rh}(\text{L-H})$ ][PF<sub>6</sub>] and iridacycles, [ $(\eta^5\text{-Cp}^*)\text{Ir}(\text{L-H})$ ][PF<sub>6</sub>] (**7** and **11**: **L=L1**; **8** and **12**: **L=L2**). The same reaction in the absence of CH<sub>3</sub>COONa gives complexes [ $(\eta^5\text{-Cp}^*)\text{Rh}(\text{L})\text{Cl}$ ][PF<sub>6</sub>] and [ $(\eta^5\text{-Cp}^*)\text{Ir}(\text{L})\text{Cl}$ ][PF<sub>6</sub>] (**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

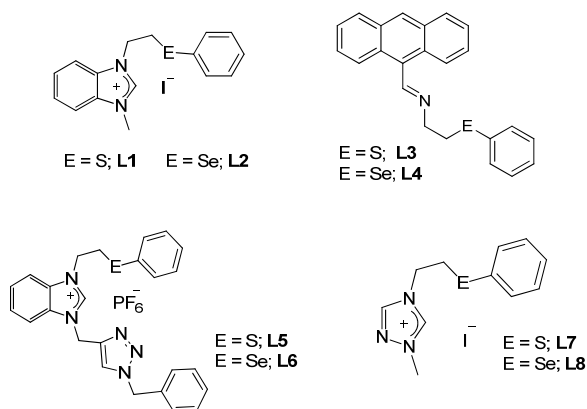
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proposed in the case of rhoda/iridacycles result due to loss of Cp\* ring. The **7-14** were also found promising for *N*-alkylation of aniline with benzyl alcohol under base free condition when their loading was 0.5 mol%. The catalytic processes are 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<sub>2</sub>O followed by transmetallation with [Pd(CH<sub>3</sub>CN)<sub>2</sub>Cl<sub>2</sub>], resulted in palladium(II) complexes, [Pd(**L5/L6-H**)Cl] [PF<sub>6</sub>] (**15-16**) and [Pd(**L5/L6-HI**)(Cl)<sub>2</sub>] (**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 ट्राइडेंटेड ऑर्गनोचालकोजन लिगेण्ड्स 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।



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 एसीटोनिट्रिल में कराने पर प्राप्त हुआ (मेटल से लिगेण्ड अनुपात 3: 2)।

सिंगल क्रिस्टल संरचनाओं (एक्स-रे डिफ्रैक्शन के साथ निर्धारित) 1 और 2 का हल किया गया है और जौ पैलेडियम की स्कवायर प्लेनर 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) स्पीशीज़ डिराइव क्रमशः इंटरकोनवर्जन और सोनोगशिरा कपलिंग।

एंथ्रेसीन कोर युक्त शिफ बेस [PhS(CH<sub>2</sub>)<sub>2</sub>C=N-9-C<sub>14</sub>H<sub>9</sub>] (**L3**)/[PhSe(CH<sub>2</sub>)<sub>2</sub>C=N-9-C<sub>14</sub>H<sub>9</sub>] (**L4**), 2- (फिनाइल-सल्फैनियल/सेलेनियल) एथिलअमाइन और एंथ्रेसीन-9-कार्बाल्डेहाइड के संघनन द्वारा संश्लेषित किया गया, इसे सोडियम टेट्राक्लोरोपालाडेट (II) और  $[(\eta^6\text{-benzene})\text{RuCl}(\mu\text{-Cl})_2]$  के साथ, कमरे के तापमान पर अभिक्रिया कराने बाद क्रमशः साइक्लोपेलेडेट [Pd(L-H)Cl] (**3** and **4**) और  $[(\eta^6\text{-C}_6\text{H}_6)\text{Ru}(\text{L})\text{Cl}]\text{PF}_6$  (NH<sub>4</sub>PF<sub>6</sub> के साथ अभिक्रिया कराने के बाद) (**5** and **6**) (L = **L3** or **L4**) कॉम्प्लेक्स परिणामस्वरूप प्राप्त हुआ। **3-6** की सिंगल क्रिस्टल संरचनाओं को हल किया गया था। **3** और **4** में पैलेडियम (II) की ज्यामिति विकृत स्क्वायर प्लेनर है जबकि **5** और **6** में रूथेनियम के चारों ओर स्यूडोऑक्टाइड्रल "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 लिगेंड **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  $[(\eta^5\text{-Cp}^*)\text{RhCl}(\mu\text{-Cl})_2]$  और  $[(\eta^5\text{-Cp}^*)\text{IrCl}(\mu\text{-Cl})_2]$ , और CH<sub>3</sub>COONa से 50 °C पर कराने के पश्चात NH<sub>4</sub>PF<sub>6</sub> के साथ कराने पर रोडासाइकल  $[(\eta^5\text{-Cp}^*)\text{Rh}(\text{L-H})][\text{PF}_6]$  और इरिडासाइकल  $[(\eta^5\text{-Cp}^*)\text{Ir}(\text{L-H})][\text{PF}_6]$  (**7** और **11**: L = **L3**; **8** और **12**: L = **L4**) प्राप्त हुआ। यही अभिक्रिया CH<sub>3</sub>COONa की अनुपस्थिति में कॉम्प्लेक्स  $[(\eta^5\text{-Cp}^*)\text{Rh}(\text{L})\text{Cl}][\text{PF}_6]$  और  $[(\eta^5\text{-Cp}^*)\text{Ir}(\text{L})\text{Cl}][\text{PF}_6]$  (**9**, **10**, **13** और **14**) जिसमें L = **L3** (**9** और **13**)/**L4**(**10** और **14**) बाईडेंटेड मोड में लायगेटस है। सिंगल क्रिस्टल एक्स-रे डिफ्रैक्शन 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 एनीलीन के बेस फ्री एन-एल्काइलेशन के लिए प्रयुक्त हुए जब उनकी लोडिंग 0.5 मोल% थी। रोडियम कॉम्प्लेक्स की उत्प्रेरण सामर्थ्य इरीडियम एनालॉग के तुलना में अधिक परीक्षित है।

दोनों अभिक्रियाओं में मेटल हाइड्राइड स्पीशीज़ का गठन शामिल है। 3-(1-बेंजिल-1एच-1,2,3-ट्रायज़ोल-4-वाइएल)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 मीथायल आयोडाइड के साथ अभिक्रिया द्वारा संश्लेषित किया गया था। Ag<sub>2</sub>O के साथ L5/L6 और L7/L8 की अभिक्रिया ट्रांसमेटेशन द्वारा कराने के पश्चात [Pd(CH<sub>3</sub>CN)<sub>2</sub>Cl<sub>2</sub>] के साथ कराने पर, जिसके परिणामस्वरूप पैलेडियम (II) कॉम्प्लेक्सेज़, [Pd(L5/L6-H)Cl] [PF<sub>6</sub>] (15-16) and [Pd(L5/L6-HI)(Cl)<sub>2</sub>] (17-18) प्राप्त हुआ। 17 और 18 में पैलेडियम के चारों ओर विकृत स्क्वायर प्लेनर ज्यामिति है। 15-17 की उत्प्रेरक क्षमता एक निष्क्रिय वातावरण में बेंजाइल अल्कोहल के साथ एनीलीन के एन-अल्काइलेशन और एरोबिक स्थिति में कापर और अमीन मुक्त सोनोगशिवा सी-सी कपलिंग के लिए उत्प्रेरक लोडिंग क्रमशः 0.5 और 0.02-0.1 मोल% पर परीक्षित हुई। 15 (L5 के साथ बंधित Pd) की उत्प्रेरण सामर्थ्य 16, 17 और 18 के तुलना में अधिक परीक्षित है।

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## GLOSSARY OF SYMBOLS AND ABBREVIATIONS

%	percent
$\delta$	chemical shift
$\nu$	frequency
Å	angstrom
Ar	Aryl
$\mu\text{L}$	microlitre
$^{\circ}\text{C}$	degree centigrade
br	broad signal
<i>n</i> -Bu	<i>n</i> -butyl
C <sub>q</sub>	quaternary carbon
C–C	carbon–carbon
cm	centimeter
CH <sub>2</sub> Cl <sub>2</sub>	dichloromethane
CHCl <sub>3</sub>	chloroform
CH <sub>3</sub> CN	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

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M <sup>+</sup>	molecular ion
M	molar
mmol	millimole
mol	mole
mL	milliliter
m.p.	melting point
NMP	<i>N</i> -methyl-2-pyrrolidone
NMR	nuclear magnetic resonance
Pd	palladium
Ph	phenyl
<i>n</i> -Pr	<i>n</i> -propyl
S	sulfur
Se	selenium
SMC	Suzuki-Miyaura Coupling
t	triplet
THF	tetrahydrofuran
TLC	thin layer chromatography
TMS	tetrametylsilane
XRD	x-ray diffraction