INDOLE BASED LIGANDS AND THEIR PALLADACYCLES: SYNTHESIS, STRUCTURE AND CATALYTIC APPLICATIONS

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by

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CERTIFICATE

This is to certify that the thesis entitled, **"INDOLE BASED LIGANDS AND THEIR PALLADACYCLES: SYNTHESIS, STRUCTURE AND CATALYTIC APPLICATIONS"** being submitted by **Mr. MAHABIR PRATAP SINGH** to the **Indian Institute of Technology Delhi** for the award of the degree of **Doctor of Philosophy**, is a record of bonafide research work carried out by him. Mr. Mahabir Pratap Singh 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:

New Delhi

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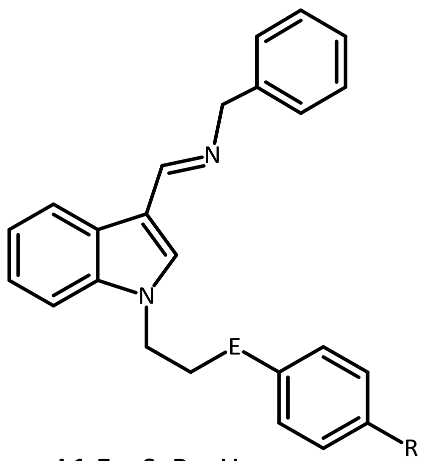
ABSTRACT

Thesis is on indole based ligands and their palladacycles. Ligands in which palladation can be managed at C-2, C-3 and C-4 of indole moiety have been designed. Mono-, bi- and tri-metallic Pd(II) complexes of indole based ligands have been prepared. The catalytic potential of palladium complexes of indole based ligands for Suzuki-Miyaura coupling, Heck coupling and allylation reactions has been explored.

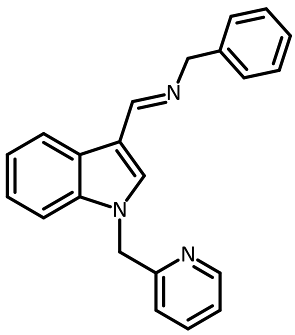
The first group is of chalcogenated indole based unsymmetrical hybrid (N,C,E)-pincer ligands (E = S/Se/Te) **L1**−**L3**. These ligands and their Pd(II) complexes **1**−**3** have been synthesized and characterized with ^{1}H, $^{13}C\{^{1}H\}$, $^{77}Se\{^{1}H\}$ and $^{125}Te\{^{1}H\}$ NMR and HR-MS. Single crystal structures of **1** and **2** have revealed square planar geometry of Pd.



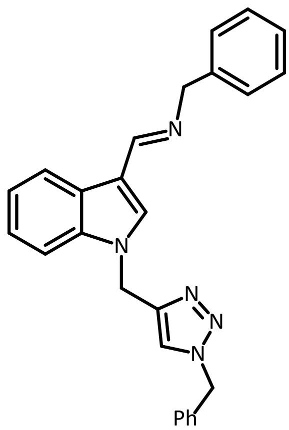
L1:E = S, R = H
L2:E = Se, R = H
L3:E = Te, R = OMe

The catalytic activities of **1**–**3** were tested for Heck coupling reactions of several aryl bromides (including deactivated ones) with *n*-butylacrylate. Palladacycles **1** and **2** was found to show better efficiency than complex **3**. Palladium(II) complexes **1** and **2** were further tested as catalyst for allylation of aldehydes and found to show excellent catalytic activity (with 1 mol% of complex **1**/**2**) for a wide substrate range.

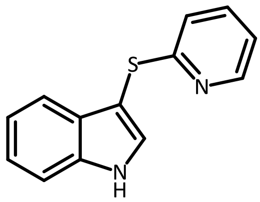
The second group of ligands prepared are unsymmetrical (N,C,N′)-pincers **L4** and **L5**. They were reacted with Na_2PdCl_4 to form Pd(II) complex **4** and **5**. Synthesis of 3-sulfenylindole ligand **L6** have been carried out by K_2CO_3 promoted sulfenylation of indole. They have been characterized with ^{1}H, $^{13}C\{^{1}H\}$ and HR-MS. Single crystal structures of Pd(II) complexes **4**−**6** have been determined with X-ray diffraction.



L4



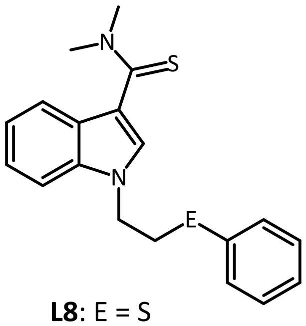
L5



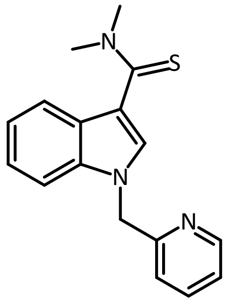
L6

The ligands **L4** and **L5** coordinate with Pd in a tridentate (N,C^{-},N′) mode forming five- and six-membered rings with palladium. The ability of the **L6** to coordinate with Pd(II) through nitrogen atom and C3 atom of the indole nucleus, forming a spiro ring is worth noting. The complexes **4** and **5** have been explored as catalyst for allylation of aldehydes and complex **6** for Suzuki-Miyaura coupling.

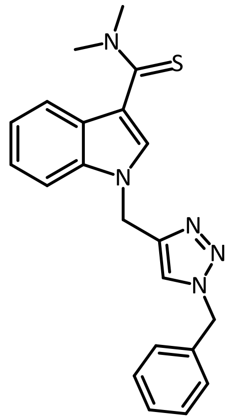
Thioamide based ligands **L7**−**L11** constitute another class of indole based ligands. Their coordination with Pd(II) has been investigated. The ligands and complexes have been characterized with ^{1}H, $^{13}C\{^{1}H\}$ and $^{77}Se\{^{1}H\}$ NMR and X-ray diffraction (on single crystals of **7A**,**7B** and **10**). Sulphur in complex **7A** bridge two palladium centers. For Suzuki-Miyaura coupling reactions the complexes of **L7−L11** are efficient as catalyst as their 0.01−0.1 mol% was found sufficient for coupling.



L8: E = S
L9: E = Se

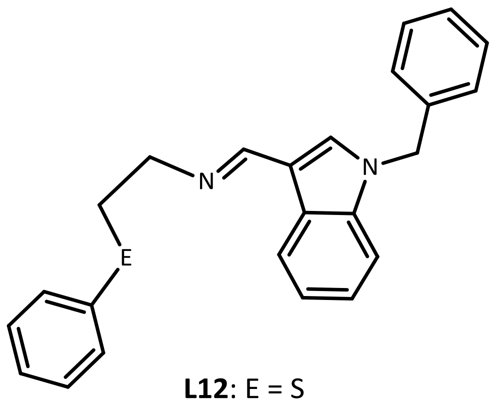


L10



L11

Terdendate ligands **L12**–**L14** constitute the last group of indole based ligands reported in the thesis. Their Pd(II) complexes have been synthesized by their reaction with sodium tetrachloropalladate(II) in presence of anhydrous sodium acetate. These ligands and their Pd(II) complexes **1−3** have been synthesized and characterized with ^{1}H, ^{13}C{^{1}H}, ^{77}Se{^{1}H} and ^{125}Te{^{1}H} NMR and HR-MS. The structure of complex **12** has been established with X-ray crystallography. It has peri-palladation (*i.e* or palladation at C-4 of the indole moiety) and distorted square-planar geometry around the metal centre.



L12: E = S
L13: E = Se
L14: E = Te

The catalytic efficiency of **12−14** for Suzuki-Miyaura coupling appears promising as their 0.05−1.0 mol % was sufficient for good conversions. Palladacycles containing S/Se donor site are better catalysts for SMC than that having Pd−Te bond.

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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	sulphur
Se	selenium
SMC	Suzuki-Miyaura Coupling
t	triplet
Te	tellurium
THF	tetrahydrofuron
TLC	thin layer chromatography
TMS	tetrametylsilane
XRD	x-ray diffraction