ORGANOCHALCOGEN LIGATED/STABILIZED PALLADIUM AND RUTHENIUM SPECIES: CATALYSTS FOR ORGANIC REACTIONS

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by

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Submitted

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

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Thesis dedicated to all my

loving friends

CERTIFICATE

This is to certify that the thesis entitled, **"ORGANOCHALCOGEN LIGATED/STABILIZED PALLADIUM AND RUTHENIUM SPECIES: CATALYSTS FOR ORGANIC REACTIONS"** being submitted by **Mr. SATYENDRA KUMAR** 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. Satyendra Kumar 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

Palladium and ruthenium complexes of organochalcogen ligands and their applications in catalysis are focus of the thesis. Multidentate organochalcogen ligands **L1**–**L10** of the thesis are depicted below (Chart 1).

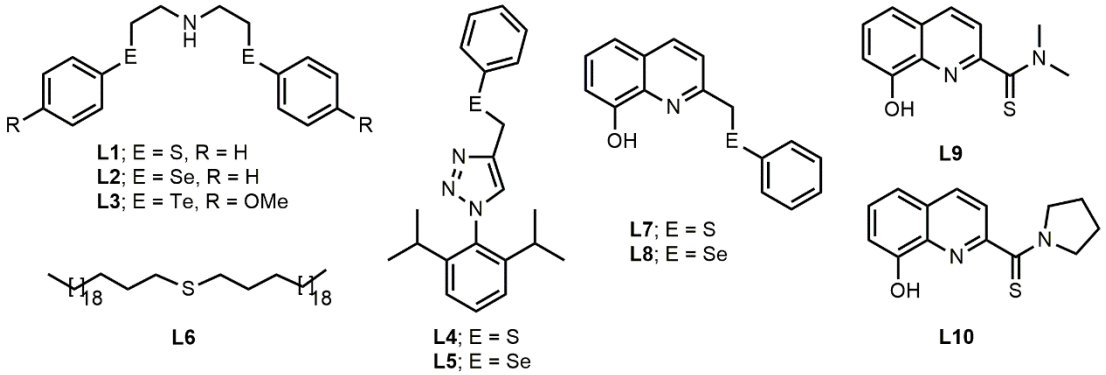

Chart 1

The (E, N, E) pincer ligands $(ArECH_2CH_2)_2NH$ (**L1**/**L2**: Ar = Ph, E = S/Se; **L3**: Ar = CH_3O-*p*-C_6H_4, E=Te) synthesized by reaction of PhS^-/$PhSe^-$/CH_3O-*p*-$C_6H_4Te^-$ with bis(2-chloroethyl)amine react with Na_2PdCl_4 in aqueous ethanol, resulting in nearly square planar diamagnetic complexes [Pd(**L**)Cl]Cl (**1**−**3**), where **L** = **L1**−**L3**. The single crystal structures (determined with X-ray diffraction) of **2** and **3** have been solved. The **1** and **2** at 2−3 mol% loading show better catalytic activity for Suzuki-Miyaura coupling (SMC) than **3**, as higher yields were observed with them in a relatively short time. The addition of TBAB was essential in some cases to get good yield of cross-coupled product. The SMC appears to be catalyzed with Pd(0) nanoparticles (NPs) generated *in situ* in the course of reaction. The NPs have been isolated and HRTEM studies on them have revealed their size as ~1−3 nm. The isolated NPs show catalytic activity for SMC independently. The two-phase test suggests a relatively low contribution of homogeneous Pd species in the catalysis.

The bidentate 1-(2,6-diisopropylphenyl)-4-(phenylthio/selenomethyl)-1*H*-1,2,3-triazole (**L4**/**L5**) synthesized by 'Click' reaction, reacts with $[Pd(CH_3CN)_2Cl_2]$ and $[\{(\eta^6\text{-benzene})RuCl(\mu\text{-}Cl)\}_2]$ (followed by reaction with NH_4PF_6), at room temperature resulting in complexes [Pd(**L**)Cl_2] (**4** and **5**) and $[(\eta^6\text{-}C_6H_6)Ru(\mathbf{L})Cl]PF_6$ (**6** and **7**) (**L** = **L4** or **L5**) respectively. Single crystal structures of **4**−**7** were solved. The geometry of Pd in **4** and **5** is distorted square planar while in case of **6** and **7** there is a pseudo-octahedral "piano-stool" type disposition of donor atoms around Ru. The catalytic activity of complexes **4** and **5** (optimum loading 0.001−2 mol% of Pd) was explored for SMC in water and Sonogashira coupling reactions. For SMC no additive or phase transfer catalyst was added. For catalysis of transfer hydrogenation (TH) of aldehydes and ketones both half sandwich Ru(II) complexes **6** and **7** were explored. Their optimum loading as catalyst was found to be 0.1−0.4 mol % of Ru. In TH both water used as a solvent, and glycerol as a hydrogen source are environmentally friendly. The **4** having sulfur ligand is more efficient than **5** (Se analog) for both SMC and Sonogashira coupling. The activity of **6** and **7** for TH is in the order Se > S.

Monodentate *n*-didocosyl sulfide (**L6**), explored as a protector of palladium nanoparticles (**1**-**6**) was synthesized by reaction of *n*-bromodocosane with Na_2S, generated *in situ* by reduction of elemental sulfur with $NaBH_4$. Pd NPs (**1-6)** protected with **L6** were prepared using different palladium precursors in the presence of varying amount of **L6** (Pd : **L6** ratio 1:2 and 4:1). The resulting spherical NPs have been characterized by powder X-ray diffraction, SEM, EDX, UV-Vis, and HRTEM. The maximum number of NPs (**1-6)** has size (nm) in the ranges: ~18-19, 4-5, 5-7, 4-6, 7-9 and 4-6 respectively. The precursor of palladium affects the size, shape and dispersion of the NPs. The reaction of Na_2PdCl_4 with **L6** resulted in complex [Pd(**L6**)$_2Cl_2$] (**8**). The NPs shows good catalytic activity for SMC of various aryl chlorides/bromides with phenylboronic acid at low

catalyst loading (0.1−0.5 mol % of Pd). The conversion is good for some aryl halides in a short reaction time of the order 1-2 h. The distinct advantage of NPs **1**−**6** is that they can be separated and reused at least up to five times. The complex **8** equivalent to 0.001 mol % Pd is efficient for SMC of some aryl halides, as good conversion into coupled products has been observed. Two phase test, conducted for complex **8** and NPs **2**, suggests the contribution of both homogeneous and heterogeneous catalytic pathway to overall catalysis.

Quinoline-based unsymmetrical pincer ligands (**L7**–**L10**) having (O^-, N, E) donor sites (where E = S/Se), and their Pd(II) complexes have been synthesized. The reaction of Na_2PdCl_4 with **L7**–**L10** results in complexes **9**–**12** easily. Thioamide based ligands **L9** and **L10** have been synthesized by Willgerodt-Kindler reaction of aldehydes/ketones. Single crystal structures of **L7** and complexes **9** and **10** have been established. The geometry around Pd in **9** and **10** is distorted square planar. Complexes **9** and **10** were explored for SMC. The required catalyst loading 0.1−0.5 mol% appears promising for good conversions of aryl bromides into coupled products. DFT calculations support that experimental results of catalysis and structural features (bond lengths and bond angles) of complexes of **9** and **10**. One pot thermolysis of complex **9** in the presence of TOP/ OA+ODE (1:1 mixture) surfactant at moderate temperature results in cubic palladium oxide (PdO) nanoparticles. HRTEM, SEM–EDX and powder XRD have authenticated these NPs. The phase of PdO NPs was authenticated by matching their powder XRD patterns with those reported in JCPDS (Card No. 65−5261).

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GLOSSARY OF SYMBOLS AND ABBREVIATIONS

%	percent
δ	chemical shift
ν	frequency
Å	angstrom
Ar	Aryl
AAS	Atomic Absorption Spectroscopy
µL	microlitre
°C	degree centigrade
br	broad signal
n-Bu	*n*-butyl
C−C	carbon−carbon
cm	centimeter
CH_2Cl_2	dichloromethane
$CHCl_3$	chloroform
CH_3CN	acetonitrile
d	doublet
dipp	2,6-diisoprpylphenyl
DCM	dichloromethane
DMF	dimethylformamide
DMSO	dimethyl sulfoxide
DFT	density functional theory
EDX	energy dispersive X-ray analysis
e.g.	for example
g	gram
h	hour
HR	high resolution
Hz	hertz
HC	Heck coupling
Hg	Mercury
HOMO	higest occupied molecular orbital
i.e.	that is

kV	kilovolt
LUMO	lowest unoccupied molecular orbital
m	multiplet
m/z	mass/charge
MHz	megahertz
M^+	molecular ion
M	molar
mmol	millimole
mol	mole
mL	milliliter
m.p.	melting point
nm	nanometer
NP	nano-particle
NMR	nuclear magnetic resonance
Pd	palladium
Ph	phenyl
n-Pr	*n*-propyl
Ru	ruthenium
s	singlet
S	sulphur
Se	selenium
SEM	scanning electron microscopy
SMC	Suzuki-Miyaura Coupling
t	triplet
TH	transfer hydrogenation
THF	tetrahydrofuron
TEM	transmission electron microscopy
TMS, TBAB, TOP	tetrametylsilane, tetrabutyl ammonium bromide, trioctyl phosphine
XRD	X-ray diffraction
P-XRD	powder X-ray diffraction