QUINOXALINE AND TRIAZOLE BASED SULFUR / SELENIUM LIGANDS: METAL COMPLEXES FOR CATALYTIC ACTIVATION

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by

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Department of Chemistry

Submitted

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CERTIFICATE

This is to certify that the thesis entitled, **"QUINOXALINE AND TRIAZOLE BASED SULFUR / SELENIUM LIGANDS: METAL COMPLEXES FOR CATALYTIC ACTIVATION"** being submitted by **Mrs. FARIHA SALEEM** 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. Mrs. Fariha Saleem 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:

New Delhi

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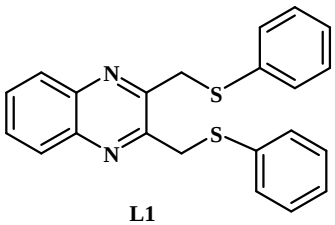
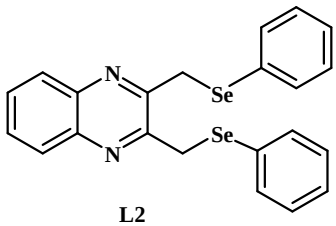
ABSTRACT

The focus of thesis is on (i) designing of bidentate chalcogenoether ligands containing S or Se along with N donor site (from quinoxaline or click generated 1,2,3-triazole moietie), (ii) exploring their coordination chemistry with Pd(II), (η^6-benzene)Ru(II) and (η^5-pentamethylcyclopentadiene) Rh(III) / Ir(III) and (iii) investigating the designed metal complexes of organochalcogen ligands for various catalytic organic transformation *viz.* C−C coupling reactions, NMO based oxidation of alcohols, Oppenauer-type oxidation of alcohols and transfer hydrogenation reaction of carbonyl compounds. Attempts to understand the nature of true catalytic species generated *in situ* from palladium(II) complexes has been made. The following new multidentate organochalcogen ligands with **L1**–**L10** were designed:



L1



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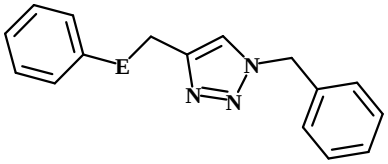
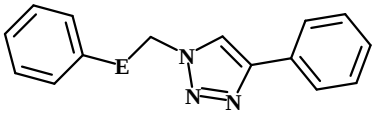
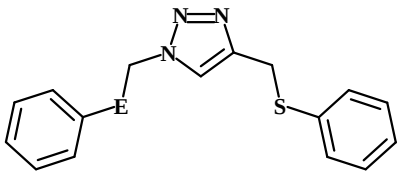


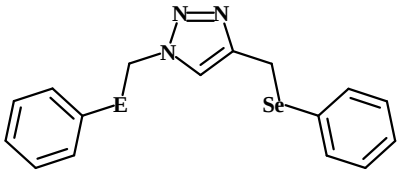
E = S; L3
E = Se; L4



E = S; L5
E = Se; L6



E = S; L7
E = Se; L8



E = S; L9
E = Se; L10

All the ligands and complexes exhibit characteristic HR-MS, IR, ^{1}H, ^{13}C{H}, and ^{77}Se{H} NMR spectra.

The bidentate 2,3-di[(phenylthio/-seleno)methyl]quinoxaline (**L1** / **L2**) synthesized by the reaction of *in situ* generated PhS^- / $PhSe^-$ with 2,3-bis(bromomethyl)quinoxaline, on reaction with Na_2PdCl_4, results in complexes $[Pd_2(\mathbf{L1}-H)_2Cl_2]$ (**1**) / $[Pd\mathbf{L_2}Cl_2]$ (**2**) respectively. Structures of Single crystals by X-ray diffraction of ligands and complexes have been determined. The **1** is a palladacycle, formed by external base free activation of benzyl group's C(sp^3)−H of **L1** whereas **L2** behaves in **2** as a bidentate ligand resulting in formation of seven membered chelate ring with Pd(II) center. In both the complexes **1** and **2**, the geometry around Pd centre is distorted square planar. Complexes **1** and **2** were explored to catalyzed Suzuki−Miyaura coupling reactions of several aryl bromides (including deactivated ones). The palladacycle **1** shows better catalytic efficiency than complex **2**. The catalysis with **1 / 2** has been found to proceed *via in situ* generated nanoparticles (size < 2 nm) composed of palladium and sulfur or selenium and protected by **L1** or **L2**. These NPs were characterized by SEM, TEM and EDX and found catalytically active independently. The catalysis appears to be of cocktail type (i.e. homogeneous and heterogeneous in parts), on the basis of two phase tests.

The bidentate 1-benzyl-4-((phenylthio)-/(phenylseleno)methyl)-1H-1,2,3-triazole (**L3** / **L4**) and 4-phenyl-1-((phenylthio)-/(phenylseleno)-methyl)-1H-1,2,3-triazole (**L5** / **L6**) were synthesized by the 1,3-dipolar cycloaddition of azides to terminal alkynes (click reaction). Their metal complexes **(3−8)** are formed by direct reaction with $[Pd(CH_3CN)Cl_2]$ and $[\{(\eta^6\text{-benzene})RuCl(\mu\text{-}Cl)\}_2]$. The coordination geometry around Pd is almost square planar. There is a "pseudo-octahedral" half sandwich "Piano-Stool" geometry around the Ru center in **7**−**8**. The Pd(II) complexes were explored for C−C coupling reactions (Suzuki-Miyaura and Heck), whereas Ru(II) complexes were investigated to catalyze oxidation of alcohols and transfer hydrogenation of ketones. The order of optimum loading of **3** / **4** as a catalyst has been found to be 0.01 mol%.

Complexes **3** / **4** are more efficient for Suzuki than Heck coupling. Further the efficiency of catalyst **3** has been found to be higher than that of complex **4**. Complexes **3** and **4** are probably pre-catalysts and dispense catalytically active Pd NPs in the course of reaction. Nps (size 3−11 nm) appear to have a role in the catalysis, as they show catalytic activity after isolation also. The particles were isolated and subjected to SEM, SEM-EDX and HR-TEM. The two-phase test has suggested that the catalysis is cocktail type. Complexes **5**–**8** have been used for oxidation of alcohols and transfer hydrogenation of ketones. Complex **7** was found to be most efficient for the two catalytic reactions (conversion 95%–97%). Oxidation of alcohols appears to involve the formation of Ru(IV)=O species, whereas catalytic transfer hydrogenation reactions proceed *via* formation of a metal-hydride intermediate. The catalytic processes are more efficient with complexes, in which N(2) of the triazole is involved in coordination with Ru metal. These efficiency orders are supported by HOMO−LUMO energy gaps estimated by DFT calculations.

The half-sandwich Cp*Rh(III) / Ir(III) complexes of bidentate ligands **L3**–**L6**, prepared by reacting them with $[(\eta^5\text{-Cp*})\text{RhCl}(\mu\text{-Cl})]_2$, and $[(\eta^5\text{-Cp*})\text{IrCl}(\mu\text{-Cl})]_2$ at room temperature followed by treatment with NH_4PF_6. The crystal structures of **10**, **11** and **14** established by X-Ray crystallography reveal a pseudo-octahedral “piano-stool” disposition of donor atoms around metal centre. These complexes have been explored as a catalyst in transfer hydrogenation of carbonyl compounds using 2-propanol as hydrogen donor, N-methylmorpholine-N-oxide (NMO) based and Oppenauer-type oxidation of alcohols. Efficiency for Oppenauer type oxidation is somewhat slower than that based on NMO. Both the type of oxidation of alcohols reactions involves the formation of metal hydride species. In TH the species formed with loss of Cp* appears to be involved in catalysis. The catalytic processes are more efficient with Rh complexes than the corresponding Ir analogue. Results of DFT calculations are consistent with the various experimental results.

A multidentate 1,2,3-triazole based chalcogen ligands **L7**–**L10** and their Pd(II) and Ru(II) complexes have been synthesized by their reaction with [Pd(CH_3CN)Cl_2] and [{(η^6-benzene)RuCl(μ-Cl)}$_2$] respectively. The structures of complexes (**19**–**24**) have been established with X-Ray crystallography. Pd(II) complexes (**17**–**20**) were explored for Suzuki-Miyaura coupling reactions and Ru(II) complexes in transfer hydrogenation of carbonyl compounds (2-propanol and glycerol as hydrogen donor). The oxidation of alcohols using NMO as an oxidant and Oppenauer-type oxidation of alcohols are also catalysed by these Ru complexes. The catalytic efficiency of **17**−**20** appears promising as their 0.01 mol % was sufficient for good conversions. DFT calculations on Ru(II) complexes (**21**−**24)** have been made which support experimental results of catalysis and structural aspects of complexes.

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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−C	carbon−carbon
cm	centimeter
CH_2Cl_2	dichloromethane
$CHCl_3$	chloroform
CH_3CN	acetonitrile
Cp*	pentamethylcyclopendadiene
CuAAC	copper(I) catalyzed azide–alkyne cycloaddition
d	doublet
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
Ir	iridium
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
NMO	*N*-methylmorpholine-*N*-oxide
Pd	palladium
Ph	phenyl
n-Pr	*n*-propyl
Ru	ruthenium
Rh	Rhodium
S	sulphur
Se	selenium
SEM	scanning electron microscopy
SMC	Suzuki-Miyaura Coupling
t	triplet
TH	transfer hydrogenation
THF	tetrahydrofuron
TEM	transmission electron microscopy
TMS	tetrametylsilane
XRD	x-ray diffraction
PXRD	powder x-ray diffraction