PALLADIUM(II) AND RUTHENIUM(II) COMPLEXES OF ORGANOCHALCOGEN LIGANDS: APPLICATIONS IN CATALYTIC ORGANIC SYNTHESIS

By

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CERTIFICATE

This is to certify that the thesis entitled, "**PALLADIUM(II) AND RUTHENIUM(II) COMPLEXES OF ORGANOCHALCOGEN LIGANDS: APPLICATIONS IN CATALYTIC ORGANIC SYNTHESIS**" being submitted by Ms. DIPANWITA DAS 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. Dipanwita Das 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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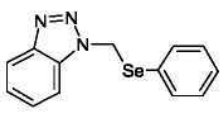
DIPANWITA DAS

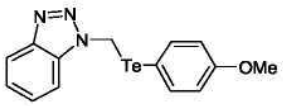
ABSTRACT

The chemistry of multidentate organochalcogen ligands has got attention in the recent past due to their potential for several applications including catalytic ones. The present thesis is thus focused on designing of bi-, tri- and tetradentate compounds containing S, Se and Te donor sites along with/without N and exploring their co–ordination chemistry with Pd(II) and Ru(II) species. The Pd(II) and (η^6-benzene/*p*-cymene)Ru(II) complexes of these chalcogenated ligands have been studied for catalytic C–C coupling reactions and oxidation of alcohols and results are presented in the thesis. Half sandwich complexes of Ru(II) having (η^6-benzene / *p*-cymene) unit because some of them are known for their diverse catalytic activities and promising anticancer activity. As such the piano-stool type species containing organoselenium or organotellurium moiety are very little known and therefore worth exploring.

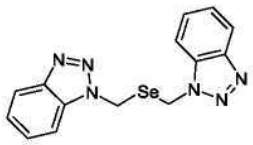
The following new multidentate organochalcogen ligands with $\mathbf{L^1}$–$\mathbf{L^9}$ were designed:



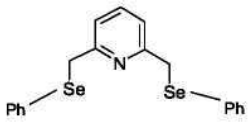
$\mathbf{L^1}$



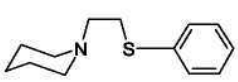
$\mathbf{L^2}$



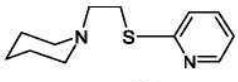
$\mathbf{L^3}$



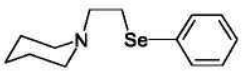
$\mathbf{L^4}$



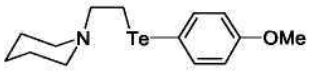
$\mathbf{L^5}$



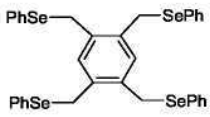
$\mathbf{L^6}$



$\mathbf{L^7}$

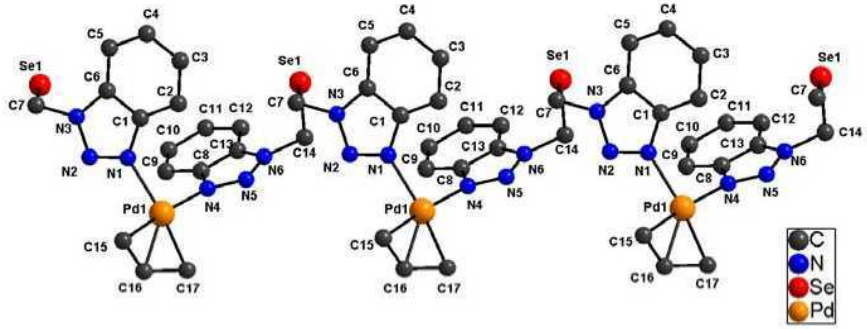


$\mathbf{L^8}$



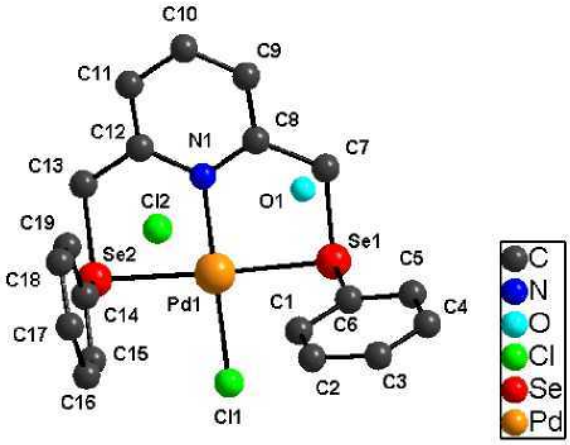
$\mathbf{L^9}$

The crystal structures of $\mathbf{L^1}$, $\mathbf{L^2}$ and $\mathbf{L^3}$ have been solved by X-ray crystallography. The complexes $[PdCl_2(\mathbf{L})]$ (where $\mathbf{L} = \mathbf{L^1}$: **1**, $\mathbf{L} = \mathbf{L^2}$: **2**) have been found promising for Heck and Suzuki–Miyaura C–C coupling reactions. The half sandwich species $[RuCl(\eta^6$-*p*-cymene)$(\mathbf{L})][PF_6]$ ($\mathbf{L} = \mathbf{L^1}$:**3**, $\mathbf{L} = \mathbf{L^2}$: **4**) have been found promising for catalytic oxidation of primary alcohols with N-methylmorpholine-N-oxide (NMO). Palladium complexes **1** and **2**, show $^{77}Se\{^1H\}/^{125}Te\{^1H\}$ NMR spectra having signals at higher frequency relative to the corresponding free ligand which support the formation of metal–chalcogen bond. The single crystal structures of complexes **3** and **4** have been solved. In the molecular structures of cation of **3** and **4** Ru exhibits the pseudo-octahedral half sandwich ''piano-stool" disposition around Ru. The ring of *p*-cymene occupies one face of octahedron and the other is occupied by Se/Te, Cl and N. The $\mathbf{L^3}$ has been found to form polymeric complex with (η^3-allyl)Pd(II) unit unexpectedly in which 'soft' donor site Se remains dormant instead of forming bond with "soft" palladium preferentially. These polymeric palladium complexes are also promising for catalyzing Heck C-C coupling reactions homogeneously. The crystal structures of $[Pd(\eta^3\text{-}C_3H_5)(L)]\cdot ClO_4$ (**5**) and $[Pd(\eta^3\text{-}C_3H_5)(L)]\cdot PF_6$ (**6**) have been solved and it was observed that on changing anion ClO_4^- with PF_6^- the nature of chain is not affected.



Molecular structure of a part of polymeric chain in **5**

The pincer (Se, N, Se) ligand, $\mathbf{L^4}$ forms two types of complexes, [PdCl($\mathbf{L^4}$)]Cl (**7**) and Na[PdCl($\mathbf{L^4}$)][$PdCl_4$](**8**), when reacted with $Na_2[PdCl_4]$ depending upon solvent. The complex **8** is formed in MeOH and **7** in acetone-water mixture. Complex cation **8** [{PdCl($\mathbf{L^4}$)}$^+$] crystallizes with counter anion $[PdCl_4]^{2-}$ available from the unreacted $Na_2[PdCl_4]$. The $\mathbf{L^4}$, **7** and **8** have been characterized by ^1H, ^{13}C, ^{77}Se NMR spectra and X-ray crystallography. Se-77 NMR has indicates that both Se donor sites of $\mathbf{L^4}$ are engaged in coordination with Pd which is also supported by X-ray data. The geometry of palladium is nearly square planar. The molecular structure of **7** is shown below.



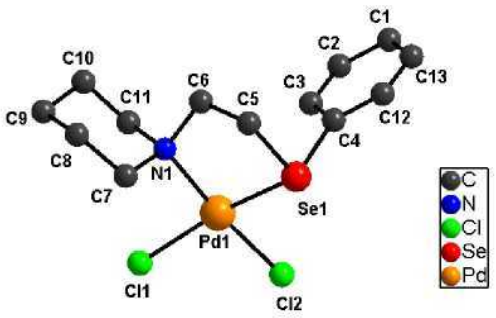
Molecular structure of **7**

$\mathbf{L^4}$ on reaction with di-μ-chlorobis{η^6-benzene)dichlororuthenium(II)}(**a**) forms $[Ru(CH_3CN)_2Cl(\mathbf{L^4})][PF_6]$ (**9**), when $\mathbf{L^4}$**:a** = 2:1 and stirring time of reactants is 2 h in a 1:1 mixture of acetonitrile and methanol, whereas for $\mathbf{L^4}$**:a** = 4:1 in methanol with stirring time 2 h the complex formed is $[Ru(\mathbf{L^4})_2][ClO_4]_2$ (**10**). This is first example in which the

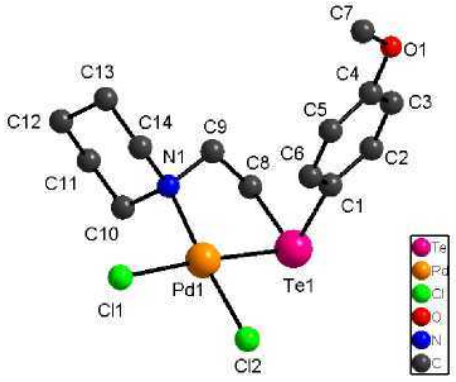
benzene ring is substituted irrespective of metal:ligand ratio. The geometry around Ru in complexes **9** and **10** is distorted octahedral.

The complexes **7** and **8** were explored as catalysts for Heck coupling reaction. The compound **8** has two palladium centres and therefore is expected to be a catalyst of higher activity than **7**, which is found to be experimentally true. The TON values for complexes **7** and **8** are upto 97 % and 9.7 x 10^4 respectively.

Piperidine derivatives are important building blocks in organic synthesis and biologically active. The ligands $\mathbf{L^5}$, $\mathbf{L^6}$, $\mathbf{L^7}$ and $\mathbf{L^8}$ have been designed and their ligand chemistry with Pd(II) has been explored. All the ligands $\mathbf{L^5}$, $\mathbf{L^6}$, $\mathbf{L^7}$ and $\mathbf{L^8}$ and their complexes **11-14** have been characterized by ^{1}H, ^{13}C, ^{77}Se and ^{125}Te NMR spectra. The ^{77}Se and ^{125}Te NMR spectra of $\mathbf{L^7}$ and $\mathbf{L^8}$ show peaks at 279 and 200 ppm respectively which shift to higher frequency on complex formation. The crystal structures of **12**, **13** and **14** have been solved. The molecular structures of **13** and **14** are shown in Figs. Given below. The geometry around Pd is square planar. The Pd—Se and Pd—Te bond lengths are found to be 2.3632(15) and 2.5145(6) Å respectively. The Se–Pd–N and Te–Pd–N bond angles are found to be 89.1(2)° and 90.20(14)° respectively.



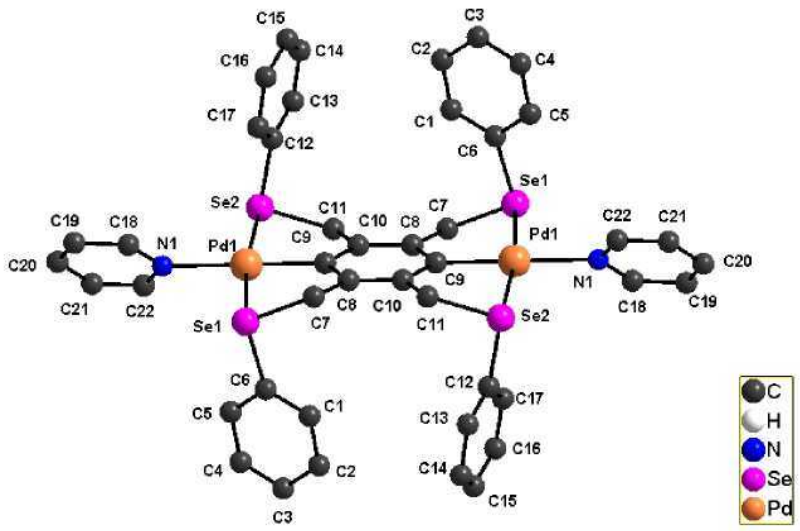
Molecular structure of **13**



Molecular structure of **14**

The catalytic potential of complexes **11-14** has been explored for Heck C-C coupling reactions with aryl bromides. These results are promising. Yields upto >90% are obtained for some substrates in case of **13** and **14**. The electron– withdrawing groups on the aryl ring are observed to increase the reaction rate. The Pd(II) complexes of seleno- and telluroether are found to be more efficient than thioethers.

The syntheses of ligand $\mathbf{L^9}$ and its bimetallic complexes with and [(η^3-allyl)Pd(II)] (**15**), bispincer Pd(II) complex (**16**) and [(η^6-benzene)Ru(II)] (**17**) have been carried out. Two Se atoms coordinate with one metal ion forming seven-membered chelate ring in **15** and **17** (on each side of phenyl ring) while in **16** two Se and one C atom coordinate with each Pd forming a bispincer complex. The ligand $\mathbf{L^9}$ and its complexes **15, 16** and **17** have been characterized by ^{1}H, ^{13}C and ^{77}Se spectra as well as X-ray crystallography. The ^{77}Se NMR spectrum of $\mathbf{L^9}$ shows a signal at 361.8 ppm which shift to higher frequencies by ~30-37 ppm on complexation. The molecular structures of **16** is shown below. The geometry around Ru is pseudo-octahedral and geometry around Pd roughly square planar.



Molecular structure of **16**

The complexes **15** and **16** have been explored as catalyst for Heck reaction at concentration 0.001 mol % using *n*-butylamine as base. Complex **16** shows much higher catalytic activity than **15** with high yield upto 95% and TON value upto 95000. The substrates with electron withdrawing groups give better yields.

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