ORGANOCHALCOGEN LIGATED PALLADIUM(II) AND PALLADIUM(0) FOR CARBON–CARBON COUPLING REACTIONS

By

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DEDICATED

TO

MY PARENTS

CERTIFICATE

This is to certify that the thesis entitled, **"ORGANOCHALCOGEN LIGATED PALLADIUM(II) AND PALLADIUM(0) FOR CARBON–CARBON COUPLING REACTIONS"** being submitted by **Mr. GYANDSHWAR KUMAR RAO** 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 him. Mr. Gyandshwar Kumar Rao 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: 07/11/2012

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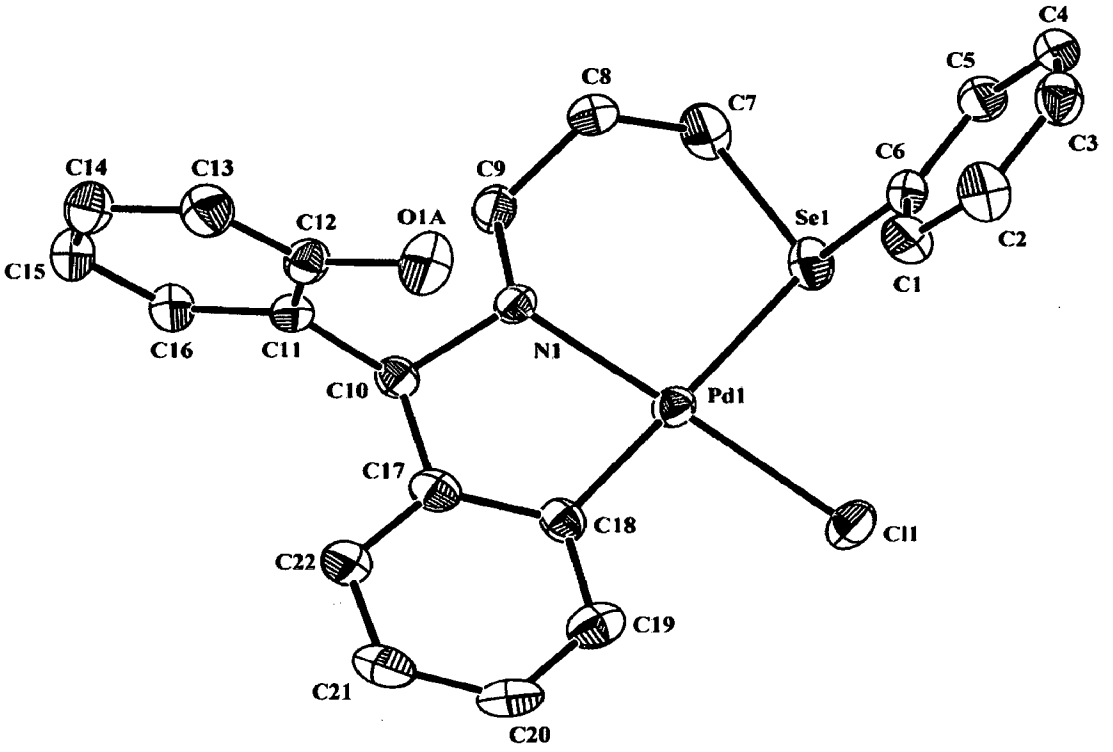
ABSTRACT

Palladium(II) complexes of hybrid organochalcogen ligands containing O and N along with S, Se and Te have emerged as a new class of efficient catalysts/precatalysts for C–C coupling reactions such as Suzuki–Miyaura, Heck and Sonogashria. For coupling of aryl chlorides and electron-rich aryl bromides, Pd(II) complexes of bulky and electron-rich phosphines, carbenes, pincer and palladacycles are known to be efficient catalysts/precatalysts. Generation of Pd(0) species including Pd nano-particles has been noticed in most of the cases in the course of catalysis and therefore these Pd complexes are considered many times as dispensers of Pd(0) species. The Pd nano-particles stabilized by dendrimers, organic/organofluorous ligands, polymers, ionic liquids and surfactants have been found independently efficient and recyclable catalysts for Suzuki-Miyaura coupling reactions. However, most of the Pd-complex based catalysts or pre-catalysts mentioned above known for cross coupling are sensitive to air and/or moisture. The Pd(II) complexes of chalcogenated Schiff bases, chalcogeno-ether and palladacycles have emerged as catalysts which are air stable, moisture insensitive and efficient for reactions such as Suzuki-Miyaura and Heck coupling. The catalytic efficiency of these Pd(II) complexes depends on the nature of other donor groups present in the ligand. The strong donor properties of chalcogens, particularly sulphur and selenium may be one of the reasons for the efficiency shown by Pd-complexes of organochalcogen ligands for catalytic C–C coupling.

The present thesis is focused on designing of mono-, bi- and tri-dentate chalcogenoether ligands containing S, Se and Te donor sites with or without N and O and exploring their coordination chemistry with Pd(II) and Pd(0) species. The Pd(II) complexes of and Pd nano-particles stabilized with selenoether have been studied for

catalytic C–C coupling reactions. The role of species generated *in situ* from molecular complexes during catalysis has been investigated.

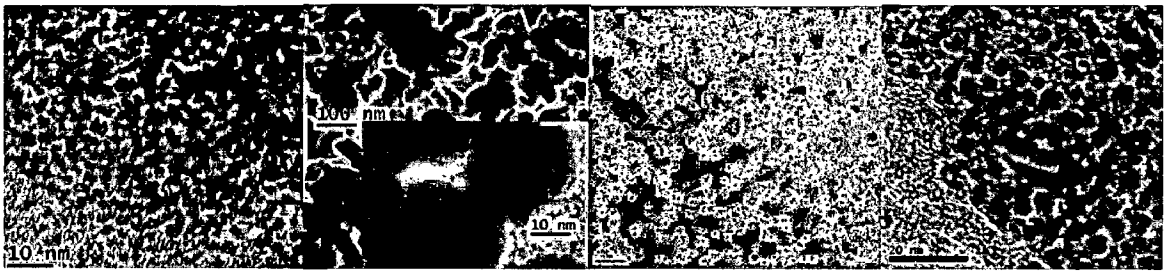
The secondary amine ligands (**L1–L4**) [**L1**: $C_6H_5S–(CH_2)_3–NH–HC(Ph)–C_6H_4–2–OH$; **L2**: $C_6H_5Se–(CH_2)_3–NH–HC(Ph)–C_6H_4–2–OH$; **L3**: $MeO–4–C_6H_4–Te–(CH_2)_3–NH–HC–(Ph)C_6H_4–2–OH$; **L4**: $C_6H_5S–(CH_2)_3–NH–HC–(Ph)C_6H_4–4–OMe–2–OH$] were prepared by the reduction of corresponding Schiff bases with $NaBH_4$ in ethanol. The ligands on reaction with Na_2PdCl_4 give complexes [PdCl(C^-, N, E)] (**1–4**) [**1**: (C^-, N, S) = **L1**–H, **2**: (C^-, N, Se) = **L2**–H, **3**: (C^-, N, Te) = **L3**–H, **4**: (C^-, N, S) = **L4**–H] were synthesized by reacting with corresponding ligands. All these compounds were authenticated by ^1H, $^{13}C\{^1H\}$, $^{77}Se\{^1H\}$ and $^{125}Te\{^1H\}$ NMR spectroscopy. The ligands bind in (C^-, N, Se) mode with Pd(II) in **2** and **4** as established by single crystal X-ray diffraction leaving the OH group uncoordinated which is probably the result of preferable *ortho*-palladation of the ligand.



ORTEP Diagram of Complex **2**

The catalytic activity of **1–4** for Suzuki-Miyaura coupling was tested by reacting aryl/heteroaryl halide with phenylboronic acid. The order of efficiency is Se palladacycle > S palladacycle > Te palladacycle. The catalytic activity of sulphated palladacycle (**1**) was significantly reduced, when –OMe group was incorporated in its architecture.

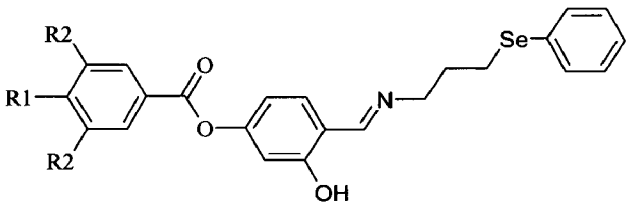
The *in situ* generated species during the course of Suzuki-Miyaura cross coupling were investigated by separating and analyzing the decomposition products



Nanoparticles of $\mathbf{Pd_{16}S_7}$, $\mathbf{Pd_{17}Se_{15}}$, $\mathbf{Pd_3Te_2}$ and $\mathbf{Pd_{16}S_7}$ obtained from **1–4** respectively obtained from **1–4**. It appears that palladium chalcogenides are true catalytic species formed from pre-catalysts **1–4** during the course of reaction. The composition of these species were found to be $\mathbf{Pd_{16}S_7}$, $\mathbf{Pd_{17}Se_{15}}$, $\mathbf{Pd_3Te_2}$ and $\mathbf{Pd_{16}S_7}$ for **1–4** respectively. The size of nano-particles obtained from **4** has been found to be significantely higher (~6 nm) than those obtained from palladacycle **1** (~2 nm). This probably results in significant lower catalytic activity of **4**.

The reaction of (3-aminopropyl)phenylselenide with benzoate esters of 2,4-dihydroxybenzaldehyde in dry ethanol gave four Schiff bases (**L5–L8**; differing in lengths and numbers of alkyl chain) containing (Se, N, O^-) donor sites. Their Pd(II)-complexes [PdCl(**L**–H) (**5–8**); **L** = **L5–L8**] have been synthesized by reacting them with Na_2PdCl_4. All of them were characterized by ^1H, $^{13}C\{^1H\}$ and $^{77}Se\{^1H\}$ NMR and elemental analyses. The nearly square planar geometry around Pd in structure of **5**

has been elucidated by X-ray diffraction on its single crystals. The ligand is coordinated with Pd in a (Se, N, O^-) mode and forms two six membered chelate rings.



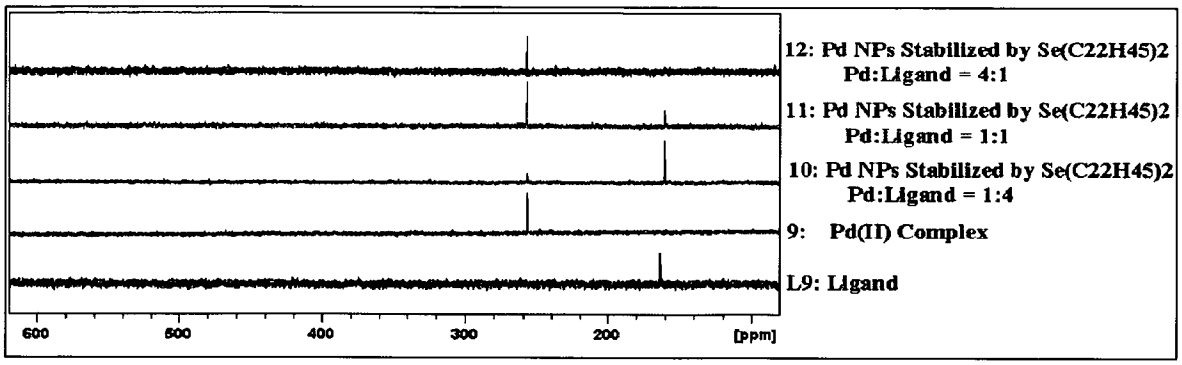
L5: R1 = OMe, R2 = H
L6: R1 = $OC_{10}H_{21}$, R2 = H
L7: R1 = R2 = $OC_{10}H_{21}$
L8: R1 = $OC_{18}H_{37}$, R2 = H

The studies on Suzuki-Miyaura, Heck and Sonogashira coupling reactions in the presence of **5–8** have revealed that catalytic efficiency increases with alkyl chain length of pendent arms of ligand for Suzuki and Heck coupling but not for Sonogashira coupling. Further investigation have suggested that **5–8** are pre-catalysts and give nano-sized Pd(0) species during the catalytic reaction. The spherical shaped nano-particles of average size ~3 nm were formed in case of both the complexes. The nano-particles, formed in case of **8** are much more uniformly dispersed than those formed from **5** and may be among the reason of its higher efficiency.

The liquid crystalline properties of ligands **L5–L8** and their Pd-complexes were investigated by differential scanning calorimetry (DSC) and polarized optical microscopy. The **L6** and **L8** have been found to show the liquid crystalline properties with a wide range of Smectic A phase.

The **L9** [$(C_{22}H_{45})_2Se$], prepared by reaction of docosyl bromide [$C_{22}H_{45}Br$] with nucleophile Se^{2-} generated in situ by borohydride reduction of selenium powder in dry ethanol forms complex [$PdCl_2$(**L9**)$_2$] (**9**) on reaction with Na_2PdCl_4 in 1:2 molar ratio. The **L9** and its complex has been characterized by ^1H, $^{13}C\{^1H\}$ and $^{77}Se\{^1H\}$ NMR and elemental analyses. The **L9**-stabilized Pd nano-particles (**10–12**)

having different Pd:**L9** ratio were synthesized by reaction of ligand with Na_2PdCl_4 followed by $NaBH_4$ reduction [**10**; Pd:**L9** = 1:4, **11**; Pd:**L9** = 1:1, **12**; Pd:**L9** = 4:1]. The Pd nano-particles **10–12** were characterized by powder XRD, $^{77}Se\{^1H\}$NMR spectroscopy, HRTEM, TEM–EDX and SEM. The size of NPs is ~3 nm in case **10** whereas ~5 nm in case of **11** and **12**.



$^{77}Se\{^1H\}$ NMR Spectra of **L9** and **9–12**

The coordination of the ligand **L9** *via* Se with Pd(II) and Pd(0) nano-particles was supported by $^{77}Se\{^1H\}$ NMR spectroscopy. In the spectra of **10–12** intensities of signals reveal that the ratio of weakly and strongly coordinated **L9** is higher for **10** than that of **11.** The $^{77}Se\{^1H\}$ NMR spectrum of **12** (Pd:**L9** ratio 4:1) suggest that almost all **L9** molecules are strongly coordinated to nano-particles.

The complex **9** has been found to be efficient catalyst for Suzuki-Miyaura coupling. The **9** showed catalytic activity for ArCl in the presence of its 2–5 mol%. For aryl bromides it showed high catalytic activity as its 3×10^{-5} to 0.1 mol% was found sufficient for good conversions.

The distinct feature of Suzuki coupling reactions catalyzed by **10–12** is the time for maximum conversion which is found significantly short (20 min to 3 h). The efficiency of **10** was found better than those of **11** and **12** as it was able to catalyze the reactions to give comparable conversions at lower loading. The TEM image of nano-

particles obtained after using **10** for five times suggest that aggregation of nano-particles is not extensive which probably results in their recyclability.

2–Chloroethylphenylsulfide on reaction with nucleophile $C_6H_5S^-$, $C_6H_5Se^-$ or $4\text{–}MeOC_6H_4Te^-$ to give bidentate (S, E) type chalcogeno ether ligands $C_6H_5S\text{–}(CH_2)_2\text{–}SC_6H_5$ (**L10**), $C_6H_5S\text{–}(CH_2)_2\text{–}SeC_6H_5$ (**L11**) and $C_6H_5S\text{–}(CH_2)_2\text{–}Te\text{–}C_6H_4\text{–}4\text{–}OMe$ (**L12**) respectively. Their complexes $[PdCl_2$(**L10–L12**)$]$ (**13–15**) have been synthesized by direct reaction of the ligands with Na_2PdCl_4. The ligands and complexes were characterized by ^1H, $^{13}C\{^1H\}$ and $^{77}Se\{^1H\}$ or $^{125}Te\{^1H\}$ NMR and elemental analysis. The single crystal structures of **13** and **15** have been determenied by X-ray diffraction. The distances of Pd–S bonds in **13** and **15** are 2.285(1) and 2.260(2) Å respectively. The Pd–Te bond length in **15** is 2.504(8) Å.

The catalytic efficiency of **13–15** has been studied for Suzuki-Miyaura coupling reaction of aryl bromides with phenylboronic acid. The catalytic efficiency of **13** and **14** was found promising as their 0.02 mol% are sufficient for significant conversions. However complex **15** does not show significant catalytic activity for Suzuki coupling. The major advantages of using these complexes are their air stability and moisture insensitivity.

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Supporting Information