CHALCOGENATED N-HETEROCYCLES BASED LIGANDS IN CATALYTIC ACTIVATION AND NANOPARTICLES SYNTHESIS

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by

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CERTIFICATE

This is to certify that the thesis entitled, **"CHALCOGENATED N-HETEROCYCLES BASED LIGANDS IN CATALYTIC ACTIVATION AND NANOPARTICLES SYNTHESIS"** being submitted by **Mr. KAMAL NAYAN SHARMA** 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. Kamal Nayan Sharma 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:

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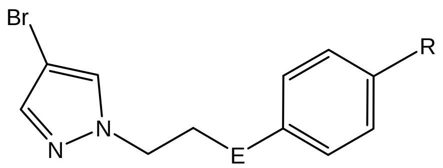
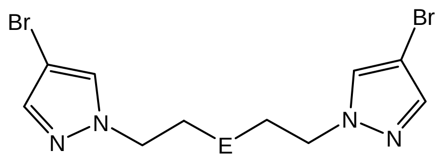
ABSTRACT

Metal complexes of chalcogenated N-heterocycles and NHCs and their application in catalysis and metal chalcogenide nanoparticles synthesis are focus of the thesis.

Synthesis and characterization of chalcogenated pyrazole based neutral bidentate (**L1**−**L3**) and tridentate (**L4**−**L6**) ligands and their Pd(II) complexes [Pd(**L1**−**L3**)Cl_2] (**1**−**3**) and [Pd(**L4**−**L6**)Cl].BF_4 (**4**−**6**) have been carried out. ^{1}H, ^{13}C{^{1}H}, ^{77}Se{^{1}H} and ^{125}Te{^{1}H} NMR, IR and HR-MS have been used to characterize them. Single crystal structures of **1**−**6** have revealed square planar geometry of Pd.



L1: E = S, R = H; **L2**: E = Se, R = H;
L3: E = Te, R = OCH_3



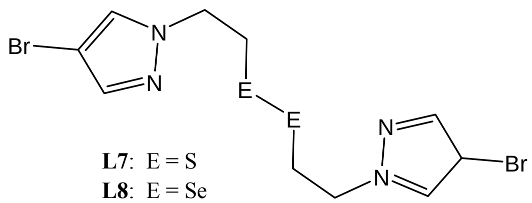
L4: E = S; **L5**: E = Se; **L6**: E = Te

Thermally stable, moisture and air insensitive complexes **1**, **2**, **4** and **5** have been found efficient catalysts (0.01 mol%) for Suzuki-Miyaura coupling reactions (Yield up to 96% in 2 h). Nanoparticles (NPs) composed of Pd and S or Se with high % of Pd (size ~3−19 nm), were formed in the beginning of these reactions. These NPs generated *in situ* from complexes **1**, **2**, **4** and **5** have been isolated and characterized with HR-TEM and SEM-EDX. The real catalysts appear to be these NPs and Pd(II) complexes **1**, **2**, **4** and **5**, most probably are the pre-catalysts.

Single source precursor (SSP) routes for the synthesis of Pd_4Se, PdSe and PdTe NPs have been developed by thermolysis of **2**, **3**, **5** and **6** at substantially lower temperature 200−250 °C. The PdP_2 NPs were formed when attempts were made to prepare nano-sized phases of palladium-sulfide by thermolysis of **1** and **4** in TOP. The

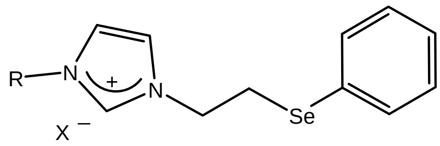
tellurium containing complexes **3** and **6** on thermolysis in TOP have given cubic PdTe nanorods whereas in OA/ODE (1 : 1) hexagonal PdTe NPs. HRTEM, SEM, SEM-EDX and powder XRD authenticate these nanostructures.

Pyrazolated disulfide and diselenide (**L7** and **L8**) and Pd(II) chalcogenolates $[PdCl(E^{\cap}N)]_2$ (**7** and **8**) and $[Pd(CH_3CN)(E^{\cap}N)]_2.2BF_4$ (**9** and **10**) [$E^{\cap}N$ = 2-(4-bromo-pyrazol-1-yl)ethanchalcogenolate; E = S/Se] have been designed and characterized with ^1H, $^{13}C\{^1H\}$ and $^{77}Se\{^1H\}$ NMR, IR and HR-MS. Single crystal structures of **8**−**10** have been determined with X-ray diffraction.



Single source precursor routes for the synthesis of palladium-chalcogenide NPs have been developed by thermolysis of **7**−**10** in 1:1 mixture of OA and ODE. $Pd_{17}Se_{15}$ NPs were formed by the thermolysis of both the Pd(II) selenolates (**8** and **10**), whereas Pd_4S NPs and a mixture of $Pd_{16}S_7$ (~68%) and PdS (~32%) NPs were obtained from Pd(II) thiolates **7** and **9**, respectively under same reaction conditions. HRTEM, SEM–EDX and powder XRD have authenticated these NPs.

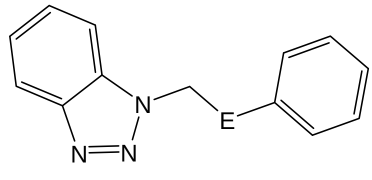
Synthesis and characterization of selenium containing imidazolium salts, (**L9**−**L11**) (differing in the chain length of alkyl substituent of N), which are precursors to (Se, C_{NHC}) ligands and Pd(II)-NHC complexes $[Pd(L{-}HX)Cl_2]$ (**11**−**13**) [L = **L9–L11**, X = I/Br] have been carried out. Single crystal structures of square planar Pd(II) complexes **11** and **12** have been established with X-ray diffraction. The complexes **11**−**13** (stable under ambient conditions) have been explored as catalyst (0.01 mol%) for Suzuki-Miyaura C−C coupling reactions and nature of real catalytic species generated *in situ* from molecular complexes established. Amongst **11–13**, the complex **13** has a pendent longest alkyl chain as a substituent on N. The length of pendent alkyl chain appears to affect catalytic activity of complex.



L9: R = CH_3; X = I
L10: R = CH_2-$(CH_2)_6$-CH_3; X = Br
L11: R = CH_2-$(CH_2)_{16}$-CH_3; X = Br

The catalytic efficiency of **13** was found to be highest whereas **11** showed significantly lower efficiency than that of **13**. As electronic properties of donor atoms remain unaffected with chain length, the variation in catalytic activities of **11−13** has been ascribed to the properties of NPs formed in the course of catalytic reactions. These NPs (~2–5 nm) were isolated and characterized by HRTEM, TEM−EDX and SEM−EDX. The NPs from **13** are much more uniformly dispersed than those formed from **11**. This appears to be cause of difference in catalytic activities of **11** and **13**.

Synthesis and characterization of benzotriazole based ligands (**L12** and **L13**), and their polymeric silver(I) complexes [$\{Ag(\mu\text{-}L)NO_3\}_n$] (**14** and **15**) have been made. The ligands and complexes have been characterized with ^1H, $^{13}C\{^1H\}$ and $^{77}Se\{^1H\}$ NMR and IR spectroscopy and X-ray diffraction (on single crystals of **14** and **15**).



L12: E = S, **L13**: E = Se

The complexes **14** and **15** (stable under ambient conditions) have been found efficient catalysts (2.0 mol%) for three-component coupling reaction between aldehyde, alkyne and amine (Yield were upto 94% in 6 h at 60 °C).

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