ORGANOSILICON LIGANDS AND THEIR METAL COMPLEXES: SYNTHESIS, STRUCTURES AND APPLICATIONS

By

NEETU RANI

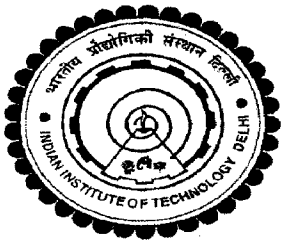
DEPARTMENT OF CHEMISTRY

Submitted

In fulfillment of the requirements of the degree of

Doctor of Philosophy

to the



Indian Institute of Technology, Delhi

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May, 2009

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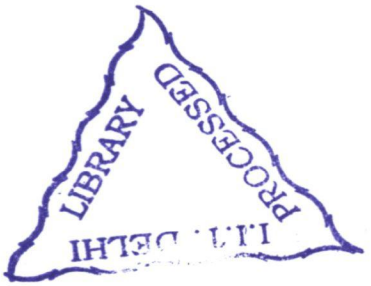

Dedicated

to my Parents

CERTIFICATE

This is to certify that the thesis entitled **"ORGANOSILICON LIGANDS AND THEIR METAL COMPLEXES: SYNTHESIS, STRUCTURES AND APPLICATIONS"**, being submitted by **Ms. NEETU RANI**, 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. Neetu Rani 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 thesis have not been submitted, in part or full, to any other university or institute for award of any degree or diploma.

Date May 13, 2009

Prof. AJAI K. SINGH

Professor

Department of Chemistry

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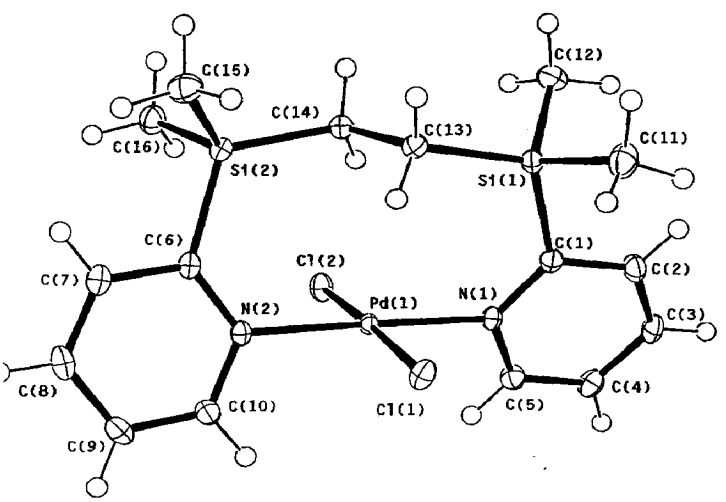
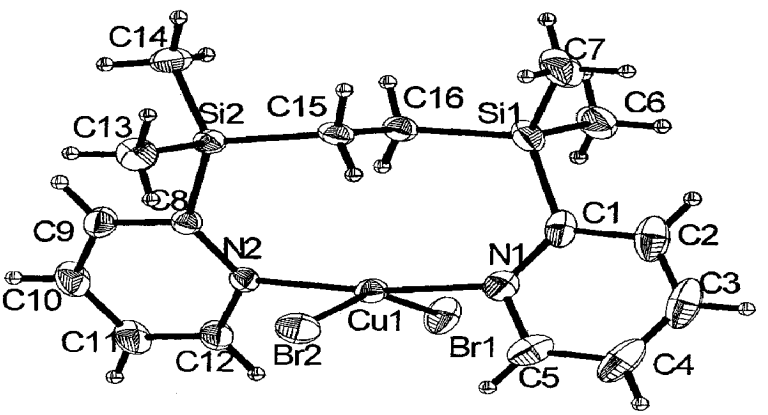
ABSTRACT

The work embodied in the present thesis deals with the synthesis and characterization of organosilicon ligands with carefully placed binding sites suitable for the construction of metallomacrocycles and extended 2/3- D supramolecular structures. The chemistry of organosilicon back bone containing ligands is first reviewed and it is recognized that it would be worthwhile to investigate such ligands by changing the length and flexibility of the spacer unit and also the donor site. The synthesis and characterization of a variety of new organosilicon ligands and their metal complexes are discussed in chapters 3-6 of the present thesis. The Pd(II) complexes of these ligands have been studied for catalytic C–C coupling Heck reactions also. Organosilicon ligands having different type of spacers and heterocyclic ring systems described in the thesis are $\mathbf{L^1}$-$\mathbf{L^7}$. 1,2-Bis(dimethyl(2-pyridylsilyl) ethane ($\mathbf{L^1}$) and 1,2-bis(dimethyl(3-pyridylsilyl)ethane ($\mathbf{L^2}$) were synthesized by the reaction of lithiated 2-pyridine and 3-pyridine respectively with 1,2-bis(chlorodimethylsilyl)ethane at low temperature (-78°C) under N_2 atmosphere. 1,2-Bis(dimethyl(3-quinolylsilyl)ethane ($\mathbf{L^3}$) was synthesized under conditions similar to those of $\mathbf{L^1}$ and $\mathbf{L^2}$. Bis(3-pyridyl)vinylmethylsilane ($\mathbf{L^4}$) was synthesized by reacting dichlorovinylmethylsilane with lithiated 3-pyridine at -78°C temperature under nitrogen atmosphere. Ligands $\mathbf{L^5}$ to $\mathbf{L^7}$ have been synthesized in which hetroaryl groups are separated by Si-Si, Si-O-Si, Si-O-Si-O-Si spacer units. 1,2-Bis(3-quinolyl)-1,1,2,2-tetramethyldisilane ($\mathbf{L^5}$), 1,3-bis(3-quinolyl)-1,1,3,3-tetramethyldisiloxane ($\mathbf{L^6}$) and 1,5-bis(3-quinolyl)-1,1,3,3,5,5-hexamethyltrisiloxane ($\mathbf{L^7}$) were synthesized by the reaction of lithiated 3-quinoline with 1,2-dichlorotetramethyldisilane, 1,3-dichloro-1,1,3,3-tetramethyldisiloxane and 1,5-dichloro-1,1,3,3,5,5-hexamethyltrisiloxane respectively at -78°C under N_2 atmosphere. These ligands are further purified by column chromatography. $\mathbf{L^1}$ and $\mathbf{L^2}$ are found to be solid at ~ 4°C and as

viscous oil at room temperature. Ligand L^3 obtained as a crystalline solid has been found to be stable under ambient conditions. L^4, L^6 and L^7 are viscous liquids while ligand L^5 is crystalline solid. The $^{13}C\{^1H\}$ and $^{29}Si\{^1H\}$ NMR of L^1 to L^7 are found to be characteristic. The $Cl_2(L^1)]$ (**1**), $[Ag(L^1)]ClO_4$ (**2**), $[Ag(L^1)]NO_3$ (**3**), $[CuBr_2(L^1)]$ (**4**), $[PdCl_2(L^2)]$ $_3SO_3$ (**6**), $[CuBr_2(L^2)]$ (**7**), $[PdCl_2(L^3)]_2$ (**8**), $[Ag(L^3)]ClO_4$ (**9**), $[CuBr_2(L^3)]$ (**10**),), $[Ag(L^4)]ClO_4$ (**12**), $[Ag(L^4)]CF_3SO_3$ (**13**), $[PdCl_2(L^5)]$ (**14**), $[PdCl_2(L^6)]$ (**15**),), $[Ag(L^5)]ClO_4$ (**17**), $[Ag(L^6)]ClO_4$ (**18**), $[Ag(L^7)]ClO_4$ (**19**), $[CuBr_2(L^5)]$ (**20**), **1**), $[CuBr_2(L^7)]$ (**22**) were synthesized and characterized by UV-Vis, IR, ^1H, $^{13}C\{^1H\}$ and $^{29}Si\{^1H\}$ NMR spectroscopy along with elemental analysis, conductance measurements. The L^1 coordinates with Pd(II) and Cu(II) through pyridyl nitrogen atoms making a nine-membered metallamacrocyclic complex.

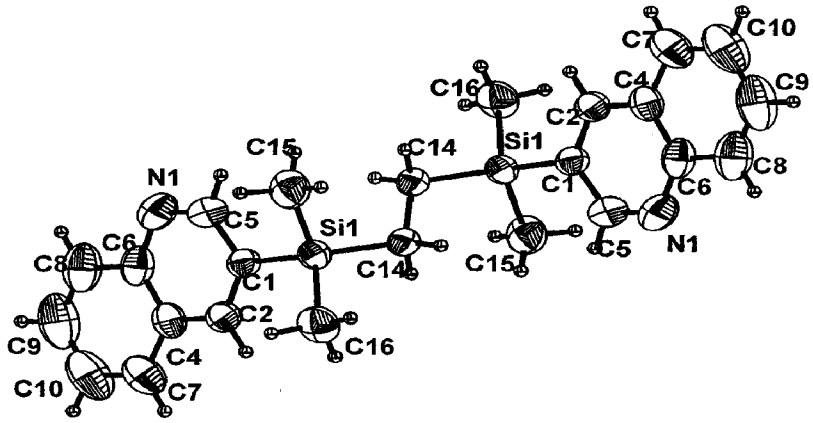


Molecular structure of $[PdCl_2(L^1)]$ (**1**)

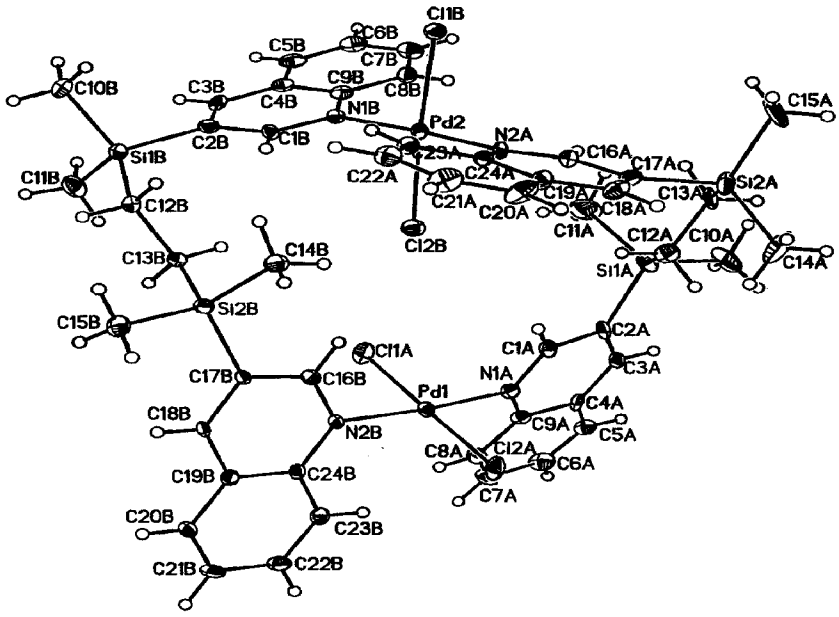


Molecular structure of $[CuBr_2(L^1)]$ (**4**)

L^3 coordinates with Pd(II) through quinolyl nitrogen atoms to make a 22-membered palladamacrocyclic ring (**8**). This is the first example of this size which has ligand containing organosilicon backbone. Ligand L^5 has also been characterization structurally.

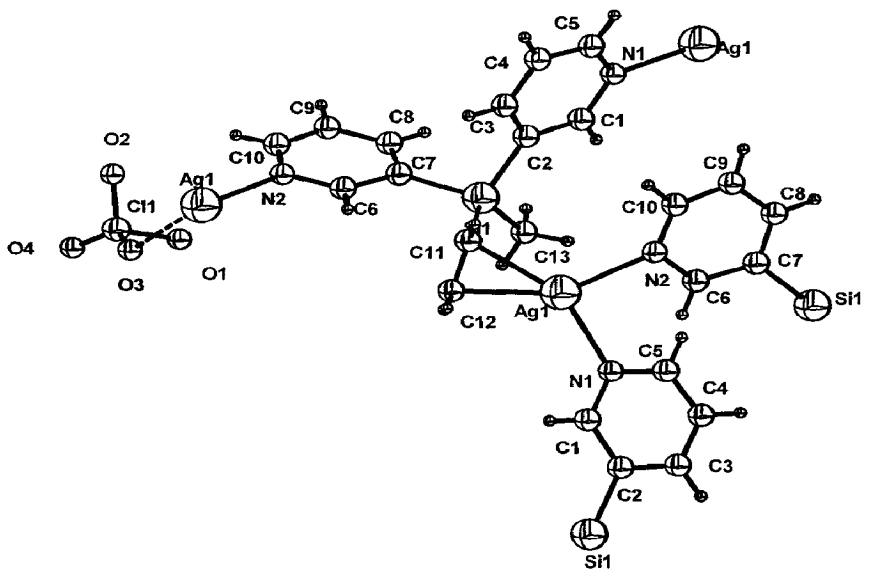


Molecular structure of L^3



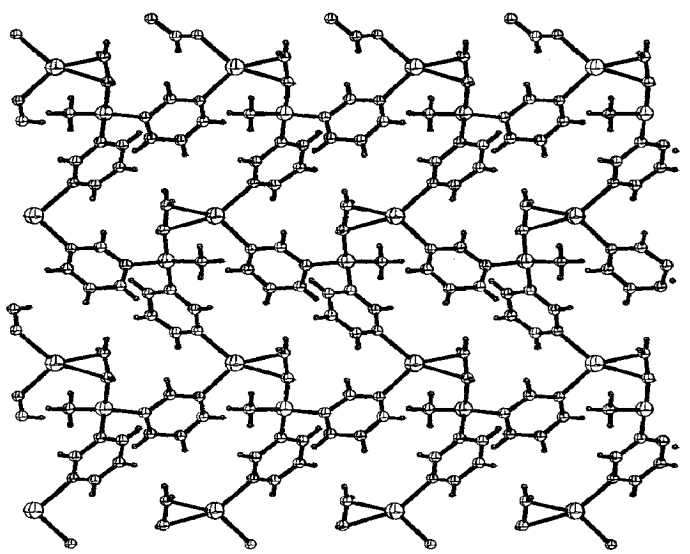
Molecular structure of $[PdCl_2(L^3)]_2$ (**8**)

The **12** has two dimensional sheet type structure having 25-membered metallamacrocycles in



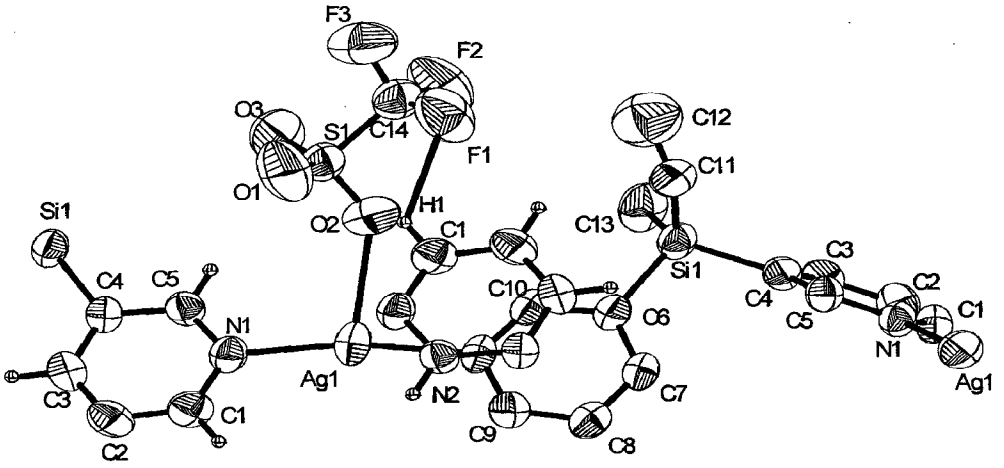
ORTEP diagram of a segment of 2-D structure of $[Ag(L^4)]ClO_4$ (**12**)

which silver is coordinated with C=C, two pyridyl groups of other molecules. The perchlorate ion has only secondary interaction with silver through oxygen. The geometry of silver is highly distorted tetrahedral.



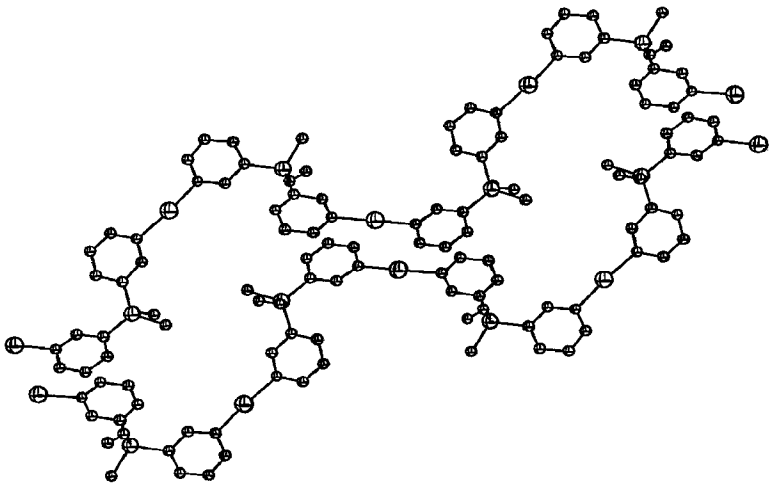
2-D structure of **12** (perchlorate ions are omitted for clarity)

The **13** has infinite molecular strands in which coordination number of silver is two. Most probably the bulkiness of $CF_3SO_3^-$ prevents the Ag-C bond formation and thus changes the structural arrangement. In **13**, $CF_3SO_3^-$ anion acts as a bridge between two molecular strands through F-H (aromatic) secondary interaction [shortest F-H distance 2.616 Å; sum of van der



ORTEP diagram of a segment of strand of **13**

Waals radii 2.90 Å). The weak Ag···O, [2.665 Å], inter-strand Ag····Ag [3.19 Å] and π- π interactions [3.66 Å] also connect two strands.



ORTEP diagram of a segment of strands of **13** (H and $CF_3SO_3^-$ are omitted for clarity)

Single crystal structure of L^5 has been solved by X-ray diffraction. The Si-C(aryl) and Si-C(alkyl) bond lengths 1.883(3) and 1.863(3) / 1.875(3) Å are consistent with the literature values 1.873(2) and 1.849(4) – 1.863(4) Å respectively reported for poly(silyl)pyridines. The palladium complexes **1**, **5**, **14**, **15** and **16** have been studied for the Heck reaction shown below. The results are promising. The advantage of using these complexes (**1**, **5**, **14**, **15** and **16**) is that they are air stable and also not moisture sensitive. The catalytic activity depends on the halide, while electron–withdrawing groups on the aryl ring increase the reaction rate. The reactivity decreases drastically in the order ArI > ArBr.

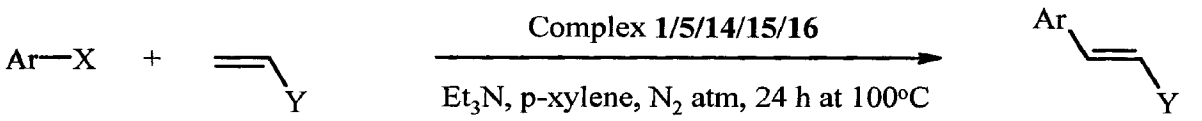


Table of contents