

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

By

**NEETU RANI**

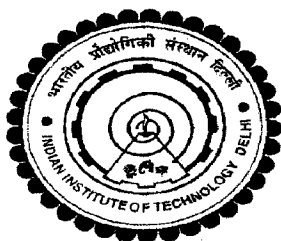
**DEPARTMENT OF CHEMISTRY**

*Submitted*

*In fulfillment of the requirements of the degree of*

**Doctor of Philosophy**

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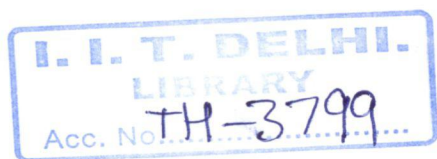


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**May, 2009**

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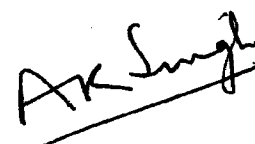
*Dedicated*  
*to my Parents*

## 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*



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*innocent smile of my son Rannvijay relieved me in a moment of anxiety and have made it possible to accomplish this task successfully.*

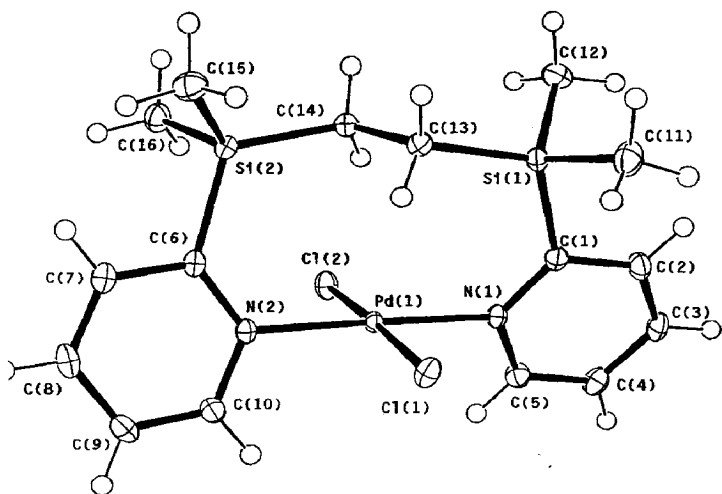
*Most of all thanks to **GOD-The Divine** who continues to make the impossible possible.*

*N. Singh*  
**NEETU RANI**

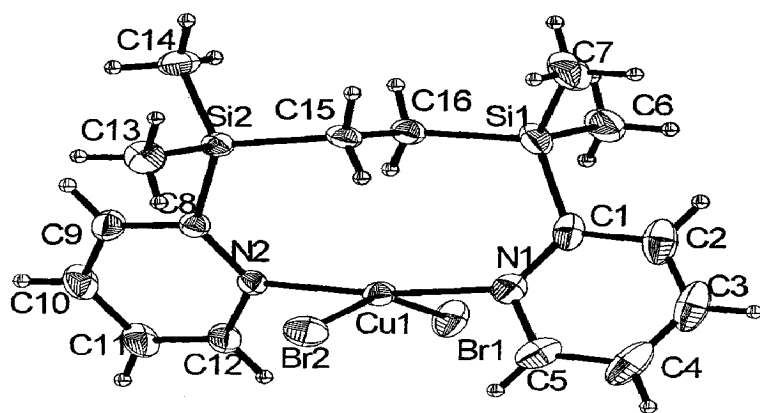
## ABSTRACT

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 L<sup>1</sup>-L<sup>7</sup>. 1,2-Bis(dimethyl(2-pyridylsilyl) ) ethane (L<sup>1</sup>) and 1,2-bis(dimethyl(3-pyridylsilyl)ethane (L<sup>2</sup>) 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<sub>2</sub> atmosphere. 1,2-Bis(dimethyl(3-quinolylsilyl)ethane (L<sup>3</sup>) was synthesized under conditions similar to those of L<sup>1</sup> and L<sup>2</sup>. Bis(3-pyridyl)vinylmethylsilane (L<sup>4</sup>) was synthesized by reacting dichlorovinylmethylsilane with lithiated 3-pyridine at -78°C temperature under nitrogen atmosphere. Ligands L<sup>5</sup> to L<sup>7</sup> 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 (L<sup>5</sup>), 1,3-bis(3-quinolyl)-1,1,3,3-tetramethyldisiloxane (L<sup>6</sup>) and 1,5-bis(3-quinolyl)-1,1,3,3,5,5-hexamethyltrisiloxane (L<sup>7</sup>) 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<sub>2</sub> atmosphere. These ligands are further purified by column chromatography. L<sup>1</sup> and L<sup>2</sup> 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. The  $^{13}\text{C}\{^1\text{H}\}$  and  $^{29}\text{Si}\{^1\text{H}\}$  NMR of  $L^1$  to  $L^7$  are found to be characteristic. The  $[\text{PdCl}_2(L^1)]$  (1),  $[\text{Ag}(L^1)]\text{ClO}_4$  (2),  $[\text{Ag}(L^1)]\text{NO}_3$  (3),  $[\text{CuBr}_2(L^1)]$  (4),  $[\text{PdCl}_2(L^2)]$  (5),  $[\text{Ag}(L^2)]\text{ClO}_4$  (6),  $[\text{CuBr}_2(L^2)]$  (7),  $[\text{PdCl}_2(L^3)]_2$  (8),  $[\text{Ag}(L^3)]\text{ClO}_4$  (9),  $[\text{CuBr}_2(L^3)]$  (10),  $[\text{Ag}(L^4)]\text{ClO}_4$  (12),  $[\text{Ag}(L^4)]\text{CF}_3\text{SO}_3$  (13),  $[\text{PdCl}_2(L^5)]$  (14),  $[\text{PdCl}_2(L^6)]$  (15),  $[\text{Ag}(L^5)]\text{ClO}_4$  (17),  $[\text{Ag}(L^6)]\text{ClO}_4$  (18),  $[\text{Ag}(L^7)]\text{ClO}_4$  (19),  $[\text{CuBr}_2(L^5)]$  (20),  $[\text{CuBr}_2(L^6)]$  (21),  $[\text{CuBr}_2(L^7)]$  (22) were synthesized and characterized by UV-Vis, IR,  $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$  and  $^{29}\text{Si}\{^1\text{H}\}$  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.

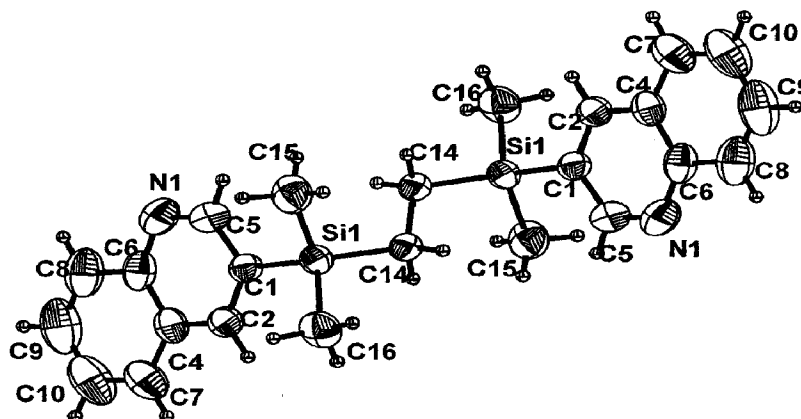


Molecular structure of  $[\text{PdCl}_2(L^1)]$  (1)

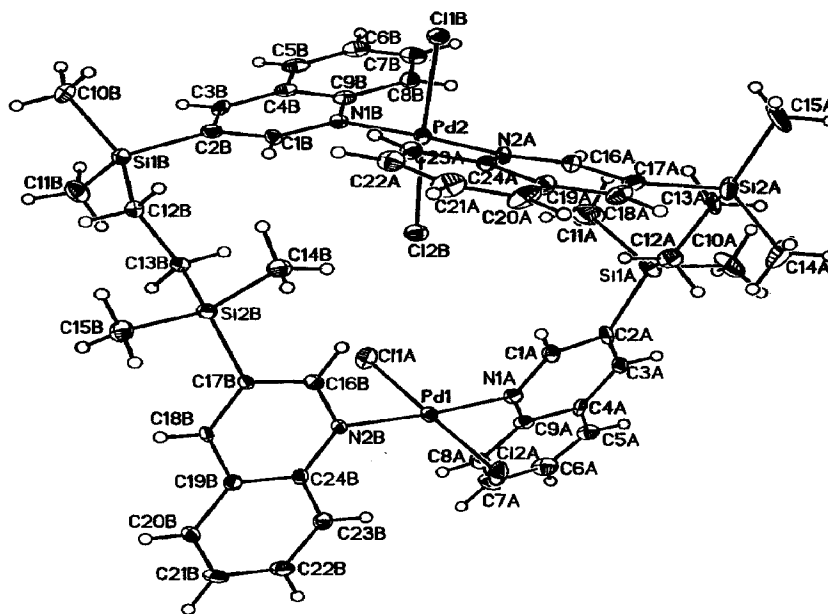


Molecular structure of  $[\text{CuBr}_2(L^1)]$  (4)

$L^3$  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.

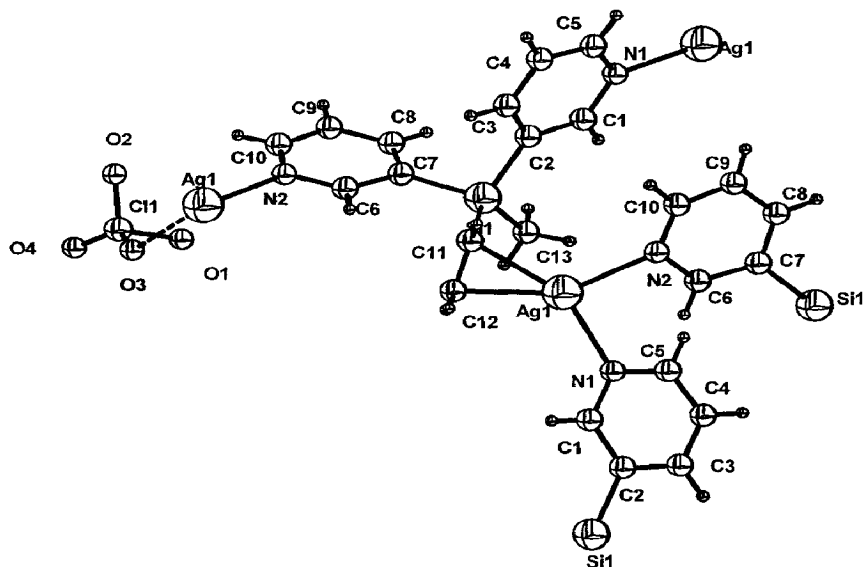


Molecular structure of  $L^3$



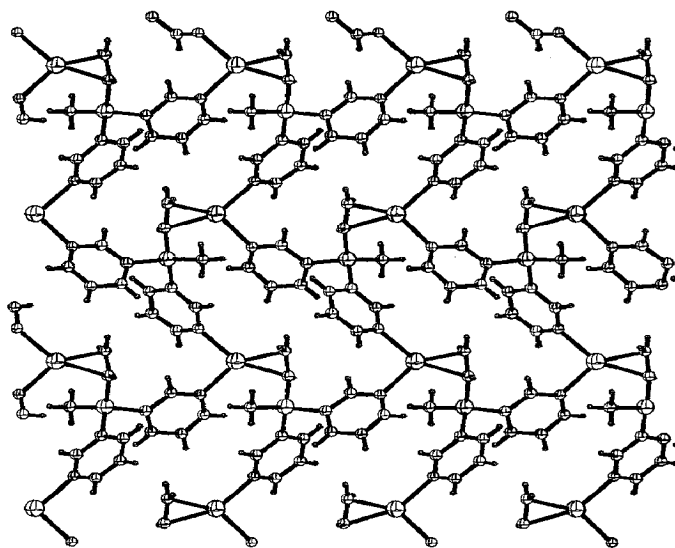
Molecular structure of  $[PdCl_2(L^3)]_2$  (8)

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



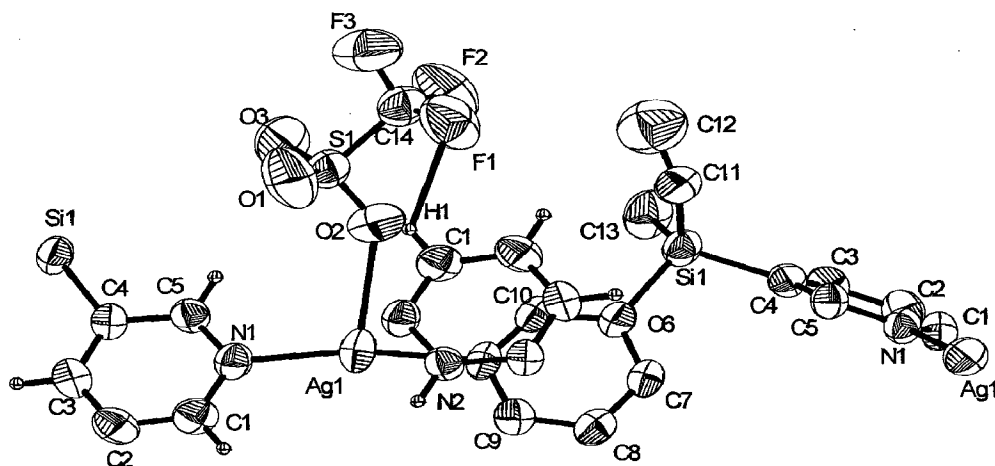
ORTEP diagram of a segment of 2-D structure of  $[\text{Ag}(\text{L}^4)]\text{ClO}_4$  (**12**)

which silver is coordinated with  $\text{C}=\text{C}$ , 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.



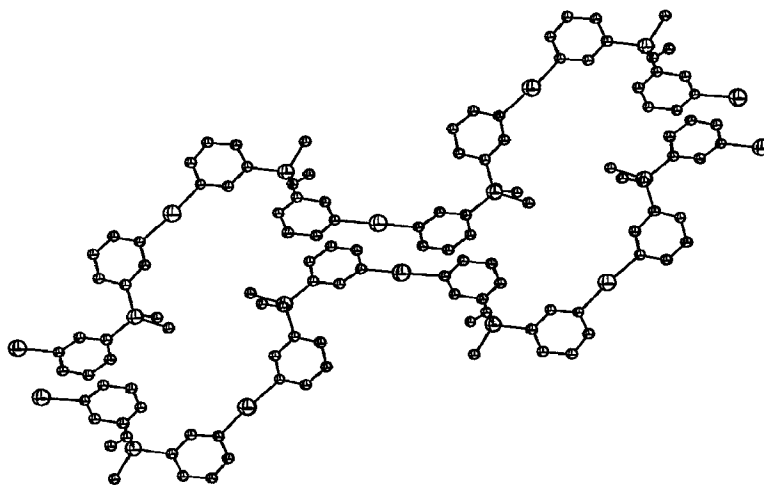
2-D structure of **12** (perchlorate ions are omitted for clarity)

The **13** has infinite molecular strands in which coordination number of silver is two. Most probably the bulkiness of  $\text{CF}_3\text{SO}_3^-$  prevents the Ag-C bond formation and thus changes the structural arrangement. In **13**,  $\text{CF}_3\text{SO}_3^-$  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



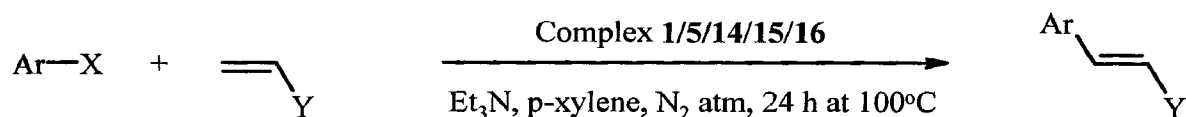
ORTEP diagram of a segment of strand of **13**

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



ORTEP diagram of a segment of strands of **13** (H and  $\text{CF}_3\text{SO}_3^-$  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

S. No.	Contents	Page No.
1	Certificate	i
2	Acknowledgements	ii
3	Abstract	iv
4	List of Figures	xv
5	List of Tables	xix
<b>Chapter 1: Introduction</b>		
	Introduction	1
1.1	Monosilane derivatives with aromatic N-heterocyclic (heteroaryl) substituents	2
1.2	Disilane derivatives with aromatic N-heterocyclic (heteroaryl) substituents	13
1.3	Siloxane derivatives with aromatic N-heterocyclic (heteroaryl) substituents	17
1.4	Organosilicon compounds with amino functionalities	21
1.5	Organosilicon compounds with phosphorus functionalities	23
1.6	Catalytic Applications of Systems having Organosilicon groups	25
1.7	Objectives and Scope of Present Work	28
1.8	References	31
<b>Chapter 2: Materials and Methods</b>		
2.1	Chemicals	38

2.2	Solvents	38
2.3	Elemental analysis	38
2.4	Melting point	39
2.5	UV spectra	39
2.6	Conductance measurements	39
2.7	Infrared spectra	40
2.8	Nuclear magnetic resonance spectra	40
2.9	Single crystal X-ray diffraction studies	40
2.10	References	41
<b>Chapter 3: Organosilicon Ligands containing 2/3- pyridyl groups</b>		
3.1	Introduction	42
3.2	Experimental	43
3.2.10	Procedure for catalytic Heck reaction	48
3.2.11	X-ray diffraction analysis	49
3.3	Results and discussion	50
3.3.1	Conductance measurements	51
3.3.2	Diffuse reflectance spectra	51
3.3.3	Infrared spectra	52
3.3.4	$^1\text{H}$ NMR spectra	53
3.3.5	$^{13}\text{C}\{^1\text{H}\}$ NMR spectra	54
3.3.6	$^{29}\text{Si}\{^1\text{H}\}$ NMR	62
3.3.7	Crystal structures	71

3.3.8	Applications in Heck reaction	74
3.4	Conclusions	82
3.5	References	83
<b>Chapter 4: Organosilicon ligands containing 3-quinolyl group</b>		
4.1	Introduction	85
4.2	Experimental	85
4.2.5	X-ray diffraction analysis	88
4.3	Results and discussion	89
4.3.1	Conductance measurements	90
4.3.2	Diffuse reflectance spectra	91
4.3.3	Infrared spectra	91
4.3.4	<sup>1</sup> H NMR spectra	92
4.3.5	<sup>13</sup> C{ <sup>1</sup> H} NMR spectra	97
4.3.6	Crystal structures	97
4.4	Conclusions	112
4.5	References	113
<b>Chapter 5: Synthesis and ligand chemistry of bis(3-pyridyl)methylvinylsilane: Formation of anion controlled Ag(I) complexes</b>		
5.1	Introduction	115
5.2	Experimental	116
5.2.5	X-ray diffraction analysis	119
5.3	Results and discussion	119

5.3.1	Infrared spectra	120
5.3.2	$^1\text{H}$ NMR spectra	122
5.3.3	$^{13}\text{C}\{^1\text{H}\}$ NMR spectra	127
5.3.4	$^{29}\text{Si}\{^1\text{H}\}$ NMR	128
5.3.5	Crystal structures	132
5.4	Conclusions	148
5.5	References	149
<b>Chapter 6: Disilane and siloxane- based ligands containing quinolyl groups , their metal complexes and applications of Pd(II) complexes in C–C coupling reaction</b>		
6.1	Introduction	151
6.2	Experimental	151
6.2.14	X-ray diffraction analysis	159
6.3	Results and discussion	160
6.3.1	Conductance	161
6.3.2	Diffuse reflectance spectra	162
6.3.3	Infrared spectra	162
6.3.4	$^1\text{H}$ NMR spectra	163
6.3.5	$^{13}\text{C}\{^1\text{H}\}$ NMR spectra	165
6.3.6	$^{29}\text{Si}\{^1\text{H}\}$ NMR	176
6.3.7	Crystal structures	184
6.3.8	Applications in Heck reaction	191
6.4	Conclusions	193

6.5	References	194
<b>Supplementary materials for 1, 4, L<sup>3</sup>, 8, 12, 13 and L<sup>5</sup></b>		196
<b>Curriculum-Vitae</b>		