Bis(3-pyridyl)methylvinylsilane (**L1**) and 1,2-di(3-quinolyl) dimethyl disilane (**L2**): Synthesis and complexation reactions. Anion controlled solid state structures of cationic Ag(I)–**L1** complex

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ABSTRACT

3-Bromopyridine and 3-bromoquinoline on reaction with *n*-butyllithium give lithiated products which on reaction with dichloromethylvinylsilane and 1,2-dichlorodimethyldisilane at $-78\,^{\circ}C$ result in the ligands bis(3-pyridyl)methylvinylsilane (**L1**) and 1,2-di(3-quinolyl)dimethyl disilane (**L2**). The complexation reactions of both these ligands with Ag(I), Pd(II) and Cu(II) have been explored. The ^1H, $^{13}C\{^1H\}$ and $^{29}Si\{^1H\}$NMR and IR spectra of both the ligands and their metal complexes have been found characteristic. The complex of **L1** with silver(I), [Ag(**L1**)]ClO₄ (**1**) gives suitable single crystals characterized by X-ray diffraction. Its structure consists of two dimensional sheets, having 25-membered metallamacrocycle ring, in which Ag has distorted tetrahedral geometry and is bonded to vinyl (η^2) group. On reacting AgCF₃SO₃ with **L1** and subjecting the single crystals of the resulting complex to X-ray diffraction it has been found that contrary to **1** there is no bond between vinyl group and silver, resulting in infinite molecular strands, in which coordination geometry of silver is distorted trigonal planar. $CF_3SO_3^-$ anion acts as a bridge between two molecular strands through $F\cdots H$ (aromatic) and $Ag\cdots O$ secondary interactions. The Ag–C distances in **1** are 2.309(5) and 2.350(12) Å. The C=C bond length does not exhibit significant change on bonding with silver in **1**.

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1. Introduction

The donor–accepter complexes of silver(I) formed with olefins have considerable potential for using in olefin/paraffin separations [1–4]. However, stable salt of tris(ethene)silver(I) cation ([Ag(η^2-C₂H₄)₃][Al{OC(CF₃)₃}₄]) was reported [5] in 2003 only. The pyridyl silanes R₂Si(3-py)₂, R₂Si(4-py)₂, RR'Si(2-py)₂, R₂Si(2-py)₂, R₂Si(2-py-3-OR')₂, RSi(4-py)₃ (py = pyridyl; R = Me, Ph; R' = vinyl, Me, Ph) and bis(3-pyridyl)cyclotetramethylenesilane [6–13] and related siloxane R₂(3-py)Si-O-Si(3-py)R₂, R₂(4-py)Si-O-Si(4-py)R₂ (R = Me, Ph) and 1,5-bis(3-pyridyl)hexamethyltrisiloxane [14,15] have been found interesting building blocks for metallamacrocycles and other interesting skeletons including supramolecular assemblies/structures. Bis(4-pyridyl)dimethylsilane and bis(3-pyridyl)dimethylsilane have been reported [16,17] recently which ligate with silver(I) resulting in diverse structures of varying Ag:ligand ratio dependent on coordinating ability of counter anions.

However, we are unaware of use as ligand of any silane having both 3-pyridyl and vinyl groups as well as of disilane containing quinolyl group. The copolymerization of bis(2-pyridyl)vinylmethylsilane with styrene and divinylbenzene has been explored [12]. It would be interesting to note the influence of vinyl group on the structure building ability of pyridylsilane derivatives. Therefore we have synthesized **L1** and **L2** and explored their complexation reactions. The single crystal structures of **L2** and complexes [Ag(**L1**)]ClO₄ (**1**) and [Ag(**L1**)]CF₃SO₃ (**2**) have been solved. The complex of Ag(I) with **L1** has two dimensional structure in which vinyl group has hapticity two, if perchlorate is counter anion. In the presence of $CF_3SO_3^-$ as counter ion different structure having molecular strands results in which vinyl group does not coordinate at all. These results are reported in this paper.

2. Experimental

The ^1H, $^{13}C\{^1H\}$ and $^{29}Si\{^1H\}$ NMR spectra were recorded on a Bruker Spectrospin DPX-300 NMR spectrometer at 300.13, 75.47 and 59.6 MHz, respectively. IR spectra in the range 4000–250 cm⁻¹ were recorded on a Nicolet Protégé 460 FT-IR spectrometer in Nujol or KBr. UV–Vis reflectance spectra were recorded Lambda Bio-20, Perkin–Elmer (USA); Model 330. The C, H and N analyses were carried out with a Perkin–Elmer elemental analyzer 240C. Dichloromethylvinyl silane (Aldrich, USA) was further purified by vacuum distillation on Mg. 3-Bromopyridine, 1,2-dichlorodimethyldisilane, AgClO₄ and AgCF₃SO₃ procured from Aldrich (USA) were used

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without further purification. The melting points determined in open capillary are reported as such.

Single crystal diffraction studies were carried out with a Bruker AXS SMART Apex CCD diffractometer using Mo Kα (0.71073 Å) radiation at 298(2) K. The software SADABS was used for absorption corrections [18] and SHELXTL for space group, structure determination and refinements [19]. The Table 1 lists the experimental parameters used for single crystal structure analysis. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in idealized positions with isotropic thermal parameters set at 1.2 times that of the carbon atom to which they are attached. The least-squares refinement cycles on F^2 were performed until the model converged.

2.1. Synthesis of L1

n-Butyllithium (20.5 mmol, 8.2 mL of 2.5 M solution in n-hexane) was added drop wise to a solution of 3-bromopyridine (3.16 g, 20 mmol) made in dry diethyl ether (30 mL) at −78 °C under nitrogen atmosphere. The resulting mixture was allowed to warm to 40 °C and stirred at that temperature for 30 min to obtain yellow suspension which was again cooled to −78 °C. Dichloromethylvinylsilane (1.41 g, 10 mmol) was slowly added to the yellow suspension at −78 °C. The crude L1 was obtained by work up given in Supplementary material and purified to yellow coloured viscous oil by column chromatography on silica gel with ethylacetate–hexane mixture (40:60). Yield: 0.165 g, 69%. NMR: (^{1}H, CDCl$_3$, 25 °C vs TMS) δ (ppm): 8.69 (s, 2H, H$_5$), 8.65 (d, $^3J_{H,H}$ = 5.7 Hz, 2H, H$_4$), 7.80 (d, $^3J_{H,H}$ = 7.5 Hz, 2H, H$_2$), 7.32 (t, $^3J_{H,H}$ = 6.6 Hz, 2H, H$_3$), 6.45 (dd, $^3J_{H,H}$ = 19.8 Hz, $^3J_{H,H}$ = 14.7 Hz, 1H, H$_6$), 6.29 (dd, $^3J_{H,H}$ = 14.7 Hz, $^2J_{H,H}$ = 3.6 Hz, 1H, H$_{7a}$), 5.85 (dd, $^3J_{H,H}$ = 19.8 Hz, $^2J_{H,H}$ = 3.6 Hz, 1H, H$_{7b}$), 0.72 (s, 3H, Me), (^{13}C{^{1}H}, CDCl$_3$, 25 °C vs TMS) δ (ppm): 154.0 (C$_5$), 150.0 (C$_4$), 142.9 (C$_2$), 137.1 (C$_7$), 133.0 (C$_3$), 130.5 (C$_1$), 123.6 (C$_6$), −4.6 (Me), (^{29}Si{^{1}H}, CDCl$_3$, 25 °C vs TMS) δ (ppm): 15.68. IR (KBr, cm^{-1}): 3024 (m; $\upsilon_{C-H\ (aromatic)}$), 2955 (s; $\upsilon_{C-H\ aliphatic}$), 1646 (w; $\upsilon_{(vinyl\ C=C)}$), 1257 (m; υ_{Si-Me}), 788 (vs; $\upsilon_{Si-C(py)}$).

2.2. Synthesis of L2

A solution of 3-bromoquinoline (4.16 g, 20 mmol) was made in dry diethylether (30 mL) under nitrogen atmosphere. n-Butyllithium (20.5 mmol, 8.2 mL of 2.5 M solution in hexane) was added dropwise to it at −78 °C under nitrogen atmosphere. The mixture was stirred at −78 °C under nitrogen atmosphere for 1 h. The resulting dark brown suspension was obtained to which 1,2-dichlorodimethyldisilane (1.8 g, 10 mmol) was added dropwise at −78 °C. The reaction mixture was slowly allowed to warm to room temperature and kept for 12 h. After workup as described in Supplementary material crude L2 was obtained as dark yellow oil which was purified by column chromatography (silica gel; 30:70 ethyl acetate–hexane mixture). The colourless single crystals of L2 were obtained by slow evaporation of solvents from the eluent. Yield 2.1 g, ∼56%; m.p. 119 °C. Anal. Calc. for Si$_2$C$_{22}$H$_{24}$N$_2$: C, 70.93; H, 6.44; N, 7.52. Found: C, 71.13; H, 6.40; N, 7.49%. NMR (^{1}H, CDCl$_3$, 25 °C vs TMS) δ (ppm): 8.86 (s, 2H, H$_9$), 8.07 (bs, 4H, H$_2$ + H$_7$), 7.72–7.66 (m, 4H, H$_4$ + H$_6$), 7.50 (t, $^3J_{H,H}$ = 7.5 Hz, 2H, H$_5$), 0.47 (s, 12H, Me); (^{13}C{^{1}H}, CDCl$_3$, 25 °C, vs TMS) δ (ppm): 153.8 (C$_9$), 148.0 (C$_8$), 142.5 (C$_2$), 131.0 (C$_1$), 129.8 (C$_7$), 129.2 (C$_6$), 127.8 (C$_3$), 127.6 (C$_4$), 126.5 (C$_5$), −4.1 (Me); ^{29}Si NMR (CDCl$_3$, 25 °C vs TMS) δ (ppm): −21.93; IR (KBr, cm^{-1}): 3055 (w; $\upsilon_{C-H\ (aromatic)}$), 2950 (m; $\upsilon_{C-H\ (aliphatic)}$), 1246 (s; υ_{Si-Me}), 788 (vs; $\upsilon_{Si-C(qu)}$).

2.3. Synthesis of [Ag(L1)]ClO$_4$ (1)

A solution of L1 (0.07 g, 0.3 mmol) made in methanol (5 mL) was slowly diffused into solution of AgClO$_4$ (0.06 g, 0.3 mmol) made in 3 mL of water (deionized) to obtain colourless crystals of 1, which have been found air stable. Yield 0.11 g, 82%; m.p.(d) 213 °C. Anal. Calc. for C$_{13}$H$_{14}$AgN$_2$SiClO$_4$: C, 35.97; H, 3.23; N,

Table 1
Crystallographic data and refinements of 1, 2 and L2.

Compound	1	2	L2
Empirical formula	C$_{13}$H$_{14}$AgN$_2$SiClO$_4$	C$_{14}$H$_{14}$AgF$_3$N$_2$O$_3$SSi	C$_{22}$H$_{24}$N$_2$Si$_2$
Formula weight	433.67	483.29	372.61
Crystal size (mm)	0.463 × 0.215 × 0.167	0.463 × 0.215 × 0.167	0.465 × 0.211 × 0.169
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	Pbca	P2(1)/c	P2(1)/c
Unit cell dimension			
a (Å)	14.877(3)	7.3882(15)	12.805(4)
b (Å)	14.616(2)	13.156(3)	6.6410(19)
c (Å)	15.239(3)	19.195(4)	12.933(4)
α (°)	90.00		
β (°)	90.00	99.10(3)	102.302(5)
γ (°)	90.00		
Volume (Å^3)	3313.6(11)	1842.3(7)	1074.5(5)
Z	8	4	2
Density (calc.) (Mg m^{-3})	1.739	1.742	1.149
Absorption coefficient (mm^{-1})	1.467	1.309	0.172
$F(000)$	1728.0	960.0	396.0
θ range (°)	2.37–25.00	1.88–25.00	1.63–25.50
Index ranges	−17 ⩽ h ⩽ 17	−8 ⩽ h ⩽ 8	−15 ⩽ h ⩽ 15
	−17 ⩽ k ⩽ 17	−15 ⩽ k ⩽ 15	−8 ⩽ k ⩽ 8
	−18 ⩽ l ⩽ 18	−22 ⩽ l ⩽ 22	−15 ⩽ l ⩽ 15
Reflections collected	29338	16940	10279
Independent reflections [R$_{(int)}$]	2910	3224	1999
Completeness to maximum θ (%)	99.8	99.4	100
Maximum/minimum transmission	0.785/0.691	0.810/0.725	0.969/0.959
Data/restraints/parameters	2910/0/200	3224/0/227	1999/0/120
Goodness-of-fit on F^2	1.344	1.063	1.187
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.1061, wR_2 = 0.2230	R_1 = 0.0422, wR_2 = 0.1106	R_1 = 0.0765, wR_2 = 0.1610
R indices (all data)	R_1 = 0.1091, wR_2 = 0.2248	R_1 = 0.0492, wR_2 = 0.1150	R_1 = 0.0944, wR_2 = 0.1719
Largest difference peak/hole (e Å^{-3})	1.228/−1.266	0.840/−0.656	0.445/−0.299

6.46. Found: C, 35.86; H, 3.25; N, 6.50%. NMR: (^{1}H, CDCl$_3$ (+2–3 drops DMSO-d_6), 25 °C vs TMS) δ (ppm): 8.83 (s, 2H, H$_5$), 8.68 (bs, 2H, H$_4$), 8.05 (bs, 2H, H$_2$), 7.51(t, $^3J_{H,H}$ = 5.3 Hz, 2H, H$_3$), 6.51 (dd, $^3J_{H,H}$ = 19.8 Hz, $^3J_{H,H}$ = 14.7 Hz, 1H, H$_6$), 6.36 (dd, $^3J_{H,H}$ = 14.8 Hz, $^2J_{H,H}$ = 3.6 Hz, 1H, H$_{7a}$), 5.93 (dd, $^3J_{H,H}$ = 19.8 Hz, $^2J_{H,H}$ = 3.6 Hz, 1H, H$_{7b}$), 0.78 (s, 6H, Me). IR (Nujol, cm^{-1}): 3049 (m; $\upsilon_{C-H\ (aromatic)}$), 2956 (m; $\upsilon_{C-H\ (aliphatic)}$), 1581 (w; $\upsilon_{(vinyl\ C=C)}$), 1263 (w; υ_{Si-Me}), 789 (m; $\upsilon_{Si-C(py)}$), 1087 (s; υ_{Cl-O}) and 621 (m; υ_{Cl-O}).

2.4. Synthesis of [Ag(L1)]CF$_3$SO$_3$ (2)

It was synthesized in the form of single crystals by the method given for **1**, except, AgCF$_3$SO$_3$ replaced AgClO$_4$, and found air stable. Yield 0.09 g, 66%; m.p.(d) > 230 °C. Anal. Calc. for C$_{14}$H$_{14}$-AgF$_3$N$_2$O$_3$SSi: C, 34.76; H, 2.89; N, 5.79. Found: C, 34.91; H, 2.73; N, 5.70%. NMR: (^{1}H, CDCl$_3$, 25 °C, vs TMS) δ (ppm): 8.84 (s, 2H, H$_5$), 8.70 (d, $^3J_{H,H}$ = 5.1 Hz, 2H, H$_4$), 8.01 (d, $^3J_{H,H}$ = 7.2 Hz, 2H, H$_2$), 7.51 (b, 2H, H$_3$), 6.49 (dd, $^3J_{H,H}$ = 19.5 Hz, $^3J_{H,H}$ = 14.7 Hz, 1H, H$_6$), 6.35 (dd, $^3J_{H,H}$ = 14.7 Hz, $^2J_{H,H}$ = 3.6 Hz, 1H, H$_{7a}$), 5.93 (dd, $^3J_{H,H}$ = 19.6 Hz, $^2J_{H,H}$ = 3.6 Hz, 1H, H$_{7b}$), 0.77 (s, 6H, Me). IR (Nujol, cm^{-1}): 3041 (m; $\upsilon_{C-H\ (aromatic)}$), 2959 (m; $\upsilon_{C-H\ (aliphatic)}$), 1640 (m; $\upsilon_{vinyl\ C=C}$), 1257(vs, br; υ_{Si-Me} + υ_{S-O}), 789 (vs; $\upsilon_{Si-C(py)}$).

2.5. Synthesis of [Ag (L2)]ClO$_4$ (3)

A solution of **L2** (0.11 g, 0.3 mmol) made in acetone (5 mL) was reacted with AgClO$_4$ (0.06 g, 0.3 mmol) dissolved in 3 mL of water as described for **1**. However, **3** was found light and air sensitive. The solid can be stored under nitrogen protected from light for several days. Yield 0.10 g, 61%; m.p.(d) 180 °C. Anal. Calc. for Si$_2$C$_{22}$H$_{24}$N$_2$AgClO$_4$: C, 45.55; H, 4.14; N, 4.83. Found: C, 45.50; H, 4.03; N, 4.85%. NMR (^{1}H, CDCl$_3$, 25 °C, vs TMS) δ (ppm): 9.18 (s, 2H, H$_9$), 8.29 (s, 2H, H$_2$), 7.98 (bs, 2H, H$_7$), 7.77–7.75 (m, 4H, H$_4$ + H$_6$), 7.60 (bs, 2H, H$_5$), 0.63 (s, 12H, Me). IR (Nujol, cm^{-1}): 3055 (w; $\upsilon_{C-H\ (aromatic)}$), 2950 (m; $\upsilon_{C-H\ (aliphatic)}$), 1256 (m; υ_{Si-Me}), 1093 (vs), and 627 (m) (υ_{Cl-O}), 790 (s; $\upsilon_{Si-C(qu)}$).

2.6. Synthesis of [Pd(L1)Cl$_2$] (4) and [Pd(L2)Cl$_2$] (5)

To a solution of **L1** (0.07 g, 0.30 mmol) or **L2** (0.11 g, 0.30 mmol) made in 10 mL of acetone was added Na$_2$[PdCl$_4$] (0.08 g, 0.25 mmol) dissolved in 10 mL of water. The resulting mixture was stirred for 1 h at room temperature and poured into 100 mL of water. The dark yellow coloured compounds **4** or **5** were obtained by work up procedure given in Supplementary material.

4: Yield 0.048 g, 40%; m.p.(d) > 250 °C; Anal. Calc. for C$_{13}$H$_{14}$N$_2$SiPdCl$_2$: C, 37.72; H, 3.78; N, 5.25. Found: C, 37.79; H, 3.77; N, 5.20%. NMR: (^{1}H, CDCl$_3$ 25 °C vs TMS) δ (ppm): 8.85 (m, 4H, H$_5$ + H$_4$), 7.84 (bs, 2H, H$_2$), 7.36 (bs, 2H, H$_3$), 6.59 (m, 1H, H$_6$), 6.41 (m, 1H, H$_{7a}$), 5.90 (m, 1H, H$_{7b}$), 0.74 (s, 6H, Me). (^{13}C{^{1}H}, CDCl$_3$, 25 °C vs TMS) δ (ppm): 157.9 (C$_5$), 151.8 (C$_4$), 144.8 (C$_2$), 139.3 (C$_7$), 135(C$_3$), 131.4 (C$_1$), 124.9 (C$_6$), −2.7 (Me). IR(KBr, cm^{-1}): 3056 (m; $\upsilon_{C-H\ (aromatic)}$), 2955 (s; $\upsilon_{C-H\ (aiiphatic)}$), 1626 (m; $\upsilon_{(vinyl\ C=C)}$), 1259 (s; υ_{Si-Me}), 793 (vs; $\upsilon_{Si-C(py)}$).

5: Yield 0.13 g, 86%; m.p.(d) > 210 °C. Anal. Calc. For C$_{22}$H$_{24}$N$_2$Si$_2$PdCl$_2$: C, 48.12; H, 4.37; N, 5.10. Found: C, 48.14; H, 4.39; N, 5.03%. (^{1}H, CDCl$_3$ 25 °C vs TMS) δ (ppm): 10.01 (s, 2H, H$_9$), 9.54 (s, 2H, H$_2$), 8.42 (b, 2H, H$_7$), 8.07 (b, 2H, H$_6$), 7.84 (bd, $^3J_{H,H}$ = 7.50 Hz, 2H, H$_4$), 7.70 (bt, $^3J_{H,H}$ = 6.9 Hz 2H, H$_5$), 0.58 (s, 12H, Me). (^{13}C{^{1}H}, CDCl$_3$, 25 °C vs TMS) δ (ppm): 158.2 (C$_9$), 145.1 (C$_2$), 131.9 (C$_7$), 129.4 (C$_6$), 128.4(C$_4$), 127.9 (C$_5$), −2.3 (Me); signals of quaternary carbons of quinoline had very low intensity in comparison to noise; (^{29}Si{^{1}H}, CDCl$_3$, 25 °C vs TMS) δ (ppm): −20.86. IR(KBr, cm^{-1}): 3043 (w; $\upsilon_{C-H\ (aromatic)}$), 2957 (m; $\upsilon_{C-H\ (aliphatic)}$), 1259 (s; υ_{Si-Me}), 788 (vs; $\upsilon_{Si-C(qu)}$).

2.7. Synthesis of [CuBr$_2$(L2)] (6)

The solid CuBr$_2$ (0.066 g, 0.3 mmol) was added to a solution of **L2** (0.11 g, 0.3 mmol) made in 10 mL of methanol and the resulting mixture stirred for 15 min. A clear dark green coloured solution was formed. This solution was kept at 5 °C for 2 days. The dark green powder of **6** was obtained, which was found air stable. Yield 0.13 g, 72%; m.p.(d)165 °C. Anal. Calc. for Si$_2$C$_{22}$H$_{24}$N$_2$CuBr$_2$: C, 44.35; H, 4.03; N, 4.70. Found: C, 44.30; H, 4.10; N, 4.63%. IR (KBr, cm^{-1}): 3056 (w; $\upsilon_{C-H\ (aromatic)}$), 2948 (ms; $\upsilon_{C-H\ (aliphatic)}$), 1254 (s; υ_{Si-Me}), 790 (vs; $\upsilon_{Si-C(qy)}$). (UV reflectance: 725 nm).

3. Result and discussion

The ligands **L1** and **L2** synthesized by the reactions given in Scheme 1 using Schlenk techniques at low temperature are air stable. The single crystals of **3–6** could not be grown. The **L1** was viscous oil, therefore its elemental analyses could not be carried out. The change in metal: ligand ratio and the concentrations of reactants did not affect the nature of the resulting metal complexes. Both the palladium complexes were found air stable. The complexes **1–3** were found sparingly soluble in water and common organic solvents. Their solutions in Me$_2$SO and acetonitrile were not found very stable. The complexes **4–5** were found soluble in common organic solvents. The **6** was also found moderately soluble in common organic solvents except MeOH and EtOH. In IR spectra of **1** and **3** bands around 1087/1093 and 621/627 cm^{-1} were observed, which indicate that ClO$_4^-$ is nearly uncoordinated in them. In IR spectrum of **L1** band at 788 cm^{-1} appears due to Si–C(py) vibrations The bands at 1257 and 1246 cm^{-1} are due to Si–CH$_3$ vibrations in IR spectra of **L1** and **L2**, respectively. In the spectrum of **2** the ν(S–O) appears to overlap Si–CH$_3$ vibrations. The C=C stretching vibration has been found red shifted by 75 and 20 cm^{-1} on the formation **1** and **4**, respectively, indicating bonding between C=C and metal. ^{1}H NMR spectra of both the ligands and their metal complexes **1–5** were found characteristic. The proton NMR of **6** was not recorded due to its paramagnetic nature. The poor solubility of **1–3** restricted us from recording their carbon-13 or silicon-29 NMR spectra, which were found characteristic in the case of **4** and **5**, revealing their purity. On formation of **1**, **2** and **4** signal of H$_5$ in proton NMR spectra shows deshielding ($\sim$0.15 ppm) with respect to that of free **L1**. In carbon-13 NMR spectrum of **4** signal of C$_5$ also shows deshielding (3.9 ppm) relative to that of free ligand. In proton NMR spectra of **1** and **2**, signals
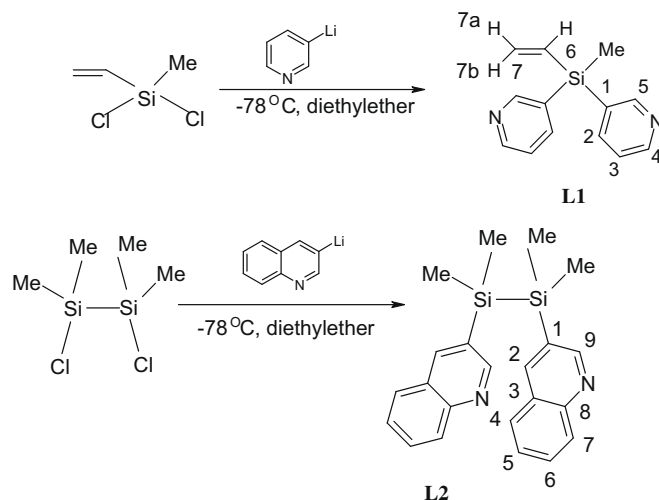
Scheme 1.

of H_2 and H_3 exhibit deshielding (0.19–0.25 ppm) relative to those of free **L1**. It appears from the proton NMR spectral data that in solution **1** and **2** have almost similar coordination of silver. The difference occurs probably in the course of crystal formation [16,17]. The signals of olefinic protons in proton NMR spectrum show small deshielding (~0.1 ppm) on the formation of **4**. In case of **1** deshielding of these protons is <0.1 ppm. The corresponding carbon signals in carbon-13 spectrum of **4** also exhibit deshielding (<2 ppm) relative to those of free **L1**. The signals of C_2 and C_7 also show deshielding (upto 2.2 ppm) in carbon-13 NMR spectrum of **4** in comparison to those of free ligand. The signal of methyl carbon in carbon-13 NMR spectrum of **4** appears deshielded by 2.7 ppm relative to that of free **L1**. Thus it appears that in **4**, Pd is probably bonded with C=C (bond strength may be moderate only) and pyridyl nitrogen. The structure may be polymeric or metallamacrocyclic as chelation is going to give a chelate ring of size bigger than 6-membered. In proton NMR spectrum of **5** various protons are downfield than those of **3**. In comparison to signals of ^{1}H NMR of free **L2** also, the signals in the spectra of **3** and **5** both are deshielded. The deshielding is highest in the signals of H_9 (proton NMR) and C_9 (C-13 NMR) relative to those of free **L2**, when **3** and **5** are formed. Most probably **L2** coordinates through ring nitrogen and probability of metallamacrocycle formation or polymeric structure in case of **3** and **5** is strong. The reflectance spectra of copper complex **6** in UV–Vis region was recorded as solubility was inadequate in non-coordinating organic solvents. It shows maxima at 725 nm (d–d transition) indicating the probability of coordination number four or five for the copper.

3.1. Crystal structures

Single crystal structures of **1**, **2** and **L2** have been solved by X-ray diffraction. The selected bond lengths and angles are given in Table 2. The structure of silver complex **1** is two dimensional sheet type which has 25-membered metallamacrocycles. Silver is coordinated with C=C, and two pyridyl groups of two different ligand molecules (Figs. 1 and 2). The perchlorate ion has strong secondary interaction with silver through oxygen (Ag···O = 2.719(15) Å; sum of van der Waal radii 3.24 Å). The sum of bond angles N(2)–Ag(1)–N(1), N(2)–Ag(1)–C(12) and N(1)–Ag(1)–C(12) is 357.1°(≈360°), indicating that N(1), N(2) and C(12) constitute a trigonal planar geometry around Ag(1). The sum of six angles at Ag (viz N(2)–Ag(1)–N(1), N(2)–Ag(1)–C(11), N(2)–Ag(1)–C(12), N(1)–Ag(1)–C(11), N(1)–Ag(1)–C(12) and C(12)–Ag(1)–C(11) is ≈657° (for tetrahedral structure around Ag expected value is ~655°). Out of the six angles C(12)–Ag(1)–C(11) is only 32.2(5)°. Thus two vinyl carbon atoms and two pyridyl nitrogen are at corners of highly distorted tetrahedron enveloping silver. Therefore coordination geometry of Ag may be described as distorted tetrahedral and distortion is caused by rigidity of carbon–carbon double bond. The secondary interaction between perchlorate oxygen and silver also contributes to distortion. The angle O(3)–Ag(1)–C(11) is 99.1(9)° and rules out any correlation of coordination geometry around silver to a trigonal bipyramidal arrangement. On reacting AgCF$_3$SO$_3$ with **L1** complex **2** was obtained. On subjecting its single crystals to X-ray diffraction it was found that contrary to **1** there is no bond between vinyl group and silver, resulting in infinite molecular strands (Fig. 3A). Formally by replacing perchlorate ion with CF$_3$SO$_3^-$, the **2** can be derived from **1**. It changes the structure drastically as infinite molecular strands constitute the structure of **2**. The sum of bond angles N(1)–Ag(1)–N(2) N(1)–Ag(1)–Ag(1) and N(2)–Ag(1)–Ag(1) ≈354°, which indicates that on including the weak interaction of Ag(I) with oxygen of CF$_3$SO$_3^-$ coordination number of silver becomes three (Fig. 3B) and its coordination geometry is distorted trigonal planar. The geometry may also be described as linear distorted by weak interaction between Ag and

Table 2
Selected bond lengths (Å) and bond angles (°) for **1**, **2** and **L2**.

| Bond length		Bond angles	
1			
Ag(1)–N(1)	2.281(10)	N(2)–Ag(1)–N(1)	92.0(4)
Ag(1)–N(2)	2.255(9)	N(2)–Ag(1)–C(12)	144.7(4)
Ag(1)–C(11)	2.350(12)	N(2)Ag(1)–C(11)	115.8(4)
Si(1)–C(11)	1.818(12)	N(1)–Ag(1)–C(12)	120.4(5)
Si(1)–C(2)	1.854(13)	C(12)–Ag(1)–C(11)	32.2(5)
Si(1)–C(7)	1.885(11)	N(1)–Ag(1)–C(11)	152.1(4)
Si(1)–C(13)	1.910(14)	N(1)–Ag(1)–O(3)	79.29(42)
C(11)–C(12)	1.290(2)	N(2)–Ag(1)–O(3)	97.38(42)
Ag(1)–C(12)	2.309(15)	O(3)–Ag(1)–C(11)	99.1(9)
Ag(1)···O(3)	2.719(15)	C(2)–Si(1)–C(7)	106.4(5)
		C(2)–Si(1)–C(13)	109.7(6)
		C(11)–Si(1)–C(13)	113.7(7)
		C(11)–Si(1)–C(7)	105.3(5)
		C(6)–N(2)–Ag(1)	116.6(7)
		C(1)–N(1)–Ag(1)	121.3(8)
		Ag(1)···O(3)–Cl(1)	127.3(1)
2			
Ag(1)–N(1)	2.135(3)	N(1)–Ag(1)–N(2)	167.87(13)
Ag(1)–N(2)	2.141(3)	N(1)–Ag(1)–Ag(1)	77.35(9)
Ag(1)···Ag(1)	3.191(1)	N(2)Ag(1)–Ag(1)	108.33(9)
Si(1)–C(11)	1.849(5)	C(11)–Si(1)–C(13)	111.8(3)
Si(1)–C(13)	1.866(5)	C(11)–Si(1)–C(4)	109.5(2)
Si(1)–C(4)	1.880(4)	C(4)–Si(1)–C(6)	106.50(17)
Si(1)–C(6)	1.885(4)	C(13)–Si(1)–C(6)	110.2(2)
C(11)–C(12)	1.262(9)	C(1)–H(1)···F(1)	68.7(2)
F···H(shortest)	2.616(11)	Ag(1)···O(2)–S(1)	129.6(3)
Ag···O(shortest)	2.665(19)		
π···π	3.663(5)		
L2			
Si(1)–Si(1)	2.3369(17)	C(3)–Si(1)–Si(1)	107.22(11)
C(3)–Si(1)	1.883(3)	C(2)–Si(1)–Si(1)	109.81(13)
C(7)–N(1)	1.313(4)	C(3)–Si(1)–C(1)	110.44(15)
C(6)–N(1)	1.358(4)	C(1)–Si(1)–C(2)	110.60(18)
C(1)–Si(1)	1.875(3)	C(7)–N(1)–C(6)	117.1(3)
C(2)–Si(1)	1.863(3)		
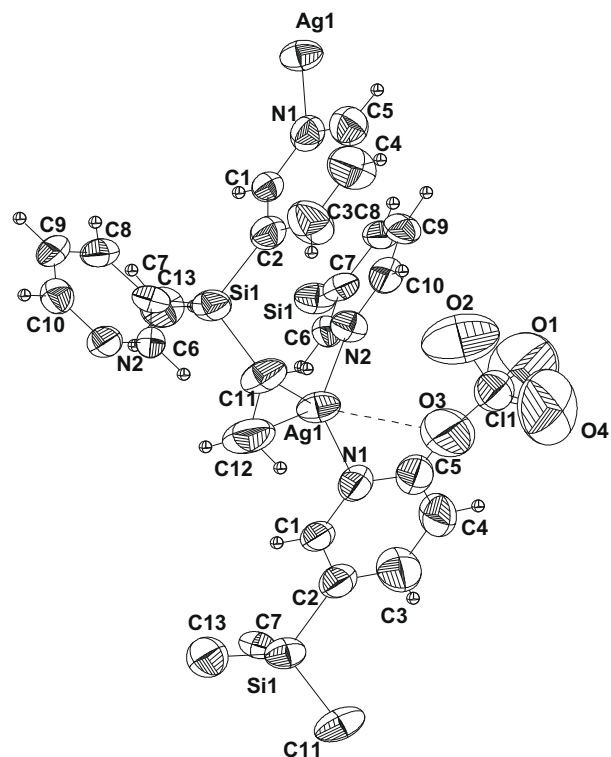
Fig. 1. ORTEP diagram of a segment of two dimensional structure of [Ag(**L1**)]ClO$_4$ (**1**) with 50% probability ellipsoids.
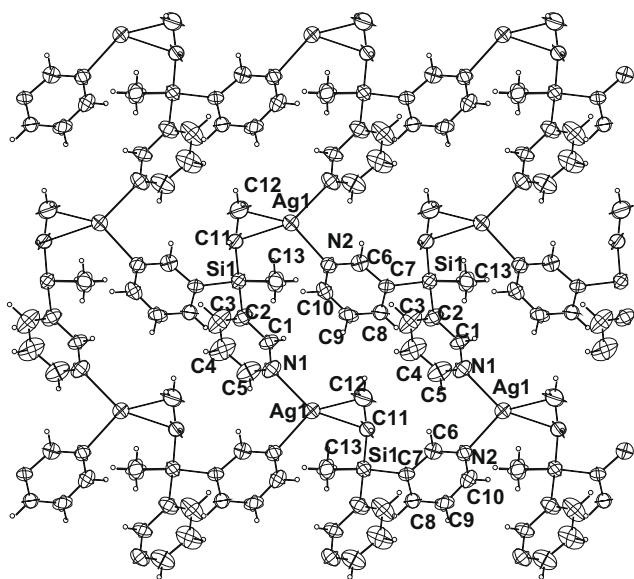
Fig. 2. Two dimensional structure of **1** with 50% probability ellipsoids (perchlorate ions are omitted for clarity).

oxygen of $CF_3SO_3^-$. Probably the bulkiness of $CF_3SO_3^-$ prevents the bond formation between silver and C=C and thus changes the structural arrangement. In a recent study made on silver complexes of bis(4-pyridyl)dimethylsilane containing different counter ions it has been observed that among the coordinating anions $CF_3SO_3^-$ (others NO_2^-, NO_3^- and PF_6^-) being bulkiest restricts [16,17] the coordination number of Ag to three as in case of **2**. The bigger bite of $CF_3SO_3^-$ has been reported responsible for stretch of transannular Ag⋅⋅⋅Ag interactions [15]. These facts support the argument that one of the reasons of change in structural features of Ag(I)–**L1** complex when counter ion perchlorate is replaced with CF_3SO_3, may be the bulkiness of later. However, it should not be ignored that the formation of structure of Ag(I)–**L1** complex has to be

attributed to the felicitious combination of size influence with the electronic effects character. In **2**, $CF_3SO_3^-$ anion acts as a bridge between two molecular strands through F–H (aromatic) secondary interaction [shortest F–H distance 2.616(11) Å; sum of van der Waal's radii 2.90 Å]. The secondary Ag⋅⋅⋅O, [2.665(19) Å], argentophilic Ag⋅⋅⋅Ag [3.191(1) Å] and π–π interactions [3.663(5) Å] also connect the strands. The Ag–N bond distances 2.281(10) and 2.255(9) Å of **1** are longer than literature reports, 2.127(4)–2.159(5) Å for metallamacrocycle of Ag formed with bis(3-pyridyl)dimethylsilane [8]. However, Ag–N bond distances of **2**, 2.135(3) and 2.141(3) Å are consistent with these reports. Probably Ag–N bonds of **1** are elongated due to formation of 2-D structure which probably also contributes in distorting coordination geometry around silver. The Ag–C bond lengths 2.350(12) and 2.309(15)) Å of **1** are somewhat shorter than bond distances 2.385(5)–2.410(5) Å reported [5] for $[Ag(\eta^2\text{-}C_2H_4)_3]^+$. The C=C bond length of 1.290(2) Å found in **1** is consistent with the value 1.304 Å reported [5] for $[Ag(\eta^2\text{-}C_2H_4)_3]^+$ and 1.313 Å reported for solid ethene [20]. This indicates that C=C bond length remains almost unchanged on coordination with Ag in **1**. In iso-electronic $[Pt(\eta^2\text{-}C_2H_4)_3]$ average C=C bond length is elongated to 1.402(7) Å [21]. The N–Ag–N bond angle in **2** is 167.87(13)°, deviated from linearity due to Ag⋅⋅⋅O secondary interaction (2.665(19) Å; sum of van der Waal' radii 3.24 Å) and probably also due to argentophilic Ag⋅⋅⋅Ag interactions (3.191(1) Å; sum of van der Waal' radii 3.44 Å). The Ag⋅⋅⋅Ag distance (3.191(1) Å) of **2** is consistent with earlier reports of 3.145(1) Å for metallamacrocycle of Ag formed with bis(3-pyridyl)dimethylsilane [8], which has a perchlorate counter anion. The C=C bond length of **2** is shorter than that of **1** (Table 2) as expected. The argentophilic, Ag⋅⋅⋅Ag interactions in **2** are much stronger than those observed in Ag complexes of $O(SiMe_2(4\text{-}py))_2$ formed with different anions (Ag⋅⋅⋅Ag distance = 3.20(1)–3.81(1) Å) [15].

The ORTEP diagram of **L2** is shown in Fig. 4. 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 [22] 1.873(2) and 1.849(4)–1.863(4) Å, respectively, reported for poly(silyl)pyridines. The Si–Si bond distance 2.3369(17) Å of **L2** is slightly shorter than
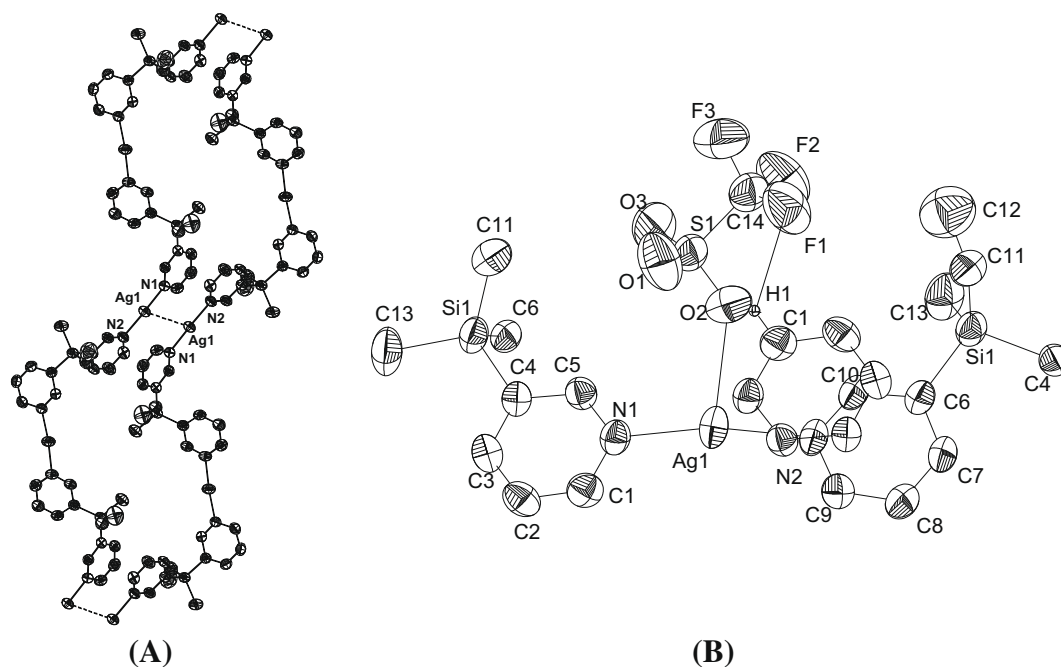

(A)

(B)

Fig. 3. (A) ORTEP diagram of a segment of strands of **2** with 50% probability ellipsoids, H and $CF_3SO_3^-$ are omitted for clarity; (B) coordination sphere of Ag in **2** including secondary interaction with $CF_3SO_3^-$.
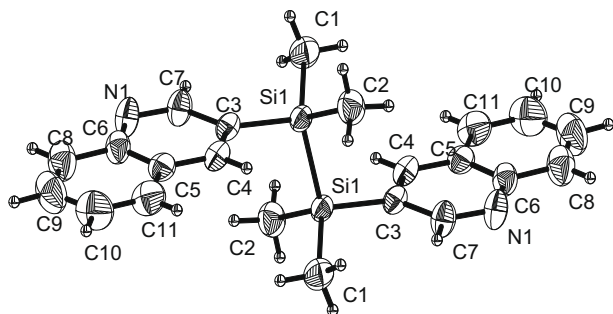
Fig. 4. ORTEP diagram of **L2** with 50% probability ellipsoids.

the earlier reported values 2.3539(14) Å for known disilanes [23,24] and 2.353(3) Å for $(Me_2SiSiMe_2)[\eta^5-C_5H_4Fe(CO)_2I]_2$ [25]. The present value is more consistent with Si–Si bond length, 2.346(4) Å, reported for $(Me_2SiSiMe_2)[\eta^5-C_5H_4Fe(CO)_2]_2$ [25]. The geometry of silicon in **L2** is tetrahedral The steric congestion is known to elongate Si–Si bond as in case of 1,2-bis(1,1,2-trimethyl-propyl)-1,1,2,2-tetrakis(diethylamino)disilane and 1,2-di-*tert*-bu-tyl-1,1,2,2-tetrakis(diethylamino)disilane which have Si–Si bond lengths as 2.539(2) and 2.4764(9) Å, respectively [26]. The present Si–Si bond length is much shorter than these, indicating less steric crowding in case of **L2**. The Si–Si bond distance of disilane-bridged [2] ruthenocenophane 2.370(2) Å [27] is somewhat elongated than the present one. 2,2,5,5-Tetramethyl-3,3,4,4-tetrakis(trimethyl-silyl)-2,3,4,5-tetrasilahexane also shows [28] some what longer Si–Si bond distances (2.3738(9)–2.403(2) Å) in comparison to that of **L2**, again due to steric crowding. The Si–Si bond length of bicy-clic disilane (2.307(4) Å) [29] is some what shorter than that of **L2**. The Si–Si bond length of the order of 2.697(2) Å has also been re-ported for hexa-*tert*-butyldisilane [30]. For simple disilane $Me_3Si–Si–Ph_3$ the Si–Si bond length 2.355(1) Å [31] has been found to be somewhat longer than that of **L2**. In perchloropolysilane, which consists of infinite parallel-aligned all-*trans* chains of $SiCl_2$ repeat units, Si–Si bond length is found longer (2.372 (5) Å) [32] than that of **L2**. In 1,2-bis(ferrocenyl)-1,1,2,2-tetramethyldisilane and (1,1′-ferrocenediyl)tetramethyldisilane Si–Si bond lengths have been reported as 2.340(2) and 2.351(1) Å, respectively [33]. The first value is consistent with that of **L2** whereas second one is somewhat longer.

4. Conclusion

New organosilicon backbone containing pyridyl/quinolyl li-gands, bis(3-pyridyl)methylvinylsilane (**L1**) and 1,2-di(3-quinolyl)dimethyl disilane (**L2**) have been synthesized and characterized by NMR, IR and X-ray diffraction (when single crystals could be grown). The [Ag(**L1**)]ClO$_4$ (**1**) has two dimensional sheet type structure having 25-membered metallamacrocycles in which Ag has distorted tetrahedral geometry and is bonded to vinyl group. AgCF$_3$SO$_3$ forms with **L1** infinite molecular strands in which coor-dination geometry of silver is distorted trigonal planar. CF$_3$SO$_3^-$ an-ion acts as a bridge between two molecular strands through F···H (aromatic) and Ag···O secondary interactions. The Ag–C distances in **1** are 2.309(5) and 2.350(12) Å. The C=C bond length does not exhibit significant change on bonding with silver in **1**.

Appendix A. Supplementary material

CCDC 702626, 702628 and 702627 contains the supplementary crystallographic data for **1**, **2** and **L2**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.03.012.

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