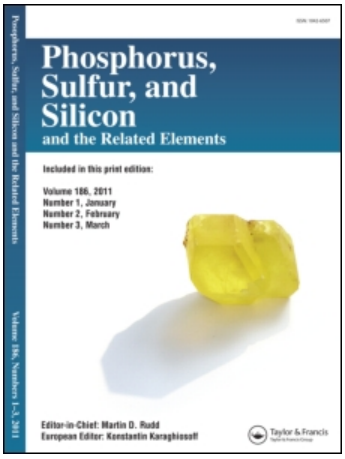

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DIORGANOSILICON(IV) COMPLEXES OF FLUORO-IMINES: SYNTHETIC, SPECTROSCOPIC AND BIOLOGICAL ASPECTS

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DIORGANOSILICON(IV) COMPLEXES OF FLUORO-IMINES: SYNTHETIC, SPECTROSCOPIC AND BIOLOGICAL ASPECTS

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The synthetic, spectroscopic and biological studies of some diorganosilicon(IV) complexes derived from fluoroimines having NS and NO donor systems have been undertaken. The fluoroimines were prepared by the condensation of 2-Fluorobenzaldehyde and 1-(2-Fluorophenyl)-ethanone with hydrazinecarbothioamide and hydrazinecarboxamide. These imines, on interaction with diorganosilicon(IV) chlorides, yield complexes having Si—S/Si—O and Si←N bonds. The structures of these compounds have been elucidated by microestimations and spectral [(UV), (IR), (proton-1, carbon-13, fluorine-19 and silicon-29 NMR)] studies which unerringly point to a trigonal bipyramidal and octahedral geometries for unimolar and bimolar reactions, respectively, around silicon(IV), as the active lone pair of nitrogen is also included in the coordination sphere. Studies were conducted to assess the comparative growth inhibiting potential of the synthesized complexes against the fluoroimines for a variety of fungal and bacterial strains. The studies demonstrate that the concentrations reached levels which are sufficient to inhibit and kill the pathogens. The results of biological studies have also been compared with the conventional standards, Bavistin and Streptomycin, taken for antifungal and antibacterial activities, respectively.

Key words: Diorganosilicon(IV) complexes, fluoroimines, thioimines, spectral studies, biocidal activity.

INTRODUCTION

The interest in organosilicon compounds is generated by the wide applicability of organo-siloxane elastomers, resins and liquid polymers.[1,2] Since, organosilicon chemistry involves hydrides, halides, alkoxides, oxides, nitrides, and sulfides, it is in many ways a counterpart of the inorganic chemistry of silicon. Tetrahedral geometry dominates the structural chemistry of organometallic halides of silicon (R_nMX_{4-n}; $n = 1 - 3$, R = Me, Ph) which exhibits this stereochemistry in all the three phases.[3] Higher coordination numbers in organosilicon chlorides can also arise by intramolecular coordination of a donor atom remote in the organic ligand.[4] Many five- and six-coordinated silicon complexes have been characterised and are recent examples illustrating the trigonal bipyramidal[5,6] and octahedral[7] geometries, respectively, typically adopted by such compounds. Lukevics *et al.*[8] reported anticancer properties for several quinoline derivatives bearing a trialkylsilyl group towards a panel of animal tumour systems. Silatrane derivative, migugen containing an unusual five coordinate geometry at the silicon atom exhibits 50% inhibition of Walker 256 carcinosarcoma.[9] Generally, organosilicon compounds seem to owe their antitumour properties to the stimulation of the immunodefensive system of the organism.[10]

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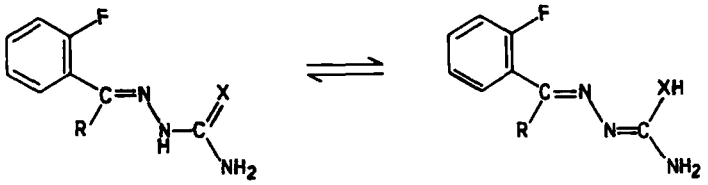
The reason for application of fluoro organometallic compounds in pharmaceutical field is because of their positive results in biological activity.[11] This has also been attested by the available literature.[12] It possibly appears that fluorine can alter the activity of molecules or make them specific irreversible enzyme inhibitors.[13]

The overall picture of silicon in relation to biological systems is that of a ubiquitous, passive and almost always benign element. However, its organo-derivatives display appreciable potential in biological systems. An objective of this account is to highlight a systematic study of the stereochemical and biochemical aspects of the diorganosilicon(IV) complexes of fluoroimines. The metal chelates along with their chelating agents have been tested in vitro against pathogenic fungi, viz., Fusarium oxysporum, Aspergillus niger and Macrophomina phaseolina and bacteria, viz., Klebsiella aerogenous, Pseudomonas cepacicola, Staphylococcus aureus and Escherichia coli. The results of these investigations are quite encouraging. Based on the coordination sites available in the ligand systems, these may be classified as monobasic bidentate as shown below:



where , R= H or CH_3 and X = S or O

RESULTS AND DISCUSSION

The 1:1 and 1:2 molar reactions of Me_2SiCl_2 and Ph_2SiCl_2 with fluoroimines have led to the formation of $Me_2SiCl(N\frown X)$, $Me_2Si(N\frown X)_2$, $Ph_2SiCl(N\frown X)$ and $Ph_2Si(N\frown X)_2$ types of complexes. The reactions have been carried out in perfectly dry methanolic medium and proceed smoothly with the precipitation of KCl. These reactions can be represented by the following general equations:

$$R_2SiCl_2 + N\frown X.K \xrightarrow{1:1} R_2SiCl(N\frown X) + KCl$$

$$R_2SiCl_2 + 2N\frown X.K \xrightarrow{1:2} R_2Si(N\frown X)_2 + 2KCl$$

(where, $N\frown X$ is the donor system of the potassium salt of fluoroimine $N\frown X.K$, X = S or O and R = Me or Ph)

The resulting coloured solids are soluble in most of the common organic solvents. These have been found to be monomeric as evidenced by their molecular weight determinations. The low values of molar conductivity (8–15 $ohm^{-1}\ cm^2\ mol^{-1}$) of the resulting silicon complexes in anhydrous DMF show them to be non-electrolytes in nature.

U.V. Spectra

The electronic spectra of 2-(2-Fluorophenylmethylene)hydrazine carboxamide and its 1:1 and 1:2 dimethylsilicon complexes have been recorded. The spectrum of the

ligand shows a broad band at 365 nm which can be assigned to the $n - \pi^*$ transitions of the azomethine group. This band shows a blue shift in the silicon complexes appearing at 340 and 346 nm for 1:1 and 1:2 derivatives respectively, due to the polarisation within the >C=N chromophore caused by the silicon-ligand electron interaction. The bands at 270 and 300 nm due to $\pi - \pi^*$ transitions, appear almost in the same region in the spectra of organosilicon derivatives.

IR Spectra

The assignments of characteristic IR frequencies for the resulting complexes may be discussed as follows:

The IR spectra of these derivatives do not show any band in the region 3250–3100 cm^{-1} which could be assigned to νNH. This clearly indicates the deprotonation of the ligands as a result of complexation with the metalloid atom. A sharp band at ca. 1620 cm^{-1} due to ν(>C=N) frequency of the free azomethine group in the ligands shifts to the lower frequency (ca. 15 cm^{-1}) in the silicon complexes and indicating thereby the coordination of the azomethine nitrogen to the silicon atom. A shift of this frequency to the higher[14] and lower[15] wavenumber side as well as no change has also been reported in the literature.[16]

In dimethylsilicon(IV) complexes, a band at ca. 1420 cm^{-1} has been ascribed to the asymmetric deformation vibrations of (CH_3—Si) group,[17] whereas the band at ca. 1270 cm^{-1} to the symmetric deformation mode of (CH_3—Si) group.

Several new bands are observed in the spectra of the complexes at ca. 620 cm^{-1}, 580 cm^{-1} and 540 cm^{-1} and these are due to ν(Si—O),[18] ν(Si←N)[19] and ν(Si—S)[20] vibrations, respectively. These remain absent in the spectra of the ligands. A band due to ν(Si—Cl)[21] at ca. 510 cm^{-1} is observed in 1:1 diorganosilicon(IV) derivatives.

It has been reported that the cis form of such complexes gives rise to two ν(M—N) bands, whereas in the transform only one IR active ν(M—N) band[22] is observed. The presence of only one ν(Si←N) band in the present case, suggests that the complexes exist in the trans form.

^1H NMR Spectra

The proton magnetic resonance spectral data of hydrazinecarboxamides and hydrazinecarbothioamides of 2-Fluorobenzaldehyde, [1-(2-Fluorophenyl)ethanone] and their corresponding silicon complexes have been recorded in DMSO-d_6. The chemical shift values relative to the TMS peak are listed in Table I.

The broad signal due to the —NH proton in the ligands disappears in the case of silicon complexes showing the coordination of silicon to sulphur/oxygen after the deprotonation of the functional group. The azomethine proton signal $\left(\mathrm{H—\overset{|}{C}=N}\right)$ appears at δ8.42 and δ8.33 ppm in the ligands L_1H and L_2H. Further, the signals observed at δ1.88 and 2.12 ppm in the ligands L_3H and L_4H are due to methyl protons of $\left(\mathrm{H_3C—\overset{|}{C}=N}\right)$ group. The downfield shift of these positions

TABLE I

^{1}H NMR spectral data (δ, ppm) of fluoroimines and their corresponding diorganosilicon(IV) complexes

Compound	-NH (bs)	$-NH_2$ (bs)	H-C=N/ H_3C-C=N(s)	Aromatic (m)	Si-CH_3/C_6H_5
L_1H	11.67	2.35	8.42	7.68-6.65	-
$Me_2SiCl(L_1)$	-	2.32	8.68	7.88-6.74	0.74
$Me_2Si(L_1)_2$	-	2.36	8.72	7.96-6.90	0.98
L_2H	11.24	2.16	8.33	7.78-6.70	-
$Ph_2SiCl(L_2)$	-	2.14	8.68	7.92-6.76	6.24
$Ph_2Si(L_2)_2$	-	2.16	8.70	8.04-6.84	6.44
L_3H	9.30	3.08	1.88	7.52-6.16	-
$Me_2SiCl(L_3)$	-	3.00	2.08	7.77-6.38	0.66
$Me_2Si(L_3)_2$	-	3.04	2.12	7.84-6.46	0.84
L_4H	10.24	3.16	2.12	8.28-6.92	-
$Me_2SiCl(L_4)$	-	3.12	2.32	8.44-7.10	0.76
$Me_2Si(L_4)_2$	-	3.14	2.28	8.48-7.08	0.94
$Ph_2SiCl(L_4)$	-	3.16	2.28	8.32-7.00	6.32
$Ph_2Si(L_4)_2$	-	3.12	2.26	8.36-7.04	6.36

DMSO-d_6-2.54(s)

bs-broad singlet, s-singlet, m-multiplet.

in the spectra of the complexes substantiates the coordination of azomethine nitrogen to the silicon atom. The additional signals in the region δ0.66–0.98 ppm and δ6.24–6.44 ppm in $Me_2SiCl(N\frown X)$, $Me_2Si(N\frown X)_2$, $Ph_2SiCl(N\frown X)$ and $Ph_2Si(N\frown X)_2$ types of complexes are due to Me_2Si and Ph_2Si groups, respectively.

^{13}C *NMR Spectra*

The conclusions drawn from the UV, IR and ^{1}H NMR spectra are concurrent with the ^{13}C NMR spectral data regarding the authenticity of the proposed structures. The ^{13}C NMR spectra of ligands L_2H, L_3H and their 1:1 and 1:2 diorganosilicon derivatives have been recorded in Table II. The chemical shift values of the carbon atoms attached with the azomethine nitrogen, thiolic sulphur or amido oxygen lends further support to the proposed coordination in these complexes. The new carbon signals due to Si—Me/Ph are also reported.

^{19}F *NMR Spectra*

The ^{19}F NMR spectra of L_3H and L_4H display a sharp singlet at $\delta - 108.36$ and -109.00 ppm, respectively. The diorganosilicon(IV) complexes of these ligands

TABLE II

^{13}C NMR spectral data of fluoroimines and their respective diorganosilicon(IV) complexes

Compound	Chemical shift values (δ, ppm)				
	Amido/ Thiolo	Azomethine	Methyl	Aromatic	Si-Me/Ph
L_2H	179.52	157.38	-	143.66,127.85,126.54, 123.34,122.17,120.33	-
$Me_2SiCl(L_2)$	167.42	146.82	-	143.82,127.96,126.68, 123.32,122.36,120.66	14.34
$Me_2Si(L_2)_2$	168.34	148.24	-	143.92,127.88,126.66, 123.46,122.48,120.68	15.56
L_3H	164.58	156.51	15.88	141.29,129.64,129.10, 126.72,123.52,123.41	-
$Ph_2SiCl(L_3)$	157.32	148.76	16.12	141.28,129.76,129.43, 126.87,124.01,123.58	130.18,134.26, 137.33,139.15
$Ph_2Si(L_3)_2$	159.73	149.16	16.22	141.34,129.75,129.48, 126.79,123.24,123.58	133.24,136.17 137.86,139.32

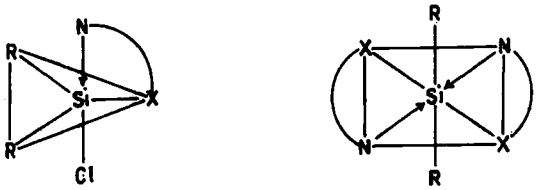
Methanol - 50.5

give signals ranging in between $\delta - 108.42$ to -110.16 ppm and thus supporting the non-involvement of fluorine in complexation.

^{29}Si NMR Spectra

The ^{29}Si NMR spectra of $Me_2SiCl(L_1)$ and $Me_2Si(L_1)_2$ give a sharp signal at $\delta - 95.45$ and -108.07 ppm clearly indicating the penta- and hexacoordinated environment, respectively, around the silicon atom.[23]

On the basis of the results so far discussed including the analytical as well as spectral data, suitable pentacoordinated trigonal bipyramidal and hexacoordinated octahedral geometries have been suggested for 1:1 and 1:2 diorganosilicon(IV) derivatives, respectively.



(1:1 complex) (1:2 complex)

(where, X = S or O and R = Me or Ph)

TABLE III

Fungicidal screening data of fluoroimines and their diorganosilicon(IV) complexes

Compound	Average percentage inhibition after 96 hrs (conc. in ppm)								
	Aspergillus niger			Fusarium oxysporum			Macrophomina phaseolina		
	50	100	200	50	100	200	50	100	200
Bavistin	91	100	100	86	100	100	82	100	100
L_1H	68	77	80	72	80	84	66	74	78
$Me_2SiCl(L_1)$	74	86	100	80	88	100	72	85	100
$Me_2Si(L_1)_2$	86	94	100	92	100	100	87	96	100
$Ph_2SiCl(L_1)$	82	100	100	88	94	100	84	95	100
$Ph_2Si(L_1)_2$	86	100	100	96	100	100	93	100	100
L_2H	70	78	84	74	80	84	69	78	80
$Me_2SiCl(L_2)$	77	84	100	80	86	100	74	86	100
$Me_2Si(L_2)_2$	88	96	100	94	100	100	89	98	100
$Ph_2SiCl(L_2)$	86	98	100	88	100	100	83	100	100
$Ph_2Si(L_2)_2$	89	100	100	98	100	100	94	100	100
L_3H	72	78	80	74	79	86	72	81	84
$Me_2SiCl(L_3)$	78	87	100	79	88	100	84	89	100
$Me_2Si(L_3)_2$	86	94	100	84	95	100	88	92	100
$Ph_2SiCl(L_3)$	84	96	100	82	100	100	86	100	100
$Ph_2Si(L_3)_2$	96	100	100	92	100	100	95	100	100
L_4H	74	80	86	83	88	92	85	88	92
$Me_2SiCl(L_4)$	80	88	100	88	92	100	88	92	100
$Me_2Si(L_4)_2$	88	97	100	95	100	100	96	100	100
$Ph_2SiCl(L_4)$	86	100	100	92	100	100	96	100	100
$Ph_2Si(L_4)_2$	98	100	100	96	100	100	98	100	100

BIOCIDAL ACTIVITY

Fungicidal and bactericidal activities of fluoroimines and their respective diorganosilicon(IV) complexes against pathogenic fungi and bacteria are recorded in Tables III and IV.

Mode of Action

The degradative enzymes produced by the microorganisms are important in host infection, food deterioration and breakdown of organic matter.[24] The enzyme production is here intended to mean both, synthesis of the enzyme by the microorganism and activity of the enzyme in the medium after it is produced. Since, the diorganosilicon(IV) complexes inhibit the growth of microorganisms, it is assumed that the production of the enzymes is being affected and hence the organism is unable to utilize the food and consequently the growth ceases. The enzymes which require free sulfhydryl groups (—SH) for activity appear to be especially susceptible to deactivation by ions of the complexes. Due to greater lipid solubility, complexes

TABLE IV

Bactericidal screening data of fluoroimines and their diorganosilicon(IV) complexes

Compound	Diameter of inhibition zone (mm) after 24 hours (conc. in ppm)							
	Escherichia coli[-]		Klebsiella aerogenous[-]		Pseudomonas cepacicola[-]		Staphylococcus aureus[+]	
	500	1000	500	1000	500	1000	500	1000
Streptomycin	1	2	3	5	2	3	15	17
L_1H	4	6	5	7	4	7	7	10
$Me_2SiCl(L_1)$	5	7	6	9	6	8	8	11
$Me_2Si(L_1)_2$	7	9	8	12	7	10	9	12
$Ph_2SiCl(L_1)$	7	9	8	11	6	9	9	11
$Ph_2Si(L_1)_2$	10	13	10	14	8	10	12	16
L_2H	5	8	6	8	6	9	9	12
$Me_2SiCl(L_2)$	7	9	8	10	7	11	11	14
$Me_2Si(L_2)_2$	9	12	10	13	8	12	13	15
$Ph_2SiCl(L_2)$	8	11	10	12	9	12	11	14
$Ph_2Si(L_2)_2$	12	14	12	15	10	14	14	18
L_3H	5	9	6	8	7	10	10	14
$Me_2SiCl(L_3)$	6	10	8	10	8	11	12	16
$Me_2Si(L_3)_2$	8	11	8	12	9	12	14	19
$Ph_2SiCl(L_3)$	9	12	8	14	10	12	12	16
$Ph_2Si(L_3)_2$	12	15	14	17	13	16	16	19
L_4H	7	10	7	10	8	12	12	16
$Me_2SiCl(L_4)$	8	11	9	11	9	13	14	18
$Me_2Si(L_4)_2$	10	13	10	13	10	14	17	21
$Ph_2SiCl(L_4)$	9	13	10	12	11	13	14	16
$Ph_2Si(L_4)_2$	12	16	14	17	15	18	17	21

facilitate their diffusion through the spore membrane to the site of action within spores and ultimately killing them by combining with —SH groups of certain cell enzymes.[25] The variation in the effectiveness of different biocidal agents against different organisms as suggested by Lawrence *et al.*[26] depends on the impermeability of the cell. Rich and Horsfall[27] have adducted evidence that the hydrocarbon tail functions as a lipophilic group to drive the compound through the semipermeable defenses of the cell.

The effect of resonating rings on toxicity may be appraised in the light of modern electronic theory. According to Gilman,[28] resonant energy is energy in excess of the sum of the energy of the separate bonds, making up the molecule. The Arrhenius activation theory states that excess molecular energy seems to activate molecules and produce a more rapid rate of chemical reaction. Resonating structures, such as benzene rings (in the present case) may serve as powerhouse to activate potentially reactive groupings. If toxicity is dependent on one or more chemical reactions, then any molecule which would increase the rate of chemical reactions must, perforce, enhance toxicity.[29]

The toxicity of diorganosilicon(IV) complexes can well be understood by considering the chelation theory.[30] The chelation reduces the polarity of the central

ion mainly because of the partial sharing of its positive charge with the donor groups and possible π-electron delocalisation within the whole chelate ring. This chelation increases the lipophilic nature of the central atom, which favours its permeation through the lipid layer of the membrane.

From bactericidal activity, it is apparent that the complexes were more toxic towards Gram(+) stain as compared to Gram(−) stain. The reason is the difference in the structures of the cell walls. The walls of Gram(−) cells are more complex than those of Gram(+) cells. The lipopolysaccharide forms an outer lipid membrane and contributes to the complex antigenic specificity of Gram(−) cells.

Further, the results of biocidal activity have been compared with the conventional fungicide, Bavistin and conventional bactericide, Streptomycin, taken as standards in either case. It is evident that though the fluoro ligands alone were quite toxic but their activity synergized on undergoing complexation. From Table III it is clear that some of the newly synthesized complexes killed the pathogens at 100 ppm concentration while at 200 ppm concentration all the complexes killed the pathogens completely, hence this concentration is absolutely fatal for the microorganisms. The data reveal that the complexes $Ph_2Si(L_3)_2$ and $Ph_2Si(L_4)_2$ were found to be even more toxic than the standard, Bavistin.

Further the sequence of toxicity in increasing order as evidenced from Tables III and IV is

$$Me_2SiCl(L) < Me_2Si(L)_2 \simeq Ph_2SiCl(L) < Ph_2Si(L)_2$$

The results of Tables III and IV also reveal that there is a direct relation between the activity and the coordination environment of the silicon. The six coordinated silicon displayed better results as compared to the five coordinated silicon.

EXPERIMENTAL

Adequate care was taken to keep the diorganosilicon(IV) complexes, chemicals and glass apparatus free from moisture. The clean and well dried glass apparatus fitted with quickfit interchangeable standard ground joints was used throughout the experimental work. All the chemicals and solvents used were dried and purified by standard methods.

Preparation of ligands. The fluoroimines were prepared by the condensation of 2-Fluorobenzaldehyde and 1-(2-Fluorophenyl)ethanone with hydrazinecarboxamide in presence of sodium acetate and hydrazinecarbothioamide in equimolar ratio in absolute alcohol. The contents were refluxed for 45 minutes, recrystallised from the same solvent and dried under reduced pressure. The physical properties of these fluoroimines are as follows:

Fluoroimine, Colour and M.P. (°C)
[2-(2-Fluorophenylmethylene)hydrazinecarboxamide], L_1H
Off White, 218
[2-(2-Fluorophenylmethylene)hydrazinecarbothioamide], L_2H
White, 190
[2-{1-(2-Fluorophenyl)ethyledene}hydrazinecarboxamide], L_3H
White, 194
[2-{1-(2-Fluorophenyl)ethyledene}hydrazinecarbothioamide], L_4H
White, 122

Synthesis of diorganosilicon(IV) complexes. To a calculated amount of potassium salt of fluoroimine [prepared by adding corresponding weight of potassium (0.24–0.74 g) to the fluoroimine (1.27–3.73 g)], L_1H, L_2H, L_3H or L_4H in dry methanol was added the methanolic solution of diorganosilicondichloride (Me_2SiCl_2 or Ph_2SiCl_2) in 1:1 or 1:2 stoichiometric proportions. The contents were refluxed

TABLE V

Analyses and physical properties of diorganosilicon(IV) complexes

Product formed and colour	M.P. (°C)	Yield (%)	Analyses (%) N Found (Calcd.)	S Found (Calcd.)	Cl Found (Calcd.)	Si Found (Calcd.)	Mol.wt. Found (Calcd.)
$Me_2SiCl(L_1)$	226	65	15.21	-	12.89	10.03	245
Yellow			(15.35)		(12.95)	(10.26)	(274)
$Me_2Si(L_1)_2$	230	75	20.21	-	-	6.58	451
Cream			(20.08)			(6.71)	(418)
$Ph_2SiCl(L_1)$	227	76	10.65	-	8.87	6.94	420
Yellow			(10.56)		(8.91)	(7.06)	(398)
$Ph_2Si(L_1)_2$	100	69	15.26	-	-	5.05	510
Cream			(15.49)			(5.18)	(543)
$Me_2SiCl(L_2)$	64d	72	14.42	10.92	12.18	9.52	318
Yellow			(14.50)	(11.06)	(12.23)	(9.69)	(290)
$Me_2Si(L_2)_2$	162	77	18.68	14.11	-	6.02	426
Light yellow			(18.65)	(14.23)		(6.23)	(451)
$Ph_2SiCl(L_2)$	240d	69	10.02	7.63	8.51	6.53	444
Cream			(10.15)	(7.75)	(8.56)	(6.78)	(414)
$Ph_2Si(L_2)_2$	173	72	14.55	11.02	-	4.71	603
Dim purple			(14.62)	(11.16)		(4.89)	(575)
$Me_2SiCl(L_3)$	168d	72	14.43	-	12.26	9.58	312
Cream			(14.60)		(12.32)	(9.76)	(288)
$Me_2Si(L_3)_2$	196	78	18.56	-	-	6.07	424
Light yellow			(18.82)			(6.29)	(447)
$Ph_2SiCl(L_3)$	174	64	10.03	-	8.49	6.63	452
Light pink			(10.20)		(8.61)	(6.82)	(412)
$Ph_2Si(L_3)_2$	182	58	14.56	-	-	4.72	603
Light yellow			(14.73)			(4.92)	(571)
$Me_2SiCl(L_4)$	158d	68	13.69	10.49	11.48	9.02	325
White			(13.83)	(10.55)	(11.67)	(9.24)	(304)
$Me_2Si(L_4)_2$	170d	74	17.38	13.24	-	5.72	504
White			(17.56)	(13.40)		(5.87)	(479)
$Ph_2SiCl(L_4)$	128	70	9.55	7.27	8.17	6.32	456
Cream			(9.82)	(7.49)	(8.28)	(6.56)	(428)
$Ph_2Si(L_4)_2$	122	58	13.71	10.48	-	4.33	576
Cream			(13.94)	(10.64)		(4.66)	(603)

over a ratio-head for 16–18 hours and the white precipitate of potassium chloride obtained, was removed under suction. The excess of the solvent was then removed and the compounds were dried under reduced pressure for 3–4 hours. These were purified by repeated washing with a (1:1) mixture of dry methanol and cyclohexane. Inspite of our best efforts, it has not been possible to obtain suitable crystal for the X-ray crystal structure studies. All the compounds were isolated as powdered solids. The details of these reactions and the analyses of the resulting products are recorded in Table V.

Analytical methods and physical measurements. Carbon and hydrogen analyses were performed at the micro-analytical laboratory of the department. Nitrogen and sulfur were estimated by Kjeldahl's and Messenger's methods, respectively. Silicon was determined gravimetrically as SiO_2. The conductance was measured with a conductivity bridge type 304 Systronics model and the molecular weights were determined by the Rast method. IR spectra were recorded on a Perkin-Elmer 577 Grating Spectrophotometer in the range 4000–200 cm^{-1}, as Nujol mulls using KBr optics. ^1H and ^{19}F NMR spectra were recorded in DMSO-d_6, ^{13}C and ^{29}Si NMR spectra were recorded in methanol, using TMS as the internal/external standard for ^1H, ^{13}C and ^{29}Si NMR spectra and C_6F_6 as the external reference for ^{19}F NMR spectra.

Biocidal activity. A culture of test organism was grown on PDA media (starch, glucose, agar-agar and water, for fungi) and agar media (peptone, beef extract, agar-agar, NaCl and water, for bacteria) for seven days at the optimum temperature for growth. All the glasswares used were sterlized in an autoclave before use. The radial-growth method and the paper-disc plate method were employed to evaluate the fungicidal and bactericidal activities, respectively.[31]

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