

Organosilicon (IV) Complexes with Schiff Bases

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Analytical and spectroscopic (infrared and PMR) data are presented for organosilicon complexes of general formulae $R_2Si(\widehat{ONS})$, $R_3Si(\widehat{XN})$ and $R_2Si(\widehat{NX})_2$ (where $\widehat{XN}$ and $\widehat{ONS}$ represent the donor systems of schiff bases). These complexes adopt five- and six-coordinated structures in possibly trigonal bipyramid and octahedral geometries respectively.

Mehrotra and coworkers^{1,2} reported the preparation and characterization of organosilicon complexes of O,

N donors. Earlier reports from our laboratories dealt with the preparation of organosilicon complexes of schiff bases with N, S donor^{3,4} schiff bases. In continuation of this we report in this note the preparation and characterization of organosilicon (IV) complexes of schiff bases (I-III).

Organosilicon chlorides were distilled before use. Ligands were prepared by the reported methods⁵⁻⁷. Preparations and analyses of the metal complexes were carried out as already reported³.

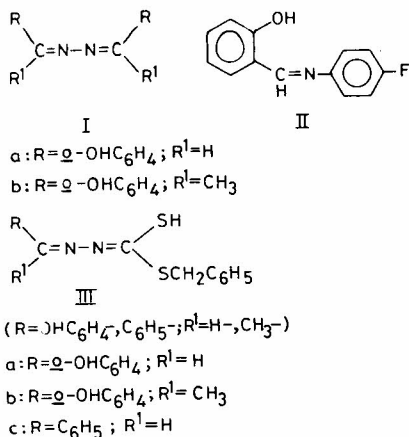
Infrared spectra were recorded in nujol on a Perkin-Elmer 577 spectrophotometer and PMR spectra on a Perkin-Elmer RB-12 spectrometer in $CDCl_3$ or $DMSO-d_6$ using TMS as an internal standard.

The reactions of dimethyl-, diphenyl-, diphenylmethyl-, and trimethyl-silicon chlorides with the

Table 1—Physical Characteristics of Organosilicon Complexes

Silicon derivatives	Ligand	Molar ratio	Yield %	Product Colour and State	m.p./b.p./mm °C	Mol. wt found (calc.)	Found (calc.) (%)		
							Si	C	H
Me_2SiCl_2	II	1:2	76	$Me_2Si(C_{13}H_9NFO)_2$ Yellow solid	70 145/5	500.0 (486.08)	5.63 (5.96)	69.00 (69.13)	4.34 (4.94)
Ph_2SiCl_2	II	1:2	90	$Ph_2Si(C_{13}H_9NFO)_2$ Orange solid	115/5	635 (610.08)	4.90 (4.76)	74.90 (74.74)	4.83 (4.58)
Me_3SiCl	II	1:1	81	$Me_3Si(C_{13}H_9NFO)$ Yellow brown solid	68 160/7	312.0 (288.08)	10.52 (10.06)	67.80 (66.64)	6.28 (6.24)
$Ph_2MeSiCl$	II	1:1	83	$Ph_2MeSi(C_{13}H_9NFO)$ Yellowish red semisolid	210/8	443.0 (412.08)	7.20 (7.05)	75.03 (75.71)	5.95 (5.33)
Me_2SiCl_2	Ib	1:1	96	$Me_2Si(C_{16}H_{14}N_2O_2)$ Yellow solid	157	339.0 (324.08)	8.58 (8.94)	66.33 (66.65)	6.01 (6.17)
Ph_2SiCl_2	Ib	1:1	87	$Ph_2Si(C_{16}H_{14}N_2O_2)$ Yellow foamy semisolid	—	—	6.65 (6.47)	74.86 (74.99)	5.39 (5.35)
Ph_2SiCl_2	Ib	1:1	94	$Ph_2Si(C_{14}H_{10}N_2O_2)$ Cream yellow foamy solid	122	445.0 (420.00)	6.68 (6.92)	73.52 (74.27)	4.05 (4.76)
Me_2SiCl_2	Ia	1:1	91	$Me_2Si(C_{14}H_{10}N_2O_2)$ Yellow semisolid	—	—	9.80 9.82	64.38 64.84	5.95 5.40
Me_3SiCl	Ib	2:1	90	$(Me_3Si)_2(C_{16}H_{14}N_2O_2)$ Yellow solid	184	—	13.68 13.59	64.16 64.07	7.43 7.76
Me_3SiCl	Ia	2:1	89	$(Me_3Si)_2(C_{14}H_{10}N_2O_2)$ Yellow solid	199	353.05 386.18	14.93 14.50	62.25 62.17	7.05 7.38
Me_2SiCl_2	IIIa	1:1	96	$Me_2Si(C_{15}H_{12}N_2S_2O)$ Yellow solid	164	369.0 358.08	7.95 8.09	56.64 56.97	5.05 5.02
Me_2SiCl_2	IIIc	1:2	88	$Me_2Si(C_{15}H_{13}N_2S_2)_2$ Buff solid	153	653.0 628.08	4.05 4.61	61.23 61.13	5.62 5.09
Ph_2SiCl_2	IIIa	1:1	89	$Ph_2Si(C_{15}H_{12}N_2S_2O)$ Wine red semisolid	—	—	6.32 6.15	68.45 68.63	4.03 4.66
Ph_2SiCl_2	IIIc	1:2	96	$Ph_2Si(C_{15}H_{13}N_2S_2)_2$ Yellow brown semisolid	—	—	3.15 3.83	66.83 66.55	4.35 4.76
Me_2SiCl_2	IIIb	1:1	82	$Me_2Si(C_{16}H_{14}N_2S_2O)$ Yellow semisolid	—	—	7.63 7.79	58.58 58.61	5.52 5.40
Ph_2SiCl_2	IIIb	1:1	85	$Ph_2Si(C_{16}H_{14}N_2S_2O)$ Brown semisolid	—	—	5.90 5.64	67.53 67.74	4.18 4.83

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sodium salts of bifunctional tridentate azines and monofunctional and bifunctional schiff bases of *p*-fluoroaniline and S-benzylthiocarbamate were carried out in 1:1 and 1:2 molar ratios in refluxing benzene. It took 10-12 hr of refluxing for the completion of the reaction. The complexes are yellow to orange red in colour and low melting (Table 1). These are soluble in most of the common organic solvents and are susceptible to moisture.

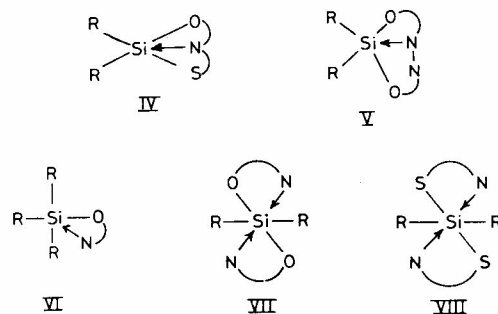
The absence of IR bands in the region, 3300-2850 cm^{-1} , due to νOH or νNH in the complexes indicates deprotonation of ligands on complexation. A sharp band observed $\sim 1590 \text{ cm}^{-1}$ in all the compounds has been assigned to $\nu(\text{C}=\text{N})$.

In the case of $\text{R}_2\text{Si}(\widehat{\text{O}}\text{N}-\widehat{\text{N}}\text{O})$ type of derivatives, two bands are observed around 1615 and 1590 cm^{-1} indicating the coordination of one of the nitrogen atoms of two $\text{C}=\text{N}$ groups, while in $(\text{R}_2\text{Si})_2(\widehat{\text{O}}\text{N}-\widehat{\text{N}}\text{O})$ type of compounds, only a single band around 1590 cm^{-1} is observed suggesting the coordination through nitrogen atoms of both the $\text{C}=\text{N}$ groups. In all the derivatives, except those of the type, $\text{R}_2\text{Si}(\widehat{\text{N}}\text{S})_2$, the sharp bands $\sim 1305 \text{ cm}^{-1}$ may be assigned to the phenolic $\nu\text{C}-\text{O}$ modes.

In dimethyl-, diphenylmethyl-, and trimethyl-silicon derivatives, bands around 1420 and 1270 cm^{-1} have been assigned to the asymmetric and symmetric deformation modes of $\text{CH}_3\text{-Si}$ respectively⁸. Strong bands around 755 cm^{-1} may be due to $\nu\text{Si}-\text{C}$ modes. In diphenyl complexes, four medium to strong intensity bands around 1430, 1120, 725 and 690 cm^{-1} are observed and these have been assigned to $\nu\text{Si}-\text{C}_6\text{H}_5$ modes⁹. In these complexes, the medium intensity bands around 835 cm^{-1} have been assigned to $\nu\text{Si}-\text{O}$ ¹⁰, whereas $\nu\text{Si}-\text{N}$ ¹¹ is observed around 560 cm^{-1} . In complexes of schiff bases of S-benzylthiocarbamate, the medium intensity bands appearing around 520 cm^{-1} have been assigned to $\nu\text{Si}-\text{S}$ ¹².

The PMR spectra of complexes are devoid of signals due to OH and NH groups, indicating deprotonation on complex formation. The coordination of azomethine nitrogen is indicated by the downfield shift in the proton signals attached to $\text{C}=\text{N}$ group. In all the complexes signals due to the protons of the group R in $\text{R}-\text{Si}$ are also observed (Table 2).

The following tentative structures (IV-VIII) can be proposed for the complexes synthesized.



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Table 2— ^1H NMR Spectral Data (δ , ppm) of Organosilicon Derivatives

Sl. No.	Structure	1	2	3	4
1	$\text{Me}_2\text{Si}(\text{O.C}_6\text{H}_4\text{.CH:N.C}_6\text{H}_4\text{.F})_2$	0.13	6.8-7.5	8.56	—
2	$\text{Ph}_2\text{Si}(\text{O.C}_6\text{H}_4\text{.CH:N.C}_6\text{H}_4\text{.F})_2$	—	6.6-7.45	8.43	—
3	$\text{Ph}_2\text{SiMe}(\text{O.C}_6\text{H}_4\text{.CH:N.C}_6\text{H}_4\text{.F})$	6.80-7.75	0.53	8.58	—
4	$\text{Me}_2\text{Si}(\text{O.C}_6\text{H}_4\text{.C(CH}_3)_2\text{:N.N(CH}_3)_2\text{C.C}_6\text{H}_4\text{O})$	0.3	6.90-8.05	2.67	—
5	$\text{Ph}_2\text{Si}(\text{O.C}_6\text{H}_4\text{.C(CH}_3)_2\text{:N.N(CH}_3)_2\text{C.C}_6\text{H}_4\text{O})$	—	6.65-7.81	2.51	—
6	$\text{Ph}_2\text{Si}(\text{O.C}_6\text{H}_4\text{.(CH}_3)_2\text{:N.N.C.S.SCH}_2\text{C}_6\text{H}_5$	—	7.20-7.90	2.38	4.48
7	$\text{Me}_2\text{Si}(\text{O.C}_6\text{H}_4\text{.C(CH}_3)_2\text{:N.N.C.S.SCH}_2\text{C}_6\text{H}_5$	0.23	7.10-7.73	2.45	4.45

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