Synthesis of hexacoordinated organosilicon compounds - a review

Dr. Priya Duggal
Assistant Professor in Chemistry, D.A.V. College, Sector-10, Chandigarh, India

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ABSTRACT: *Hypercoordinated silicon compounds are mainly prepared by the addition reaction of nucleophilic anion or neutral reagents with tetravalent silicon derivatives respectively to anionic or neutral complexes and by the nucleophilic substitution of organosilane. This paper reviews the synthesis of hexa-coordinated organosilicon compounds.*

Key Words: *Organosilane , hypercoordinated, hexacoordinated, chelation, Schiff's base*

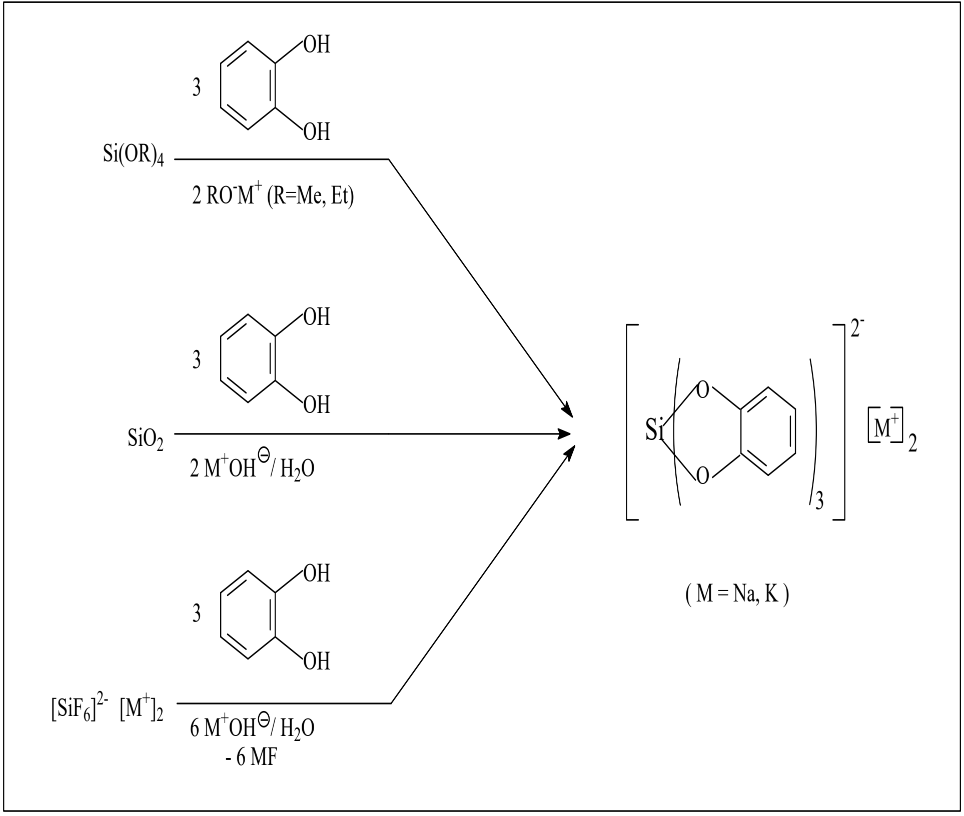
Introduction- An important offshoot in organosilicon chemistry is the study of penta and hexa-coordinated silicon complexes. The studies on the reactivity of penta and hexa-coordinated compounds have revealed the enhanced electrophilicity of silicon in these compounds as compared to their tetra-coordinated analogues **[1-4]**. Due to this property, the hypervalent silicon compounds have been employed in the synthesis of various organic / organometallic compounds. Hypervalent species of silicon are of particular interest because of their importance as starting materials and reactive intermediates in synthesis and because of their biological activity**[5-8]**.

Synthetic methods of hexacoordinated silicon (IV) complexes

Hexa-coordinate silicon species may be prepared according to the following methods:

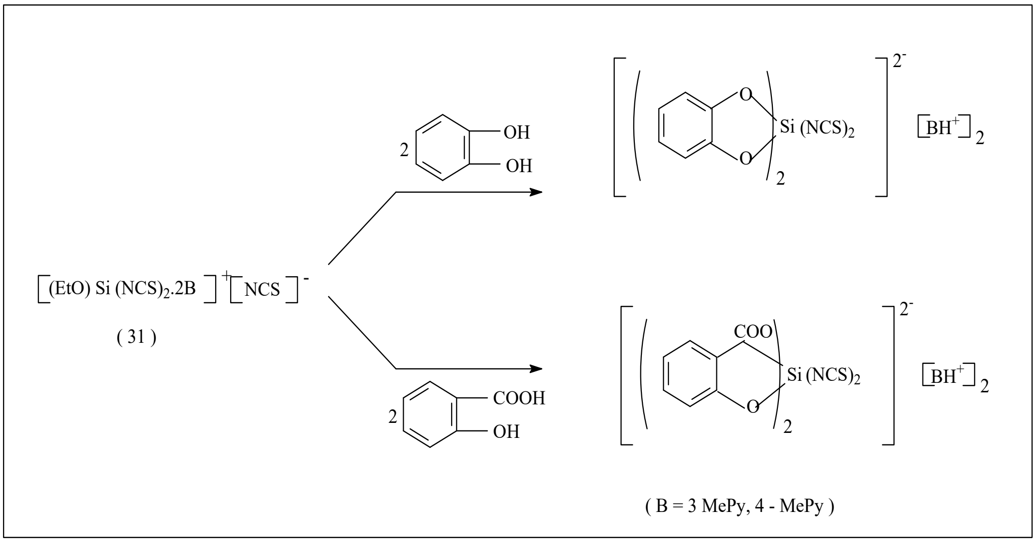
1. Intermolecular coordination to an organosilane

The hexa-coordinated anionic complexes are prepared by the reaction of catechol with teramethoxy (or tetraethoxy) silane under basic conditions **[9,10].** Also these complexes can be obtained directly from silica and $[SiF_6]^{2-}$ $[M^+]_2$ where M=Na, K **[11,12]** (Scheme – 1)



Scheme-1

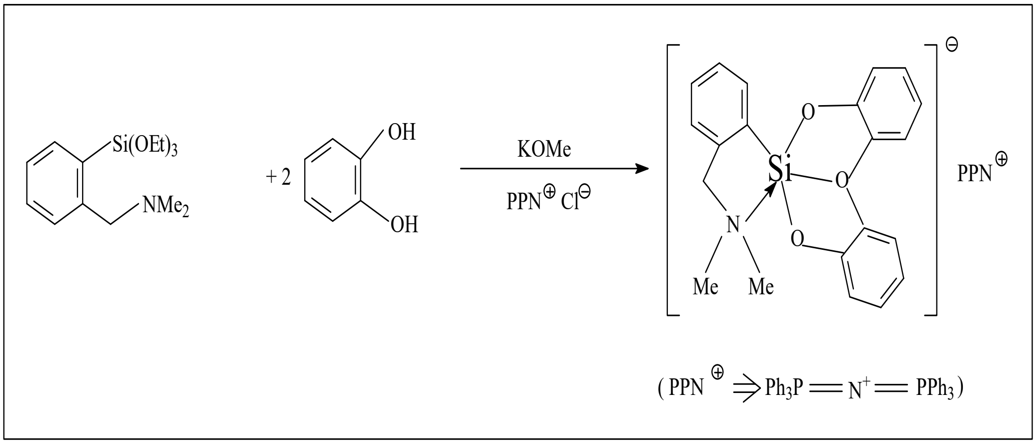
Hexa-coordinated bicyclic dianionic silicates could be prepared from the reaction of cationic silicon species (31) with suitable ligands **[13,14]** (Scheme – 2).



Scheme - 2

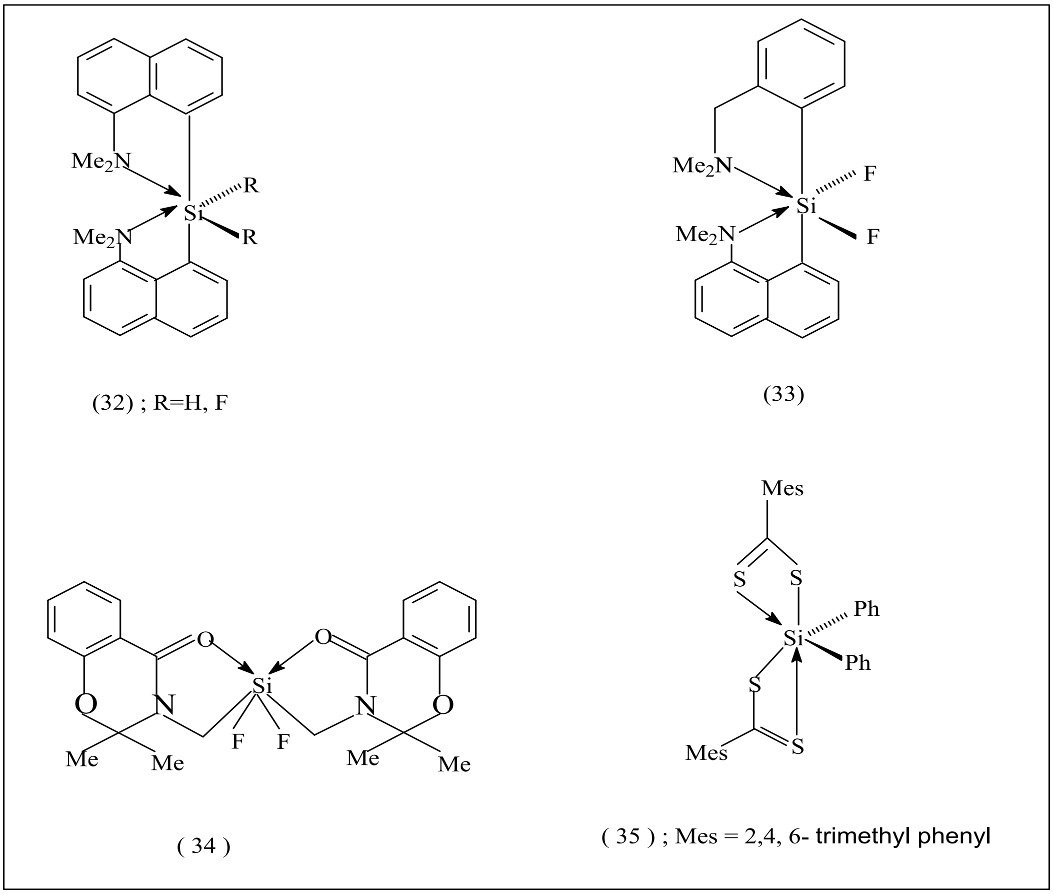
2. Intramolecular coordination to an organosilane

Hexa-coordination in silicon compounds can also be achieved by intramolecular coordination wherever the ligand permits **[15,16].** (Scheme-3)



Scheme- 3

Neutral bis chelated compounds which contain bidentate, monoanionic, C,N ;C,O-coordinated ligands were well investigated compounds of hexa-coordinated silicon. For example complexes (32) and (33) were potentially hexa-coordianted and involved intramolecular donation by the dimethyl amino group to the silicon atom **[17].** Similarly bis(2,2–dimethylbenzo[2H]-4-oxo-1,3-oxazino-3-methyl)difluorosilane(34) achieved hexa-coordination by the intermolecular donation from lactam oxygen **[18].** The complex (35) was synthesized by the reaction of diphenyldicholorosilane with potassium-2,4,6-trimethyl dithiobenzoate. In case of complex (35) hexa-coordination at silicon was achieved by the intramolecular coordination of thiocarbonyl sulfur atoms to the silicon atom **[19].** Hexa-coordination at silicon in these compounds was inferred from variable temperature NMR studies and X-ray data (Fig – 1).



(32) ; R=H, F

(33)

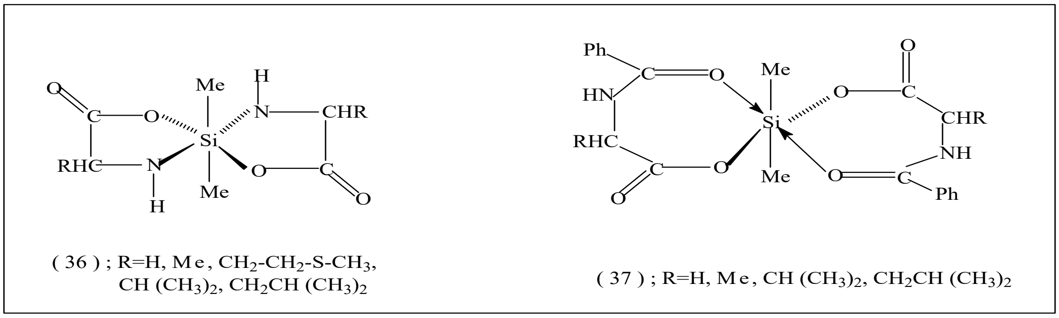
(34)

(35) ; Mes = 2,4, 6- trimethyl phenyl

Fig. 1

3. Substitution by a bidentate ligand in functional organosilane

Hexa-coordinated silicon (IV) complexes (36) and (37) were synthesized by the treatment of dimethyldicholorosilane with the sodium salt of amino acids **[20]** and N-benzoyl amino acids **[21]** in 1:2 molar ratios. A distorted octahedral structure with trans methyl groups was suggested for the complexes (Fig. 2).

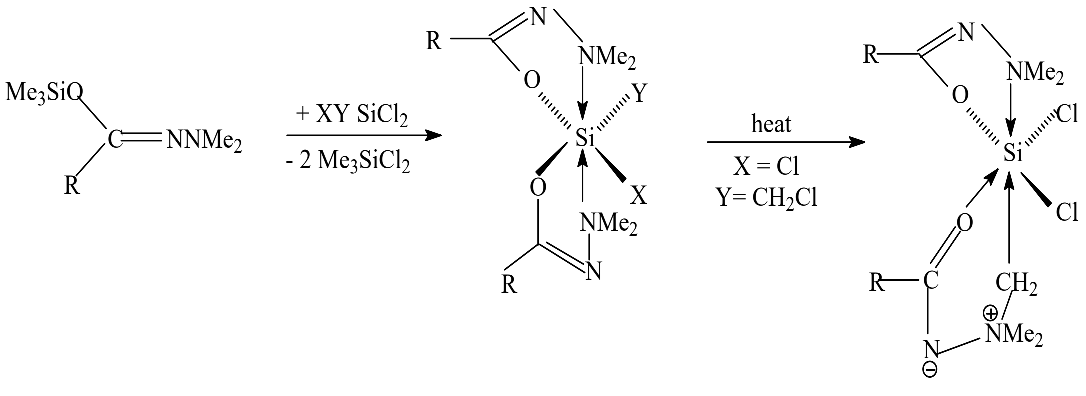


(36) ; R=H, Me, CH_2-CH_2-S-CH_3, CH $(CH_3)_2$, CH_2CH $(CH_3)_2$

(37) ; R=H, Me, CH $(CH_3)_2$, CH_2CH $(CH_3)_2$

Fig. 2

Hexa-coordinate bis (N-Si) chelate (39) was synthesized using a simple ligand exchange reaction between two tetra-coordinated silicon compounds, o-trimethylsilylated-N,N-dimethylhydrazides (38) and a polyhalosilane **[22,23]**. When (choloromethyl)tricholorosilane was used with compound (38), the initially formed neutral octahedral complexes (39) upon heating were irreversibly converted to the isomeric hexa-coordinated zwitterionic silicates (40). This molecular rearrangement was rather unusual, since it involved chelate ring expansion from the common five membered ring to a six membered ring in the thermodynamically favoured product (40). This rearrangement illustrated a transilylation reaction followed by internal displacement of chloride by NMe_2 group, leading to ring expansion and O-Si coordination (Scheme – 4).

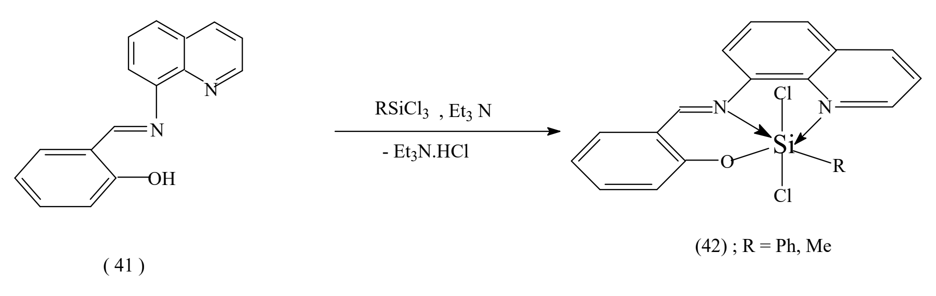


(38) (39) ; R, X, Y = alkyl, aryl, halogen (40)

Scheme 4

4. Substitution by a tridentate ligand in functional organosilane

Condensation of salicylaldehyde with 8-aminoquinoline afforded (ONN) tridentate ligand 2-N(quindine-8-yl)iminomethylphenol (41). Reaction between (41) and methyl / phenyl tricholorosilanes in the presence of triethylamine resulted in the formation of the chelate complex dichloro-[2–N-(quinoline–8yl) iminomethylphenolato] methyl / phenylsilane (42) bearing a hexa-coordinate silicon atom **[24].** The crystal structure of the complex (42) (R=Ph) revealed a rare coordination pattern. Although carrying two chlorine atoms, the hexa-ccordinate Si atom coordinated the tridentate ligand's imine N atom in the trans position to the phenyl group (Scheme-5).



(41) (42) ; R = Ph, Me

Scheme – 5

5. Substitution by a tetradentate ligand in functional organosilane

Hexa-coordinated complexes (43) were prepared by reaction of diorganodichlorosilanes with disodium salt of tetradentate Schiff's base ligand N,N′–ethylenebis(2-hydroxyacetophenoneimine) **[25].** The ligand was prepared by the condensation of 2-hydroxyacetophenone and ethylenediamine (Fig – 3).

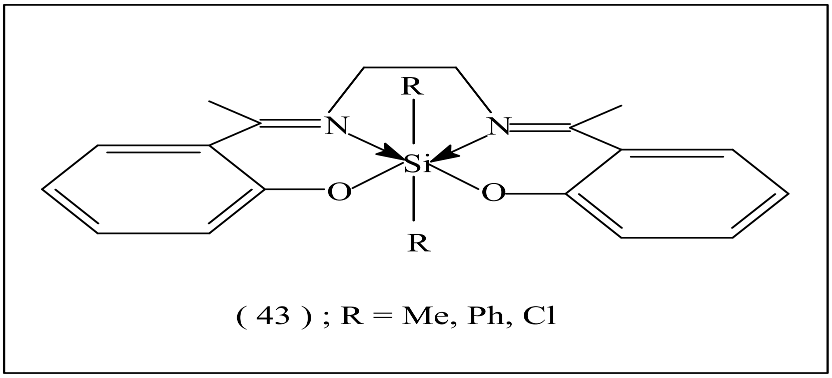
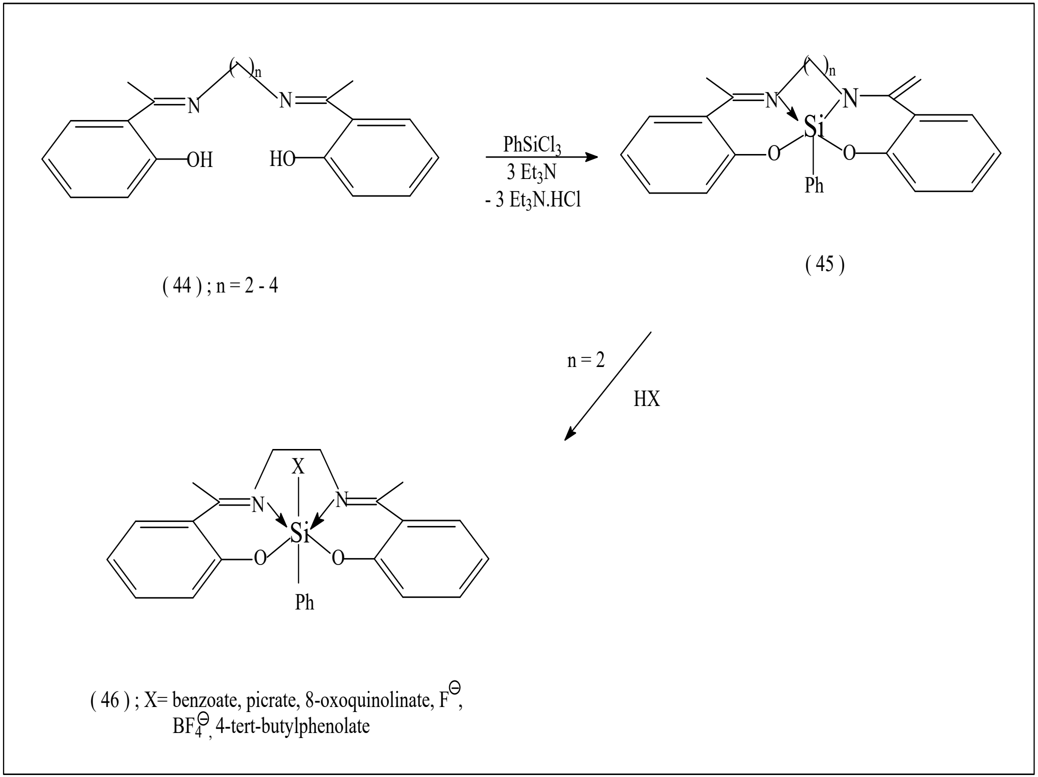

(43) ; R = Me, Ph, Cl

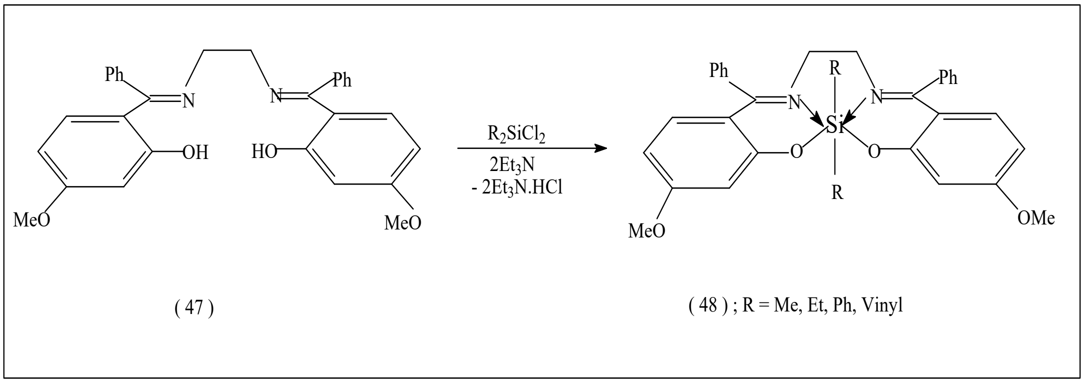
Fig. 3

The reaction between phenyltrichlorosilane and the tetradentate ligand (44) supported by an amine base, yielded penta-coordinated silicon complex (45) with enamine functionalized ligand **[26].** The resulting penta-coordinated silicon complexes were reacted with a variety of bronsted acids HX to yield hexa-coordinated salen silicon complexes (46) (Scheme-6)



Scheme-6

However the reacton between diorganodichlorosilanes and the tetradentate salen type ligand (47) in the presence of triethylamine yielded hexa-coordinate diorganosilanes (48). In all these complexes the silicon atom was situated in a distorted octahedral coordination sphere **[27].** The organic substituents at the Si atom were trans-positioned (Scheme-7). This type of complexes with different salen type ligands, were also synthesized by Roewer etal **[28].**



(47)

(48) ; R = Me, Et, Ph, Vinyl

Scheme – 7

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