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Short Review

Structurally characterised silyls

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Abstract

This review summarises the inorganic and organic compounds containing the silyl (i.e. $–SiH_3$) fragment that have been characterised by single-crystal X-ray diffraction in the solid-state. Relevant features of these silicon-containing materials are compared and contrasted. © 2000 Published by Elsevier Science S.A.

Keywords: Silyl; X-ray crystal structure; Solid-state; Silicon; Organosilane; Silane

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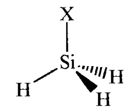
1. Introduction

There has been relatively little work devoted to the solid-state characterisation of silyl (i.e. $–SiH_3$) containing compounds. This seems puzzling when one contrasts this fact with the widespread interest in the organic and organometallic chemistry of silicon and the obvious relationship that exists between the methyl group and its silicon congener. One reason for the vacuum of information is no doubt a direct consequence of the air sensitivity and the relatively low melting point properties of many silanes. However, this class of silicon-containing materials includes some very important precursors to, for example, polysilane polymers (e.g. $[–SiR_2–]_n$) [1]. Silanes themselves are very useful as a source of silicon for the deposition of the element in high purity at semiconductor junctions [2,3a–c]. Related carbosilanes (e.g. SiH_2Et_2) may find application as precursors to both elemental silicon, β-SiC and/or thin films of silicon dioxide [3d].



Compound (X)	Reference
F	5
Cl	6a, 6b
Br	6c
I	6c
- CN	9
-N=C=O	19

Fig. 1.

Interest in the structural properties of silyls was first sparked over 40 years ago. It was in 1955 that trisilylamine (i.e. $N[SiH_3]_3$) was examined by gas phase electron diffraction [4]. Interestingly, this molecule is not isostructural to trimethylamine. Instead, the first example of planar triangular geometry about a N atom was indicated (i.e. the N atom and all three Si atoms are coplanar). Work in more recent years has centred on comparing the solid-state structure of silyls with those of the gas phase investigations (e.g. $Me_2N–SiH_3$ is a pentamer in crystal form but monomeric in the gas phase) and in varying the atom and/or fragment to which the Si atom is bonded. This work is aimed at the understanding of some fundamental aspects of structural silicon chemistry.

This short review will provide a compilation of the known solid-state X-ray crystal structure determinations for organic and inorganic silyls.

1.1. Simple silyls: $E–SiH_3$ ($E =$ main group element)

Although the solid-state crystal structure of the parent of all silyl compounds, silane (i.e. SiH_4), is not

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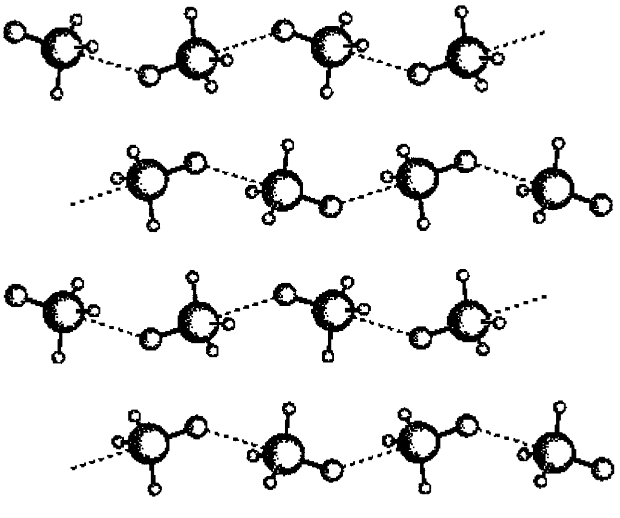
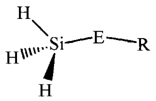


Fig. 2. The orientation of $FSiH_3$ molecules within the crystal. Note the close intermolecular contacts between the large spheres (representing Si atoms) and the medium sized spheres representing the F atoms.



E	R	Reference
O	Me	7
O	SiH_3	8a
S	SiH_3	8b
Se	SiH_3	8b

Fig. 3.

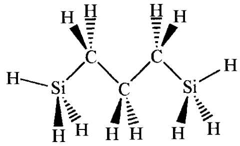


Fig. 4.

currently known,[1] the structural characterisation of a number of simple silyls derivatives (Fig. 1) has been carried out. Structural parameters have been known for sometime from gas phase data and solid-state infrared spectroscopy in combination with deuterium isotopic labelling, revealing that many of these compounds exhibit intermolecular interactions in the solid-state. This situation is almost invariably absent in the gas phase. Halide derivatives that contain the silyl group include the fluoro and chloro compounds. The solid-state investigation of $FSiH_3$ (at 96 K) has clearly shown the presence of intermolecular interactions between neighbouring molecules that form 'zigzag' chains. These chains consist of close F···Si–F interatomic distances [$d = 2.8941(14)$ Å], which are well within the sum of the van der Waals radii for Si and F [5]. Fig. 2 depicts the orientation of $FSiH_3$ in the crystal phase; note the close interatomic contact between the F atom (medium-sized spheres) and the silicon atom (large spheres) of an adjacent molecule (data taken from Ref. [5]). In a similar way, dimethyl ether forms a strong adduct with $ClSiH_3$ [i.e. an O···Si interaction; data at 100 K, $d = 2.2724(12)$ Å] in the solid-state. This results in a lengthening of the Si–Cl bond when compared with that found in the gas phase [$\Delta d = 0.096$ Å]; in addition, a virtually linear O–Si–Cl angle (178.56(4)°) is observed [6a,b]. Further work in the halogen series includes the characterisation of the mono-bromo and iodo compounds [6c]. These species also contain linear chains within the crystals, although in the latter case there is no cross-linking of the infinite chains as seen in the fluoro derivative.

Methoxysilane and its disilyl congener disiloxane have also been investigated by X-ray diffraction in the solid-state (Fig. 3). The former is a monomer in the both the gas and solid (data at 110 K) phases with almost identical bond lengths and angles [7]. However, disiloxane (108 K data) forms infinite chains in the crystalline form as a result of weak [$d = 3.115(5)$ Å] intermolecular Si···O interactions [8a]. Related structural studies of disilyl sulfide and selenide (Fig. 3) also show these properties, but in this case the calcogen atoms each have two close intermolecular Si contacts, in contrast to the one found in disiloxane [8b].

Carbosilyl compounds that have been studied include the X-ray characterisation of silyl cyanide [9] and 1,5-disilapentane. The latter adapts the preferred *anti–anti* conformation in the solid-state (Fig. 4) with respect to the carbosilane chain. Electron diffraction studies have indicted that there are three stable forms for 1,5-disilapentane in the gas phase: *anti–anti*, *anti–gauche* and *gauche*(+)–*gauche*(−) conformers. In addition, there appears to be no molecular interactions in the crystalline form [10]. The cyano compound, however, contains strong intermolecular binding via the N-atom lone pair (i.e. $Si–C{\equiv}N\cdots Si–C{\equiv}N$; $d = 2.789(2)$ Å) to form linear chains of molecules (cf. disiloxane [8a]). The behaviour appears to be mimicked in solution by $Si–C{\equiv}N\cdots$solvent interactions. These effects lead to a lengthening of the Si–C bond length in the order of solid < solution < gas phase and related changes to the $Si–C{\equiv}N$ bond angles.

Schmidbaur and co-workers have undertaken an extensive study of arylsilanes (Fig. 5). This work includes both synthetic methodology and crystallographic investigations. For example, the four-step synthesis and solid-state structure of hexasilylbenzene (i.e. $C_6[SiH_3]_6$) was reported in 1992 [11]. This compound is a high melting point solid and stable in air at room temperature. The overall molecular symmetry is very close to idealised D_{3d} point group symmetry and the crystal is

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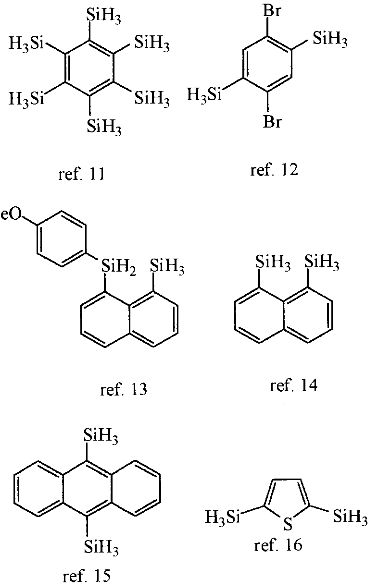
[1] The characterisation of silane by gas phase electron diffraction and by solid-state IR studies, in combination with isotopic labelling, has been known for sometime [2a].

isotypical with the high temperature form of hexamethylbenzene. Work since that time has included the characterisation by X-ray diffraction of 1,4-dibromo-2,5-disilylbenzene, which also has a relatively high melting point [12]. Schmidbaur has not restricted his work to phenylsilyls, in addition, several Si-containing naphthalenes have been produced. These investigations include the solid-state structure of 1-(*p*-anisylsilyl)-8-silylnaphthalene [13] and 1,8-disilylnaphthalene [14]. Both molecules show little distortion in the planarity of the aromatic rings, instead steric strain is reduced by in-plane outward bending of the Si–C bonds. The related species, 9,10-(disilyl)anthracene, has been produced by related synthetic protocols to the naphthyls above. This high melting solid is structurally very similar to 9,10-dimethylanthracene and exhibits a planar anthracene framework [15]. The presence of the silyl groups results in a red shift of the fluorescence wavelength relative to anthracene itself, which is greater than that observed in 9,10-dimethylanthracene. All of these aromatic silyls show very similar Si–C bond lengths (1.86–1.88 Å) and planar aromatic groups [11–15]. Very recent work by Schmidbaur and co-workers has detailed the solid-state characterisation of 2,5-disilylthiophene [16]. This species lacks intermolecular donor–acceptor interactions in the solid phase and shows little difference from the 2,5-dimethyl congener or the furan analogue.[2]



ref. 11 ref. 12

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ref. 15 ref. 16

Fig. 5.

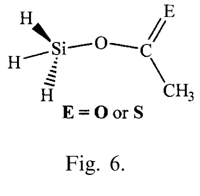

Fig. 6.

Barrow and co-workers have structurally investigated a series of compounds with the general formulae $H_3Si–OC(=E)CH_3$ (E = O or S; Fig. 6). Silyl acetate has an almost planar heavy atom skeleton with the Si–O and C=O bonds being positioned *cis* to one another [17]. Unlike methyl acetate, the silyl species has short [2.721(4) Å] intermolecular O···Si interactions that form chains within the crystal. The sulfur analogue, silyl monothioacetate, is structurally similar in many respects to the oxygen analogue. Both compounds have quite short intermolecular contacts between Si and the carbonyl [17] or thio oxygen [18] atom and different angles thereof. This gives further evidence for the highly directional nature of the intermolecular properties of these species. In addition, the intermolecular Si···S distances are longer [3.382(10) Å] than that observed in silyl acetate, suggesting that the attractive properties are much weaker. Crystalline silyl isocyanate (Fig. 1) also contains close intermolecular contacts between Si and O or N [3.303(3) and 3.311(3) Å], which are not present in the gas phase [19].

Long after the gas phase work on trisilylamine [4], Barrow and Ebsworth succeeded in growing suitable crystals at low temperature [20]. The solid-state structure shows that trisilylamine is monomeric in the solid phase with a structure that is virtually identical to the gas phase form. The deviations from C_{3h} symmetry are negligible and very similar N–Si bond lengths are observed. There appears to be no N···Si intermolecular interactions, as molecules of the compound are stacked directly on top of each other (a distance of 4.1 Å).

Unlike $[N(SiH_3)_3]$, dimethyl-silylamine ($[Me_2N\{SiH_3\}]_5$) is found to be a pentamer in the solid-state (Fig. 7: data taken from Ref. [21b]). In this case, a highly unusual structure is found in which the N atoms occupy the corners of an idealised pentagon. This leads to what is best described as a trigonal bypyramidal orientation about the Si atoms, in contrast to the pyramidal geometry observed in the gas phase [21]. The related complex *O*-methyl-*N*,*N*-disilylhydroxyamine ($MeON[SiH_3]_2$) contains intermolecular Si···O interactions ($d = 2.92$ Å) leading to a zigzag type aggregation of molecules in the solid-state. The orientation of the atoms around the N atom forms a pyramidal structure in this phase and in the gaseous form [22].

There appears to be only one structurally characterised silyl containing a Si–Si bond. This is triphenylsilylsilane (i.e. $Ph_3Si–SiH_3$), which was characterised as a

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[2] **Note added in proof**: Braddock-Wilking et al. [40] have recently described the solid-state structure of a number of aryl silanes including $H_3Si[TMP]$ (TMP = 2,4,6-trimethoxyphenyl).

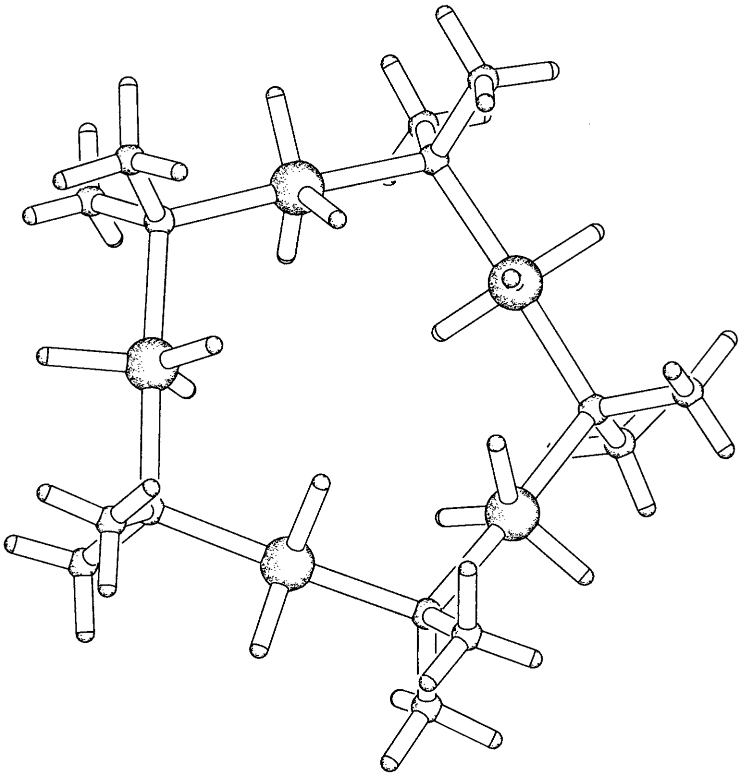

Fig. 7. The solid state structure of pentameric dimethylsilylamine.

solid in 1993. The Si–Si bond length is typical [2.336(1) Å] of disilyl bond distances [23a].[3]

The structure of a C-spiro-linked silacyclobutane has been reported. The structure of $Si_8C_3H_{20}$ (Fig. 8) contains two bridging $-SiH_2-$ units, and four terminal $-SiH_3$ fragments [23b].

Seyferth, as part of his studies on carbosilane dendrimers [24], has reported the solid-state characterisation of the silane dendrimer depicted in Fig. 9 [25]. This is no doubt the only silyl compound that has been structurally characterised that contains a dozen $-SiH_3$ groups! There is considerable thermal motion associated with the dendritic arms. This macromolecule is air sensitive but highly soluble in common organic solvents.

The only silyl compound containing a phosphorus–silicon bond to be examined by X-ray diffraction is lithium bis-(tmeda) disilylphosphanide (i.e. $[Li(tmeda)_2]^{\oplus}$ $[P(SiH_3)_2]^{\ominus}$: Fig. 10; tmeda = 1,2-bis[-dimethylamino]ethane-*N*,*N′*). The anionic portion is distinctive for its tight Si–P–Si bond angle (92.3°) and relatively short Si–P bond lengths (2.17 Å) [26]. This compound is also representative of a fairly rare class of lithium phosphanides that are truly ionic in the solid-state.

One very general trend can be made based on the available solid-state data of silyls that contain a $H_3Si–E$ (E = main group element) bond. Scheme 1 reveals the scatter plot of the general trend towards Si–E bond

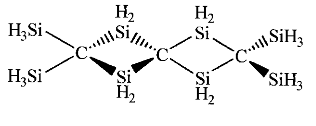

Fig. 8.

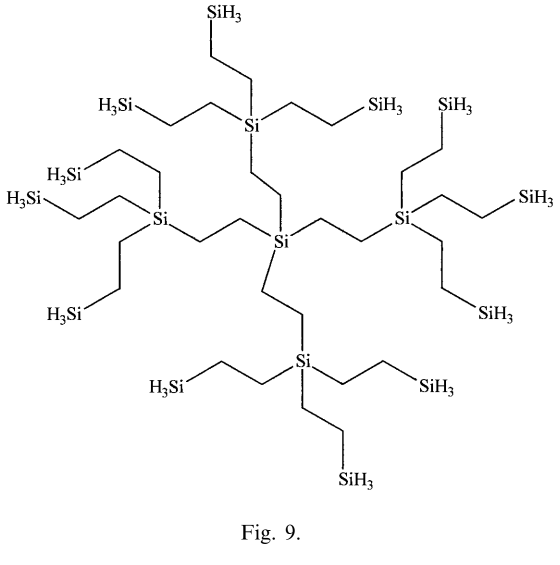

Fig. 9.

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[3] **Note added in proof**: Kawachi and co-workers [41] have recently reported the solid-state structure of $H_3Si–Ge(aryl)_3$ (aryl = 2-$Me_2NC_6H_4$).

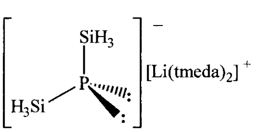


Fig. 10.

lengthening as the electronegativity of E decreases. This demonstrates a lowering of the Si–E bond order and suggests that π-donation from E to the Si d-orbitals may be a contributing factor in this lowering of the bond length. These effects are also very likely responsible for the 'hypervalent' character of many of these silicon compounds [2,3a].

2. Metal silyls [27]

2.1. η^1-Silyl compounds

The only structurally characterised metal–SiH$_3$ compound is silyl potassium, which was one of the first silyls to be structurally elucidated. It exists in a sodium chloride-like structural arrangement (Fig. 11; data taken from Ref. [28]) of alternating formal silyl anions and potassium cations [28].

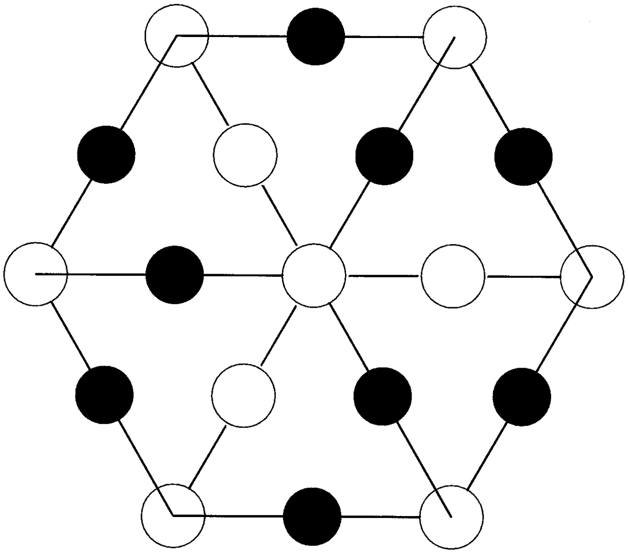
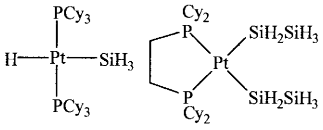


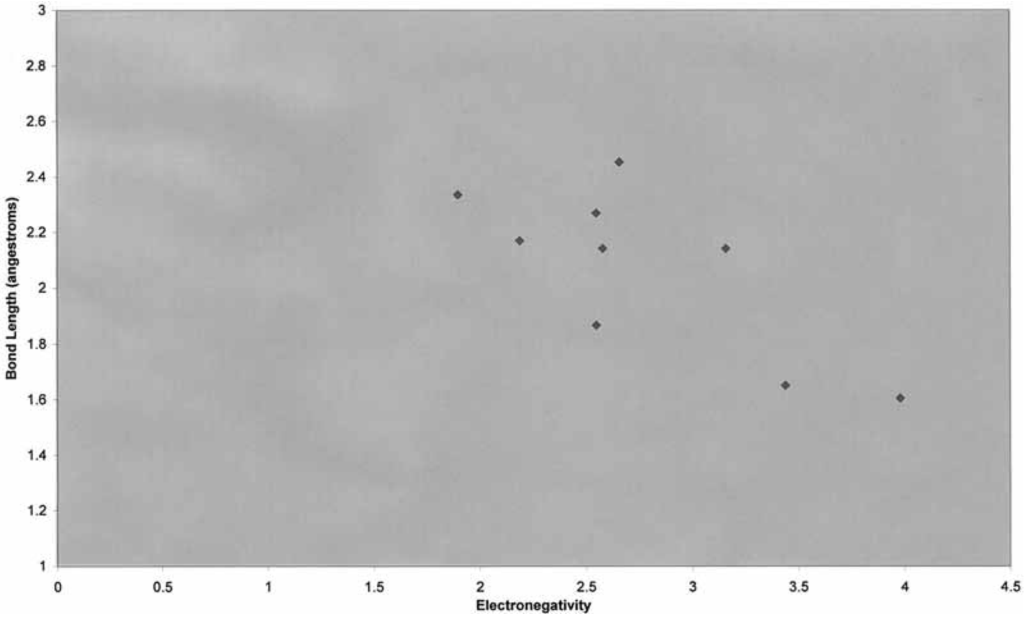
Fig. 11. The cubic NaCl-type lattice of KSiH$_3$ (black spheres are formal K$^+$ atoms, white spheres represent the [SiH$_3$]$^-$ group: this figure was generated from data given in Ref. [28]).



Cy = cyclohexyl

Fig. 12.

A number of transition metal silyls have been studied in the solid-state, although a truly systematic study of group trends has yet to be carried out. The first such example was *trans*-[Pt(SiH$_3$)(H)(PCy$_3$)$_2$] (Fig. 12; Cy = cyclohexyl) reported by Ebsworth and co-workers in 1978 [29]. It is unique, not only in being the first structurally characterised transition metal silyl, but also because it is a still fairly rare example of a complex containing a hydride ligand located *trans* to silicon. These strong *trans* influencing ligands are rarely found in this disposition [30]. The bulk of the tertiary phosphine ligands are thought to be a primary reason for



Scheme 1. Scatter plot of Si–E bond lengths vs. the electronegativity of E.

the low reactivity, *trans* stereochemistry and air-stability of this compound.

The solid-state structure of the related Pt(II) complex *cis*-[η^2-*P*,*P'*-($Cy_2PC_2H_4PCy_2$)Pt(SiH_2SiH_3)$_2$] has been briefly mentioned in the work of Michalczyk, Fink and co-workers [31]. Unfortunately, no further details of the structure are reported (unpublished results, Fig. 12).

Malisch et al. have synthesised a number of cyclopentadienyl complexes of tungsten [32] and iron [33]. The tungsten work includes the X-ray structure of [(η^5-Cp*)($OC)_2(Me_3P)W–SiH_3$] (Cp* = C_5Me_5) and the synthetic methods to a number of other organosilyl derivatives (Fig. 13). The metal–silicon bond length [2.533(3) Å] is larger than predicted, perhaps due to steric effects. The iron complex [(η^5-Cp*)$(OC)_2$-Fe–SiH_3] has been similarly synthesised and characterised by X-ray diffraction (Fig. 13) along with a number of organosilyl derivatives of both Fe and Ru [33a]. The Fe–Si bond length [2.287(2) Å] is slightly larger than that observed in the trichlorosilyl analogue. This former silyl complex readily undergoes photochemical reaction in the presence of phosphines to give [(η^5-C_5Me_5)(R_3P)(OC)Fe–SiH_3] derivatives; the Fe–Si bond is unaffected under these conditions. The closely related silylsilane (Fig. 13) complex [(η^5-Cp*)$(OC)_2$Fe–SiH_2SiH_3] has also been structurally investigated by Malisch and co-workers [33b].

The only Group IV metal silyl complex to be crystallographically characterised is the Ti(III) species [(η^5-Cp)$_2$Ti(SiH_3)(PMe_3)]. This compound is considerably more stable than its methylsilyl (i.e. –SiH_2Me) analogue and contains a short Ti–Si bond of 2.594(2) Å. A *gauche* arrangement of the silyl and phosphine fragments with respect to the Cp_2Ti unit [34] is observed (Fig. 13).

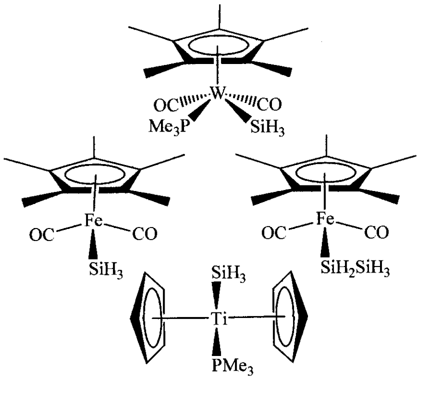
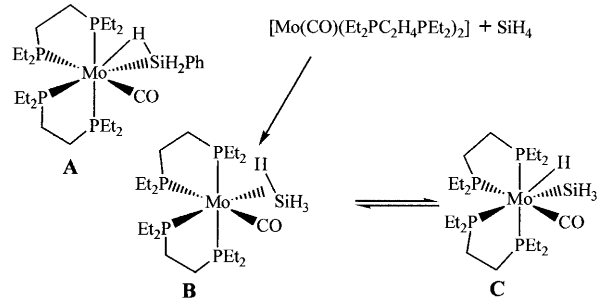


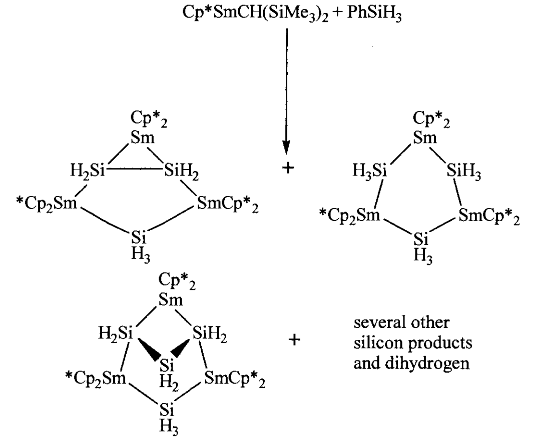
Fig. 13. Cp and Cp* complexes containing the –SiH_3 group.



Scheme 2.

2.2. *μ*-Silyl compounds

There appears to be only three silyl complexes of the lanthanide elements to be characterised by X-ray diffraction. Redistribution reactions of $PhSiH_3$ with cyclopentadienyl complexes of Sm lead to the trinuclear samarium compounds shown in Eq. (1) [35]. In these examples, the silyl unit is acting as a bridge between two metal atoms, a bonding motif, which is reminiscent of that observed in [$Me_2N\{SiH_3\}]_5$ (Fig. 7), $Si_8C_3H_{20}$ (Fig. 8) or [$(OC)_8Re_2$\{μ-η^2-Si$(OMe)_3$\}(μ-H)] [36]. All three of these samarium species have been structurally characterised and these clusters all co-crystallise from solution in various ratios [35].



(1)

2.3. *η*²-Silyl compounds

There are two reported examples of structurally characterised η^2-SiH_3R (R = H or Ph) compounds [37]. Both of these species have molybdenum as the central metal atom. Kubas and co-workers have characterised complex **A** (Scheme 2) [38]. In this case, the silyl group is acting as a three centre-two electron donor to the metal centre. This may be viewed as a 'snapshot' of the Si–H bond during bond rupture (i.e. activation; cf. hydrosilation). Later, Kubas reported that the silane derivative **B** undergoes reversible Si–H oxidative addition to produce a Mo(II) hydrido silyl (**C**). The oxidative addition product has been characterised by single-crystal X-ray diffraction methods [39].

3. Conclusions

The study of the fundamental properties of a number of simple and complex silyl compounds has revealed a wide variety of interesting solid-state structures. The propensity to which silyl derivatives are able to form chain (e.g. $FSiH_3$) or ring (as in $[Me_2N\{SiH_3\}]_5$) solid-state entities is certainly intriguing. These phenomena would have been difficult to predict based on the abundance of gas phase data to the contrary. The ability of silyls to form these complex structural motifs may have profound consequences in the design of silyl-containing materials, polymers, etc. This brief review has shown the wide variety of silicon compounds that can be produced from a very simple fragment. The silyl group has been shown to be very different in many respects its carbon congener, the methyl group.

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