Chapter 2
Preparation and Characterization of Polyhedral Oligosilsesquioxanes

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2.1 General Comments

Polyhedral OligoSilSesquioxanes are often abbreviated by the acronym POS or POSS® and are compounds of the general formula $Si_nO_{3n/2}R_n$ (often denoted as T_nR_n). The commonest of these compounds are the cubic T_8R_8 POS species since many hydrolysis/condensation reactions of simple $RSiX_3$ compounds ($X = Cl$, OMe or OEt) give the T_8R_8 cage as a major product, usually along with small amounts of other T_nR_n cages and polymeric by-products. Few T_4R_4 POS have been prepared as they seem to require very bulky R-groups to stabilize the strained POS system and to prevent formation of larger, more stable POS cages. T_6 derivatives are more common than those containing T_4 cages, but again, only a limited number of compounds have been isolated, and ring strain is probably also a problem in these compounds. $T_{10}R_{10}$ POS are much more common than T_4 and T_6 derivatives owing to reduced ring strain, however, even larger POS are also rare and are often found as components of mixtures containing mainly T_8R_8, or polymeric materials and other T_nR_n species derived from $RSiX_3$ hydrolyses. The isolation of individual pure forms of the higher silsesquioxanes is further complicated by the existence of multiple isomers. For example, in the case of the T_nH_n POS, identification of isomers by high-resolution single-ion-detection GC has shown that although for n = 12, only one isomer was formed, four were found for n = 14, nine for n = 16, and ten or twelve isomers for n = 18 [1]. NMR studies of mixtures of isomers have allowed the structures of some to be determined: the D_{2d} form for $T_{12}H_{12}$, D_{3h} (major isomer) and C_{2v} for $T_{14}H_{14}$, and a D_{4d} structure for $T_{16}H_{16}$ [1]. The POS products that have been

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isolated include those with n = 12, 14, and 16, as well as smaller POS derivatives; however, larger POS molecules (n $\geq$ 18) have been identified using either SEC [2], or GC [1], as minor components from $RSiX_3$ hydrolyses.

2.2   Synthesis of T_nR_n Compounds where R = H, Alkyl or Alkenyl

2.2.1   *Hydrolysis*

2.2.1.1 T_4 and T_6 Compounds

Only two alkyl T_4 POS, $T_4(i\text{-Pr})_4$, and $T_4(t\text{-Bu})_4$, have been prepared by hydrolysis; using acidic conditions i-PrSiCl$_3$ and t-BuSiCl$_3$ afford the T_4 derivatives with yields of 55% and 95%, respectively [3]. Hydrolysis of other alkyl RSiCl$_3$ compounds, e.g. R = Me or Et, leads to the formation of larger T_nR_n compounds or polymeric siloxanes, see below.

The synthesis of a small number of T_6 alkyl-POS has been reported including early work on compounds identified as T_6R_6, obtained as sublimable solids in low yield, by the distillation of products from the hydrolysis of RSi(OEt)$_3$ (R = Me, Et) [4, 5]. The properties of these materials were noted to be different to those of the previously known T_8 compounds, and as a result were identified as T_6R_6 species.

The attempted hydrolysis in organic solvents of alkyltrichlorosilanes with alkyl substituents the size of a cyclohexane ring or larger, has a tendency to produce incompletely condensed products, such as $T_7Cy_7(OH)_3$ [6]. If, however, the reaction uses solely aqueous HCl as the hydrolysis medium, then the products consist of mixtures of fully condensed species, including T_6R_6 derivatives, for the cases when R = n-C$_7$H$_{15}$ [7], n-C$_8$H$_{17}$, or i-C$_9$H$_{19}$ [8]. Vacuum distillation of the n-octyl and i-nonyl products was found to lead to thermal rearrangement of the compounds and the isolation of pure T_6R_6 derivatives. In a similar fashion T_6Cy_6 may be prepared by the aqueous hydrolysis/condensation of CySiCl$_3$, giving the pure product in 10% yield [9]. For trichlorosilanes with alkyl groups in most cases smaller than cyclohexane, the presence of non-aqueous, or scarce-water, hydrolysis media can give rise to the desired T_6R_6 products. For trichlorosilanes with R = i-Bu, c-C$_5$H$_9$, Cy, Ph, n-Oct, (CH$_2$)$_3$C$_6$H$_4$-4-OMe, and (CH$_2$)$_2$CMe$_2$CH$_2$CO$_2$Me, hydrolysis in DMSO led to T_6R_6 in moderate yields [10].

2.2.1.2 T_8 Compounds

A range of T_8 POS substituted with alkyl and related derivatives can be prepared by hydrolysis and condensation reactions. These include substituents from the very simplest, such as T_8H_8 and T_8Me_8 to more complicated functional groups, for example $T_8[(CH_2)_3Cl]_8$. Details for the preparation of these POS derivatives are presented in Table 2.1. It may be seen that the reaction products show a very wide range of yields, this being one of the biggest problem areas in the use of hydrolysis reactions to prepare POS compounds. Optimization of reaction conditions can lead to yields being improved, significantly in some cases, and the use of the basic tetrabutylammonium fluoride as a catalyst [11] has allowed synthesis of previously inaccessible, simple T_8 POS, and led to significantly improved yields of others. Several of these compounds are useful precursors to a wide range of other POS derivatives. For example, T_8H_8 yields alkylated products via hydrosilylation, $T_8(CH=CH_2)_8$ undergoes metathesis reactions, additions, and Heck reaction chemistry, and $\{T_8[(CH_2)_3NH_3]_8\}Cl_8$ and its deprotonated derivative $T_8[(CH_2)_3NH_2]_8$, are precursors to a range of amides.

The synthetic route to T_8H_8 has improved significantly, from the initially reported yield of less than 1% for the acid-hydrolysis of $HSiCl_3$ [12], to the current yield of 18% for the scarce-water acid hydrolysis of $HSiCl_3$ [13]. Similarly, the yield of $T_8(CH=CH_2)_8$ has been increased from 6% [14], to a best yield of 41%, when the hydrolysis is carried out in the presence of acidic Amberlite (IR-120 PLUS) ion exchange resin [15]. A contemporary preparation for $T_8(CH=CH_2)_8$ shows a significantly higher yield (80%), from a phase-transfer-catalysed hydrolysis of $CH_2=CHSi(OEt)_3$ [16]. In contrast to these two compounds, the synthetic yields of $\{T_8[(CH_2)_3NH_3]_8\}Cl_8$ have stayed constant at about 35% despite a number of minor variations to synthetic conditions. This salt can be deprotonated using basic Amberlite IRA-400 ion exchange resin to give the unstable free amine in quantitative yield [17]. However, there have been recent reports claiming the synthesis of the free amine directly from the starting silane in yields ranging up to 93% [18]. These direct preparations of the free amine are reported to lead to a much more stable material.

Table 2.1 Hydrolytic routes to T_8R_8 compounds, R = H, alkyl or alkenyl

R or T_8R_8	Starting materials	Yield (%)	Refs.
-H	$HSiCl_3 + FeCl_3$, HCl	18	[13]
-Me	$MeSi(OEt)_3$ + poly(2-hydroxyethyl methacrylate), NH_3 or HCl	23	[19]
-Me	$MeSi(OEt)_3 + NEt_3$, HCl, AcOH	88	[20]
-CH=CH$_2$	$CH_2=CHSiCl_3$ + acid Amberlite,	41	[15]
-CH=CH$_2$	$CH_2=CHSi(OEt)_3 + NMe_4OH$	80	[16]
i-Bu	*i*-BuSi(OEt)$_3$ + NBu$_4$F	26	[11]
i-Bu	*i*-BuSi(OMe)$_3$ + KOH	96	[21]

R or T_8R_8	Starting materials	Yield (%)	Refs.
$-(CH_2)_2(CF_2)_3CF_3$	$CF_3(CF_2)_3(CH_2)_2Si(OEt)_3 + KOH$	99	[22]
$-(CH_2)_3NH_2$	$H_2N(CH_2)_3Si(OEt)_3 + NMe_4OH$	93	[18]
$\{T_8[(CH_2)_3NH_3]_8\}Cl_8$	$H_2N(CH_2)_3Si(OEt)_3 + HCl$	35	[17]
$-(CH_2)_3SH$	$HS(CH_2)_3Si(OMe)_3 + HCl$	17	[23]
$-(CH_2)_3Cl$	$Cl(CH_2)_3Si(OEt)_3 + HCl$	37	[24]
$-(CH_2)_3Br$	$Br(CH_2)_3SiCl_3 + FeCl_3, HCl$	3	[25]
$-n\text{-}C_6H_{13}$	$n\text{-}C_6H_{13}Si(OEt)_3 + NBu_4F$	44	[11]
$-c\text{-}C_5H_9$	$c\text{-}C_5H_9Si(OEt)_3 + NBu_4F$	95	[11]
$-Cy$	$CySi(OEt)_3 + NBu_4F$	94	[11]

The mechanism by which the T_8 POS cage is formed during the hydrolytic reactions of simple $HSiX_3$ compounds, via $HSi(OH)_3$ condensation, to give T_8H_8 has been the subject of a theoretical study showing that the overall formation of T_8H_8 is exothermic by 48.3 kJ mol^{-1}, and that H-bonding is a significant factor in determining the nature of the intermediates and the mechanistic route [26].

The capping of partially condensed silsesquioxanes, $R_7Si_7O_9(OH)_3$, by reaction with chloro- or alkoxysilanes to give T_8R_7R' derivatives follows the same general reaction scheme (Eq. 2.1). The partially condensed trisilanol species have been known since 1965 [27], and the recent interest in the synthesis of T_8R_7R' derivatives derives from their utility in incorporating POS cage substituents into other materials via a single connection point. The most useful compounds for this are thus T_8R_7R' species where the R groups are inert and the lone R' substituent contains a functional group.

$$R_7Si_7O_9(OH)_3 \quad + \quad R'SiX_3 \quad \xrightarrow{\text{base}} \quad T_8R_7R' \qquad \textbf{(Eq. 2.1)}$$
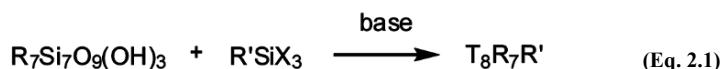
$$X = Cl, \text{O-alkyl}$$

In T_8R_7R' compounds with a sufficiently bulky R group, an R' group that would normally be too reactive to give a stable $T_8R'_8$ compound may be incorporated, as for example in the preparation of $T_8R_7(CH_2)_3NH_2$ (R = i-Bu, c-C_5H_9 or Ph), T_8R_7Cl (R = i-Bu, c-C_5H_9 or Cy), and $T_8Cy_7OSiCl_3$. The synthetic routes to a selection of representative T_8R_7R' compounds are presented in Table 2.2.

Table 2.2 Alkyl-T_8R_7R' compounds prepared by corner capping of $R_7Si_7O_9(OH)_3$

Substituents		Starting materials	Yield (%)	Refs.
R	R'			
$-i$-Bu	$-H$	$(i\text{-Bu})_7Si_7O_9(OH)_3 + HSiCl_3, NEt_3$	67	[28]
$-i$-Bu	$-(CH_2)_3NH_2$	$(i\text{-Bu})_7Si_7O_9(OH)_3 + NH_2(CH_2)_3Si(OEt)_3, NEt_3$	-	[29]

Substituents		Starting materials	Yield (%)	Refs.
R	R'			
-i-Bu	-$(CH_2)_3Cl$	$(i\text{-}Bu)_7Si_7O_9(OH)_3$ + $Cl(CH_2)_3SiCl_3$, NEt_3	73	[30]
-$(CH_2)_2CF_3$	-H	$Na_3\{[CF_3(CH_2)_2]_7Si_7O_9(O)_3\}$ + $HSiCl_3$, NEt_3	76	[31]
-$(CH_2)_2CF_3$	-Me	$Na_3\{[CF_3(CH_2)_2]_7Si_7O_9(O)_3\}$ + $MeSiCl_3$, NEt_3	72	[32]
-c-C_5H_9	-CH_2Cl	$(c\text{-}C_5H_9)_7Si_7O_9(OH)_3$ + $ClCH_2SiCl_3$, NEt_3	78	[33]
-c-C_5H_9	-$(CH_2)_3Cl$	$(c\text{-}C_5H_9)_7Si_7O_9(OH)_3$ + $Cl(CH_2)_3SiCl_3$	82	[34]
-c-C_5H_9	-$(CH_2)_3NH_2$	$(c\text{-}C_5H_9)_7Si_7O_9(OH)_3$ + $NH_2(CH_2)_3Si(OMe)_3$	78	[35]
-Cy	-H	$T_7Cy_7(OH)_3$ + $HSiCl_3$, NEt_3	88	[36]
-Ph	-$(CH_2)_3NH_2$	$Ph_7Si_7O_9(OH)_3$ + $NH_2(CH_2)_3Si(OMe)_3$, toluene	68	[37]

2.2.1.3 T_{10}, T_{12} and Larger Compounds

A small number of alkyl-POS compounds larger than T_8 have been prepared by hydrolysis of their parent trichloro- or trialkoxysilanes. Among the most common syntheses are the scarce-water hydrolyses, for example, $HSiCl_3$ affords $T_{10}H_{10}$ in less than 4% yield, as a by-product of the formation of T_8H_8 [13]. An alternative hydrolysis route leads to the formation of $T_{12}H_{12}$, again as a by-product, in similar yield [1]. Another scarce-water hydrolysis, in this case using tetrabutylammonium fluoride and c-$C_5H_9SiCl_3$, has been reported to produce $T_{10}(c\text{-}C_5H_9)_{10}$ in 12% yield [38].

A more conventional aqueous hydrolysis of $CF_3(CH_2)_2SiCl_3$ gives $T_{12}[(CH_2)_2CF_3]_{12}$, although no yield was reported for this reaction [39]. A study of the acidic hydrolysis and condensation of vinyltrimethoxysilane showed that a mixture of products was formed. This was reported to include the large vinyl-POS $T_n(CH=CH_2)_n$ for n=14 and 16, although neither compound was isolated from the product mixture [40].

2.2.2   Substitution

Substitution reactions at the corner silicon atoms of alkyl POS compounds can produce a very wide range of products. The simplest of these reactions is that of preparing T_8D_8 from T_8H_8 using deuterium gas, catalysed by palladium on carbon [41]. The most common reaction involving substitution at silicon is hydrosilylation, a simple platinum-catalyzed reaction allowing the addition of a Si-H to an unsaturated compound such as an alkene or alkyne. The general hydrosilylation reaction can be summarized in Eq. 2.2, and the syntheses of a range of T_8R_8 derivatives are presented in Table 2.3. The potential problems of hydrosilylation reactions are two-fold; first that the product can be either the α- or the β-isomer, and second that reaction may take place at functional groups other than alkene or alkyne within the added compound, most often at oxygen.

The first problem may be overcome by the strong directing effect of silicon, which favours the α-product, leaving the β-product generally as an impurity to be removed. The occurrence of reaction at other functionalities can often be reduced during optimization of a reaction by careful choice of the platinum catalyst, solvent and reaction conditions. A wide variety of functional groups may be introduced into POS systems by hydrosilylation including those, such as alcohols, that could not be introduced via the hydrolysis of $RSiX_3$ monomer synthetic route. Similar reactions are also seen for the T_8R_7H compounds, giving rise to T_8R_7R' species.

$$T_8X_8 \ + \ \underset{}{\diagup\!\!\!\!\diagup}\!\!-R \ \xoverset{\text{Pt catalyst}}{\longrightarrow} \ T_8(CH_2)_2R \ \text{or} \ T_8OSiMe_2(CH_2)_2R \qquad \textbf{(Eq. 2.2)}$$

$$X = H, \ OSiMe_2H$$
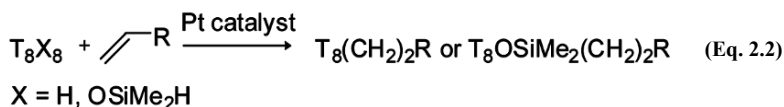
Table 2.3 Alkyl-T_8R_8 compounds prepared by hydrosilylation

R	Starting materials	Yield (%)	Refs.
$-C_nH_{2n+1}$ (n = 2-10)	$T_8H_8 + CH_2=CH_2$, or $CH_2=CH_2C_{n-2}H_{2n-3}$, H_2PtCl_6	76-92	[42]
$-(CH_2)_2CMe_2OH$	$T_8H_8 + CH_2=CHCMe_2OH$, H_2PtCl_6	62	[43]
$-(CH_2)_2C_6H_4$-4-Br	$T_8H_8 + CH_2=CHC_6H_4$-4-Br, Pt(dvs)	81	[44]
$-(CH_2)_2C_6H_4$-4-CH_2Cl and $-CHMeC_6H_4$-4-CH_2Cl	$T_8H_8 + CH_2=CHC_6H_4$-4-CH_2Cl, H_2PtCl_6, $Cl(CH_2)_2Cl$	85[a]	[45]
$-(CH_2)_3Cy$	$T_8H_8 + CH_2=CHCH_2Cy$, H_2PtCl_6, $Cl(CH_2)_2Cl$, $MeO(CH_2)_2OMe$	94	[46]
$-(CH_2)_3Ph$	$T_8H_8 + CH_2=CHCH_2Ph$, H_2PtCl_6, $Cl(CH_2)_2Cl$, $MeO(CH_2)_2OMe$	69	[46]
$-(CH_2)_3CN$	$T_8H_8 + CH_2=CHCH_2CN$, H_2PtCl_6	-	[47]
$-(CH_2)_5OH$	$T_8H_8 + CH_2=CH(CH_2)_3OH$, H_2PtCl_6	-	[48]
$-(CH_2)_3OCH_2CH(O)CH_2$	$T_8H_8 + CH_2=CHCH_2OCH_2CH(O)CH_2$, Pt(COD)Cl$_2$	24	[23]
$-(CH_2)_3SiMe_3$	$T_8H_8 + CH_2=CHCH_2SiMe_3$, H_2PtCl_6	93	[23]
$-(CH_2)_3SiCl_3$	$T_8H_8 + CH_2=CHCH_2SiCl_3$, H_2PtCl_6	-	[49]
$-(CH_2)_4CH(O)CH_2$	$T_8H_8 + CH_2=CH(CH_2)CH(O)CH_2$, Pt(dvs)	99	[50]
$-(CH_2)_nBr$ (n = 4, 5, 7, 8)	$T_8H_8 + CH_2=CH(CH_2)_{n-2}Br$, H_2PtCl_6	88-99	[51]

R	Starting materials	Yield (%)	Refs.
-CH=CHCMe$_2$OH and –OCMe$_2$C≡CH	T$_8$H$_8$ + CH≡CCMe$_2$OH, H$_2$PtCl$_6$	-[a]	[49]
-CH=CH(CH$_2$)$_4$Cl and –C(=CH$_2$)(CH$_2$)$_4$Cl	T$_8$H$_8$ + CH≡C(CH$_2$)$_4$Cl, H$_2$PtCl$_6$	79[a]	[51]

[a] Consists of a mixture of these products.

A similar method can be used to prepare unusual T$_8$ compounds derived from monohydrosilylation of T$_8$H$_8$, to give T$_8$H$_7$R products. Thus, treatment of T$_8$H$_8$ with 9,10-dibromo-1-decene in the presence of H$_2$PtCl$_6$ gives the mono-substituted compound T$_8$H$_7$[(CH$_2$)$_8$CHBrCH$_2$Br] [52] and further substitution was realized by reaction with ethylene, again using H$_2$PtCl$_6$ catalyst, to give T$_8$Et$_7$[(CH$_2$)$_8$CHBrCH$_2$Br]. Likewise T$_8$H$_8$ has been treated with three long-chain alkenes using H$_2$PtCl$_6$ to give the T$_8$H$_7$(CH$_2$)$_n$Me (n = 18, 20, 22) products [53]. The substitution patterns resulting from the reaction of T$_8$H$_8$ with varying molar ratios of either phenol and undec-1-ene or phenol and 3,3-dimethylpent-4-enoate have been studied [54]. When complicated mixtures of products were clearly present, patterns observed in the ^{29}Si NMR spectra of the product mixtures suggest that identification of particular substitutional isomers may still be possible. The unusual hydrosilylation reaction of T$_8$H$_8$ with 1,3-divinyl-1,1,3,3-tetramethyldisiloxane proceeds with an α : β product ratio of 3.4 : 1, but it also shows signs of creating some linkages between adjacent T$_8$ cages [55]. Similar reactions, but using more complicated divinyl derivatives, and Pt(dcp) as catalyst, allow preparation of di-POS compounds when using a divinyl compound to POS ratio of 1:2, polymeric POS systems were seen at other reagent ratios [56].

2.2.3   Cage Rearrangement

Fragmentation and rearrangement of existing POS cages can be an effective method for the preparation of new larger POS cage materials. The expansions of a series of T$_8$ alkyl-POS functionalized with either linear alkyl chains, or a variety of 3-substituted propyl chains, (CH$_2$)$_3$R (R = Cl, Br, I, NCS, C$_6$F$_5$) have been prepared by the action of basic catalysts such as K$_2$CO$_3$, NaOH, or Na$_2$SiF$_6$ on the corresponding T$_8$ compounds [57, 58]. The resulting products comprised mixtures of the corresponding T$_8$, T$_{10}$, and sometimes T$_{12}$, POS compounds with the T$_8$ species predominating, although the individual cage forms were not isolated. Another T$_{10}$ derivative that can be prepared by fragmentation and rearrangement reactions is T$_{10}$[(CH$_2$)$_3$N$_3$]$_{10}$ which was discovered serendipitously when attempting to prepare T$_8$[(CH$_2$)$_3$N$_3$]$_8$ from T$_8$[(CH$_2$)$_3$Cl]$_8$ and NaN$_3$ [30]. A mixture of products is again produced by this reaction; however, in this case, the major product is the T$_{10}$ POS, with T$_8$ and T$_{12}$ as minor products.

2.2.4   *Modification of R*

2.2.4.1 T_8 Compounds

One of the largest categories of reactions producing alkyl POS is that of modification of R groups using a variety of reactions such as substitutions, reactions involving acid derivatives and reactions of unsaturated systems. There has been a wide range of reported substitution reactions for alkyl-POS compounds. These range from relatively conventional substitutions, taking place close to the POS core, to more complicated reactions, often taking place at a greater remove. These more complicated reactions have included Sonogashira couplings, oxidations, and reactions with lithium reagents. An unusual alkyl-POS substitution reaction involving an enzymatically catalyzed substitution of $T_8[(CH_2)_3NH_2]_8$ by catechin was reported in 2005 [59]. The product was reported to be disubstituted, with catechin bound to two of the amine groups of the POS, either as an imide or as a secondary amine. Unsurprisingly, given the nature of the reaction, the substitution pattern on the POS cube is unknown. Of the simpler reactions, a large proportion of these have involved substitution of the chlorine in $T_8[(CH_2)_3Cl]_8$ by a wide range of nucleophiles. A selection of these substitution reactions is presented in Table 2.4.

Table 2.4 Alkyl-T_8R_8 compounds prepared by substitution reactions of functional groups

R	Starting materials	Yield (%)	Refs.
-CH=CHC$_6$H$_4$-4-C≡CSiMe$_3$	T_8(CH=CHC$_6$H$_4$-4-Br)$_8$ + HC≡CSiMe$_3$, [Pd(PPh$_3$)$_2$Cl$_2$], CuI, PPh$_3$, NEt$_3$	37	[60]
-(CH$_2$)$_2$P(=O)(OEt)$_2$	T_8(CH$_2$)$_2$Br + P(OEt)$_3$	-	[61]
-(CH$_2$)$_2$Si(CH$_2$PMe$_2$)$_3$	T_8[(CH$_2$)$_2$SiCl$_3$]$_8$ + LiCH$_2$PMe$_2$	97	[62]
-(CH$_2$)$_2$Si(CH$_2$PPh$_2$)$_3$	T_8[(CH$_2$)$_2$SiCl$_3$]$_8$ + LiCH$_2$PPh$_2$	93	[63]
-(CH$_2$)$_2$SiMe$_2$H	T_8[(CH$_2$)$_2$SiMe$_2$Cl]$_8$ + LiAlH$_4$	61	[64]
-(CH$_2$)$_2$SiMe$_2$OH	T_8[(CH$_2$)$_2$SiMe$_2$H]$_8$ + H$_2$O, Pd	65	[64]
-(CH$_2$)$_2$SiMe[(CH$_2$)$_2$SiMe$_2$OH]$_2$	T_8{(CH$_2$)$_2$SiMe[(CH$_2$)$_2$SiMe$_2$H]$_2$}$_8$ + H$_2$O, Pd	96	[64]
-(CH$_2$)$_2$SiMe$_n$[C$_6$H$_4$-3-P(NMe$_2$)$_2$]$_{3-n}$ (n =0, 1, 2)	T_8[(CH$_2$)$_2$SiMe$_n$Cl$_{3-n}$]$_8$ + BrC$_6$H$_4$-3-P(NMe$_2$)$_2$, n-BuLi	-	[65]
-(CH$_2$)$_3$NHCH$_2$PPh$_2$	T_8[(CH$_2$)$_3$NH$_2$]$_8$ + H$_2$CO/Ph$_2$PH	37	[17]
-(CH$_2$)$_3$N$_3$	{T_8[(CH$_2$)$_3$NH$_3$]$_8$}Cl$_8$ + CF$_3$(CF$_2$)$_3$SO$_2$N$_3$, CuSO$_4$·5H$_2$O, NaHCO$_3$	67	[66]
-(CH$_2$)$_3$OH	T_8[(CH$_2$)$_3$Cl]$_8$ + Ag$_2$O	91	[67]
-(CH$_2$)$_3$ONO$_2$	T_8[(CH$_2$)$_3$I]$_8$ + AgNO$_3$	99	[17]
-(CH$_2$)$_3$PPh$_2$	T_8[(CH$_2$)$_3$Cl]$_8$ + KPPh$_2$	83	[23]

R	Starting materials	Yield (%)	Refs.
-(CH$_2$)$_3$SMe	T$_8$[(CH$_2$)$_3$Cl]$_8$ + NaSMe	55	[23]
-(CH$_2$)$_3$SCN	T$_8$[(CH$_2$)$_3$Cl]$_8$ + NaSCN	90	[23]
-(CH$_2$)$_3$I	T$_8$[(CH$_2$)$_3$Cl]$_8$ + NaI	97	[23]

Similar reactions to those used on the T$_8$R$_8$ systems have also been applied to T$_8$R$_7$R' compounds to produce an equally wide variety of products with varying substitutions. Formation of bis-T$_8$ derivatives can be achieved in the unusual reaction between T$_8$(*i*-Bu)$_7$(CH$_2$)$_3$SH and the *ortho*-chloro substituted benzene derivative 1,2-(CN)$_2$-C$_6$H$_2$-4,5-Cl$_2$ in the presence of a base, leading to the formation of 1,2-(CN)$_2$C$_6$H$_2$-4,5-[S(CH$_2$)$_3$T$_8$(*i*-Bu)$_7$]$_2$ in 94% yield [68]. Similarly, treatment of T$_8$(*c*-C$_5$H$_9$)$_7$(CH$_2$)$_3$I with the *para*-hydroxy substituted compound HOC$_6$H$_2$-2,5-Br$_2$-4-OH, again in the presence of base, led to the formation of the bis-T$_8$ derivative C$_6$H$_2$-2,5-Br$_2$-1,4-[O(CH$_2$)$_3$T$_8$(*c*-C$_5$H$_9$)$_7$]$_2$, although in only 15% yield [69].

Those reactions involving formation of a carboxylic acid derivative break down fairly evenly between those forming amides and esters; however hydrolysis of esters being used as protecting groups can also be used to give CO$_2$H groups. Perhaps somewhat surprisingly, most reactions involving the formation of an amide or ester do not involve a POS compound containing a CO$_2$H group, this probably being associated with the difficulty of introducing unprotected acid functionalities into POS species. A selection of reactions involving acid derivatives is presented in Table 2.5. Although some of these reactions occur without a catalyst, most do require one, even when using reactive acid derivatives. This may be due to the steric interactions arising when attempting to fully functionalize all eight substituents in an alkylated T$_8$R$_8$ compound. Many of the hydrolyses of alkyl-T$_8$ derivatives involve the deprotection of an alcohol but there are some where hydrolysis of an ester leads to the formation of carboxylic acid.

Table 2.5 Preparation of alkyl-T$_8$R$_8$ compounds involving carboxylic acid derivatives

R	Starting materials[a]	Yield (%)	Refs.
-(CH$_2$)$_3$NH(L-Lys) TFA salt	T$_8$[(CH$_2$)$_3$NH$_3$]$_8$Cl$_8$ + BLDCH, HBTU, HOBT, N(*i*-Pr)$_2$Et, citric acid, CF$_3$CO$_2$H	47	[70]
-(CH$_2$)$_3$N[(CH$_2$)$_2$CO$_2$H]$_2$	T$_8${(CH$_2$)$_3$N[(CH$_2$)$_2$CO$_2$-*t*-Bu]$_2$}$_8$ + HCO$_2$H,	99	[71]
-(CH$_2$)$_3$N[(CH$_2$)$_2$C(=O)NH(CH$_2$)$_2$NH$_2$]$_2$	T$_8${(CH$_2$)$_3$N[(CH$_2$)$_2$CO$_2$Me]$_2$}$_8$ + H$_2$N(CH$_2$)$_2$NH$_2$	92	[72]
-(CH$_2$)$_3$NHC(O)Ph	{T$_8$[(CH$_2$)$_3$NH$_3$]$_8$}Cl$_8$ + PhC(O)Cl	49	[17]
-(CH$_2$)$_3$NAc$_2$	T$_8$[(CH$_2$)$_3$NH$_3$]$_8$Cl$_8$ + Ac$_2$O	59	[73]
-(CH$_2$)$_3$NCO	T$_8$[(CH$_2$)$_3$NH$_2$]$_8$ + C(O)Cl$_2$	11-47	[17]

[a] BLDCH - N$_\alpha$N$_\epsilon$-di(Boc)-L-Lys dicyclohexylammonium salt; HBTU - 2-(1*H*-benzotriazole-1-yl)-1,1,3,3-tetramethyluronium hexafluorophosphate; HOBT - 1-hydroxybenzotriazole hydrate

Some interesting differences in product have been observed upon varying the reaction conditions when treating $T_8[(CH_2)_3NH_2]_8$ with a series of anhydrides. At room temperature, succinic, maleic [17], and acetic [74] anhydrides all react to form primary amides; however, at 180° C, the reaction with succinic anhydride affords a cyclic secondary amide [74].

Various biologically-relevant acid derivatives of alkyl-POS compounds have been prepared, usually derived from the octa-amine $T_8[(CH_2)_3NH_2]_8$. Amino acids and oligopeptides have been introduced in their N-protected forms by reaction with $\{T_8[(CH_2)_3NH_3]_8\}Cl_8$ to give the amides in yields ranging from 44% to 94% [75]. It has also proven possible to synthesize oligopeptide POS derivatives using protection/deprotection methods, as well as by reaction with a pre-prepared oligopeptide [75]. More recently, this idea has been applied to making biologically-based dendrimers by repeatedly functionalising $T_8[(CH_2)_3NH_2]_8$ with Boc-protected lysine salts. Four sequential reactions led to the formation of the lysine-dendrimers $T_8[(CH_2)_3NH(\text{L-Lys})]_8$, $T_8[(CH_2)_3NH(\text{L-Lys})(\text{L-Lys})_2]_8$, $T_8[(CH_2)_3NH(\text{L-Lys})(\text{L-Lys})_2(\text{L-Lys})_4]_8$ and $T_8[(CH_2)_3NH(\text{L-Lys})(\text{L-Lys})_2(\text{L-Lys})_4(\text{L-Lys})_8]_8$ as their TFA salts [70]. $T_8[(CH_2)_3NH_2]_8$ has also been coupled with the lactones δ-lactonolactone, ε-caprolactone, δ-maltonolactone, and δ-gluconolactone, to give octa-amide products, reactions proceeding in 23% to 53% yield [17].

Some of the first work on the synthesis of vinyl POS derivatives was carried out as a study of cross-metathesis reactions of $T_8(CH=CH_2)_8$ with a selection of simple and substituted alkenes [76]. Two different catalysts were compared; the first generation Grubbs catalyst, $[RuCl_2(=CHPh)(PCy_3)_2]$, and Schrock's catalyst, $\{Mo[=NC_6H_3\text{-}2,6\text{-}(i\text{-Pr})_2](=CHCMe_2Ph)[OCMe(CF_3)_2]_2\}$, and the results from the more successful syntheses are presented in Table 2.6 [76].

Table 2.6 Alkynyl-T_8R_8 compounds prepared by alkene metathesis

R	Starting materials[a]	Yield (%)
-CH=CHPh	$T_8[CH=CH_2]_8 + CH_2=CHPh$, [Mo]	81
-CH=CHCH$_2$Si(OMe)$_3$	$T_8[CH=CH_2]_8 + CH_2=CHCH_2Si(OMe)_3$, [Mo]	99
-CH=CH(CH$_2$)$_2$CH$_3$	$T_8[CH=CH_2]_8 + CH_2=CHC_3H_7$, [Mo]	99
-CH=CH(CH$_2$)$_3$Br	$T_8[CH=CH_2]_8 + CH_2=CH(CH_2)_3Br$, [Ru]	76
-CH=CH(CH$_2$)$_3$OH	$T_8[CH=CH_2]_8 + CH_2=CH(CH_2)_3OH$, [Ru]	<10
-CH=CH(CH$_2$)$_6$Si(OMe)$_3$	$T_8[CH=CH_2]_8 + CH_2=CH(CH_2)_6Si(OMe)_3$, [Mo]	99
-CH=CH(CH$_2$)$_8$CO$_2$Et	$T_8[CH=CH_2]_8 + CH_2=CH(CH_2)_8CO_2Et$, [Mo]	99

[a] [Mo] - $\{Mo[=NC_6H_3\text{-}2,6\text{-}(i\text{-Pr})_2](=CHCMe_2Ph)[OCMe(CF_3)_2]_2\}$, [Ru] - $[RuCl_2(=CHPh)(PCy_3)_2]$

This study was followed by another, looking at the preparation of other T_8-vinyl

derivatives by either cross-metathesis, using the first or second generation Grubbs catalysts, or silylative coupling, using $[RuHCl(CO)(PCy_3)_2]$ [77]. It was found that the choice of either metathesis or silylative coupling catalysts does not affect the product yield for 1-hexene, allyltrimethylsilane and styrene, but that the silylative coupling reactions for 1-hexene and allyltrimethylsilane produce a mixture of *cis/trans* isomers. In contrast, however, for the reactions of vinyltrimethylsilane, 1-vinyl-2-pyrrolidinone, butylvinyl ether, *tert*-butyl vinyl ether, and trimethylsilyl vinyl ether, only the silylative coupling catalyst led to the production of product [77]. No reaction was observed for *tert*-butyl vinyl sulfide using either the first generation Grubbs catalyst or the silylative coupling catalyst; however when the second generation Grubbs catalyst was tried, the reaction proceeded. A related cross-metathesis study involved contrasting the couplings carried out using the first generation Grubbs catalyst, and silylative coupling catalyst $[RuHCl(CO)(PCy_3)_2]$, of $T_8(i\text{-Bu})_7CH=CH_2$, with $CH_2=CHR$ (R = Ph, C_6H_4-4-Me, C_6H_4-4-OMe, C_6H_4-4-Cl, C_6H_4-4-Br, CH_2Ph and CH_2SiMe_3) to produce monovinyl-substituted products [78]. Further studies on metathesis reactions of T_8 POS derivatives have been more focused on the synthesis of specific products, using the first generation Grubbs catalyst, for example, the formation of dendrimers derived from $T_8(CH=CH_2)_8$, by coupling the POS core to functionalized styrenyl derivatives [60, 79, 80], and of photoluminescent compounds, by decorating it with vinylbiphenyl derivatives [81]. In addition to this, $T_8[CH=CHC_6H_4C_6H_3\text{-}3,5\text{-}(CHO)_2]_8$ has been prepared by the cross-metathesis of octavinyl POS with 4'-vinylbiphenyl-3,5-dicarbaldehyde [81]. Upon the subsequent reduction of the aldehyde to the alcohol, using either $NaBH_4$ or $LiAlH_4$, the internal carbon-carbon double bond was found to be unaffected.

As well as metathetic reactions, a range of addition reactions to unsaturated compounds involving POS species to give alkyl-POS compounds is known. Most of these reactions take place between an unsaturated POS derivative, whether simple systems like $T_8(CH=CH_2)_8$ or more complex, and an appropriate reagent; however, there are a small number of reactions known between a T_8 POS derivative and an unsaturated compound. A selection of these addition reactions are presented in Table 2.7.

Table 2.7 Alkyl-T_8R_8 compounds prepared by addition reactions of alkenes

R	Starting materials	Yield (%)	Refs.
-Et	$T_8(CH=CH_2)_8 + H_2$, Pd/C	89	[82]
-$CHDCH_{1.14}D_{1.86}$	$T_8(CH=CH_2)_8 + D_2$, Pd/C	-	[82]
-$(CH_2)_2CHO$	$T_8(CH=CH_2)_8 + CO/H_2$, $PtCl_2$(sixantphos), $SnCl_2$	-	[21]
-$(CH_2)_2CO_2Me$	$T_8(CH=CH_2)_8 + CO + MeOH$, $MeSO_2OH$, Pd_2dba_3, C_6H_4-1,2-$[CH_2P\text{-}(t\text{-}Bu_2)]_2$	43	[83]
-$(CH_2)_2Ph$	$T_8(CH=CH_2)_8 + C_6H_6 + AlCl_3$	73	[84]
-$(CH_2)_2PEt_2$	$T_8(CH=CH_2)_8 + HPEt_2$, AIBN	> 90	[63]
-$(CH_2)_2S(CH_2)_2(CF_2)_nCF_3$ (n = 5, 7)	$T_8(CH=CH_2)_8 + HS(CH_2)_2(CF_2)_nCF_3$, AIBN	90, 91	[85]
-$(CH_2)_2SiMe_nCl_{3-n}$ (n = 2, 1, 0)	$T_8[CH=CH_2]_8 + HSiMe_nCl_{3-n}$, H_2PtCl_6	93-99	[86]

R	Starting materials	Yield (%)	Refs.
$-(CH_2)_2SiMe_n(CH=CH_2)_{3-n}$ (n = 2, 1, 0)	$T_8[(CH_2)_2SiMe_nCl_{3-n}]_8 + CH_2=CHMgBr$	52-81	[86]
$-(CH_2)_2SiMe_2C_6H_4$-4-Br	$T_8(CH=CH_2)_8 + HSiMe_2C_6H_4$-4-Br, Pt(dvs)	67	[60]
$-(CH_2)_2Br$	$T_8(CH=CH_2)_8 + HBr$, (BzO)$_2$	65	[83]
$-CH=CHPh$	$T_8(CH=CH_2)_8 + PhI$, [Pd(OAc)$_2$], PPh$_3$, NEt$_3$	51	[60]
$-(CH_2)_3NHC(O)NHCH_2CH=CH_2$	$T_8[(CH_2)_3NH_2]_8 + CH_2=CHCH_2NCO$	90	[17]
$-(CH_2)_3N[(CH_2)_2CO_2Me]_2$	$T_8[(CH_2)_3NH_2]_8 + CH_2=CHCO_2CH_3$	73	[87]
$-CH_2CH(O)CH_2$	$T_8(CH_2CH=CH_2)_8 + MCPBA$	75	[88]
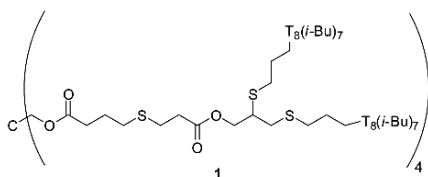
Phosphorus-containing derivatives of alkyl-POS have been prepared by UV-promoted photoaddition of phosphines to carbon-carbon double bonds. Both $T_8(CH=CH_2)_8$ and $T_8(CH_2CH=CH_2)_8$ were converted to the respective octa-substituted dimethylphosphino derivative by UV irradiation in the presence of Me$_2$PH [89]. The ethyldimethylphosphine derivative was further functionalized by reaction with sulphur to give $T_8[(CH_2)_2P(=S)Me_2]_8$, and then complexed to a series of metal carbonyl fragments.

An octa-POS compound has recently been prepared by the addition reaction of the mono-thiol POS $T_8(i\text{-Bu})_7(CH_2)_3SH$ with the tetra-alkyne $C[CH_2OC(=O)(CH_2)_3S(CH_2)_2CO_2CH_2C\equiv CH]_4$ [90]. Spectroscopic analysis indicated the reaction had proceeded to give the octa-POS compound **1**.

Two related addition reactions of dichlorocarbene (derived from chloroform) to $T_8(CH=CH_2)_8$ in the presence of base have been seen to give rise to either the octa- or the tetra-substituted derivatives, $T_8(2,2\text{-Cl}_2\text{-}c\text{-C}_3H_3)_8$ and $T_8(CH=CH_2)_4(2,2\text{-Cl}_2\text{-}c\text{-C}_3H_3)_4$ in about 40% yield [84]. Several other cyclization reactions are known for unsaturated POS derivatives. Two octa-substituted cyclohexane-epoxides, differing in the tether to the POS core, have been prepared from the cyclohexene compounds using Oxone® or MCPBA [50]; and the partial epoxidation of $T_8(CH=CH_2)_8$ by MCPBA resulted in the formation of $T_8(CH=CH_2)_6[CH(O)CH_2]_4$ [91].

Other alkyl-POS compounds containing more than one type of substituent can be prepared by addition reactions. On treatment of $T_8(CH=CH_2)_8$ with HOTf, the monoaddition product $T_8(CH=CH_2)_7(CH_2)_2OTf$, resulted. This product can be hydrolyzed to give the monoalcohol (which can be reduced to $T_8Et_7(CH_2)_2OH$) or

treated with 2-mercaptopyridine to give the monopyridyl derivative [92].

A limited number of cycloaddition reactions involving alkyl-POS compounds have been carried out, the majority of which were aimed at making T_8R_7R' products [93-95]. However, there has very recently been a series of nine T_8 POS-octatriazole compounds prepared using "click" reactions. These syntheses involved the treatment of $T_8[(CH_2)_3N_3]_8$ with a series of alkynes, ranging from simple alkynes like phenylacetylene, to complicated alkyne derivatives involving protected systems, and a pyrazolylborate derivative. Various different catalyst and solvent systems were tested for these alkynes, and optimization of conditions led to generally high yields (63% to 90%) [66].

Of the studies of cycloaddition reactions leading to T_8R_7R' products, the most simple of these involved the reaction of a POS-azide derivative with phenylacetylene to form a 1,2,3-triazole derivative by a "click" reaction [93, 94]. An in-depth investigation of a series of cycloadditions has compared the efficacies of microwave-assisted and conventional reaction conditions for the synthesis of a series of POS derivatives containing isoxazolidine or isoxazoline rings [95]. The microwave-assisted reactions often performed better, resulting in higher yields, and product mixtures that could be separated to give individual isomers.

2.2.4.2 T_{10} and T_{12} Compounds

There have been two recent reports of reactions modifying the functional groups of T_{10} alkyl-POS compounds, both starting from $T_{10}(CH=CH_2)_{10}$. Starting from a mixture of T_{10} and T_{12} cages, comprising one or two phenyl substituents, the rest being vinyl, or vice versa, a number of reactions were carried out at the vinyl groups of these compounds [96]. These included metathesis reactions with 4-bromostyrene, and Heck couplings; both with vinyltriethoxysilane, and with the pre-metathesis product, to form oligomeric species. Starting from a simpler vinyl-POS mixture comprising T_8, T_{10} and T_{12} POS compounds, thiol-ene reactions have been attempted with large alkyl-POS compounds [97]. Following free-radical-initiated reaction of the POS mixture with $HS(CH_2)_2CO_2Bu$, the products $T_{10}[(CH_2)_2S(CH_2)_2CO_2Bu]_{10}$ and $T_{10}[(CH_2)_2S(CH_2)_2CO_2Bu]_4(CH=CH_2)_6$ were identified, depending on the ratio of the starting materials.

2.2.5   *Other Synthetic Methods*

2.2.5.1 T_6 Compounds

With sufficiently large R groups, hydrolysis of $RSiCl_3$ can lead to stable, isolable silane triols, $RSi(OH)_3$, or 1,1,3,3-tetrahydroxydisiloxanes, $[RSi(OH)_2]_2O$. Following isolation of such silanols, it has been found possible to dehydratively couple them

using dicyclohexylcarbodiimide (DCC), giving rise to T_6R_6 species in yields ranging from 20 %, where R is 2,4,6-i-Pr$_3$C$_6$H$_2$ [98], to 26% or 41%, where R is t-Bu or CMe$_2$-i-Pr, respectively [99]. Similarly, 1,3-diisopropyl-1,1,3,3-tetrahydroxydisiloxane can be converted to the cyclotetrasiloxane, which, when treated with (i-PrSiCl$_2$)$_2$O, gives $T_6(i$-Pr)$_6$ in 25% yield [100]. Another unusual route to $T_6(t$-Bu)$_6$, involves reaction of t-BuSi(OH)$_3$ with NaH to give a mixture of silsesquioxane products from which the T_6 compound can be isolated in 35% yield [101].

2.2.5.2 T_8 Compounds

Two reactions related to the conventional hydrolysis and condensation reactions have also provided unusual routes to T_8 alkyl-POS. One is the cleavage, hydrolysis and condensation reaction that takes place by the action of potassium hydroxide on a mixture of tetraethylcyclotetrasiloxane and pentaethylcyclopentasiloxane resulting in the formation of T_8Et_8 in 37% yield [102]. The second involves the reaction between tetrabutylammonium fluoride and [Me(MeO)SiO]$_4$, producing T_8Me_8 in 52% yield, which is one of the better yields for this compound [103]. Other reactions have been used to prepare alkyl-POS from siloxanes; with DCC effecting the dehydration of the cyclotetrasiloxane [i-Pr(OH)OSi]$_4$ to give $T_8(i$-Pr)$_8$ [104], and of the disiloxane [Cy(OH)$_2$Si]$_2$O to give T_8Cy_8 [105]. Another unusual synthetic route to alkyl-POS arises from the depolymerization of a combination of polymethylsilsesquioxane and polyvinylsilsesquioxane, using tetrabutylammonium fluoride, NBu$_4$F. This results in the formation of a mixture of T_n cages (n = 8, 10, 12) in reasonable yield, but the only characterization of the cages formed and their pattern of substitution was obtained using MALDI-ToF mass spectrometry [106].

2.2.5.3 T_{10} and T_{12} Compounds

Two more unusual routes to T_{10} and T_{12} alkyl-POS compounds have been reported. Firstly, the base-catalyzed reformation of mixtures of methycyclosiloxanes, which resulted in a sublimable product, $T_{10}Me_{10}$, suitable for single crystal X-ray diffraction [107]; and secondly, the preparation of $T_{10}(CH=CH_2)_{10}$ and $T_{12}(CH=CH_2)_{12}$ in moderate yields by hydrolysis of [CH$_2$=CHSi(OEt)$_2$]$_2$O in the presence of NBu$_4$F [38].

2.3 Synthesis of T_nR_n Compounds where R = Aryl

2.3.1 Hydrolysis

2.3.1.1 T_8 Compounds

There are surprisingly few aryl- or heteroaryl-POS compounds that have been prepared by the hydrolysis of chloro- or alkoxysilane precursors, especially as, until recently, it has proven difficult to functionalize T_8Ph_8 specifically without the formation of mixtures of isomers of aryl-POS. The most common hydrolytic syntheses are presented in Table 2.8, the most important being that of T_8Ph_8 [108], as it is a useful precursor to substituted aryl-T_8 derivatives. This compound was originally synthesized by the acidic hydrolysis of $PhSiCl_3$ [109], with significant improvements coming in the use of tetrabutylammonium fluoride for hydrolysis [11], and in the use of an initial hydrolysis followed by base-catalysed rearrangements of the resulting siloxane mixture [110].

Table 2.8 Examples of aryl-T_8R_8 compounds prepared by hydrolysis

R	Starting materials	Yield (%)	Refs.
-Ph	$PhSiCl_3 + PhCH_2NMe_3OH$	98	[108]
$-C_6H_4$-4-Me	$4\text{-Me-}C_6H_4SiCl_3$	19	[111]
$-C_6H_4$-3-Me	$3\text{-Me-}C_6H_4SiCl_3$	25	[112]
$-C_6H_4$-4-CH_2Cl	$4\text{-ClCH}_2C_6H_4SiCl_3$	15	[113]
$-C_6H_3$-3,5-Me_2	$3,5\text{-Me}_2C_6H_4SiCl_3$	22	[112]
$-C_6H_4$-2-NMe_2	$2\text{-NMe}_2C_6H_4Si(OMe)_3 + HCl$	84	[114]

A recent study on the synthesis of substituted-phenyl POS derivatives has led to the preparation of $T_8(C_6H_4\text{-4-R})_8$ POS in 9% to 21% yields by hydrolysis of the arylchlorosilanes $RC_6H_4\text{-4-SiCl}_3$ (R = Me, i-Pr, $SiMe_3$) [115]. The same hydrolyses carried out in the presence of NBu_4F, rather than HCl, for the methyl and trimethylsilyl species also formed the T_8 POS, albeit in lower yield. However, these reactions also produced larger POS species $T_n(C_6H_4\text{-4-R})_n$ (n = 10, R = Me, $SiMe_3$; n = 12, R = $SiMe_3$), in up to 41% yield for n = 10, and 9% yield for n = 12. Two other, little studied, aryl-POS species, the octakis(1-naphthyl) [111] and octakis(2-thienyl) [116] POS have been prepared by hydrolysis of 1-naphthyltrimethoxysilane and 2-thienyltrimethoxysilane respectively. A small number of T_8R_7R' derivatives where R is aryl have also been prepared. These include the capping of $R_7Si_7O_9(OH)_3$ (R = c-C_5H_9, [117] or Cy [118]) with $ClCH_2C_6H_4\text{-4-SiCl}_3$ to give $T_8R_7C_6H_4\text{-4-CH}_2Cl$ in good yield.

2.3.1.2 T_{10} and T_{12} Compounds

Only three larger aryl-POS compounds, other than the three $T_8(C_6H_4$-4-R$)_8$ compounds described above, seem to have been prepared via simple hydrolyses. Thus, T_nPh_n, n = 10, 12, are isolable following base-treatment of the initial hydrolysis products resulting from PhSiCl$_3$ [110], and T_{12}(2-thienyl)$_{12}$ has been prepared by the basic hydrolysis of (2-thienyl)Si(OMe)$_3$ [116].

2.3.2   *Modification of R*

2.3.2.1 T_8 Compounds

A significant amount of effort has been devoted to exploring the possibility of achieving a uniform substitution of the phenyl rings via nitration, halogenation, and recently, sulfonation [119, 120], but, with a few exceptions, most of these attempts have given rise to mixtures. A selection of these reactions is presented in Table 2.9. The nitration of T_8Ph_8 to give $T_8(C_6H_4NO_2)_8$ is important as the nitro derivative is the precursor to $T_8(C_6H_4NH_2)_8$, which is widely used as an additive in polymers [120]. This reaction was first observed on the dissolution of T_8Ph_8 in HNO$_3$ [109], and more recently was reinvestigated and optimized [121]. It was observed that $T_8(C_6H_4NO_2)_8$ did not form regioselectively, as a mixture of predominantly monosubstituted *meta*- and *para*-isomers are formed. In contrast, the di-nitration of T_8Ph_8, although reported to give a mixture of nitration products, [122] can, under the appropriate conditions, afford predominantly the 2,4-dinitrated product [123].

Bromination of T_8Ph_8 gives an apparently monobrominated T_8 product comprising a mixture of 3- and 4-substituted phenyl rings [124], but the product containing, on average, 5.3 bromine atoms, $T_8Ph_8Br_{5.3}$, was chosen as the most suitable for further reaction due to its comprising a mixture of compounds with the fewest multiply-brominated rings, and the highest proportion of 4-brominated rings [125]. As a result of the incomplete substitution, reactions of this product result in complicated product mixtures. Compounds with higher or lower proportions of bromination can be produced by this method, including products with an average of 15.7 bromines per T_8 core [125]. While it has not been possible to exclusively brominate all eight rings of T_8Ph_8 in the 4-position, an important recent report has shown that $T_8(C_6H_4$-4-I$)_8$ can be prepared which will be a useful precursor to a range of novel $T_8(C_6H_4$-4-R$)_8$ species via a variety of synthetic routes [126]. The use of chlorosulfonic acid to introduce SO$_3$H has been reported to give $T_8(C_6H_4$-3-SO$_3$H$)_8$ in 74% yield [127].

Other studies report that the product has only an average of 40% of the phenyl rings bearing a sulfonic acid group after milder sulfonating conditions were used [128], or that no preference for one substitutional isomer over another was observed in the product [129] (see also discussion in Section 7.6, Chapter 7). Friedel Crafts alkylation of T_8Ph_8 was also reported [127]. The unusual multiple bromination of

T_8(2-thienyl)$_8$ to give the tribromothiophene product in excellent yield has also been reported [116]. Four different aryl-T_8 compounds, T_8Ph_8, $T_8(C_6H_4$-n-Me)$_8$ (n = 3 or 4), and $T_8(C_6H_3$-3,5-Me$_2)_8$, have been hydrogenated in yields ranging from 88 to 95 % using palladium on charcoal as catalyst to give the saturated analogues [112].

Table 2.9 Aryl-T_8R_8 compounds prepared by direct substitution at the aromatic ring

R or T_8 compound	Starting materials	Yield (%)	Refs.
-C$_6$H$_4$NO$_2$	T_8Ph_8 + HNO$_3$	90[a]	[121]
-C$_6$H$_3$(NO$_2$)$_2$	T_8Ph_8 + HNO$_3$, H$_2$SO$_4$	78[a]	[122]
-C$_6$H$_3$-2,4-(NO$_2$)$_2$	T_8Ph_8 + HNO$_3$, H$_2$SO$_4$	82	[123]
-C$_6$H$_4$-3-SO$_3$H	T_8Ph_8 + ClSO$_2$OH	74	[127]
-C$_6$H$_4$Br	T_8Ph_8 + Br$_2$, FeCl$_3$	60[a]	[124]
-C$_6$H$_4$-4-I	T_8Ph_8 + ICl	90	[126]
$T_8Ph_8Br_{5.3}$	T_8Ph_8 + Br$_2$, Fe	87[a]	[125]

[a] Contains a mixture of substitutions.

A wide range of reactions has been successfully carried out at substituents on aryl-POS compounds without cleaving the T_8 cage. These include substitutions at benzylic carbons by a variety of nucleophiles, and reaction at substituted benzene rings by lithiations, Grignard reactions, and catalyzed reactions such as Heck, Sonogashira and Suzuki chemistries. A selection of these reactions is presented in Table 2.10. One unusual substitution reaction involving T_8 aryl-POS is the recent preparation of an iminofullerene-POS compound, prepared in 36% yield by the reaction of $T_8(i\text{-Bu})_7C_6H_4$-4-CH$_2$N$_3$ with C$_{60}$ [130]. Another unusual reaction is that of $T_8(C_6H_4Br)_8$ with the Grignard reagent formed from 2-bromo-3-(2'-ethylhexyl) thiophene to give the predominantly octa-substituted product [131], although some of the analytical data may suggest that the Grignard reagent has partially degraded the silsesquioxane core.

Table 2.10 Aryl-T_8R_8 compounds prepared by substitution reactions at functional groups

R	Starting materials	Yield (%)	Refs.
-C$_6$H$_4$-4-CH$_2$I	$T_8(C_6H_4$-4-CH$_2$Cl)$_8$ + NaI	99	[113]
-C$_6$H$_4$-4-CH$_2$OH	$T_8(C_6H_4$-4-CH$_2$I)$_8$ + AgClO$_4$	95	[113]
-C$_6$H$_4$-4-CH$_2$ONO$_2$	$T_8(C_6H_4$-4-CH$_2$I)$_8$ + AgNO$_3$	93	[113]
-C$_6$H$_4$-4-CH$_2$OPPh$_2$	$T_8(C_6H_4$-4-CH$_2$OH)$_8$ + Ph$_2$PCl	70	[132]
-C$_6$H$_4$-4-CH$_2$P(O)Ph$_2$	$T_8(C_6H_4$-4-CH$_2$I)$_8$ + Ph$_2$P(O)Et	83	[132]
-C$_6$H$_4$-4-CH$_2$PPh$_2$	$T_8[C_6H_4$-4-CH$_2$P(O)Ph$_2]_8$ + AlH$_3$	64	[132]
-C$_6$H$_4$-4-CH=CH-4-C$_5$H$_4$N	$T_8(C_6H_4$-4-I)$_8$ + CH$_2$=CH-4-C$_5$H$_4$N, Pd$_2$dba$_3$, tri-o-tolylphosphine, H$_2$CuSn, NEt$_3$	48	[126]

R	Starting materials	Yield (%)	Refs.
$-C_6H_4-4-CH=CHC_6H_4-4-Me$	$T_8(C_6H_4-4-I)_8$ +CH_2=CHC$_6H_4$-4-Me, Pd$_2$dba$_3$, tri-o-tolylphosphine, Cu, NCy$_2$Me	87	[126]
$-C_6H_4-4-C\equiv CPh$	$T_8(C_6H_4-4-I)_8$ + HC≡CPh, CuI, Pd(PPh$_3$)$_4$, NEt$_3$	90	[126]
$-C_6H_4-4-Ph$	$T_8(C_6H_4-4-I)_8$ + PhB(OH)$_2$, Pd$_2$dba$_3$, tri-o-tolyl-phosphine, Ag$_2$O	83	[126]
$-C_6H_4NH_2$	$T_8(C_6H_4NO_2)_8$ + HCO$_2$H, Pd/C, NEt$_3$	82[a]	[121]
$-C_6H_4N_3$	$T_8C_6H_4NH_2$ + H$_2$SO$_4$, NaNO$_2$, NaN$_3$	-[a]	[133]
$-C_6H_3(NH_2)_2$	$T_8[C_6H_3(NO_2)_2]_8$ + HCO$_2$H, Pd/C, NEt$_3$	70[a]	[122]
Methylstyrene derivatives of $T_8Ph_8Br_{5.3}$	$T_8Ph_8Br_{5.3}$ + CH$_2$=CHC$_6H_4$-4-Me, Pd[P(t-Bu)$_3$]$_2$, Pd$_2$dba$_3$, NCy$_2$Me	78[a]	[125]
Phenylacetylene derivatives of $T_8Ph_8Br_{5.3}$	$T_8Ph_8Br_{5.3}$ + CH≡CPh, CuI, Pd$_2$(dba)$_3$, Pd[P(t-Bu)$_3$]$_2$, NEt$_3$	85[a]	[134]
Phosphonic phenylester derivatives of $T_8Ph_8Br_{5.3}$	$T_8Ph_8Br_{5.3}$ + P(=O)(OPh)$_2$Cl, n-BuLi	78[a]	[127]

[a] Contains a mixture of substitutions.

One of the most frequently used aryl-POS derivatives, $T_8(C_6H_4NH_2)_8$, can be prepared from $T_8(C_6H_4NO_2)_8$ in high yield by reduction using formic acid in the presence of Pd/C, to give a product suitable for incorporation into a wide variety of polymers [121]. Similarly, mixed isomer hexadecanitro POS, $T_8[C_6H_3(NO_2)_2]_8$, can be converted to $T_8[C_6H_3(NH_2)_2]_8$, the hexadecamine compound [122]; however, the preparation of the isomer-specific 2,4-dinitrate has not been reported. Further to this, $[T_8(C_6H_4NH_3)_8]Cl_8$, has recently been prepared from $T_8(C_6H_4NH_2)_8$ for use in DNA-detection experiments [135]. Recently, reaction of HNO$_3$ with $T_8(C_6H_4-4-SiMe_3)_8$ has been shown to give exclusively the *para*-substituted isomer $T_8(C_6H_4-4-NO_2)_8$ in 94% yield [115], and the related nitro-derivative $T_8(C_6H_3-3-NO_2-4-Me)_8$ can be prepared by the nitration of $T_8(C_6H_4-4-Me)_8$ using either nitric acid or a copper (II) nitrate, acetic anhydride mixture [115]. These pure compounds should open up routes to a range of new precursors for materials chemistry, as will the recent synthesis of the specifically iodinated $T_8(C_6H_4-4-I)_8$, which can be used to prepare many novel compounds via Heck, Suzuki and Sonogashira reactions [126, 134].

Carboxylate derivatives of T_8 aryl-POS compounds have been prepared. For example, esters can be prepared from $T_8(C_6H_4-4-CH_2OH)_8$ by reaction with the reactive acid derivatives acetic anhydride and 4-nitrobenzoyl chloride, and by reaction with terephthaloyl chloride and methanol to give $T_8[C_6H_4-4-CH_2OC(O)Me]_8$, $T_8[C_6H_4-4-CH_2OC(O)C_6H_4-4-NO_2]_8$, and $T_8[C_6H_4-4-CH_2OC(O)C_6H_4-4-CO_2Me]_8$ respectively in near quantitative yield [113]. Similarly, several amino acid-derived POS compounds were prepared by the reaction of $T_8(C_6H_4-4-CH_2OH)_8$ with N-protected amino acids and oligopeptides [75]. Hydrolysis of the ester $T_8[C_6H_4N(CH_2CO_2Me)_2]_8$ can be used to give the acid functionalized POS

$T_8[C_6H_4N(CH_2CO_2H)_2]_8$ [136].

2.3.2.2 T_{10} and T_{12} Compounds

Reactions of functional groups in T_{10} and T_{12} aryl-POS compounds are usually similar to those observed for the T_8 analogues. Thus, $T_{12}Ph_{12}$ may be nitrated using HNO_3, giving $T_{12}(C_6H_4NO_2)_{12}$ in 95% yield [122], although as is the case for the T_8 systems, this is not a regiospecific reaction, with predominantly *meta*, some *para* and a trace of *ortho* substitution. These nitro groups can be converted to amines using Pd/C, in the presence of formic acid, in 70% yield [122]. Similarly, the specifically substituted 4-nitrophenyl T_n POS (n = 10 and 12) has been prepared in 80% and 33% yield, respectively, by treating $T_n(C_6H_4$-4-$SiMe_3)_n$ with HNO_3 [115]. Hydrogenation of $T_{12}Ph_{12}$ using palladium on charcoal proceeds with an excellent 93% yield, but the equivalent reaction for $T_{10}Ph_{10}$ has not been reported [112]. Again in parallel to what has been done for the T_8 compounds, T_{12}(2-thienyl)$_{12}$ has been triply brominated to give the dodeca(tribromothiophene) derivative in 90% yield [116].

2.3.3   *Other Synthetic Methods*

The potentially highly useful regiospecifically brominated T_8Ph_8 derivative $T_8(C_6H_4$-4-$Br)_8$ has been prepared by acid polycondensation of the cyclic sodium silanolate Na_4-c-[BrC_6H_4-4-$SiO(O)]_4$, followed by base-catalyzed rearrangement to give the product in moderate 58% yield [137]. While this synthetic route may prove highly useful in a limited number of cases, given the necessity of preparing the starting cyclotetrasiloxane sodium silanolate, it is unlikely to be widely used, especially given the relative ease of preparation of $T_8(C_6H_4$-4-$I)_8$, see above.

The ethynyl derivative $T_8(C_6H_4C{\equiv}CSiMe_3)_8$ has been prepared, along with the related T_4 and T_6 species (detectable by MALDI-TOF mass spectrometry in the crude T_8 product), by the hydrolysis of an unusual starting material, the ionic λ^5-substituted spirosilicate, pyridinium bis(2,3-naphthalendiolato)-4'-(trimethylsilylethynyl) phenylsilicate [138]. However, although the hydrolysis proceeded in 88% yield, this methodology is unlikely to become widespread, since the starting spirosilicate requires a seven-step synthesis.

2.4   Synthesis of T_nR_n Compounds where R = Alkoxy

There have been only a very limited number of alkoxy-POS compounds prepared, all of which are $T_8(OR)_8$ derivatives, and all of which result from substitution reactions at the cage silicon atoms. The first synthesis of $T_8(OMe)_8$ used the reaction of T_8Cl_8 with methyl nitrite [139]; however, due to the toxicity and potentially explosive nature of methyl nitrite, an alternative route was sought. Thus, T_8Cl_8 was found to react with trimethyl orthoformate to give $T_8(OMe)_8$ in 68% yield [140]. It is perhaps somewhat surprising that the preparation of further analogues of this compound have not been attempted, using other orthoesters. The remaining synthetic work in this area has all been based around the same reaction, that between T_8H_8 and an alcohol in the presence of catalytic amounts of NEt_2OH base. The first alkoxy-POS compounds prepared in this manner were $T_8[O(CH_2)_3CH=CH_2]_8$ and $T_8[O(CH_2)_5Me]_8$ [48], although no yields were reported. This has been followed by a report in the patent literature, using an optimized version of the same methodology, and preparing T_8R_8, where R is OEt, O-i-Pr, O-t-Bu, OOct and OCy in 54 to 87 % yields [141].

2.5   Synthesis of T_nR_n Compounds where R = Siloxy

2.5.1   Corner Capping

Two compounds, $T_8Cy_7OSiCl_3$, and the siloxy-bridged $O(T_8Cy_7)_2$ can be prepared in 62 or 69% yield, respectively, by the corner capping of $T_7Cy_7(OH)_3$ using either one or a half equivalent of $O(SiCl_3)_2$, and NEt_3 or pyridine as base [142].

2.5.2   Substitution

2.5.2.1 T_8 Compounds

Most new siloxy-POS compounds are prepared by modification of the substituents at a pre-existing siloxy centre rather than by introduction of a completely new siloxy group via a substitution reaction. Those that have been prepared by this method generally contain a simple siloxy substituent, or derive from a reactive group at silicon. Thus, $T_8(OSiMe_3)_8$ can be prepared either in quantitative yield by

reaction of T_8H_8 with $Me_3SiOSbMe_4$ [143], or in 54% yield by reaction of T_8H_8 with Me_3SiOH in the presence of a base [141]. Four other compounds, $T_8[OSi(CD_3)_3]_8$ [144], $T_8(OSiMe_2CH=CH_2)_8$ and $T_8(OSiMe_2CH_2Cl)_8$ [145], and $T_8Cy_7OSiMe_3$. [36] have been prepared by a similar route, but using the trimethylamine-*N*-oxide adduct of the relevant chlorosilane. A limited number of other T_8R_7R'-siloxy POS, where R' is a bridging group, has been prepared by substitution at silicon. These reactions involve a monochloro POS, T_8R_7Cl, being treated with either a lithiated monohydroxy POS, or a lithiated dihydroxy-containing partial-cage POS [146]. These reactions result in the formation of the di-POS compounds $(T_8R_7)_2O$ (R = *c*-C_5H_9, Cy) and the tri-POS compound $(T_8Cy_7)_2(exo,exo$-$Si_8O_{11}Cy)$ in 65% to 73% yield.

2.5.2.2 T_{10}, T_{12} and T_{14} Compounds

A series of larger siloxy-POS compounds has been prepared, as in the case of the T_8 analogue, via the trimethylamine-N-oxide adduct of the relevant chlorosilane. This has allowed the synthesis of $T_{10}(OSiMe_2CH=CH_2)_{10}$ and $T_{10}(OSiMe_2CH_2Cl)_{10}$ in 65% and 52% yields [145], and $T_{12}(OSiMe_3)_{12}$ [147], and $T_{14}(OSiMe_3)_{14}$ [147], both in 95% yield.

2.5.3   Modification of R

2.5.3.1 T_6 Compounds

The majority of the functional group modification reactions involving T_6 siloxy-POS compounds either involve formation from isolated $[T_6O_6]^{6-}$ salts [148], or the modification of these siloxy compounds. The silylation reactions include the formation of $T_6(OSiMe_2H)_6$, from the treatment of $[NEt_4]_6[T_6O_6]^{6-}$ with HMe_2SiCl [148], and $T_6(OSiMe_3)_6$, from treatment with Me_3SiCl [149]. The silane $T_6(OSiMe_2H)_6$ can be converted to the bromide $T_6(OSiMe_2Br)_6$, by catalytic bromination using $Rh(acac)_3$ and allyl bromide [148]. Both POS species have been used in the preparation of porous polymeric POS-based materials, with $T_6(OSiMe_2H)_6$ undergoing hydrosilylation with $T_8(CH=CH_2)_8$, and $T_6(OSiMe_2Br)_6$ being hydrolyzed [150].

2.5.3.2 T_8 Compounds

The most common functional group modification reaction of siloxy-POS compounds is hydrosilylation, but other methods are available, such as the reaction involving

an alkene in T_8 siloxy-POS compounds, exemplified by the cross-metathesis of $T_8(OSiMe_2CH=CH_2)_8$ with either styrene or 1-pentene, using Schrock's catalyst [76].

The reactions of acid derivatives include examples of both hydrolysis and esterification, with $T_8[OSiMe_2(CH_2)_2C_6H_4\text{-}4\text{-}OAc]_8$ having been hydrolyzed to give the alcohol [151], and a number of different siloxy-POS being reacted with methacryloyl chloride to give the methacrylate derivatives, $T_8[OSiMe_2(CH_2)_3O(CH_2CH_2O)_nOC(=O)CMe=CH_2]_8$ (n = 2, 3, 4, 6) [152], and $T_8[OSiMe_2(CH_2)_3OC(O)CMe=CH_2]_8$ [153].

A wide range of substitution reactions of siloxy-POS compounds has been observed and a selection of these is presented in Table 2.11. While some of these reactions are of very similar type to those observed for other POS, some of them take advantage of the additional distance between reacting centres and the POS cage, and the added steric shielding provided by the siloxy groups being between the rest of the functional group and the POS core, which allows the use of reagents, such as Grignard reagents, that have been known to attack the POS cage in less well protected systems. One particular compound of interest is $T_8(OSiMe_2C_6H_4\text{-}4\text{-}CO_2H)_8$ [154], containing a carboxylic acid group held in a comparatively constrained orientation by the $-OSiMe_2C_6H_4-$ linker. This compound has been prepared in two steps from $T_8(OSiMe_2C_6H_4\text{-}4\text{-}Me)_8$, and opens up possibilities for a further range of carboxylate-functionalized POS compounds to be prepared.

Table 2.11 Siloxy-T_8R_8 compounds prepared by substitution reactions of functional groups

R	Starting materials	Yield (%)	Refs.
$-OSiMe_2CH(O)CH_2$	$T_8(OSiMe_2CH=CH_2)_8 + m\text{-}CPBA$	87	[155]
$-OSiMe_2CH(CO_2Et)_2$	$T_8(OSiMe_2H)_8 + BrCH(CO_2Et)_2$, Na	27	[156]
$-OSiMe_2(CH_2)_2SiMe(CH_2CH=CH_2)_2$	$T_8[OSiMe_2(CH_2)_2SiMeCl_2]_8 +$ $CH_2=CHCH_2MgBr$	-	[157]
$-OSiMe_2(CH_2)_2SiMe(OCH_2CH=CH_2)_2$	$T_8[OSiMe_2(CH_2)_2SiMeCl_2]_8 +$ $CH_2=CHCH_2OH$, pyridine	-	[157]
$-OSiMe_2(CH_2)_2Si(CH=CH_2)_3$	$T_8[OSiMe_2(CH_2)_2SiCl_3]_8 + CH_2=CHMgBr$	78	[158]
$-OSiMe_2(CH_2)_2Br$	$T_8(OSiMe_2CH=CH_2)_8 + HBr$, $(PhO)_2$	79	[156]
$-OSiMe_2C_6H_4\text{-}4\text{-}CBr_3$	$T_8(OSiMe_2C_6H_4\text{-}4\text{-}Me)_8 + NBS$, AIBN	86[a]	[154]
$-OSiMe_2C_6H_4\text{-}4\text{-}CO_2H$	$T_8(OSiMe_2C_6H_4\text{-}4\text{-}CBr_3)_8 + AgNO_3$, HCOOH	90	[154]
$-OSiMe_2Br$	$T_8(OSiMe_2H)_8 + CH_2=CHCH_2Br$, Rh(acac)$_3$	99	[159]

[a] Contains a mixture of products with varying degrees of bromination.

Hydrosilylation has led to the preparation of a wide range of T_8 siloxy-POS compounds with various functional groups appended to them; a selection of these is presented in Table 2.12. The starting POS compounds are generally either

$T_8(OSiMe_2H)_8$ or $T_8(OSiMe_2CH=CH_2)_8$, with the former being the reagent of choice in recent years, probably due to both its ease of preparation, and commercial availability. Of those reactions starting from $T_8(OSiMe_2CH=CH_2)_8$, most of them are hydrosilylations with simple silane derivatives, introducing new silicon centres into the POS compounds. For the reactions starting from $T_8(OSiMe_2H)_8$, the hydrosilylation generally introduces functionalized organic groups to provide the desired chemical functionality. Alcohols and ethylene glycol oligomers have been commonly prepared by this method, but more exotic derivatives have included a carborane cage compound, $T_8[OSiMe_2(CH_2)_3C\equiv CMeB_{10}H_{10}]_8$ [160].

Table 2.12 Siloxy-$T_8 R_8$ compounds prepared by hydrosilylation

R	Starting materials	Yield (%)	Refs.
$-OSiMe_2(CH_2)_2C_6H_4$-4-NH_2	$T_8(OSiMe_2H)_8 + CH_2=CHC_6H_4$-4-$NH_2$, Pt(dvs)	-	[161]
$-OSiMe_2(CH_2)_2SiMe_nCl_{3-n}$ (n=1,2)	$T_8(OSiMe_2CH=CH_2)_8 + HSiMe_nCl_{3-n}$, H_2PtCl_6	86,97	[160]
$-OSiMe_2(CH_2)_2SiMe(OSiMe_3)_2$	$T_8(OSiMe_2CH=CH_2)_8 + HSiMe(OSiMe_3)_2$, H_2PtCl_6	-	[162]
$-OSiMe_2(CH_2)_2Si(OEt)_3$	$T_8(OSiMe_2CH=CH_2)_8 + HSi(OEt)_3$, H_2PtCl_6	83	[160]
$-OSiMe_2(CH_2)_2SiCl_3$	$T_8(OSiMe_2CH=CH_2)_8 + HSiCl_3$, H_2PtCl_6	95	[158]
$-OSiMe_2(CH_2)_3C\equiv CMeB_{10}H_{10}$	$T_8(OSiMe_2H)]_8 + CH_2=CHCH_2C\equiv CMeB_{10}H_{10}$, Pt(dvs)	85	[160]
$-OSiMe_2(CH_2)_3CN$	$T_8(OSiMe_2H)_8 + CH_2=CHCH_2CN$, H_2PtCl_6	43	[163]
$-OSiMe_2(CH_2)_3OH$	$T_8(OSiMe_2H)_8 + CH_2=CHCH_2OH$, Pt(dvs)	86	[153]
$-OSiMe_2(CH_2)_3O(CH_2)_2OH$	$T_8(OSiMe_2H)_8 + CH_2=CHCH_2O(CH_2)_2OH$, Pt(dvs)	87	[153]
$-OSiMe_2(CH_2)_3OCH_2CH(O)CH_2$	$T_8(OSiMe_2H)_8 + CH_2=CHCH_2OCH_2CH(O)CH_2$, Pt(dcp)	91	[164]
$-OSiMe_2(CH_2)_3O(CH_2CH_2O)_nH$ (n = 2, 3, 4, 6)	$T_8(OSiMe_2H)_8 + CH_2=CHCH_2O(CH_2CH_2O)_nH$, Pt(dvs)	-	[165]
$-OSiMe_2(CH_2)_3O(CH_2CH_2O)_nMe$ (n = 2, 3, 4, 6, 8, 12.5)	$T_8(OSiMe_2H)_8 + CH_2=CHCH_2O(CH_2CH_2O)_nMe$, Pt(dvs)	-	[166]
$-OSiMe_2(CH_2)_3OSiMe_3$	$T_8(OSiMe_2H)_8 + CH_2=CHCH_2OSiMe_3$, Pt(dvs)	82	[153]
$-OSiMe_2(CH_2)_3Cl$	$T_8(OSiMe_2H)_8 + CH_2=CHCH_2Cl$, H_2PtCl_6	48	[167]
$-OSiMe_2(CH_2)_3Br$	$T_8[OSiMe_2H]_8 + CH_2=CHCH_2Br$, H_2PtCl_6	50	[168]

The other common reactions of T_8 siloxy-POS compounds are those where reaction occurs at the siloxy-silicon centres. These reactions are often silicon-specific substitution reactions, with silylation being most common. As well as reactions where additions to the siloxy groups occur, reactions resulting in the removal of part or all of a siloxy substituent are known, for example by desilylation or alcoholysis. A selection of compounds resulting from these reactions is presented in Table 2.13. There have been recent attempts to prepare highly silylated T_8 siloxy-POS compounds by treatment of simple starting materials, $[T_8O_8]^{8-}$ or T_8H_8, with either $(Me_3SiO)_3SiCl$ or $(Me_3SiO)_3SiOH$. In all cases the reaction proceeded, but

not to completion, with two or three corners of the cube showing no substitution [169], presumably due to the steric bulk of the silylating agents. While the desired $T_8[OSi(OSiMe_3)_3]_8$ has not yet been produced, a closely related compound, $T_8[OSi(OSiMe_3)_3]_7OSi(OSiMe_3)_2OH$, has been obtained by silylation of $T_8[OSi(OEt)_3]_8$ with Me_3SiCl [169].

Table 2.13 Siloxy-T_8R_8 compounds prepared by reaction at cage-silicon atoms

R or T_8R_8	Starting materials	Yield (%)	Refs.
$[T_8O_8]^{8-}$	$T_8(OSiMe_2H)_8 + H_2O$	-	[170]
$-OSiMe_2H$	$[NMe_4]_8[T_8O_8] + HMe_2SiCl$	87	[168]
$-OSiMe_3$	$T_8(OSiMe_2H)_8 + Me_3SiCl, AcOH$	98	[171]
$-OSiMe_2CH_2Cl$	$T_8(OSiMe_2H)_8 + ClCH_2Me_2SiCl, AcOH$	94	[171]
$-OSiMe_2CH_2Br$	$T_8(OSiMe_2H)_8 + BrCH_2Me_2SiCl, AcOH$	90	[171]
$-OSiMe_2CH=CH_2$	$[NMe_4]_8[T_8O_8] + CH=CH_2Me_2SiCl$	87	[156]
$-OSiMe_2CH_2CH=CH_2$	$[NMe_4]_8[T_8O_8] + CH=CH_2CH_2Me_2SiCl$	52	[172]
$-OSiMe_2Ph$	$[NMe_4]_8[T_8O_8] + PhMe_2SiCl$	54	[173]
$-OSiMe_2(CH_2)_3OH$	$T_8[OSiMe_2(CH_2)_3OSiMe_2-t-Bu]_8 + NBu_4F$	81	[174]
$-OSiMe_2C_6H_4-4-Me$	$[NMe_4]_8[T_8O_8] + Me-4-C_6H_4Me_2SiCl$	40	[154]
$-OSiMe_2OH$	$T_8(OSiMe_2H)_8 + Pd/C$	-	[175]
$-OSiMe_n(OEt)_{3-n}$ (n = 2, 1, 0)	$[NMe_4]_8[T_8O_8] + (EtO)_{3-n}Me_nSiCl$	-	[176]
$-OSiMe_2OSiMe_2H$	$T_8(OSiMe_2OH)_8 + HMe_2SiCl$	-	[175]
$-OSiMe_2OSiMe_3$	$T_8(OSiMe_2H)_8 + (Me_3Si)_2, HCl$	97	[170]

2.5.3.3　　*T_{10} Compounds*

Only two T_{10} siloxy POS compounds have been prepared by modification of their functional groups, both using the same methodology. These are $T_{10}(OSiMe_2H)_{10}$ [177], and $T_{10}(OSiMe_3)_{10}$ [178], prepared by the silylation of $[NBu_4]_{10}[T_{10}O_{10}]$ with HMe_2SiCl and Me_3SiCl, respectively.

2.6　　Synthesis of T_nR_n Compounds where R = Metal Complex

2.6.1　　*Hydrolysis*

There have been very few reports of fully condensed POS compounds containing metal ions directly prepared by hydrolysis and condensation. One of these,

$[NMe_4]_7Na[T_8O_8]$, can be prepared by the hydrolysis of sodium silicate in the presence of NMe_4OH and $NaOH$ [179], while another is a more complicated system comprising $\{T_8[(CH_2)_3NH_3]_8\}^{8+}$ cations and a mixture of Cl^- and $[ZnCl_4]^{2-}$ anions, formed by the acidic hydrolysis of $H_2N(CH_2)_3Si(OEt)_3$ in the presence of $ZnCl_2$ [73].

2.6.2   *Substitution*

2.6.2.1 T_8 Compounds

A small range of metal-containing T_8 POS compounds has been prepared by substitution at their cage silicon atoms. Three alkyltin compounds, $T_8(OSnBu_3)_8$ and $T_8(OSnBu_3)_8 \cdot 4H_2O$ [180], and $T_8(OSnMe_3)_8$ [143], were all prepared by treating T_8H_8 with the appropriate hexaalkyldistannoxane. Reaction yield varied depending on the alkyl ligands, with butyltin products being obtained in up to 95% yield, and methyltin products in 54% yield. The cobalt compound, $T_8[Co(CO)_4]_8$ was obtained by reaction between T_8H_8 and dicobaltoctacarbonyl, in 87% yield [181] and a mono-ferrocenyl derivative was prepared by hydrosilylation of T_8H_8 with vinylferrocene to afford $T_8H_7(CH_2)_2Fc$ in 14% yield [182] (see also Section 1.8.2, Chapter 1).

2.6.2.2 T_{10} Compounds

Only one metal-containing T_{10} compound has been prepared by a substitution reaction at the cage silicon atoms. Thus, $T_{10}(OSnBu_3)_{10} \cdot 4H_2O$ can be prepared, as for the T_8 analogue, in 93% yield by the direct reaction of $T_{10}H_{10}$ with hexamethyldistannoxane [180].

2.6.3   *Modification of R*

The most common method of preparing metal-containing POS compounds has been by modification of their functional groups. Of the metallated POS compounds, those containing eight metal atoms, as a T_8R_8 compound, are rarer than the T_8R_7R' compounds, as these latter are often employed as either model compounds for catalytic systems, or as catalysts in their own right (see Chapter 3). A selection of octametallated T_8 compounds is presented in Table 2.14 which includes examples of metals binding to suitable T_8 compounds such as a series of $T_8[(CH_2)_3NH_2]_8$ transition metal complexes [73] and a tetramethylstibine compound [143], as well as reaction with a vinylferrocene derivative [183].

Table 2.14 T_8R_8 metal complexes prepared by modification of functional groups

R or T_8R_8	Starting materials	Yield (%)	Refs.
$T_8[(CH_2)_3NH_2]_8M_2X_4$ [MX$_2$ = Ni(NO$_3$)$_2$, Cu(NO$_3$)$_2$, CuBr$_2$, Zn(NO$_3$)$_2$, ZnI$_2$, Cd(BF$_4$)$_2$, Cd(NO$_3$)$_2$]	$T_8[(CH_2)_3NH_2]_8$ + MX$_2$·nH$_2$O	60-90	[73]
$T_8[(CH_2)_3NH_3]_8[MCl_4]_4$ (M = Co, Cu, Cd)	$T_8[(CH_2)_3NH_3]_8Cl_8$ + MCl$_2$·nH$_2$O	27-82	[73]
-OSiMe$_2$(CH$_2$)$_2$Fc	$T_8(OSiMe_2H)_8$ + CH$_2$=CHFc, Pt(dvs)	57	[183]
-OSiMe$_2$(CH$_2$)$_2$SiMe$_2$Fc	$T_8(OSiMe_2CH=CH_2)_8$ + HSiMe$_2$Fc, H$_2$PtCl$_6$	70	[160]
-OSiMe$_2$Co(CO)$_4$	$T_8[OSiMe_2H]_8$ + Co$_2$(CO)$_8$	99	[159]
-OSbMe$_4$	$T_8(OSnMe_3)_8$ + Me$_3$SiOSbMe$_4$	60	[143]
-OTiClCp$_2$	$T_8(OSnMe_3)_8$ + Cp$_2$TiCl$_2$, CH$_2$Cl$_2$	84	[180]

A broad selection of complexes of T_8R_7R' POS derivatives has been prepared for use, for example, in the modelling of silica-anchored catalyst systems involving metals such as Ti, Zr, Mo, W, Mn, Os, Rh, Pd and Pt (see Chapter 3). Such a variety of introduced metals allows for an equally broad range of catalyst systems that have been modelled, or complexes that have been determined to be catalytically active in their own right. A selection of the T_8R_7R' metal complexes that have been prepared, both for catalytic studies and other uses, is presented in Table 2.15. Other complexes that have been prepared include osmium complexes, from the reaction of a dimethylcyclohexenyl-POS derivative with K$_2$OsO$_2$(OH)$_4$, resulting in the formation of a chelated osmate ester complex [35].

Table 2.15 T_8R_7R' metal complexes prepared by modification of R'

T_8 derivative	Starting materials	Yield (%)	Refs.
$[(T_8Cy_7-\mu-O)Sc(acac)]_2$	T_8Cy_7OH + Sc(acac)$_2$Cp*	61	[184]
$T_8(c-C_5H_9)_7OTiCl_2Cp'$	$T_8(c-C_5H_9)_7OH$ + Cp'TiCl$_3$, n-BuLi	51	[185]
$T_8(c-C_5H_9)_7OTi(O-i-Pr)_3$	$T_8(c-C_5H_9)_7OH$ + Ti(O-i-Pr)$_4$	80	[186]
$T_8(c-C_5H_9)_7OTi(CH_2Ph)_2C_5H_3$-1,3-(SiMe$_3$)$_2$	$T_8(c-C_5H_9)_7OH$ + Ti(CH$_2$Ph)$_3$C$_5$H$_3$-1,3-(SiMe$_3$)$_2$	-	[187]
$[T_8(c-C_5H_9)_7O]_2[Mn(TMEDA)_2]$	$T_8(c-C_5H_9)_7OH$ + [Mn(CH$_2$-t-Bu)$_2$(TMEDA)]	54	[188]
$T_8(c-C_5H_9)_7C_6H_4$-4-CH=CHFc	$[T_8(c-C_5H_9)_7C_6H_4$-4-CH$_2$PPh$_3$]Cl + FcCHO, NaOEt	89[a]	[189]
$T_8(c-C_5H_9)_7OMo(=NH)(CH_2-t-Bu)_3$	$T_8(c-C_5H_9)_7OH$ + Mo(≡N)(CH$_2$-t-Bu)$_3$	76	[190]
$T_8(c-C_5H_9)_7OMo(=NC_6H_3$-2,6-$i$-Pr$_2$)(CH$_2$-$t$-Bu)(=CH-$t$-Bu)	$T_8(c-C_5H_9)_7OH$ + Mo(=NC$_6$H$_3$-2,6-i-Pr$_2$)(CH$_2$-t-Bu)$_2$(=CH-t-Bu)	99	[191]
$[T_8(c-C_5H_9)_7O]_2Mo[NH(t-Bu)C_6H_3$-3,5-($i$-Pr)$_2$][N($t$-Bu)C$_6H_3$-3,5-($i$-Pr$_2$)](≡CEt)	$T_8(c-C_5H_9)_7OH$ + Mo[N(t-Bu)C$_6$H$_3$-3,5-(i-Pr)$_2$]$_3$(≡C-Et)	60	[192]
$[T_8Cy_7OP(NMe_2)_2]_2Mo(CO)_4$	$T_8Cy_7OP(NMe_2)_2$ + norbornadienemolybde-numtetracarbonyl	95	[193]

T_8 derivative	Starting materials	Yield (%)	Refs.
$T_8Cy_7OSnMe_3$	$T_8Cy_7H + Me_3SnCl\cdot Me_3NO$	87	[36]
$T_8Cy_7OSbMe_4$	$T_8Cy_7H + Me_3SiCl\cdot Me_3NO$	83	[36]
$[T_8Cy_7\text{-}\mu\text{-}O]_2[SmCp^*_2][Li(THF)]$	$T_8Cy_7OH + Cp^*_2Sm(\mu\text{-}Cl)Li(THF)_2$, MeLi	68	[184]
$T_8(c\text{-}C_5H_9)_7OW[=NC_6H_3\text{-}2,6\text{-}(i\text{-}Pr_2)](CH_2\text{-}t\text{-}Bu)(=CH\text{-}t\text{-}Bu)$	$T_8(c\text{-}C_5H_9)_7OH + W[=NC_6H_3\text{-}2,6\text{-}(i\text{-}Pr_2)](CH_2\text{-}t\text{-}Bu)_2(=CH\text{-}t\text{-}Bu)$	-	[194]
$[T_8(c\text{-}C_5H_9)_7O]_2W[=NC_6H_3\text{-}2,6\text{-}(i\text{-}Pr_2)](CH_2\text{-}t\text{-}Bu)_2$	$T_8(c\text{-}C_5H_9)_7OH + W[=NC_6H_3\text{-}2,6\text{-}(i\text{-}Pr_2)](CH_2\text{-}t\text{-}Bu)_2(=CH\text{-}t\text{-}Bu)$	-	[195]
$T_8Cy_7ORe(CO)_5$ and dimer	$T_8Cy_7OH + Re(CO)_5CF_3SO_3$, n-BuLi, CO	-	[196]
$T_8(c\text{-}C_5H_9)_7ORe(CH_2\text{-}t\text{-}Bu)(=CH\text{-}t\text{-}Bu)(\equiv C\text{-}t\text{-}Bu)$	$T_8(c\text{-}C_5H_9)_7OH + Re(CH_2\text{-}t\text{-}Bu)_2(=CH\text{-}t\text{-}Bu)(\equiv C\text{-}t\text{-}Bu)$	95	[197]
$[T_8Cy_7OP(NMe_2)_2]_2PtCl_2$	$T_8Cy_7OP(NMe_2)_2 + Pt(cod)Cl_2$	96	[193]

[a] Mixture of E and Z isomers.

Four mono- and one di-POS complex have been prepared with three different metals starting from the POS-fluorenyl compound $T_8(c\text{-}C_5H_9)_7CH_2Flu$ (Flu = 9-H-fluorene) [34]. These include trimethylsilyl and trimethylstannyl derivatives, sandwich compounds with $ZrCl_2Cp^*$ and $ZrCl_2Cp''$, and a di-POS sandwich compound with two fluorenyl rings sandwiching a $ZrCl_2$ fragment. Two titanium alkoxide complexes containing either one or three (1R,2S,5R)-2-isopropyl-5-methylcyclohexyloxy groups at the titanium centre have been prepared using $T_8(c\text{-}C_5H_9)_7OH$ as a precursor [198]. A second series of four titanium compounds was also prepared from $T_8(c\text{-}C_5H_9)_7OH$ [199]; reaction with Cp^*TiMe_3 gave the di-POS compound $[T_8(c\text{-}C_5H_9)_7O]_2TiCp^*Me$ which, when treated with either $B(C_6F_5)_3$ or $[C_6H_5NHMe_2][B(C_6F_5)_4]$, gave the adducts $[T_8(c\text{-}C_5H_9)_7O]_2TiCp^*(\mu\text{-}Me)B(C_6F_5)_3$ and $\{[T_8(c\text{-}C_5H_9)_7O]_2TiCp^*(\kappa\text{-}NMe_2Ph)\}[B(C_6F_5)_4]$, respectively. The $B(C_6F_5)_3$ adduct reacts with $[Ph_3C][B(C_6F_5)_4]$ to give $\{[T_8(c\text{-}C_5H_9)_7O]_2TiCp^*\}B(C_6F_5)_4$ along with several by-products [199]. In order to confirm the identity of the major product, this mixture was further treated with N,N-dimethylaniline, resulting in the quantitative formation of $\{[T_8(c\text{-}C_5H_9)_7O]_2TiCp^*(\kappa\text{-}NMe_2Ph)\}[B(C_6F_5)_4]$.

A series of three iridium-POS complexes has recently been prepared, starting from $T_8(c\text{-}C_5H_9)_7OSiMe_2H$, which undergoes hydrosilylation with three different iridium complexes containing ligands derived from 2-pyridylbenzene, and a ligand containing a pentene group [200] (see also Section 7.2.4, Chapter 7). The octa-silane $T_8(OSiMe_2H)_8$ was similarly hydrosilylated sequentially with one equivalent of one of the complexes, followed by an excess of N-allylcarbazole, to give mono-iridium, hepta(propylcarbazole) POS compounds.

An unusual series of metallo-POS compounds are phthalocyanines functionalised with eight POS thiol groups, $T_8(i\text{-}Bu)_7(CH_2)_3S\text{-}$ [68, 201]. These were prepared by the reaction of the di-POS compound 1,2-$(CN)_2C_6H_2$-4,5-$[S(CH_2)_3T_8(i\text{-}Bu)_7]_2$ with $CoCl_2\cdot 6H_2O$, $CuCl$, $Zn(OAc)_2\cdot 2H_2O$, $Lu(OAc)_3\cdot 6H_2O$ or $Gd(OAc)_3\cdot 6H_2O$, resulting in the formation of the phthalocyanine, and assembly of the single- [68] or double-layer complexes [201]. The single layer complexes, with Co, Cu and Zn, showed yields ranging from 33% to 71%, while the double layer complexes, with Lu and

Gd, showed 2% and 17% yields, respectively.

2.7   Synthesis of Miscellaneous $T_n R_n$ Compounds

2.7.1   *Hydrolysis*

The contribution of the tetraalkylammonium cation to the stability of anionic POS oxides in aqueous solution has been shown to be more important than merely balancing the charge. The anionic species exist in solution as a large number of different silicate anions produced by the action of the base on the silicon source [202]. These silicate anions can be stabilized as the T_6, T_8, or larger POS anion by the presence of the appropriate tetraalkylammonium cation or non-aqueous co-solvents [203]. Molecular dynamics studies on $[T_8O_8]^{8-}$ / $[NMe_4]^+$ / H_2O solutions (1 $[T_8O_8]^{8-}$: 16 $[NMe_4]^+$: 450 H_2O) show that the $[NMe_4]^+$ ions are preferentially sited above the POS cage faces to form a coordination sphere that excludes water molecules and decreases the ease of cage hydrolysis [204]. This exclusion of water molecules by $[NMe_4]^+$ is much less significant for the $[T_6O_6]^{6-}$ ion, and $[T_8O_8]^{8-}$ is found to be ca. 290 kJ mol^{-1} more stable in an aqueous $[NMe_4]^+$ solution [205].

2.7.1.1 T_6 Compounds

The hexameric silicate anion, $[T_6O_6]^{6-}$ can be prepared and isolated as a salt by the action of an appropriate base, most commonly tetraethylammonium hydroxide, on a silicon source such as tetraethoxysilane [148], or fumed silica [206], both of which can give an isolable solid product in good yield.

2.7.1.2 T_8 Compounds

The octasilicate anion $[T_8O_8]^{8-}$ can be prepared by hydrolysis/condensation as a salt, usually with either $[NMe_4]^+$ or $[NMe_3(CH_2)_2OH]^+$ as counterion, and it is an important precursor to the vast majority of the octasiloxy POS compounds. It is commonly prepared and used in solution, where it exists as the major silicate product from the reaction of $Si(OEt)_4$ and NMe_4OH [207]. It can also be precipitated as a solid with a large amount of water of crystallization, either as the tetramethylammonium [159] or choline [208] (trimethylhydroxyethylammonium) salts. There are also a few T_8R_7Cl compounds that have been prepared by corner capping of the partially condensed cubic species, $R_7Si_7O_9(OH)_3$ with $SiCl_4$. These include the R = *i*-Bu

[209], c-C$_5$H$_9$ and Cy compounds [146], which are reported with yields around 90%.

2.7.1.3   T$_{10}$ Compounds

The [NBu$_4$]$_{10}$[T$_{10}$O$_{10}$] salt, which can be isolated as a solid, appears to be stabilized by the [NBu$_4$]$^+$ cation, much as [NMe$_4$]$^+$ stabilizes the T$_8$ and [NEt$_4$]$^+$ the T$_6$ cages [178].

2.7.2   Co-Hydrolysis

The co-hydrolysis and condensation of different chloro- or alkoxysilanes has proven only a marginally successful route for the preparation of POS compounds with different functional groups, as a variety of different products are generally formed, including POS of varying sizes, and substitutions, and different substitutional isomers (see also Section 1.8.1, Chapter 1). Even when relatively few products are formed during a particular reaction, separating individual products is often impractical. However, a few cases have been reported where individual products could be identified, and sometimes separated from the product mixture.

The co-hydrolysis of a 5:1 mixture of HSiCl$_3$ and PhSiCl$_3$ leads to a mixture comprising T$_8$H$_8$, T$_8$H$_7$Ph, T$_{10}$H$_9$Ph and other unidentified silsesquioxane products [210]. Following the removal of the T$_8$H$_8$, size-exclusion HPLC led to a mixture of T$_8$H$_7$Ph and T$_{10}$H$_9$Ph, recrystallization of this led to pure T$_8$H$_7$Ph in 3 % yield, and T$_{10}$H$_9$Ph in 0.5% yield. When the co-hydrolysis of MeSiX$_3$ and CH$_2$=CHSiX$_3$ (X = Cl or OAc) is carried out using varying ratios of starting materials, nine products T$_8$Me$_n$(CH=CH$_2$)$_{8-n}$ (n = 0–8) are formed, as identified by GLC and MS [211]. The co-hydrolysis of a combination of CH$_2$=CHSiCl$_3$ and PhSiCl$_3$ in a 5:3 ratio gave T$_8$(CH=CH$_2$)$_7$Ph and T$_8$(CH=CH$_2$)$_6$Ph$_2$ as the main products with the expected T$_8$(CH=CH$_2$)$_5$Ph$_3$ being obtained in a lower yield [212]. The related co-hydrolysis of CH$_2$=CHSiCl$_3$ and PhCH$_2$SiCl$_3$ in a 6:2 ratio gave a surprising mixture of products, characterized by GCMS, including T$_8$(CH=CH$_2$)$_8$, T$_8$(CH=CH$_2$)$_7$CH$_2$Ph, and T$_8$(CH=CH$_2$)$_6$(CH$_2$Ph)$_2$, along with compounds containing hydroxy and alkoxy substituents [213]. Products from the co-hydrolysis of RSiX$_3$ and R'SiX$_3$ [R = Pr, R' = (CH$_2$)$_3$Cl, (CH$_2$)$_3$I, (CH$_2$)$_3$SH, CH$_2$CH=CH$_2$; R = Et, R' = CH=CH$_2$] in a constant 7:1 ratio, have been studied in detail [214]. The product mixtures comprised T$_8$R$_{8-n}$R'$_n$ (n = 0, 1 or 2) that can be separated by HPLC, and in addition, three isomeric disubstituted products can be readily distinguished both from each other and from other products by ^{29}Si NMR spectroscopy. A more complicated co-hydrolysis reaction, between NH$_2$(CH$_2$)$_3$Si(OMe)$_3$, i-OctSi(OMe)$_3$, and CF$_3$(CF$_2$)$_5$(CH$_2$)$_2$Si(OEt)$_3$ led to the formation of a product mixture with a nominal composition of T$_8$[(CH$_2$)$_3$NH$_2$]$_2$$i$-Oct$_4$[(CH$_2$)$_2$(CF$_2$)$_5CF_3$]$_2$ [215]. Further treatment of

this product with $OCN(CH_2)_3Si(OEt)_3$ led to the recovery of a product with nominal composition of $T_8[(CH_2)_3NHC(O)NH(CH_2)_3Si(OEt)_3]_2i\text{-}Oct_4[(CH_2)_2(CF_2)_5CF_3]_2$.

2.7.3   *Substitution and Modification of Functional Groups*

The photochemical chlorination of T_8H_8 using chlorine gas was found to give rise to T_8Cl_8 in 95% yield [139], and there have also been attempts to convert simple T_8R_8 compounds, like T_8H_8 into specific $T_8R_{8-n}R'_n$ compounds by substitution at the cage silicon atoms, the main disadvantage to this method being the production of complicated product mixtures. There are, however, some simple synthetic routes to $T_8R_{8-n}R'_n$ compounds. For example, the disilanol $T_8[OC(=CH_2)Me]_6(OH)_2$ was serendipitously produced during an attempted synthesis of $T_8[OC(=CH_2)Me]_8$ by the $[Co_2(CO)_8]$ catalyzed reaction between T_8H_8 and acetone, the product being isolated as a single isomer in 35% yield [43]. A series of monoamine-containing T_8 POS compounds has also been prepared, generally via a substitution reaction at the corner of the cage [216]. Thus, T_8Cy_7Cl reacts with NH_3, $NH=C(NMe_2)_2$, and $NH=C(NHC_6H_4\text{-}2\text{-}Me)_2$ to give T_8Cy_7R [$R = NH_2$, $N=C(NMe_2)_2$, or $N=C(NHC_6H_4\text{-}2\text{-}Me)_2$] in greater than 80% yield. Furthermore, the $T_8Cy_7NH_2$ could be silylated using Me_3SiCl, to give $T_8Cy_7NHSiMe_3$ in 87% yield [216].

2.7.4   *Other Synthetic Methods*

2.7.4.1 T_4 Compounds

Evidence has been found for the existence of an unusual T_4 derivative detectable by mass spectrometry and prepared by laser ablation of porous silica targets using a XeCl excimer laser [217]. A variety of clusters was produced including an anionic cluster corresponding in molecular weight to $[T_4(OH)_3O]^-$, which appears as a more stable, magic-number cluster, as does the related T_8 cluster. The production of the T_4 cluster can be optimized such that it is the major cluster produced. While there is no direct evidence for this cluster to have the T_4 structure, calculations at the HF/6-31G** level show it to be the most stable form for this molecular formula [217].

2.7.4.2 T_8 Compounds

There are several unusual preparative methods for T_8 POS, one being the basic hydrolysis/condensation reaction of the silica extracted from rice hull ash, which was found to lead to the formation of the anionic $[T_8O_8]^{8-}$ POS core [218].

There have been a number of attempts to prepare T_8 cages in stepwise fashion, beginning with a cyclotetrasiloxane, but these are usually unsatisfactory. The reaction of $(MeClSiO)_4$ with $CH_2=CHSiCl_3$ was found to give $T_8Me_6(CH=CH_2)_2$ as the major product following purification; although there was evidence to suggest that the desired $T_8Me_4(CH=CH_2)_4$ might exist as a by-product [211]. Similarly, $Na_4[PhSiO(O)]_4$ was treated with $MeSiCl_3$, followed by a condensation reaction under acidic conditions to give a very insoluble product, which could be brominated on the phenyl rings, resulting in a more soluble derivative, readily identified as $T_8Me_4(C_6H_4Br)_4$ [219]. The $T_8Ph_4(CH=CH_2)_4$ analogue could be prepared in the same manner, but an attempt to produce $T_8Cy_4Ph_4$ produced predominantly polymeric species [219].

The attempted preparation of $T_8R_4R'_4$ by condensation of two cyclotetrasiloxanes is rare; early attempts used the reaction of $[PhSi(OH)O]_4$ and $[MeSi(OH)O]_4$ in low concentration in the presence of a base catalyst [220]. This reaction proceeded in 95% yield, giving the desired $T_8Me_4Ph_4$, but the susceptibility of the $[RSi(OH)O]_4$ species to other condensation reactions severely limits the wider applicability of this reaction. More recent studies have shown that both n-Bu$_4$NF and PhCH$_2$Me$_3$NOH will catalyze the formation of symmetrical T_8 species from $[RSi(OH)O]_4$ (R = phenyl, p-tolyl, isobutyl and naphthyl) [137].

2.7.4.3 T_{10} Compounds

The reaction of polyphenyl and polyvinyl silsesquioxanes with n-Bu$_4$F leads to reorganization and rearrangement of the polymers to give mixed cage species such as T_{10} and T_{12} compounds with a mixture of phenyl and vinyl substituents, which may be identified using MALDI-TOF MS [96].

2.8   Synthesis of Endohedral T_8R_8 Compounds

A limited number of T_8 POS derivatives wherein the silsesquioxane cage encapsulates an atom or ion as an endohedral complex have been prepared. While there is little space within the cage, it is big enough to take up monoatomic species, both during synthesis and via post-synthetic modification. The most common endohedral species is the fluoride anion, which can be introduced using either method, generally through the use of n-Bu$_4$NF. Including n-Bu$_4$NF during some hydrolysis and condensation reactions may afford endohedral complexes, for example, formation of $[NBu_4][F@T_8Ph_8]$ [221], $[NBu_4][F@T_8(CH=CH_2)_8]$, and $[NBu_4][F@T_8(C_6H_4$-4-Me)$_8]$ [222]. Single crystal X-ray diffraction and multinuclear NMR studies have confirmed the presence of the fluoride anion within the cage. When T_8R_8 compounds

with electron-withdrawing substituents are treated with n-Bu$_4$NF [R = CH=CH$_2$, CH=CHPh, (CH$_2$)$_2$CF$_3$, (CH$_2$)$_2$(CF$_2$)$_3$CF$_3$, (CH$_2$)$_2$(CF$_2$)$_5$CF$_3$, Ph] then endohedral fluoride complexes may be isolated [223], but with electron-donating substituents (R = Me, Et, Cy, i-Bu), no fluoride encapsulation was observed [223]. The presence of mixed electron donating and withdrawing substituents led to products resulting from cage opening and rearrangement.

The encapsulation of atomic hydrogen has been found to occur, first demonstrated using γ-irradiation of T$_8$(OSiMe$_3$)$_8$ in air to form H@T$_8$(OSiMe$_3$)$_8$ [224], and more recently by glow discharge using a Tesla coil for a series of different POS compounds to form H@T$_8$R$_8$ (R = Me, i-Bu, Cy, Ph, OSiMe$_3$) [225]. The latter method is both faster and safer than the use of γ-irradiation. These endohedral compounds have relatively long lifetimes, enough that the interactions of H@T$_8$(OSiMe$_3$)$_8$ with metal complexes have been studied by EPR Spectroscopy [226].

2.9   Introduction to the Physical Properties of POS Compounds

Most simple T$_8$R$_8$ and T$_8$R$_7$R' compounds are air-stable, white or off-white powders, colorless crystals, or oils, and low molecular weight compounds such as T$_8$H$_8$ and T$_8$Me$_8$ may be readily sublimed. The electronic effect of the T$_8$ cage in T$_8$R$_8$ and T$_8$R$_7$R' compounds has been shown by ^{13}C NMR chemical shift studies to be electron-withdrawing, similar to that of the CF$_3$ group [113] and this has an effect on reactions taking place on rings in T$_8$ compounds, see Section 2.3.2. The incompletely condensed trisilanols Si$_7$O$_9$(OH)$_3$ are closely related to the T$_8$R$_8$ and T$_8$R$_7$R' polyhedral cage compounds and their extensive use as models for silica-grafted catalysis has been reviewed recently [227].

2.10   NMR and EPR Spectroscopy of POS Compounds

2.10.1   Solution ^{29}Si NMR Studies

Solution NMR spectroscopy is a useful tool for investigating the structures of POS compounds, since the organic derivatives of the cages are often soluble in common NMR solvents and ^{1}H and ^{13}C spectra of substituents are not greatly affected by the POS cage and are usually as expected by comparison with simple, non-

POS analogues. The sensitivity of ^{29}Si chemical shifts to changes in substituents in POS cage silicon atoms make ^{29}Si NMR spectroscopy an important technique for compound identification, for monitoring reaction progress, for elucidating the composition of isomer mixtures, and for checking the purity of POS compounds. For example, the progress of the free radical polymerization of $T_8(CH=CH_2)_8$ and acetoxystyrene can readily be monitored by using the significant chemical shift difference of the $SiCH=CH_2$ and $SiCH_2CH_2$- at -79 and -66 ppm respectively [228]. The ^{29}Si NMR chemical shift difference can be used to show that the product from hydrosilylation of T_8H_8 with $HC\equiv CCMe_2OH$ is mainly the C-substituted $T_8(CH=CHCMe_2OH)_8$ and not $T_8(OCMe_2C\equiv CH)_8$ [49], and to determine α/β adduct ratio in the hydrosilylation reactions between T_8H_8 and alkynyl stilbenes [229], or with azobenzene derivatives [56, 230]. Monitoring the cage rearrangement reactions of various $T_8[(CH_2)_3X]_8$ (X = Cl, NCS etc.) compounds to give mixtures of $T_8[(CH_2)_3X]_8$, $T_{10}[(CH_2)_3X]_{10}$, and $T_{12}[(CH_2)_3X]_{12}$ compounds shows that upon going from compounds where the Si is just involved in 8-membered rings, $T_8[(CH_2)_3X]_8$, to two 8- and one 10-membered, $T_{10}[(CH_2)_3X]_{10}$, to one 8 and two 10-membered, $T_{12}[(CH_2)_3X]_{12}$, there is increased shielding of ca. 2-3 ppm for each change, see Table 2.16 [57].

Characteristic ^{29}Si chemical shifts for alkyl-T_8 compounds come in the range of ca. -65 to -70 ppm, as shown in Table 2.16, and similar shifts are found for the POS cages when such precursors are incorporated into polymeric materials. The chemical shifts for aryl-T_8 compounds are found in the range ca. -77 to -83 ppm, although for the substituted compounds such as $T_8(C_6H_4NH_2)_8$ many of these spectra are complicated by the presence of several isomers. The chemical shift range for T_8 compounds with siloxy substituents is usually observed at ca. -110 ppm, as is seen in Table 2.16.

POS cages containing a fluoride ion [223, 231], for example, $[NBu_4]$ $[F@T_8(CH=CH_2)_8]$ (δ ca. -83 ppm), show an upfield shift of a few ppm compared to their empty cage counterparts, Table 2.16, with only one chemical shift seen for the endohedral anion, consistent with the fluoride interacting equally with all eight of the Si atoms in the T_8 cage.

Table 2.16 Selected solution phase ^{29}Si NMR data for T_nR_n compounds[a]

R, or T_nR_n compound	^{29}Si NMR chemical shift (ppm from Me$_4$Si)	Refs.
	n = 6	
-i-Bu	-55.4	[10]
-c-C$_6$H$_{11}$	-56.6	[10]
-Ph	-66.9	[10]
$[n$-Pr$_4$N]$_6$[T$_6$O$_6$][b]	-88.2	[232]
-OSiMe$_3$	-99.1, 14.5 (SiMe$_3$)	[233]
	n= 8	
-H	-84.12	[234]
-CH$_2$CH$_3$	-65.5	[82]
-CH$_2$CH$_2$Br	-70.45	[83]

R, or T_nR_n compound	^{29}Si NMR chemical shift (ppm from Me$_4$Si)	Refs.
-CH=CH$_2$	-80.21	[235]
-CH=CH$_2$[c,d]	-83.0	[223]
-CH=CHPh	-78.2	[223]
-CH=CHPh[c,d]	-81.0	[223]
-CH$_2$CH=CH$_2$	-70.77	[88]
-CH$_2$CH$_2$SiMe$_2$OMe[e]	-65.91, 18.62 (SiMe$_2$OMe)	[236]
-i-Pr	-66.26	[104]
-(CH$_2$)$_3$Ph	-66.8	[46]
-(CH$_2$)$_3$NH$_2$	-66.5	[237]
{T$_8$[(CH$_2$)$_3$NH$_3$]$_8$}Cl$_8$[f]	-66.4	[238]
-(CH$_2$)$_3$N(CH$_2$CO$_2$H)$_2$[b]	-67.2	[239]
-(CH$_2$)$_3$N$_3$	-67.0	[66]
-(CH$_2$)$_3$PPh$_2$[g]	-66.41	[23]
-(CH$_2$)$_3$OH[f]	-65.9	[17]
-CHMeCH$_2$OCH$_2$CH(O)CH$_2$	-67.6	[240]
-(CH$_2$)$_3$SH	-66.80	[241]
-(CH$_2$)$_3$Cl	-67.28	[242]
-(CH$_2$)$_3$I	-66.2	[243]
-(CH$_2$)$_2$CF$_3$[c]	-66.7	[223]
-(CH$_2$)$_2$CF$_3$[c,d]	-70.4	[223]
-CH$_2$CH(O)CH$_2$	-69.7	[88]
-(CH$_2$)$_2$CO$_2$Me	-67	[83]
-i-Bu	-67.9	[244]
-c-C$_5$H$_9$	-66.6	[11]
-Cy	-68.7	[11]
-Ph[c]	-78.1	[223]
-Ph[c,d]	-80.7	[223]
-C$_6$H$_4$-4-Me	-77.62	[245]
-C$_6$H$_4$NO$_2$[e]	-79.22	[115]
-C$_6$H$_4$-4-Br[h]	-78.3	[137]
-C$_6$H$_4$-4-SiMe$_3$	-78.4, -3.83 (SiMe$_3$)	[115]
-naphthyl[c]	-77.02	[137]
[NMe$_4$]$_8$[T$_8$O$_8$][b,i]	-98.122	[202]
-OEt	-103	[141]
-OSiMe$_2$H	-112.48, -3.95 (SiMe$_2$)	[246]
-OSiMe$_2$OSiMe$_3$[c]	-108.986, -21.990 (SiMe$_2$O), 12.469 (SiMe$_3$)	[170]
-OSiMe$_2$CH=CH$_2$	-100.4, 8.58, 9.026 (SiMe$_2$)	[247]
-OSiMe$_2$(CH$_2$)$_3$NMe$_2$[e]	-107.3, 14.9 (SiMe$_2$)	[248]

R, or T_nR_n compound	^{29}Si NMR chemical shift (ppm from Me$_4$Si)	Refs.
-OSiMe$_2$(CH$_2$)$_3$OH	-100.4, 8.6 (SiMe$_2$)	[249]
-OSiMe$_2$(CH$_2$)$_4$CH(O)CH$_2$	-101, 21.3 (SiMe$_2$)	[250]
-OSiMe$_3$	-109, 13 (SiMe$_3$)	[141]
-OSnMe$_3$	-110.144	[180]
-O[TiClCp$_2$]	-101.9	[180]
-SiMe$_2$-t-Bu	-71.31, -12.67 (SiMe$_2$-t-Bu)	[251]
	$n = 10$	
-H	-86.25	[1]
-CH=CH$_2$	-81.48	[38]
-(CH$_2$)$_3$N$_3$	-68.94	[30]
-(CH$_2$)$_3$Cl	-68.97	[57]
-c-C$_5$H$_9$	-69.20	[38]
-C$_8$H$_{17}$	-68.68	[57]
-C$_6$H$_4$-4-Me	-79.5	[115]
-OSiMe$_2$CH$_2$Cl	-110.82, 6.96 (SiMe$_2$)	[180]
	$n = 12$	
-H	-85.78, -97.76	[1]
-CH=CH$_2$	-81.34, -83.35	[38]
-(CH$_2$)$_3$N$_3$	-68.69, -71.36 (1:2)	[30]
-(CH$_2$)$_3$Cl	-68.73, -71.37	[57]
-Cy	-71.29, -74.29	[112]
-C$_6$H$_4$-4-SiMe$_3$	-81.5, -79.4; -4.13, -4.06 (SiMe$_3$)	[115]
	$n = 14$	
-H	-87.89, -88.03, -89.71	[1]

[a] Unless otherwise stated, chemical shifts are for CDCl$_3$ solutions and are referenced with respect to Me$_4$Si. [b] H$_2$O/D$_2$O solution. [c] THF-d_8 solution. [d] Anionic endohedral fluoride, [NBu$_4$]$^+$ cation. [e] (CD$_3$)$_2$CO solution. [f] (CD$_3$)$_2$SO solution. [g] C$_6$D$_6$ solution. [h] CD$_2$Cl$_2$ solution. [i] Enriched in ^{29}Si.

The chemical shifts for T_8R_7R' compounds (Table 2.17) are similar to those found for the corresponding TR or TR' groups in T_8R_8 and $T_8R'_8$ compounds, as might be expected, but the three signals expected for the TR environments in T_8R_7R' compounds are often difficult to resolve and can appear as a single broad signal, along with the TR' signal. One of the few detailed NMR studies of an isomeric mixture of POS compounds showed that complicated mixtures of all possible isomers of $T_8(OPh)_n(R)_{8-n}$ [n = 0-8; R = n-C$_{11}$H$_{23}$ or (CH$_2$)$_2$CMe$_2$CH$_2$CO$_2$Me] were formed in reactions of T_8H_8 with PhOH and undec-1-ene or 3,3-dimethylpent-4-enoate. Computational models of the spectra suggest that the predominant products bear dissimilar substituents on adjacent Si atoms [54]. In a related study, products having ^{29}Si NMR signals at -108.84 (*Si*O$_4$), 12.67 [Ph(CH$_2$)$_3$*Si*Me$_2$O] and 12.78 ppm (C$_6$H$_{11}$*Si*Me$_2$O) corresponding to a mixture of isomers of $T_8[OSiMe_2(CH_2)_3Ph]_{8-n}$ (OSiMe$_2$C$_6$H$_{11}$)$_n$ (n = 0-6) are formed on hydrosilylation of $T_8(OSiMe_2H)_8$ with

a 6:2 mixture of allylbenzene and 1,5-hexadiene [252]. The ^{29}Si NMR spectrum of the mixture formed by co-hydrolysis of $H_2N(CH_2)_3Si(OMe)_3$, i-OctSi(OMe)$_3$, and $F_3C(CF_2)_5CH_2CH_2Si(OEt)_3$ gives a broad signal at ca. -68 ppm with several shoulders indicating that several POS species are present, and provides an example of how ^{29}Si NMR spectroscopy is limited in distinguishing between closely related POS compounds [215]. The silicate anion, $[T_8(O)_4(OT)_4]^{16-}$, in which the T-unit substituents are at alternate corners of the T_8 cage is formed in silicate solutions containing $[NMe_3(CH_2CH_2OH)]^+$ and has ^{29}Si NMR chemical shifts attributable to the exocyclic Si, the cage T-O-Si, and the cage SiO$^-$ silicon atoms at -82, -99 and -109 ppm respectively [253].

Table 2.17 ^{29}Si NMR data for T_8R_7R' compounds in solution[a]

R and R'		^{29}Si NMR chemical shift (ppm from Me$_4$Si)	Refs.
R	R'		
-(CH$_2$)$_2$CF$_3$	-Me[b]	-64.8, -67.5, -68.0	[32]
-(CH$_2$)$_2$CF$_3$	-(CH$_2$)$_2$OH	-67.65, -67.66, -67.84	[254]
-(CH$_2$)$_2$CF$_3$	-(CH$_2$)$_2$Ph[c]	-66.4, -67.4, -67.7	[32]
-(CH$_2$)$_2$CF$_3$	-(CH$_2$)$_2$(CF$_2$)$_5$CF$_3$[d]	-67.2, -67.4	[254]
-(CH$_2$)$_2$CF$_3$	-C$_6$H$_4$-4-OCF=CF$_2$[c]	-68, -71.5	[255]
-i-Bu	-CH=CH$_2$[e]	-66.9, -67.4, -80.9(SiCH=)	[78]
-i-Bu	-(CH$_2$)$_2$OH	-67.1, -67.3, -69.1 (3:4:1)	[256]
-i-Bu	-(CH$_2$)$_3$Cl	-67.57, -67.87, -68.10 (3:4:1)	[30]
-i-Bu	-OSiMe$_2$H	-2.98, -66.84, -67.76, -67.79, -108.97	[257]
-c-C$_5$H$_9$	-H	-66.47 (SiCH), -83.90 (Si-H)	[258]
-c-C$_5$H$_9$	-OH	-63.48, -64.18, -97.75 (4:3:1 ratio)	[185]
-c-C$_5$H$_9$	-Cl	-65.74, -66.32, -66.36 (3:3:1), -89.53 (SiCl)	[146]
-c-C$_5$H$_9$	-(CH$_2$)$_2$OH	-65.9, -68.1 (7:1)	[256]
-c-C$_5$H$_9$	-(CH$_2$)$_3$Cl	-66.52, -67.11	[259]
-c-C$_5$H$_9$	-C$_6$H$_4$-4-CH$_2$Cl[f]	-67.8, -68.2, -79.6	[260]
-c-C$_5$H$_9$	-OSiMe$_2$C≡CH	-15.79, -65.58, -66.24, -108.13 (1:3:4:1)	[261]
-c-C$_5$H$_9$	-OTiMeCp*(OT$_8$(C$_5$H$_9$)$_7$)[e]	-110.8 (SiO$_4$), -66.0, -65.9, -65.8(3:1:3)	[199]
-Cy	-(CH$_2$)$_3$SiMe$_2$C$_6$H$_4$-4-SiMe$_2$H	-3.43 (SiMe$_2$), -17.03 (SiMe$_2$H), -68.38 (4 SiCy), -68.56 (3 SiCy), -66.47 (SiCH$_2$)	[262]
-Cy	-C$_6$H$_4$-4-CH$_2$Cl[f]	-67.8, -68.2, -79.6	[118]
-Cy	-SiCl$_3$	-62.0 (SiSiCl$_3$), -31.4 (SiCl$_3$), -67.7, -67.8, -67.9, -68.4	[142]
Cy	-OSiMe$_3$[e]	11.29, -67.54, -68.09, -68.12, -107.81 (1:3:3:1:1)	[36]
-Cy	-OSiCl$_3$	-66.0 (SiOSiCl$_3$), -56.6 (OSiCl$_3$), -67.8, -68.0, -68.6, -69.0, -69.6, -69.8, -70.2	[142]

R and R'		^{29}Si NMR chemical shift (ppm from Me$_4$Si)	Refs.
R	R'		
-Cy	-O[Re(CO)$_5$]^g	-68.06, -68.66, -99.40 (1:6:1)	[196]
-Ph	-(CH$_2$)$_2$C$_6$H$_4$-4-SO$_2$Cl	-66.69 (SiCH$_2$), -78.35, -78.41, -78.67	[263]
-Ph	-(CH$_2$)$_3$NH$_2$	-64.76, -78.30, -78.78 (1:4:3)	[37]
-Ph	-(CH$_2$)$_2$OH	-67.31 (SiCH$_2$), -78.42, -78.79	[263]
-Ph	-(CH$_2$)$_3$SiMe$_2$C$_6$H$_4$-4-SiMe$_2$H	-3.61 (SiMe$_2$), -17.22 (SiMe$_2$H), -78.23 (4 SiPh), -78.71 (3 SiPh), -65.25 (SiCH$_2$)	[262]
-OEt	-(CH$_2$)$_2$CO$_2$C$_{16}$H$_{33}$	-102.80, -102.75, -102.72, -65.26 (SiCH$_2$)	[264]
-OEt	-C$_{16}$H$_{33}$	-102.56, -102.63, -102.69, -64.12 (SiCH$_2$)	[53]

[a] Unless otherwise stated, all data are for CDCl$_3$ solutions or were not reported, and are referenced with respect to Me$_4$Si. [b] (CD$_3$)$_2$CO/CDCl$_3$ solution. [c] (CD$_3$)$_2$CO solution. [d] (CD$_3$)$_2$CO/THF solution. [e] C$_6$D$_6$. [f] THF solution.

Besides ^{29}Si NMR, heteronuclear studies of POS compounds have sometimes been carried out when looking at applications of the POS species. For example, ^{11}B NMR spectra have been used to monitor the interaction of T$_8$(c-C$_5$H$_9$)$_7$(OH) with (C$_6$F$_5$)$_3$B via B···OH coordination [265], and ^{19}F NMR spectroscopy can be used to monitor enzymatic activity by using the high number of fluorine nuclei in POS species derived from T$_8$[(CH$_2$)$_3$NH$_2$]$_{8-n}$[(CH$_2$)$_3$NHC(=O)CF$_3$]$_n$ (where n = 3–5) when attached to the surface of silica nanoparticles [266]. Applications of T$_8$ POS compounds in MRI imaging studies have also recently become of interest, owing to their potential to bind a high concentration of Gd(III) as a relaxation agent [267] (see also Section 7.5.1, Chapter 7).

2.10.2   *Solid State NMR Studies*

The use of solid state ^{29}Si NMR spectroscopy for the analysis of both molecular and polymer materials containing POS cages has become widespread in the last 10 years. It is a technique used extensively to help determine whether a polymerization or mechanical process has caused degradation of the POS cage, when the cage is a component in a polymeric or composite material. Chemical shifts for a range of molecular T$_8$R$_8$ and T$_8$R$_7$R' compounds are shown in Table 2.18, and show well-defined chemical shift ranges for alkyl (-65 to -70 ppm), aryl (-75 to -81 ppm), and siloxy (-95 to -120 ppm) substituted POS cages. The solid state chemical shift values for molecular species are generally close to those for analogous solution data (see Section 2.10.1) and can be used for comparison with spectra recorded on polymeric materials containing POS cages when confirmation is needed that a POS cage is still intact. For example, upon reaction of T$_8$[CH$_2$CH(O)CH$_2$]$_8$ with diamines [88], the product exhibits signals at -68.56, and -67.46 ppm and the radical-induced polymerization of methyl methacrylate with T$_8$(OSiMe$_2$H)$_8$ gives a product with

signals at -108.6 (POS) and 13.3 (OSiMe$_2$CH$_2$-) ppm, both spectra indicating that little rearrangement has occurred [268]. Similarly, solid state ^{29}Si NMR spectra for nanocomposites prepared using T$_8$[OSiMe$_2$(CH$_2$)$_4$CH(O)CH$_2$]$_8$ or T$_8$(C$_6$H$_4$NH$_2$)$_8$ precursors indicate that the POS cores are largely unchanged during the process [269], and while broadening of the solid state ^{29}Si NMR signal from {T$_8$[(CH$_2$)$_3$NH$_3$]$_8$} -Cl$_8$ occurs in the presence of Pd nanoparticles, the chemical shift is not much altered, suggesting that the POS core is not cleaved by the nanoparticles [270].

Table 2.18 Solid state ^{29}Si NMR chemical shifts for T$_n$R$_n$ and T$_8$R$_7$R' compounds

R or T$_n$R$_n$		^{29}Si NMR chemical shift (ppm from Me$_4$Si)	Refs.
		n = 6	
-OSiMe$_3$		-98.9, -99.2, -100.0, -100.1, -100.6 (SiO$_4$); 15.0, 14.7, 13.7, 13.1, 12.4, 12.3 (SiMe$_3$)	[149]
		n = 8	
-H		-85.5	[271]
-Me[a]		-66, -66.7	[272]
-CH=CH$_2$		-79.5	[273]
-CH$_2$CH(O)CH$_2$		-69.76	[88]
-(CH$_2$)$_3$NH$_2$		-66.4	[274]
{T$_8$[(CH$_2$)$_3$NH$_3$]$_8$}Cl$_8$		-67.0	[275]
-(CH$_2$)$_3$Cl		-66.0, -67.1	[67]
-(CH$_2$)$_2$(CF$_2$)$_5$CF$_3$		-66.7, -67.4	[276]
-c-C$_5$H$_9$		-64, -68	[277]
-Ph[a]		-79.4	[278]
-C$_6$H$_4$-4-NO$_2$		-82.6	[279]
-C$_6$H$_4$NH$_2$		-66.7	[280]
-OSiMe$_2$H		-108.69, -2.89 (SiMe$_2$)	[281]
-OSiMe$_3$		-106.0, 14.2 (SiMe$_3$)	[282]
-OSiMe$_2$(CH$_2$)$_3$CN[a]		-118 (SiMe$_2$ not seen)	[163]
-OSi(OSiMe$_3$)$_3$		-111.9 (POS), -107.5 [OSi(OSiMe$_3$)$_3$], 9.0 (SiMe$_3$)	[169]
[NMe$_4$]$_8$[T$_8$O$_8$]		-96.5	[281]
-SiMe$_2$-t-Bu[a]		-70.76, -11.20, -12.90	[251]
R	R'		
-(CH$_2$CH$_2$CF$_3$)$_7$	-H	-68.6, -58.3 (SiH)	[283]
-i-Bu$_7$	-C$_6$H$_4$-4-CH=CH$_2$	-67.8 (SiBu), ca. -80 SiC$_6$H$_4$	[284]
-Ph$_7$	-(CH$_2$)$_3$Cl	-77.02, -64.06	[285]
		n = 10	
-OSiMe$_2$H		ca. -110, ca. -2 (SiMe$_2$H)	[286]

[a] ^{13}C Solid state spectrum also recorded.

Despite the widespread use of solid state ^{29}Si NMR spectra for POS characterization, solid state ^{13}C NMR spectra of POS compounds are rarely recorded, presumably due to their more complicated nature and the lack of information obtained about the POS core in such spectra. However, comparison of the solid state ^{13}C NMR spectrum of copolymers of vinylpyrrolidine with $T_8(i\text{-Bu})_7C_6H_4\text{-4-CH=CH}_2$ show that the POS cage is incorporated intact into the polymer [284], and spectra of star polymers comprising a T_8 core and poly(ε-caprolactone) substituents are consistent with the formation of inclusion complexes with cyclodextrins [174]. The spectrum of $T_8(CH=CH_2)_8$ has been used to set up the Hartmann-Hahn conditions for magic angle spinning ^{29}Si$\rightarrow$^{13}C cross polarization transfer, a value of 136 Hz being found for $^1J_{Si\text{-}C}$ [287], and a detailed ^{13}C NMR study of $T_8(i\text{-Bu})_8$ has been used to investigate the motion of the substituents as a function of temperature [288]. Solid state ^{1}H and ^{2}H NMR spectra of T_8Et_8 and its partially deuterated derivatives are consistent with, and typical of, transitions occurring in a plastic crystal, a triclinic phase being present at low temperature, and a rhombohedral phase being present at high temperature [82].

2.10.3   EPR Spectra

EPR spectroscopy has rarely been used for the characterisation of POS compounds, but it has been used successfully for investigating the nature of certain endohedral T_8 species. Thus, a negative temperature coefficient for the ^{29}Si super hyperfine coupling constant in a mixture of the endohedral POS complexes $H@T_8(n\text{-Pr})_8$ and $D@T_8(n\text{-Pr})_8$ in toluene has been observed by EPR spectroscopy [289]. Solid and solution EPR spectra of $H@T_8[(CH_2)_nH]_8$ (where n = 0-3) species exhibit isotropic hyperfine interactions with ^{29}Si [290], and activation energies, E_a, for detrapping of H and D from T_8Me_8 are 126.7$\pm$1.2 and 127.4$\pm$1.2 kJ mol^{-1} respectively [289]. EPR spectra have also been used to monitor the rapid uptake of hydrogen atoms into the cage of T_8Me_8 upon its being subject to an electric discharge to form $H@T_8Me_8$ [225].

2.11   Vibrational Spectra of Polyhedral Oligomeric Silsesquioxane Compounds

Vibrational spectroscopy is often used in the identification of both simple molecular POS compounds and in polymeric materials as, in both cases, they give rise to a characteristic Si-O-Si band in the IR spectrum. There have been a range of values quoted for the ν_{as} band associated with the Si-O-Si linkages, even in simple POS

compounds, since although it is strong (occurring at ca. 1100 cm^{-1}) it is also broad. Table 2.19 shows IR data for a range of POS derivatives, and more data can be found in references [119] and [120]. As the bands due to Si-O-Si linkages in ladder silsesquioxanes usually occur from 1030–1055 cm^{-1} [291, 292], IR spectroscopy can be used to distinguish POS cage derivatives from ladder siloxanes. The solid state IR spectrum of T$_8$H$_8$ shows bands for δ_s (O-Si-O) at 557.9 and δ_{as} (O-Si-O) at 389.5 cm^{-1} [271], while its Si-H stretch has been variously reported at 2144 cm^{-1} [293], and at 2275 cm^{-1} [240], in CCl$_4$ solution, and as solid KBr and CsI pellets, v(Si-H) has been reported at 2277, 2294 and 2300 cm^{-1} respectively [294]. For T$_8$(OSiMe$_2$H)$_8$, the Si-H band has been reported at 2250 cm^{-1} [44], 2142 cm^{-1} [295], and at 2140 cm^{-1} [296], while its Raman spectrum shows a band due to Si-H at 2141 cm^{-1} [297]. The widely different Si-O-Si bond angles (136.35-172.13°) seen in the solid state structure of T$_8$(OSnMe$_3$)$_8$·4H$_2$O (see section 2.14.1) give rise to significant splitting of both the symmetric and antisymmetric Si-O-Si stretches [180].

Examples of the use of IR spectroscopy for monitoring whether the T$_8$ cage stays intact during a polymerization process can be seen for reactions of T$_8$[(CH$_2$)$_3$OCH$_2$CH(O)CH$_2$]$_8$ which has an Si-O-Si stretch at 1103-1110 cm^{-1}. This band can also be seen in the interpenetrating network formed in its reaction with CMe$_2$(C$_6$H$_4$-4-OH)$_2$ in the presence of poly(ethylene oxide) [298, 299], in crosslinked polymers it forms with poly(N-isopropylacrylamide) [300], and with poly(4-vinylpyridine) [301], and hybrids it makes with poly(ethylene imine) [283]. Similarly, the IR band at ca. 1109 cm^{-1} in T$_8$(CH=CH$_2$)$_8$ has been used to monitor the solution blending of the POS compound with polystyrene and with poly(4-acetoxystyrene) to show that the T$_8$ cage remains intact during the blending process [302].

Table 2.19 Infra-red stretching frequencies associated with the Si-O-Si bonds in T$_8$R$_8$ and T$_8$R$_7$R' compounds

R or T$_8$ derivative	Si-O frequencies (cm^{-1})	Refs.
-H	v$_{as}$(Si-O-Si) 1117	[303]
-Me	v$_{as}$(Si-O-Si) 1115, 1192, v$_s$(Si-O-Si) 517, and δ(O-Si-O) 465, 379	[103]
-CH=CH$_2$	1110-1112	[235]
-CH$_2$CH=CH$_2$	1105	[88]
-CH$_2$CH(O)CH$_2$	1107	[88]
-(CH$_2$)$_3$Cl	v$_{as}$(Si-O) 1230-940, δ(O-Si-O) 552	[304]
-i-Bu	1115	[244]
-Cy	1110	[305]
-(CH$_2$)$_3$N$_3$	1111	[66]
-(CH$_2$)$_3$NH$_2$	1030	[237]
{T$_8$[(CH$_2$)$_3$NH$_3$]$_8$}Cl$_8$	1105	[306]
-(CH$_2$)$_3$OCH$_2$CH(O)CH$_2$	1106	[283]
-Ph	1115	[279]
-C$_6$H$_4$NO$_2$^{a}	ca. 1100	[307]

R or T_8 derivative	Si-O frequencies (cm^{-1})	Refs.
-$C_6H_4NH_2$[a]	1100	[307]
[NMe_4]$_8$[T_8O_8]	1037	[308]
-$OSiMe_2H$	1096	[309]
-$OSiMe_2(CH_2)_2Ph$	1100	[310]

R	R'		
-H	-n-C_6H_{13}	1139	[311]
-$(CH_2)_2CF_3$	-$(CH_2)_3Br$	1090-1000	[312]
-i-Bu	-$(CH_2)_2OH$	1082	[313]
-i-Bu	-$(CH_2)_3NH_2$	ca. 1100	[314]
-i-Bu	-C_6H_4-4-CH_2Cl	1110	[130]
-Cy	-$(CH_2)_3OC(=O)C(Me)=CH_2$	1110	[315]
-Ph	-$(CH_2)_3OH$	1134	[285, 316]

[a] Contains a mixture of isomers.

The IR bands for T_8R_7R' compounds are similar to those for the related T_8R_8 species, and the same problems associated with reporting the value for the broad Si-O-Si are found; typical values for Si-O-Si IR data are given in Table 2.19. Calculated, 2350 cm^{-1}, and experimental, 2274 cm^{-1}, values of the Si-H stretch for $T_8H_7(n$-$C_6H_{13})$ are significantly different [311], and the experimental value for the Si-H stretch in $T_8(i$-Bu$)_7$H is 2215 cm^{-1} [317]. The IR spectrum of $T_8(i$-Bu$)_7$OH in KBr has been reported to show a broad hydrogen-bonded SiOH band in the 3425 cm^{-1} region [318], a sharp band due to free SiOH groups at ca. 3680 cm^{-1} and a broad band at ca. 3500 cm^{-1} attributed to a hydrogen-bonded dimeric silanol species [319]. This difference in the degree of hydrogen bonding is probably due to variations in sample concentration. Only a single sharp band due to free SiOH at ca. 3680 cm^{-1} is seen in the spectrum of a 0.1 M solution of $T_8(i$-Bu$)_7$OH in CCl$_4$ [319], whereas silanols usually exhibit strong hydrogen bonding to each other [320, 321].

As for T_8R_8 compounds, the characteristic Si-O-Si stretches in T_8R_7R' compounds can be used to monitor whether processing of monomeric species into polymers causes breakdown of the cage structure. Thus, poly(ε-caprolactone) and poly(L,L-lactide) end-capped by $T_8(i$-Bu$)_7(CH_2)_3$NH show the expected Si-O-Si T_8 band at 1099 cm^{-1} [322], and a band at 1109 cm^{-1} characteristic of the Si-O-Si stretch in $T_8(i$-Bu$)_7C_6H_4$-4-CH=CH$_2$ occurs in spectra of its copolymers with vinylpyrrolidone [284]. Conversely, the sharp absorption at 1130 cm^{-1} due to the T_8 cage in the IR spectrum of the copolymer poly(N-dodecylacrylamide-co-3-methacryloxypropylheptaphenyl POS) is lost on photooxidation and replaced by one at 1065 cm^{-1}, due to the formation of an SiO$_2$ film on breakdown of the cage [323]. Similar "SiO$_2$-like" layers have also been characterized by IR spectroscopy and shown to be formed by reaction of polymers of pendent T_8Et_7 cages with oxygen plasmas [324].

2.12   Mass Spectra of POS Compounds

Mass spectrometry has been used widely for the analysis of simple POS compounds with alkali metals or protons being readily bound by the π-electron density and electronegative atoms in the substituents on the POS cage to give positive ions. There may be difficulties in generating large ions from oligomers or polymers containing POS components without fragmentation, probably due to low ionization efficiency caused by the ability of the POS cage to delocalize electron density. It may, however, be possible to address this problem by preparing endohedral fluoride complexes having a higher ionization efficiency (see, for example, below) [223]. Mass spectrometry may be particularly useful in the analysis of complicated mixtures of POS-containing products derived from the co-hydrolysis of mixtures of simple monomers, owing to the widely differing masses of the components, the sizes of the POS cages and the number of each substituent present. Simple chemical ionization spectra can be recorded for small compounds such as $T_8[(CH_2)_3Cl]_8$ [325], but higher molecular weight T_8R_8 compounds require more sophisticated techniques such as MALDI-TOF MS and electrospray ionization (EI), possibly in conjunction with ion mobility mass spectrometry. Mass spectrometry is also important in the analysis of products arising from incomplete reaction of, for example, an octa-functional precursor, T_8R_8, not affording a clean $T_8R'_8$ product. The degree of reaction is usually easily assessed by taking into account the differing masses of the R and R' groups in the $T_8R_nR'_{8-n}$ (n = 0-8) products, but the distribution of the R and R' groups around a POS cage is better investigated by ^{29}Si NMR spectroscopy. FABMS (fast atom bombardment) has been used to characterize simple monomeric POS species such as $T_8(CH_2CH_2R)_8$ [R = Ph [84]; R = Cy, $(CH_2)_3Br$ or $(CH_2)_4Cl$ [326]].

MALDI-TOF spectra have been used to show that compounds containing from five to twenty "T" units are formed on hydrolysis of $CH_2=CHSiCl_3$ [40], to determine the ratios of T_8:T_{10}:T_{12} cages produced on the amine-catalyzed condensation of silanols such as $PhSi(OH)_3$ or $[Ph(HO)Si]_6$ derived from hydrolysis of $(MeO)_3SiR$ (R = $CH=CH_2$, Ph or C_6H_4-2-Me) [327], to determine the ratios of T_8:T_{10}:T_{12} derivatives formed on F⁻ catalyzed rearrangements of polysilsesquioxanes [106], and to investigate the structure and stabilities of the components of the mixture formed on hydrolysis of $CH_2(O)CHCH_2O(CH_2)_3Si(OMe)_3$ [328]. Similarly, UV-MALDI-TOF mass spectrometry has been used to investigate the complicated mixtures obtained by hydrolysis of $(EtO)_3Si(CH_2)_3NH_2$ in the presence of phenylglycidylether [329]. Incompletely condensed POS species as well as T_8-type compounds are shown to form as products from hydrolysis of $MeC(=CH_2)C(=O)O(CH_2)_3Si(OMe)_3$ by capillary electrophoresis-ion-trap mass spectometry [330], and LC/MS has been used to show that $T_8Me_{8-n}[(CH_2)_3OCH_2CH(O)CH_2]_n$ compounds (n = 4 or 6) are formed together with T_9 and T_{10} products from the co-hydrolysis of $MeSi(OEt)_3$ and $CH_2(O)CHCH_2O(CH_2)_3Si(MeO)_3$ [331]. The formation of silicate polyhedra such as $T_8(OH)_8$ from smaller silicate fragments has also been monitored in detail using electrospray mass spectrometry [332-334].

MALDI methods have been used to show that ruthenium-catalyzed metathesis

reactions of $T_8(CH=CH_2)_8$ do afford octa-substituted products $T_8(CH=CHAr)_8$ (Ar = Ph, C_6H_4-4-Me, C_6H_4-4-OMe, C_6H_4-4-Cl, C_6H_4-4-Br, C_6H_4-4-NO$_2$) [335], to investigate the degree of substitution in the platinum-catalyzed hydrosilylation reaction between $T_8(CH=CH_2)_8$ and $(EtO)_3SiH$ [336], and in elucidating the degree of substitution in the hydrosilylation reaction between $T_8(OSiMe_2H)_8$ and combinations of allylbenzene and 1,5-hexadiene, giving an isomeric mixture of $T_8[OSiMe_2(CH_2)_3Ph]_{8-n}(OSiMe_2C_6H_{11})_n$ (n = 0-8) compounds [252]. The extent of bromination of T_8Ph_8 using different methods, and $AgNO_3$ or AgO_2CCF_3 as ion source has been investigated using MALDI-TOF, showing that up to 17 bromines per POS molecule may be introduced [125, 337]. The formation of the tetra-POS compound $[T_8(i\text{-}Bu)_7(CH_2CH_2SiMe_2O)]_4Si$ (m/z = 3821.91) from the Pt-catalyzed reaction between $(HSiMe_2O)_4Si$ and $T_8(i\text{-}Bu)_7(CH=CH_2)$ has also been confirmed by MALDI methods [338].

MALDI-TOF mass spectrometry can be used to characterize high molecular weight POS derivatives such as glycoclusters (up to ca. m/z = 5000) prepared using $T_8(CH=CH_2)_8$ [339], a bis-POS derivative of a phthalocyanine (m/z = 3656) [340], octakis-POS substituted metallophthalocyanines (m/z = 7676-7681) [68], poly-pyrene substituted POS species (m/z = 3436) containing up to 14 pyrene groups,derived from Heck coupling of $T_8(CH=CH_2)_8$ with 1-bromopyrene [341], and poly-fluorene POS substituted compounds (m/z up to 7818) derived from coupling of $T_8(CH=CH_2)_8$ with a bromofluorene [342]. MALDI-TOF has also been used to characterize dendrimer drug carriers such as $T_8[(CH_2)_3NH(L\text{-}Lys)(L\text{-}Lys)_2(L\text{-}Lys)_4(L\text{-}Lys)_8]_8$, ($m/z$ = 16314) [70], and 4,4'-dihydroxyoctafluorobenzene has been proposed as a new matrix for MALDI spectra of POS derivatives with masses of >13 000 being observed for ethyl isobutyrate POS oligomers [343]. Recently, the use of atmospheric pressure photoionization mass spectrometry has been found to be a useful method for the characterization of POS compounds such as $T_8(i\text{-}Bu)_7CH=CH_2$ [78].

Mass spectrometry has also been used to determine the behaviour of POS cages towards electron impact; most POS cages are resistant to electron impact up to 3 keV in symmetrically substituted compounds, T_8R_8, but in $T_8(CH_2CH_2CF_3)_8$ the cage is cleaved much more easily, probably via transfer of F to a silicon atom [39]. The collision cross sections for T_8Ph_8 and $T_8(CH_2Ph)_8$ have been determined using electrospray ionization, MALDI and ion mobility methods, and, when compared with calculated data and those determined from single crystal X-ray data, show good agreement, suggesting that the POS cage is not significantly deformed in the gas phase, and that Na^+ does not cleave the cage in Na^+POS ions [344]. Similar studies have been carried out for the related $T_8(CH=CHPh)_8$ and $T_8(CH_2CH_2Ph)_8$ compounds [223, 345], and the epoxide derivatives $Na^+T_8(CH=CHPh)_x[CH(O)\text{-}CHPh]_{8-x}$ (where x = 5, 6 or 7) [346]. The collision cross sections for a range of negative POS ions $F^-@T_8R_8$ (R = $CH=CH_2$, Ph, CH=CHPh, $CH_2CH_2CF_3$ etc.) and for the related sodiated species $H^+[F^-@T_8R_8]Na^+$ have been calculated and determined experimentally by ESI or MALDI, the results from both methods being in good agreement [223].

2.13   Electronic Spectra of POS Compounds

The electronic spectra of POS compounds have only been studied intensively quite recently when their potential as tethers for photoluminescent, fluorescent and other organic fragments of optical interest was realized (see also Chapter 7). The electronic structures of T_8H_8, T_8H_7Ph, $T_8H_6Ph_2$, $T_8H_7(C_6H_4$-4-Ph) and T_8Ph_8 and crystalline T_8H_8 and $T_8Ph_8 \cdot$acetone have been calculated and show that, in contrast to T_8H_8 which has a HOMO localized at the oxygen lone pairs, the aryl-substituted compounds have HOMO and LUMO orbitals localized on the aromatic rings [347, 348]. The absorption and emission spectra for POS derivatives $T_8(CH=CHC_6H_4$-4-$CH=CHC_6H_4$-4-R)$_8$ (R = H, Me, OMe or NH_2) have been compared with simple stilbene analogues and partial cage analogues and show that the emissions for the full cage derivatives show a red shift of 60 to 100 nm. This significant effect is thought to be due to interaction of the LUMO, centred in the cage with contributions from all the cage atoms, with the stilbene substituent π^* orbitals. As the T_8 cage is symmetrical, a three-dimensional conjugation might be implied, where the cage does not act as a traditional silica-like insulator [335, 349]. DFT (density functional theory) calculations on T_8H_8 and its derivatives substituted with either 4-carbazolylphenyl (electron-donating) or 4-cyanophenyl (electron-withdrawing) groups, with the cage being either empty or containing N_2, show that the HOMO and LUMO can be independently changed and tuned, and that the T_8 cage is partially conjugated, serving as an electron acceptor [350].

The alcohol, $T_8[CH=CHC_6H_4$-4-C_6H_3-3,5$(OH)_2]_8$, has a photoluminescent quantum yield of 10% at saturation, and a bathochromic emission shift when compared to $CH_2=CHC_6H_4$-4-C_6H_3-3,5$(OH)_2$ [81], while the UV spectrum of the unusual silyl-substituted POS, $T_8(SiMe_2$-t-Bu$)_8$, exhibits a significant bathochromic shift with a lowest transition energy absorption at 285 nm compared with simple R_3SiSiR_3 (R = alkyl) species which have corresponding absorptions at ca. 200 nm [251]. Poly-pyrene species derived from Heck-coupling of $T_8(CH=CH_2)_8$ with 1-bromopyrene show solution photoluminescence bathochromic shifts of ca. 50 nm from pyrene itself, probably due to the increased conjugation due to the Si-$CH=CH_2$ fragment [341]. Aryl-substituted T_8 derivatives such as **2 – 5** have been shown by photoluminescence excitation spectra, and other techniques, to be quantum dot materials in which the organic arms are isolated by the POS cage. The spectra indicate that the emissive centers are not the cage itself, but the substituents on the cage. The compounds are soluble and the photoluminescent yields are enhanced when the conjugated arms are attached to the POS core [124, 351]. The related aryl compounds $T_8Ph_n(C_6H_4Ar)_{8-n}$ (n = 2, 3, 4 or 5; Ar = Ph, biphenyl, naphthyl, 9,9-dimethylfluorenyl etc.) have UV-VIS and photoluminescence spectra similar to those for the simple untethered aromatic compound, with a small bathochromic shift of about 20-30 nm [352].
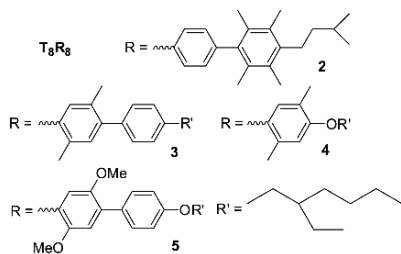
Electronic spectroscopy is also being increasingly used to probe the properties of polymeric materials containing POS groups, in particular to investigate the changes in materials induced by the presence of T_8 cage derivatives. Polyfluorenes having one or two $T_8(c\text{-}C_5H_9)_7$ substituents per fluorene unit emit blue light with high quantum efficiency in solution [353, 354], but green emission is seen for those with $T_8(c\text{-}C_5H_9)_7$ groups just as termini [355, 356], and photoluminescence studies show that polyfluorene derivatives containing $T_8(c\text{-}C_5H_9)_7OSiMe_2$- substituents may have reduced fluorescence quenching leading to increased fluorescence quantum yields [357] (see also Section 7.2, Chapter 7). As the POS content is increased in poly(phenylene vinylene)s with $T_8(c\text{-}C_5H_9)_7OSiMe_2(CH_2)_3O$- substituents their UV-vis absorption and photoluminescent emission maxima have increasing hypsochromic shifts [358], and introduction of $T_8[OSiMe_2(CH_2)_2C_6H_4\text{-}4\text{-}CH_2-]_8$ units as crosslinkers into poly(phenylene vinylene) materials has been shown to afford highly efficient green emitting materials [359].

2.14   Structural Studies of POS Compounds

2.14.1   Single Crystal X-Ray Diffraction Studies

Many T_6, T_8 and T_{10} POS derivatives have had their structures determined by single crystal X-ray diffraction and they have been reviewed in detail previously [119, 120]. Structural data for selected T_6R_6, T_8R_8 and T_8R_7R', and $T_{10}R_{10}$ compounds are given in Table 2.20. The Si-O bond lengths mostly fall in the range 1.60-1.63 Å, as expected from values in other siloxanes [360]. However, the Si-O-Si angles within a single T_8 or T_{10} POS cage may vary significantly, for example from 136.35-172.13° in $T_8(OSnMe_3)_8\cdot 4H_2O$ [180, 361] and 140.76-160.68° in T_8Cy_8 [362]. Despite the wide variations in individual angles the average Si-O-Si angles for each compound in Table 2.20 fall in the narrow range of ca. 147.5–150.8°. The variations in angles

arise from the well known flexibility of the siloxane linkage coupled with the ability of more flexible substituents to deform and adopt conformations that minimize the voids in the lattice that would form if they were to point ideally towards the vertices of a cube. The T_8 POS species with larger, flexible substituents form either a disc-like structure when substituents on two opposite faces of the core close up towards each other, or a rod-like structure when the substituents around a pair of opposite faces close up (see also Section 7.1, Chapter 7). The bond angles for the smaller, more rigid T_6R_6 compounds, are generally less varied but the structure of D_{2d} symmetric $T_{12}H_{12}$ shows Si-O-Si angles varying by up to ca. 11° [363]. Poor quality X-ray data may be obtained for T_8 POS compounds with flexible substituents, since they are prone to disorder within the lattice [83].

The potential of POS derivatives as nano-sized building blocks for materials construction has been widely described, and derives from the high symmetry of the cage, and the size of the cage, with Si$\cdots$Si distances being ca. 3.11, 4.40 and 5.39 Å for distances along an edge, across a face, and across the body diagonal of a typical cage. These cage dimensions vary little over a wide range of POS derivatives, and their values have been tabulated and discussed previously [362]. An interesting sub-group of the structures in Table 2.20 are those containing an endohedral fluoride ion, in which the Si-O-Si angles are lower than those for the empty cages and close to 141.2°, see for example, Figure 1. Attraction between the fluoride and all eight Si atoms causes the cage to contract slightly and repulsions between the oxygen atoms and the fluoride cause the Si-O-Si angle to change [222]. Analyses of the unit cell data for several alkyl-substituted T_8 derivatives crystallising in rhombohedral space groups have been tabulated, and show that packing of the molecules within the hexagonal planes is closer than the separation between the planes. A c/a ratio of ca. 1.03 in T_8R_8 and T_8R_7R' compounds for a range of alkyl substituents of varying size and nature is found, implying a related molecular arrangement in these structures. However, the parent silane T_8H_8 has a c/a ratio of 1.68, and aryl-substituted T_8 compounds do not fit this pattern [364]. The solid state structure of T_8H_7n-C_6H_{13} exhibits bilayers, owing to a preference for POS-POS and hydrocarbon-hydrocarbon interactions rather than hydrocarbon-POS interactions [311]. The preference for POS-POS interactions is often seen in more complicated materials (see WAXS and SAXS studies in Section 2.14.3) and is also shown to occur in molecular simulations of blends of $T_8(c$-$C_5H_9)_8$ and oligoethylene [365].
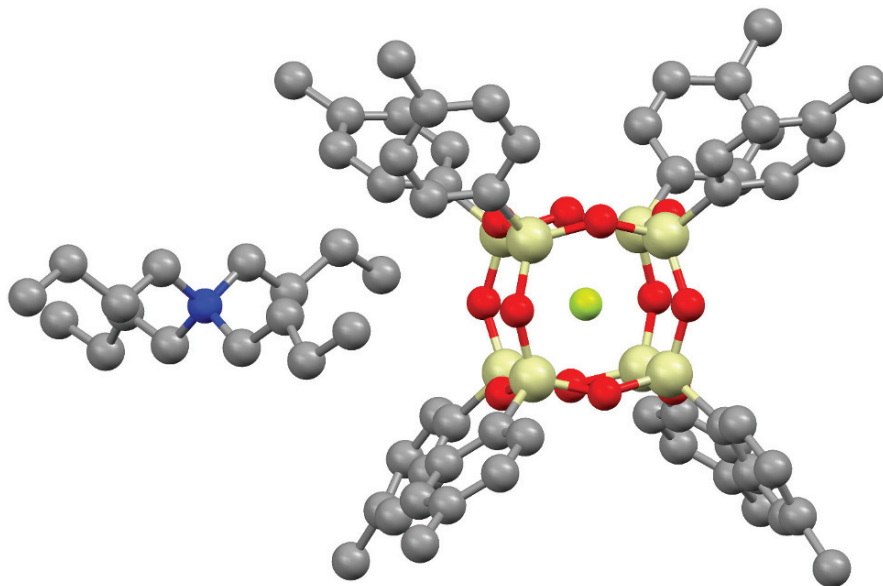
Fig. 1 The solid state structure of the endohedral POS salt $[Bu_4N][T_8(p\text{-tolyl})_8F]$, hydrogen atoms omitted for clarity [222]. (Figure drawn using data from the Cambridge Crystallographic Database, structure 229789)

Table 2.20 Selected structural data for T_nR_n, and related compounds[a]

Compound	Si-O range (Å)	Si-O-Si range (°) Si_4O_4 rings	Si-O-Si range (°) Si_3O_3/ Si_4O_4 rings (T_6) Si_5O_5 rings (T_{10})	Refs.
		$n = 6$		
T_6H_6[b]	1.634-1.643	139	131	[366]
T_6Cl_6[b]	-	136.6	126.9	[367]
T_6Me_6	1.633-1.642	141.278	131.321	[368]
$T_6(t\text{-Bu})_6$	1.623(2)-1.642(2)	137.1(1)-141.1(1)	129.7(1)-131.2(1)	[101]
T_6Cy_6	1.625(6)-1.649(6)	139.3(4)-144.7(5)	128.8(4)-130.8(5)	[9]
$T_6(2,4,6\text{-}i\text{-}Pr_3C_6H_2)_6$[c]	1.622(2)-1.646(4)	138.3(3)-141.7(3)	131.8(2)-134.0(2)	[98]
$T_6(OSiMe_3)_6$	1.56(1)-1.63(1)	136.8(8)-138.6(6)	128.9(8)-131.7(9)	[149, 369]
$T_6(OSiMe_3)_6$[d]	1.633-1.640	141.8(14)	129.2(7)	[233]
$Na_3YT_6(O^-)_6$	1.623(2)-1.651(1)	132.8(2)-135.8(2)	130.3(2)-134.1(1)	[370]
		$n = 8$		
T_8H_8	1.6168(11)-1.6195(7)	147.49(6)-147.60(7)		[371]
T_8H_8[d]	1.6143(3)	147.9(2)		[372]

Compound	Si-O range (Å)	Si-O-Si range (º) Si_4O_4 rings	Si-O-Si range (º) Si_3O_3/ Si_4O_4 rings (T_6) Si_5O_5 rings (T_{10})	Refs.
T_8Cl_8	1.595(4)-1.610(4)	148.0(3)-148.8(3)		[373]
T_8Me_8	1.610(2)-1.617(2)	148.9(1)-149.6(5)		[374]
T_8Me_8[d]	1.6174(5)	148.9(2)		[372]
$T_8(CH=CH_2)_8$	1.596(6)-1.617(7)	150.0(5) and 150.5(5)		[375]
$T_8(CH=CH)_8$[e]	1.6184(13)-1.6295(13)	138.67(9)-143.06(9)		[222]
$T_8[(CH_2)_2PMe_2]_8$	1.588(2)-1.598(2)	145.44(17)-152.37(17)		[89]
$T_8[(CH_2)_3C_6H_4-4-OMe]_8$	1.604(5)-1.627(4)	145.6(3)-156.6(3)		[362]
$T_8[(CH_2)_3Br]_8$	1.597(7)-1.633(7)	141.7(4)-153.8(5)		[25]
$T_8(CH_2CH_2CF_3)_8 \cdot THF$	1.6164(10)-1.6232(10)	144.29(7)-154.95(8)		[32]
$T_8(CH_2CH=CH_2)_8$	1.607-1.618	145.0-152.7		[88]
$T_8(CH_2CHMe_2)_8$	1.611(5)-1.622(5)	143.7(3)-152.3(3)		[11]
$T_8(CH=CHPh)_8$	1.598(4)-1.627(3)	142.52(17)-153.15(19)		[77]
$\{Si_8O_{12}[(CH_2)_3NH_3]_8\}$-$[ZnCl_4]_{2.8}Cl_{2.4}$	1.605(6)-1.636(7)	144.0(5)-157.2(5)		[73]
$T_8[(CH_2)_2(CF_2)_7CF_3]_8$	1.614(2)-1.626(2)	144.30(15)-149.94(14)		[22]
$T_8(c-C_5H_9)_8$	1.615(3)-1.630(3)	140.5(2)-156.04(19)		[11]
T_8Cy_8	1.539(2)-1.6705(17)	140.76(8)-160.68(11)		[362]
$T_8Ph_8 \cdot Me_2CO$	1.607-1.617	144.63-151.53		[376]
T_8Ph_8[e]	1.6199(15)-1.6294(16)	138.57(10)-143.87(10)		[221]
T_8Ph_8[d]	1.634(15)-1.645(19)	147.5(45)-149.8(24)		[245]
$T_8(C_6H_4-4-Me)_8$	1.610(2)-1.629(4)	144.0(2)-151.60(17)		[120]
$T_8(C_6H_4-4-Me)_8$[e]	1.6234(19)-1.628(2)	140.50(13)-142.47(13)		[222]
$T_8(C_6H_4-4-CH_2Cl)_8$	1.600(4)-1.634(4)	139.0(3)-164.3(3)		[120]
$T_8(C_6H_4-4-I)_8 \cdot EtOAc$	1.603(4)-1.616(4)	144.7(4)-152.0(3)		[126]
$T_8(OMe)_8$	1.592-1.609	145.42-151.92		[139]
$T_8[OSi(CH=CH_2)_3]_8$	1.588(3)-1.617(3)	142.8(2)-151.8(2)		[377]
$T_8(OSnMe_3)_8$	1.580(3)-1.629(4)	148.8(2)-161.2(2)		[180, 361]
$T_8(OSnMe_3)_8 \cdot 4H_2O$	1.5872(16)-1.6277(17)	136.35(10)-172.13(12)		[180, 361]
$T_8(SiMe_2-t-Bu)_8$	1.620(7)-1.630(6)	148.5(4)-152.2(4)		[251]
$T_8(Co(CO)_4)_8$	1.610(4)-1.637(4)	147.6(2)-154.1(3)		[181]
$[T_8(c-C_5H_9)_7O]_2Mn(TMEDA)_2$	1.608(2)-1.641(3)	143.95(17)-152.58(17)		[188]

Compound	Si-O range (Å)	Si-O-Si range (°) Si_4O_4 rings	Si-O-Si range (°) Si_3O_3/ Si_4O_4 rings (T_6) Si_5O_5 rings (T_{10})	Refs.
T_8Cy_7(fluorenyl)	1.596(3)-1.632(3)	142.8(2)-161.3(2)		[34]
$(T_8Cy_7)_2O$	1.6060(15)- 1.6314(14)	137.88(9)-168.09(11)		[146]
		n = 10		
$T_{10}H_{10}$	1.591(3)-1.615(3)	147.8(2)-150.2(2)	152.8(2)-157.9(2)	[378]
$T_{10}H_{10}^e$	1.616(2) and 1.622(3)	153.9(7)	155.0(5)	[379]
$T_{10}Me_{10}$	1.582-1.626	147.3-152.7	148.0-160.5	[107]
$T_{10}(OSiMe_3)_{10}$	1.574-1.609(8)	149.25-154.99	149.31-157.89	[177]
$T_{10}H_9Ph$	1.571(4)-1.620(3)	145.2(2)-150.9(2)	150.5(2)-162.7(3)	[210]

[a] Unless otherwise stated, all data are from single crystal X-ray crystallography studies. [b] Calculated structure. [c] For the right-handed enantiomer. [d] Gas phase electron diffraction structure. [e] Anionic endohedral fluoride with $[NBu_4]^+$ cation.

2.14.2   Structures Derived from Computational and Gas-Phase Electron Diffraction Studies

The structure and properties of the parent hydride, T_8H_8, have been calculated and the results described in detail in several reviews [119, 120, 289, 372, 380-382]. In the gas phase, an electron diffraction study of T_8H_8 shows it to have O_h symmetry, an Si-O-Si angle of 147.9(2)°, and Si-O and Si-H distances of 1.6141(3) and 1.454(8) Å respectively, in agreement with MP2/6-311++G(3df,3pd) calculated values of 1.629, 1.453 Å and 147.8° [372]. MP2/6-311++G(3df,3pd) calculations on T_8Me_8 give Si-O and Si-C values of 1.632 and 1.837 Å, respectively, and an Si-O-Si angle of 148.6°, which agree well with the corresponding experimental values of 1.6174(5) and 1.829(3) Å and 148.9(2)° determined by gas-phase electron diffraction methods [372]. The calculated structure [245, 347] of T_8Ph_8 agrees well with that determined by gas-phase electron diffraction methods [245]. A comparison of force fields shows that the charge-transfer reactive, and universal force fields together with COMPASS and Hybrid-COMPASS force fields all give agreement between theory and experiment for crystal packing data for both T_8H_8 and T_8Me_8, while CTR and Hybrid-COMPASS methods give good agreement with experimental data for the melting point of T_8H_8 [381]. An ab initio study of T_8R_8 (R = H, Me, SiH_3, F or Li) shows that more electropositive substituents increase the Si-O-Si angle and the Si-O bond length, while electronegative substituents do the reverse when compared to T_8H_8. The window in any given side of the POS cage is important when considering the potential of POS cages for storing hydrogen, and the same study shows that the larger $T_{14}H_{14}$ (D_{3h} isomer) and $T_{16}H_{16}$ (D_{4d} isomer) cages can accommodate two or

three H_2 molecules [383]. A detailed molecular mechanics and dynamics study of $T_8(i\text{-}Bu)_8$ in the solid state has been used to describe its phase change at ca. 319 K in terms of a dynamic disordering of the cage substituents [288].

Hartree-Fock and MP2 calculations on T_8H_7R compounds (R = Et, n-Pr, n-Bu, Cy) show that small changes occur on substituting one H for an alkyl group on one of the corners of the cage, and that combining force fields for silsesquioxanes with those for hydrocarbons may obviate the need for force fields for individual POS compounds [380, 382]. Molecular simulations of $T_8H_7(n\text{-}C_9H_{19})$ show that it forms cylindrical structures in solvents that are good for the POS cage but poor for the alkyl group, but lamellar structures if the solvent for the cage is poor [384, 385]. Related calculations on POS cubes with four substituents around a single face indicate that hexagonally arranged cylinders are the preferred structure [385]. Molecular dynamics calculations on molecules in which a hydrocarbon chain connects two T_8Me_7 fragments show that if the chain is long they are able to move independently, but if short they move together through a solution [386].

Computational studies have been carried out on several T_8 cages containing endohedral fluoride ions, to complement the single crystal X-ray diffraction studies (see Table 2.20), with MP2 calculations of $[F@T_8R_8]^-$ ions (R = Me, CF_3, $CH=CH_2$, $CH_2CH_2CF_3$) showing binding energies for the fluoride from 293 to 1130 kJ mol^{-1} [223]. Calculations at the B3LYP/6-31G(d) and B3LYP/6-311++G(d,p) levels on the binding of cations (Li$^+$, Na$^+$, K$^+$), anions (F$^-$, Cl$^-$, Br$^-$), and noble gasses (He, Ne, Ar) to T_8H_8 show that endohedral binding for the anions is preferred, as seen experimentally, but that exohedral binding is preferred for the cationic and neutral species [387]. DFT methods show that for exohedral and endohedral transition metal complexes with T_8H_8 the insertion of a metal into the cage reduces the HOMO-LUMO gap from 8.1 eV for the empty cage to between 1.2 and 4.96 eV for the endohedral species, and that the endohedral complexes $M@T_8H_8$ for M = Cr, Fe, Co, Ni, Cu, Ru and Os are more stable than the separate components [388]. However, attempts to prepare molecular T_8 cages containing endohedral cations have, so far, been unsuccessful [73]. DFT calculations on endohedral complexes of $T_{10}H_{10}$ show that endohedral binding is preferred over the separated species for complexes with Li$^+$, Na$^+$, F$^-$, Cl$^-$ and Br$^-$ [389].

2.14.3   *X-ray Diffraction Studies on Powders, Thin Films, etc.*

X-ray diffraction data have been used widely to determine the degree of dispersion of POS species within a polymer or composite, and the degree of crystallinity of any POS domains present by noting common features attributable to the POS species in diffraction patterns recorded both before and after processing POS monomers. Much of this work has been reviewed [390-402]. Diffraction peaks typical of POS cubes occur at 2θ values of 8.3, 18.9 and 24.4° corresponding to d-spacings of ca. 11, 5, and 3 Å, and can be attributed to the overall dimensions of the POS molecule,

the body diagonal of the POS cage, and the distance between opposite faces of the T_8 cage respectively [309]. Care needs to be exercised in comparing diffraction data, since the ideal cubic arrangement of the eight Si atoms in a T_8 cage is often distorted (see section 2.14.1) causing the body diagonal, face diagonal, and face-to-face distances across the POS cage to vary significantly. Several widely used T_8 POS compounds such as $T_8(CH=CH_2)_8$ [375] and $T_8(OSiMe_2H)_8$ [177] have rhombohedral structures, and the rhombohedral nature of many T_8 POS crystal structures has been commented on [364]. However, the majority of POS structures are in fact triclinic and monoclinic, and a more comprehensive discussion of the crystal structures has been published recently [120].

2.14.3.1 T_8R_8 Compounds

The powder X-ray diffraction pattern for T_8H_8 shows characteristic peaks at 2θ = 7.9, 8.4, 11.04, 18.9 and 24.13º [403]; while the pattern for T_8Me_8 is indicative of a rhombohedral structure [19, 103, 404], and has a characteristic peak at ca. 2θ = 10.8º [272, 405] which is also present in diffraction patterns from POS polyethylene nanocomposites containing >1 wt % POS, indicating that the T_8Me_8 crystallizes when dispersed in the polyethylene [404, 406, 407]. The WAXD pattern of $T_8(i\text{-}Bu)_8$ shows several sharp peaks, e.g. at ca. 2θ =7.96, 8.84, and 10.86º corresponding to d-spacings of 11.1, 10.0 and 8.1 Å, which are also seen in blends with poly(methyl methacrylate), with phenolic resin, with styrene-maleic anhydride polymers, with poly(L-lactide), and with polyethylene/ethylene-vinylacetate copolymers [314, 406, 408-411] in blends with silicone rubber [412], and also in POS- epoxy-cyanate composites, in all cases indicative of POS phase segregation [413]. A variable temperature powder XRD study of $T_8(i\text{-}Bu)_8$ showed a phase change to occur at ca. 319 K, from a low temperature $P\bar{1}$ to a high temperature $R\bar{3}m$ lattice [288]. The XRD pattern for $T_8(CH=CH_2)_8$ shows several sharp peaks at 2θ = 9.8, 20.1 and 29.9º [414-416], while the XRD pattern of $T_8[(CH_2)_3NH_2]_8$ shows several sharp peaks indicative of crystallinity and consistent with a rhombohedral unit cell, with a = 11.57 Å and α = 95.1º [417-420], and the WAXD pattern for T_8Ph_8 shows sharp diffraction peaks again indicative of crystallinity [278].

The XRD pattern for $T_8(OSiMe_2H)_8$ shows sharp peaks at ca. 2θ = 8.3, 18.9 and 24.4º corresponding to d-spacings of 11, 5, and 3 Å attributable to the distance between opposite Si_4O_4 faces of the POS core, the POS cage diagonal distance, and the size of the POS molecule respectively [151, 167, 309, 421]. WAXD studies of PEG derivatives of $T_8(OSiMe_2H)_8$ provide evidence for the presence of small disordered POS domains [421]. Conversely, although the XRD pattern for $T_8[OSiMe_2(CH_2)_3OH]_8$ is indicative of crystallinity, upon incorporation into a POS-polyimide film the crystallinity is lost [249, 422].

2.14.3.2 T_8R_7R' Compounds

As for T_8R_8 compounds, diffraction studies on T_8R_7R' compounds often concentrate on whether domains of POS cages are formed in a polymer or composite material by comparison of patterns with those from simple molecular species. The peaks in the powder X-ray diffraction pattern of $T_8(i\text{-Bu})_7(CH_2)_2C_6H_4CH_2Cl$ at $2\theta = 8.3$ and $11.0°$ are characteristic of a hexagonal POS structure and are retained when the POS compound is tethered to a dimethylimidazolium center and also when it is subsequently exchanged into a montmorillonite clay, clearly demonstrating the propensity of POS species to form crystalline domains [423]. POS domains from 1.3 to 2.7 nm across, corresponding to one to two POS units per domain are indicated from the WAXD patterns of a range of ethylene-propylene-POS polymers containing pendant $T_8(i\text{-Bu})_7$ groups [424]. Diffraction patterns also show that the mixing time has an effect on the crystallinity of the POS, for example, mixing $T_8(i\text{-Bu})_7(CH_2)_3NH$ with styrene-maleic anhydride copolymers gives a hybrid system showing the precursor diffraction pattern clearly after 2 min, but after mixing for 20 min no sharp peaks are seen [314]. The WAXD pattern of $T_8(i\text{-Bu})_7(CH_2)_3OC(=O)$-$C(=CH_2)Me$ shows sharp peaks at $2\theta = 9.5$, 12.9 and $22.4°$ corresponding to d-spacings of 10.8, 8.0 and 4.6 Å [425]; but these are largely lost on incorporation of the compound into dimethacrylate [426, 427], isobornyl methacrylate and diethylene glycol dimethacrylate networks [428], although at high loadings in copolymers with poly(octafluoropentyl acrylate) a peak at ca. $2\theta = 8°$, indicative of POS aggregation, is prominent [429]. Similarly, the sharp diffraction peaks associated with $T_8(i\text{-Bu})_7(CH_2)_3OH$ are lost on its incorporation into polylactide nanocomposites [430].

The WAXD pattern for $T_8(i\text{-Bu})_7OSiMe_2(CH_2)_3OCH_2CEt(CH_2OH)_2$ has significant reflections at ca. $2\theta = 7.9$, 10.52 and $18.6°$ corresponding to d-spacing of 11.2, 8.3 and 4.8 Å respectively and a rhombohedral or equivalent hexagonal unit cell. Some polycaprolactone networks containing this POS grouping also show these diffraction peaks indicating that the cage survives the polymerization reaction [431], and the $2\theta = 7.9°$ peak is observed in $T_8(i\text{-Bu})_7OSiMe_2(CH_2)_3OCEt(CH_2OH)_2$–polyurethane copolymers and is attributable to POS crystals (of rhombohedral unit cell; $a = 11.0$ Å, $\alpha = 104°$) in the polymer, rather than molecular level dispersion of the cages [432-435]. The XRD pattern for $[T_8(i\text{-Bu})_7(CH_2)_3NH_3]Cl$ shows reflections at $2\theta = 7.9$ and $8.8°$ [436], and for $T_8(i\text{-Bu})_7(CH_2)_3NH_2$, the highest intensity peak is seen at $2\theta = 8.3°$ [437].

A range of compounds containing the $T_8(c\text{-C}_5H_9)_7$ group have been studied by diffraction methods, for example, the WAXD pattern for $T_8(c\text{-C}_5H_9)_7(CH_2)_2C_6H_4$-4-$CH_2Cl$ shows peaks at ca. $2\theta = 8.3$, 11.3, 12.0, 19.1 and $25.9°$ corresponding to d-spacings of 10.5, 7.2, 6.9, 4.6 and 3.3 Å respectively, the 10.5 Å spacing being due to the POS molecule [438, 439], and the pattern for $T_8(c\text{-C}_5H_9)_7(CH_2)_3CN$ shows sharp peaks including one at $2\theta = 8.2°$ corresponding to a d-spacing of 10.2 Å which is also seen in cyanate ester composite materials derived from it [440]. The XRD pattern for $T_8(c\text{-C}_5H_9)_7(CH_2)_3OC(=O)C(=CH_2)Me$ shows peaks at $2\theta = 8.2$, 11.1, 12.3, 19.2 and $24.9°$ corresponding to d-spacings of 10.7, 7.9, 7.1, 4.6 and

3.6 Å respectively. The 10.7 Å peak is attributable to the size of the POS molecule, and the remaining peaks to a rhombohedral lattice [441-443]. WAXD has been used to show that the POS additives $T_8(c\text{-}C_5H_9)_7R$ [R = $(CH_2)_2(CF_2)_7CF_3$ or $CH_2CH(OH)$ CH_2OH] in polystyrene segregate at the surface, forming crystallites of 10 and 19 nm sizes respectively [444].

Diffraction studies of materials containing T_8Cy_7 or T_8Ph_7 groups have also been carried out, for example, $T_8Cy_7OSiMe_2(CH_2)_3NCO$, and polymers derived from its reaction with poly(ethylene glycol), show strong reflections at 2θ = 7.8, 10.62 and 18.20° and corresponding rhombohedral unit cell parameters of a = 11.57 Å and α = 95.5° associated with a crystalline POS phases, in both the monomeric compound and the polymers [445]. The WAXS pattern of $T_8Ph_7(CH_2)_3OC(O)C(=CH_2)Me$ shows sharp peaks that are retained in the patterns derived from copolymers with poly(octafluoropentyl acrylate), again indicative of POS aggregation [429]. The WAXD patterns for a range of ethylene-propylene-POS polymers containing T_8Ph_7 groups show POS domains from 1.3 to 9.5 nm across, suggesting from three to seven T_8Ph_7 units per domain [424].

2.15   TGA, DSC and Related Studies of POS Compounds

2.15.1   *T_8R_8 Compounds (R = H, Alkyl, Vinyl, Aryl or Silyl Derivatives)*

The thermal stability and decomposition pathways of many simple POS compounds and materials containing POS components have been studied and have been reviewed [120], and this section concentrates only on studies of simple molecular POS species. TGA studies of low molecular weight compounds such as T_8R_8 (R = H, Me, *i*-Bu, *i*-Oct, Ph) may be complicated by their ready sublimation under nitrogen, and occasional partial sublimation in air. Thus, for T_8H_8 and T_8Me_8 incomplete evaporation has been reported to occur both in air and in a N_2 atmosphere, but for $T_8(i\text{-}Bu)_8$ and $T_8(i\text{-}Oct)_8$ near complete evaporation occurs in an inert atmosphere, at approximately 265 °C for $T_8(i\text{-}Bu)_8$ [437], whereas oxidation occurs in air to give silica. However, TGA of T_8H_8 has also been reported to show rapid and near-complete mass loss at temperatures over ca. 200 °C due to sublimation [446], and TGA of T_8Me_8 and T_8Et_8 in N_2 has also been reported to show almost 100% evaporation at ca. 250-260 °C [405, 447]. POS compounds such as T_8R_8 (R = C_8H_{17} or $C_{18}H_{37}$) containing longer alkyl chains are thermally quite stable, showing 10% decomposition only at 343 and 366 °C respectively [448].

The DSC trace of $T_8(i\text{-}Bu)_8$ shows two endotherms, a sharp one at 60 °C and a broader one at ca. 265 °C probably due to the melting point, while TGA shows

that maximum evaporation occurs at 285 °C, and that complete mass loss occurs at ca. 375 °C due to evaporation of the sample in N_2, but in air a ceramic residue of 26% is formed as oxidation competes with evaporation [408, 449, 450]. The alkyl substituted cages T_8R_8 [R = $(CH_2)_5Br$, CH_2CH_2Cy, and $CH_2CH_2OCH_2CH_2Cl$] lose no mass on heating to 381, 442, and 338 ºC respectively [51, 451], but for R = CH_2CH_2Cy and $(CH_2)_5Br$, significant mass loss is seen at 460 and 380 ºC respectively by TGA [326]. The TGA analysis of the fluorinated derivatives, $T_8(CH_2CH_2R)_8$ [R = CF_3, $(CF_2)_3CF_3$, $(CF_2)_5CF_3$ or $(CF_2)_7CF_3$], in air shows that they all evaporate, the $(CF_2)_7CF_3$ derivative subliming at over 300 ºC [452] and being stable up to about 350 ºC in N_2 [453]. The TGA trace of $T_8(CH=CH_2)_8$ suggests stability to ca. 280 ºC [454, 455], but the residual mass is significantly lower than what would be expected for complete conversion to silica, and so sublimation also appears to occur [456].

The TGA analysis of $T_8[(CH_2)_3NH_2]_8$ has led to a range of results, presumably due to its hygroscopic nature and sensitivity to back-biting reactions. Thus, degradation at between 425-500 ºC of the POS cage has been reported [417], as has decomposition starting at ca. 320 ºC [418], and rapid initial mass loss occurring at ca. 350 ºC followed by steady mass loss up to 700 ºC [419]. DSC studies of $T_8[(CH_2)_3NH_2]_8$ indicate a melting point of 196.6 ºC and decomposition onset at 242 ºC, i.e. lower than determined by TGA [18]. TGA of $\{T_8[(CH_2)_3NH_3]_8\}Cl_8$ shows a two-step decomposition corresponding to initial breakdown of the alkylammonium chloride group between 305 and 420 ºC and a second step at 420-650 ºC due to degradation of the propyl chains [275].

TGA of the aryl-POS compounds T_8R_8 (R = Ph, C_6H_4-2-Me, C_6H_4-3-Me, C_6H_4-4-Me) show melting temperatures of 472, 385, 424 and 407 ºC, respectively, and onsets for decomposition at 486, 435, 431 and 413 ºC, respectively [457]. The phenyl derivative is also reported to be stable to about 480 ºC by TGA/DTA and to give SiO_2 at higher temperatures, but the dinitrated derivative $T_8[C_6H_3(NO_2)_2]_8$ detonated at 420 ºC [122, 458]. The derivative thermogravimetry traces of T_8Ph_8 and $T_8(C_6H_4NO_2)_8$ have, however, both been reported to show rapid decomposition, at 420 and 380 ºC respectively, but that $T_8(C_6H_4NH_2)_8$ undergoes a slow decomposition from 300 to 650 ºC [459].

2.15.2 T_8R_8 Compounds (R = Siloxy Derivatives)

As for the case of simple alkyl-substituted POS compounds, TGA studies of simple siloxy derivatives are complicated by sublimation occurring as well as decomposition. TGA of $T_8(OSiMe_2H)_8$, $T_8[OSiMe_2(CH_2)_3CN]_8$ and $T_8[OSiMe_2(CH_2)_3Cl]_8$ shows a tendency for sublimation, and formation of SiO_2 at high temperatures [163, 460], but under nitrogen, $T_8(OSiMe_2H)_8$ sublimes between 188 and 280 ºC [163, 460, 461]. The DSC traces of $T_8(OSiMe_2H)_8$ and $T_8[OSiMe_2(CH_2)_2C_6H_4$-4-OAc]_8$ show the latter to have a single glass transition at -15 ºC, but that $T_8(OSiMe_2H)_8$ shows no such transition [166, 462]. TGA traces for $T_8(OSiMe_2C_6H_4$-4-R)_8$ (R = Me, CBr_3, or

CO_2H) show 5 % mass loss at 370, 164 and 180 ºC respectively and a residual mass associated, as with many POS compounds, for SiO_2 [154]. Methacrylate and epoxide POS monomers are common components used for incorporation into polymer materials and have good thermal stability. Thus, TGA analysis of $T_8(OSiMe_2R)_8$ [R = $(CH_2)_3(OCH_2CH_2CH_2)_2OC(=O)C(=CH_2)Me$ or $CH=CH_2CH_2OC(=O)C(=CH_2)$-Me] reveal 5 % mass loss at ca. 257 and 302 ºC respectively [463], and TGA of $T_8[OSiMe_2(CH_2)_3OCH_2CH(O)CH_2]_8$ shows decomposition under nitrogen starting at ca. 350 ºC [464]. TGA analysis of the macromonomers $T_8[OSiMe_2(CH_2)_3(OCH_2CH_2)$-$_nOC(=O)CMe(=CH_2)]_8$ and $T_8[OSiMe_2(CH_2)_3(OCH_2CH_2)_nOH]_8$ (n = 2, 3, 4 or 6) shows that a two step decomposition takes place, that the expected ceramic yield of SiO_2 is formed, and that the T_g values for the methacrylate derivatives are ca. 10-20 ºC higher than those for the analogous ethylene glycol derivatives [152].

2.15.3 T_8R_7R' Compounds

The DSC trace of $T_8(i\text{-}Bu)_7(CH_2)_3OCH_2CH(O)CH_2$ shows melting peaks at ca. 112 and 133 ºC with a total melting heat of 26.1 J g^{-1} and crystallization peaks at ca. 119 and 139 ºC, with a total crystallization heat of 15.1 J g^{-1}, presumably indicative of two crystalline phases [465, 466]. In an inert atmosphere, TGA of $T_8(i\text{-}Bu)_7(CH_2)_3OCH_2CH(O)CH_2$ gives a char yield of 24.4%, and in oxygen a char yield of 42.7%, the onset of decomposition being slightly less than 300 ºC in both cases [465]. The TGA of $T_8(i\text{-}Bu)_7(CH_2)_3OCH_2CH(O)CH_2$ has also been reported to show significant decomposition at 220 ºC under argon [467]. TGA of $T_8(i\text{-}Bu)_7(CH_2)_3OC(=O)C(=CH_2)Me$ shows 5% decomposition in air and in nitrogen at 265 and 282 ºC respectively [425], while DSC shows that it melts at 110.4 ºC without decomposing, and that at 140 ºC it exhibits an exotherm attributable to self-polymerization [468]. TGA of $T_8(i\text{-}Bu)_7(CH_2)_3NH_2$ shows an onset of decomposition in Ar and in O_2 at ca. 277 and 265 ºC respectively [469], with rapid mass loss, possibly due to evaporation, at 293 °C [437]. Most studies on T_8R_7R' compounds are for R = i-Bu, but the T_g values for $T_8R_7(CH_2)_3OC(=O)C(=CH_2)Me$ compounds have been found to be 251 ºC and 350 ºC for R = Et and $c\text{-}C_5H_9$ respectively [470]. TGA of $T_8(c\text{-}C_5H_9)_7OSiMe_2(CH_2)_3NCO$ in air or in nitrogen shows decomposition starting at ca. 250 ºC [471], and decomposition of $T_8Cy_7(CH_2)_3OC(=O)C(Me)=CH_2$ occurs in two stages, the first at 350 °C and the second starting at 533 °C [315].

2.16   Microscopy Studies of T$_8$ POS Compounds

2.16.1   *T$_8$R$_8$ Compounds*

STM (scanning tunnelling microscopy) has been used to provide images of individual molecules of T$_8$H$_8$ chemisorbed on a Si(100)-2x1 surface. These indicate that the preferred mode of chemisorption is via one of the Si vertices rather than through an arrangement in which the cage opens up along one edge to bind via both Si and O [472]. However, when deposited on a Si(111)-7x7 surface, the cage appears to break open along one edge to bind as a "cracked cluster", the difference in reactivity between the two surfaces possibly being due to the proximity of Si surface diradicals [473]. STM images of T$_8$H$_8$ on highly oriented pyrolytic graphite show that it can form two different types of monolayer, one in which the face of the cage is in contact with the graphite and a second in which an edge contacts the surface [348]. SEM and TEM have been used to monitor the progress of siloxane formation upon hydrolysis of MeSi(OEt)$_3$ and EtSi(OEt)$_3$ and show that self assembly of the final cubic crystalline material occurs via initial spherical particle formation, followed by chains of spherical particles and bundles of rod-like structures, resulting in regular cubic crystals smaller than ca. 5 μm [103, 405, 447]. SEM of T$_8$Me$_8$ prepared from swollen poly(2-hydroxyethylmethacrylate) shows that cubic crystals having edges up to 20-30 μm long may be formed [19]. Brewster angle microscopy of T$_8$(*i*-Bu)$_8$ shows that it forms aggregates at the air/water interface at all concentrations [474], and AFM of T$_8$(*i*-Bu)$_8$ blended in phenolic resins shows that evenly dispersed POS particles occur at 20% POS content, while at 60% POS content macrophase separation occurs [409]. SEM of poly(ε-caprolactam) blended with T$_8$Ph$_8$ shows that the POS molecules adhere poorly to the polymer and instead form POS domains of 1-20 μm across [475]. SEM of {T$_8$[(CH$_2$)$_3$NH$_3$]$_8$}Cl$_8$ shows it to form crystalline microrods and particles ranging in size from 1 – 80 μm [476], while SAXS and TEM of {T$_8$[(CH$_2$)$_3$NH$_3$]$_8$}[*n*-C$_{12}$H$_{25}$SO$_3$]$_8$ show that a lamellar structure is formed with an interlayer spacing of 3.1 nm [275]. SEM of T$_8$(OSiMe$_2$H)$_8$ shows that well defined cubic particles with a porous structure and of ca. 100 μm size may be formed from the reaction of [T$_8$O$_8$]$^{8-}$ with HMe$_2$SiCl [163], but the related derivatives T$_8$[OSiMe$_2$(CH$_2$)$_3$CN]$_8$ and T$_8$[OSiMe$_2$(CH$_2$)$_3$Cl]$_8$ show a much lower degree of porosity [163, 460].

2.16.2   *T$_8$R$_7$R' Compounds*

AFM of T$_8$(*i*-Bu)$_7$(CH$_2$)$_3$OCH$_2$CH(O)CH$_2$ has been used to image crystals of size 9-10 μm across [465], and AFM studies of polyurethanes containing pendant T$_8$(*i*-Bu)$_7$ groups show that the surface of the polymer is much rougher than when no POS species are present [477]. TEM and EDXS mapping have also been used to show that the T$_8$(*i*-Bu)$_7$ segments in POS-poly(carbonate-urea)urethane nanocomposites

can form crystalline areas [478].

Specular X-ray reflectivity studies on LB multilayer films of polymers containing a pair of $T_8Cy_7OSiMe_2(CH_2)_3NHC(=O)$- groups separated by poly(ethylene glycol) chains show them to have a double layer structure with a thickness of 17.6 Å [479], while similar studies of films of the type T_8Cy_7-PEG-T_8Cy_7 show that double layers are formed with a calculated POS diameter for each POS cage of ca. 12.4 Å [480]. It has also been shown that the $T_8(c\text{-}C_5H_9)_7$–containing blocks in block copolymers of poly(n-butyl acrylate) and poly(propyl methacrylate) can be selectively stained by RuO_4 for imaging in TEM studies [443].

2.17 X-Ray Photoelectron Spectra of POS Compounds

Materials containing POS cages have not been widely studied by XPS but the Si 2p photoemission spectrum of T_8H_8 chemisorbed on a gold surface is consistent with the POS cages bonding to the surface via a single vertex as it shows two peaks in a 1:7 ratio [481]. Most XPS studies of POS-containing materials have been used to determine the presence and distribution of T_8 cages within nanocomposite materials. Thus, POS enrichment at the surface of POS-capped poly(ethylene oxide) in an epoxy resin has been inferred from the Si 2s and Si 2p signals in its XPS spectrum [31], and a higher than expected POS concentration at the surface of acrylate copolymers with pendant T_8R_7 group (R = Et or $c\text{-}C_5H_9$) is shown in the XPS spectrum [482]. XPS has also been used to show the presence of Si in polymeric materials, for example, in thermoset polymers derived from $T_8Ph_7(CH_2)_3OH$ and caprolactone [483], and to determine its concentration, for example, in POS-crosslinked polyurethane networks [484].

2.18 Electrochemistry of POS Compounds

The presence of a T_8 core was found to have little effect on the electrochemical properties of carbazole centers [485, 486], and cyclic voltammetry studies indicate that, although the monomer **6** has initial electroactivity (E_{ox} = 1.45 V in $[NBu_4][BF_4]$/ CH_2Cl_2), the current decreases on repeated cycling. Electrochemical polymerization of **6** with pyrrole affords a polypyrrole containing POS cages which shows optical contrast, switching time (0.4 versus 1.1 s) and color properties, better than those of polypyrrole itself [133]. Cyclic voltammetry studies on films cast from the lutetium(III) complex **7** show it to be electrochromic, having a green-blue transition and possible uses in electrochromic devices [201].
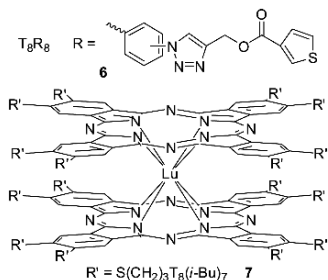
2.19   Chromatographic Methods Applied to POS Compounds

GPC has been used widely in the analysis of T_8 POS-containing materials, but studies can be complicated, since mixtures of compounds containing eight or fewer reacted substituents at a POS cage may have similar hydrodynamic radii, and, as POS materials tend to be globular compared to, for example, polystyrene, the choice of standards is important. Despite this, GPC analysis has been used to assess the purity of simple T_8 derivatives such as $T_8(C_6H_4NO_2)_8$ and $T_8(C_6H_4NH_2)_8$ [487], $T_8(c\text{-}C_5H_9)_7OSiMe_2(CH_2)_3NCO$ [471], $T_8(i\text{-}Bu)_7(CH_2)_3NH_2$ [29], and of $T_8[OSiMe_2(CH_2)_3OCH_2CH(O)CH_2]_8$ [488], and also to assess the nature of higher molecular weight materials containing POS cages. For example, GPC analysis indicates that the reaction between $T_8(C_6H_4NH_2)_8$ and $Me_2BrCC(=O)Br$ gives not only the expected $T_8[C_6H_4NHC(=O)CMe_2Br]_8$, but also higher molecular weight products [489], and that only about five of the Si-H groups per T_8 cage react in the hydrosilylation of $T_8(OSiMe_2H)_8$ with allyl-poly(ethylene oxide) [490]. It has also been used to show that the reaction between $T_8(C_6H_4Br)_8$, Mg, and 2-bromo-3-ethyl-hexylthiophene gives a fairly monodisperse product [131], to characterize the different isomers formed from the hydrosilylation of $T_8(OSiMe_2H)_8$ with a mixture of di(propylene glycol)allylethermethacrylate and 4-vinyl-cyclohexene-epoxide [463], and to determine that up to ca. 16 bromines may be introduced upon bromination of T_8Ph_8 [125].

SEC has been used to determine the purity of products derived from reactions of T_8 compounds, for example, a monomodal mass distribution was found for the polymer formed on hydrosilylation of $T_8(OSiMe_2H)_8$ with undecenyl polystyrene macromonomers [491], as was the case for a series of octa triphenylene-substituted T_8 compounds derived from $T_8[(CH_2)_3NH(CO)CH=CHCO_2H]_8$ [492]. SEC can also be used to confirm the nature of the siloxanes formed in the hydrolytic condensation reactions of trialkoxysilanes. For example, SEC methods show that T_8 species occur in the mixture formed by the hydrolysis/condensation reactions of $CH_2(O)$ $CHCH_2O(CH_2)_3Si(OMe)_3$ [493], and the formation of $T_8[(CH_2)_3Cl]_8$ resulting from

the hydrolysis of $Cl(CH_2)_3Si(OMe)_3$ [325]. SEC has also been used to show the purity of the isomeric tolyl derivatives, T_8R_8 (R = C_6H_4-2-Me, C_6H_4-3-Me or C_6H_4-4-Me) [457], and to characterize the different dendrimers formed in the preparation of globular MRI contrast agents based on $T_8[(CH_2)_3NH]_8$ cores surrounded by L-lysine [494].

2.20   Miscellaneous Physical Properties of POS Compounds

The mechanical properties (bulk modulus, averaged Young's modulus and isotropic averaged shear modulus) of $T_8(c\text{-}C_5H_9)_8$ have been calculated and suggest that, as crystalline aggregates, the POS cages can be considered as "rigid" entities when in a rubbery matrix [495]. A pristine film of $T_8(c\text{-}C_5H_9)_7CH_2CH_2C(=O)OMe$ has been shown to have a hardness and elastic modulus of 0.11 and 5 GPa respectively, but upon irradiation by Si ions it decomposes and forms an amorphous silicate-like material with hardness and elastic modulus of 6 and 65 GPa respectively [496].

Most POS derivatives are solids, but the kinematic viscosities of the viscous liquids T_8R_8 [R = $(CH_2)_7Br$, $(CH_2)_8Br$ $(CH_2)_6Cl$ and CH_2CH_2Ph] have been found to be 35, 38, ca. 42, and 48 cSt, respectively, and to have onsets for solidification of 0, +8, -5, and -20 °C [49]. The siloxy derivatives, $T_8(OSiMe_2R)_8$ where R = $(CH_2)_3OCH_2CH(O)CH_2$, $(CH_2)_2C(=O)C(=CH_2)Me$, and $OSiMe_2OSiMe_2H$, have dynamic viscosities of ca. 600, 220 and 200 mPa s respectively [497, 498].

The water contact angles for $T_8R_7(CH_2)_3OC(=O)C(=CH_2)Me$ (R = Et or $c\text{-}C_5H_9$) are 101 and 116° respectively [470], while for the fluorinated derivatives, T_8R_8 [where R = $(CH_2)_2(CF_2)_7CF_3$, $(CH_2)_2(CF_2)_5CF_3$, or $(CH_2)_2(CF_2)_3CF_3$], the surface energy decreases as the fluoroalkyl chain length increases such that the water contact angle for $T_8[(CH_2)_2(CF_2)_7CF_3]_8$ is 154°, i.e. higher than that of PTFE [22, 256] (see also Chapter 6). The related fluorinated derivatives, $T_8[OSiMe_2CH_2CH_2S(CH_2)_2(CF_2)_nCF_3]_8$ and $T_8[CH_2CH_2S(CH_2)_2(CF_2)_nCF_3]_8$ (where n = 5 or 7), when blended with poly(methyl methacrylate) give materials with water contact angles of 114-124°, which is much greater than the 71° for poly(methyl methacrylate) itself [85].

A plot of the dielectric loss of $T_8[(CH_2)_2Ph]_8$ as a function of temperature and frequency shows a dielectrically active relaxation process attributable to dynamic glass transition or α-relaxation [499], and blends of $T_8[(CH_2)_2Ph]_8$ with polystyrene and with poly(bisphenol A carbonate) have similar features [499, 500], with POS modification of polymers tending to lead to a reduction in dielectric constant [439, 441, 442, 501]. Dielectric relaxation spectroscopy and dynamic mechanical spectroscopy studies of $T_8[OSiMe_2(CH_2)_3OCH_2CH(O)CH_2]_8$ show that it undergoes two relaxation processes, both increasing in frequency as the temperature is increased [502].

2.21   Acknowledgments

2.22   References

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