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Main group and transition metal compounds with silanediolate $[R_2SiO_2]^{2-}$ and α,ω-siloxane diolate $[O(R_2SiO)_n]^{2-}$ ligands

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Contents

Abstract

This review is concerned solely with main-group and transition metal compounds incorporating D_n siloxy fragments of the type: $O(R_2SiO)_n$. Various reported routes to these metallasiloxane compounds from a range of ligand sources are discussed. Reactions involving siloxanolate ligand transfer with oligomerisation are featured. General structural and spectroscopic features of the compounds are outlined. A summary of reported chemistry for

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these metallasiloxane compounds is included. Selected information relating to the synthesis, structure and structural parameters of compounds is provided in tables organised according to periodic groups.

Keywords: Main-group; Transition metals; Siloxy fragments; Metallasiloxane compounds

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1. Scope

The co-ordination chemistry of α,ω-siloxane diolate ligands $[O(R_2SiO)_n]^{2-}$, represents a specific area of metallasiloxane chemistry. The subject area as a whole covers metal complexation by a range of other important siloxanolate ligand types, such as compounds containing the $RSiO_3$, R_2SiO_2, and R_3SiO functionalities. A recent review by Roesky [1] based upon literature published prior to 1996, described the chemistry associated with many of the metallasiloxane compounds derived from diorganosilanediols, $R_2Si(OH)_2$, α,ω-siloxane diols, $[HO(R_2SiO)_nH]$ and organosilanetriols $RSi(OH)_3$. Earlier reviews and books [2–5] have dealt more specifically with hetero- and metallasiloxanes containing siloxy groups of the type R_3SiOH. The general synthetic and structural chemistry of organosilanols has been described in a recent review by Lickiss [6].

The present review is concerned solely with coordination compounds incorporating D_n siloxy fragments of the type: $O(R_2SiO)_n$. The written format and emphasis adopted herein differs significantly from that in Ref. [1]; the discussion is presented in an integrated way rather than using a group-by-group approach. A section of the review summarises some of the chemistry that has been reported for metallasiloxane compounds having ligands $[R_2SiO_2]^{2-}$ or $[O(R_2SiO)_n]^{2-}$. Selected information relating to the synthesis, structure and structural parameters of compounds is summarised in a single set of tables organised according to periodic groups (Tables 6–30) [7,8,10,11,15–18,21,22,27,32,33,35,36,38,39,41,44,53,54,58–62,64,65].

2. Ligand sources and general synthetic/structural features

The synthesis of compounds containing diorganosilanediolate, $R_2SiO_2{}^{2-}$ or α,ω,-siloxane diolate $[O(R_2SiO)_n]^{2-}$ ligands may be achieved using a variety of source reagents. These include:

2.1 diorganosilanediols, $R_2Si(OH)_2$
2.2 alkalimetaldiorganosilanediolates, $R_2Si(OM)_2$; M = Li, Na
2.3 α,ω-siloxane diols, $[HO(R_2SiO)_nH]$
2.4 alkalimetal α,ω-siloxane diolates, $[MO(R_2SiO)_nM]$; M = Li, Na

2.5 α,ω-siloxanedichlorides
2.6 cyclic and polysiloxanes

The extent to which these reagents have been successfully employed for the synthesis of metalla- or heterosiloxanes, and the extent to which they may be considered to have general synthetic utility is considered below. Common coordination modes adopted by the ligands $R_2SiO_2^{2-}$ and $[O(R_2SiO)_n]^{2-}$ are outlined in Tables 1–5 [7–29] The ligating oxygens may coordinate to one, two or three metal centres and with the exception of the simple diorganosilanediolates, $R_2SiO_2^{2-}$, the ligands adopt chelate in addition to bridging coordination modes (the chelate mode does occur for the ligands $R_2Si(OH)O^-$ [11]). As a consequence of this, there is large degree of structural variation exhibited by these systems. In addition the conformations of the metallasiloxane ring fragments (6-, 7-, 8-, 10- and 12-membered rings known) with one hetero or metal atom present, vary from near planar to extensively puckered. The Si–O–Si angles in the 6- and 8-membered rings lie in the range 123–168° and M–O–Si angles in the range 115–140° in six-rings and 140–160° in eight-rings (see Tables 6–29). This inherent flexibility of the siloxane bond, coupled with variable coordination about the oxygen atom(s) present underpins the observed structural diversity.

2.1. Diorganosilanediols, $R_2Si(OH)_2$

The range of available compounds in the class $R_2Si(OH)_2$, is much less extensive than for the related triorganosilanol species, R_3SiOH [6]. Of the known silanediols, the compounds $Ph_2Si(OH)_2$ and $t\text{-}Bu_2Si(OH)_2$ are most frequently used for the preparation of metallasiloxanes. In reactions involving the diol $Ph_2Si(OH)_2$ as reagent, intact transfer of the diolate ligand to a target metal centre is *not* always observed. The outcome of a reaction is shown to vary with changes in the precursor metal compound used, e.g. intact transfer in $[Cp_2MOSiPh_2O]_2$ $M = Zr$ from Cp_2MCl_2 [16], oligomerisation in $[Ti(O(SiPh_2O)_4)_2]$ from $[Ti(OPr^i)_4]$ [30] and in $[Sr_3\{O(Ph_2SiO)_2\}_3(hmpa)_5{\cdot}C_6H_5Me]$ [31] from Sr/NH_3/hmpa. In contrast the diolate ligand $t\text{-}Bu_2SiO_2^{2-}$ is transferred intact, without oligomerisation, from the diol ligand $t\text{-}Bu_2Si(OH)_2$ to target metal centres in *all* reported cases e.g. $[Cl_2Ti\{Ot\text{-}Bu_2SiO\}]_2$ [32], $[Cl_2Ge\{Ot\text{-}Bu_2SiO\}]_2$ [33]. The difference in behaviour between the two ligands is most likely to be due to the relative difference in steric bulk of the R-group functionalities present. The *t*-Bu group being more sterically demanding than the phenyl ring will prevent attack at a given silicon atom, in turn, reducing the likelihood of oligomerisation. A large number of compounds having $R_2SiO_2^{2-}$ ligands adopt 1,3-dimetallacyclotetrasiloxane ring structures.

2.2. Alkalimetal diorganosilanediolates, $R_2Si(OM)_2$; $M = Li$, Na

The alkalimetal diorganosilanediolates, $t\text{-}Bu_2Si(OM)_2$ ($M = Li$, Na) [11], have been structurally characterised, but there are few reports of their use as reagents for the preparation of metallasiloxanes. The structural identity of the compound $Ph_2Si(OLi)_2$, obtained from the reaction between $Ph_2Si(OH)_2$ and BuLi (2:1), is

Table 1
Coordination modes of α,ω-siloxanolate ligands $[O(R_2SiO)_n]^{2-}$. Ligand type: $[R_2SiO_2]^{2-}$

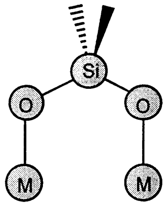
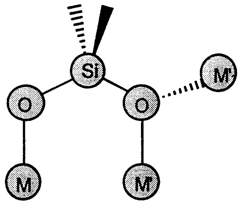
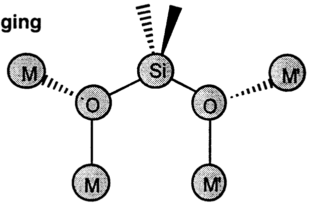
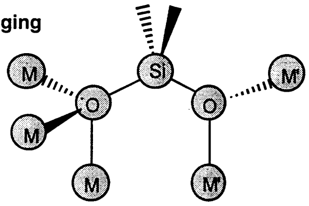
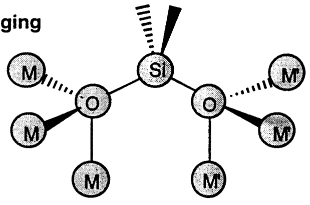
Coordination Mode	Example(s) – [Reference]
μ_2- bridging 	a) [$Cl_2Ge\{Ot\text{-}Bu_2SiO\}]_2$ [7] (8-membered rings) b) [$O_2Mo[Ot\text{-}Bu_2SiO\}]_2$ [8] (8-membered rings) c) [$t\text{-}Bu_2Si(OReO_3)_2$] [9] (acyclic)
μ_3- bridging 	d) [$Cp^*{}_2ZrOPh_2SiOLiOH]_2$ [10] (6-membered rings)
μ_4- bridging 	e) [$t\text{-}Bu_2Si(OLi)_2]_6$.8THF [11] (6-membered rings), (4-membered rings)
μ_5- bridging 	e) [$t\text{-}Bu_2Si(OLi)_2]_6$.8THF [11] (6-membered rings), (4-membered rings)
μ_6- bridging 	e) [$t\text{-}Bu_2Si(OLi)_2]_6$.8THF [11] (6-membered rings), (4-membered rings)

Table 2
Coordination modes of α,ω-siloxanolate ligands $[O(R_2SiO)_n]^{2-}$. Ligand type: $[O(R_2SiO)_n]^{2-}$, $n = 2$

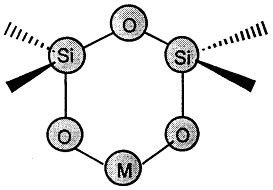
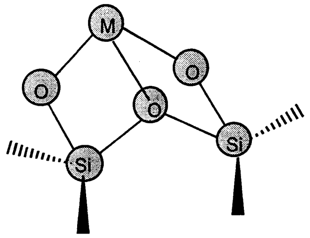
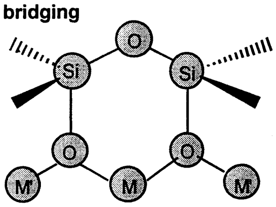
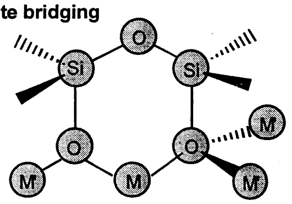
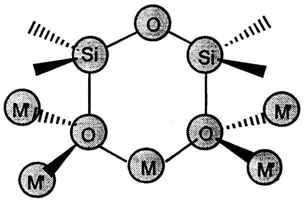
Coordination Mode	Example(s) – [Reference]
chelate 	f) $[PhBO(Ph_2SiO)]^*$ [12, 13] g) $[Zr\{O(Ph_2SiO)_2\}_3].{}_2NEt_2H_2^*$ [14] h) $[Sn\{O(t\text{-}Bu_2SiO)_2\}_2]^*$ [11] * = 6-membered ring system
chelate 	i) $[Ba_3\{O(Ph_2SiO)_2\}_3(tetraglyme)_2]$ [25] (6-membered ring)
μ_3- chelate bridging 	j) $[(THF_2Li)_2\text{-}\mu\text{-}\{Cr\{O(OPh_2SiO)_2\}]^*$ [18] k) $[(Al)_2\text{-}\mu\text{-}\{Al\{O(OPh_2SiO)_2\}]^*$ [19] * = 6-membered ring system
μ_4- chelate bridging 	l) $[O(Ph_2SiOLi.py)_2]_2$ [20] (6-membered ring)
μ_5- chelate bridging 	m) $[O(Ph_2SiONa)_2]_4.NaOH.7py.H_2O$ [21] (6-membered ring)

Table 3
Coordination modes of α,ω-siloxanolate ligands $[O(R_2SiO)_n]^{2-}$. Ligand type: $[O(R_2SiO)_n]^{2-}$, $n = 2$

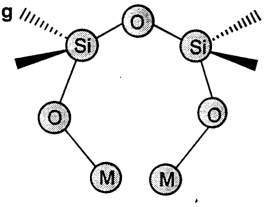
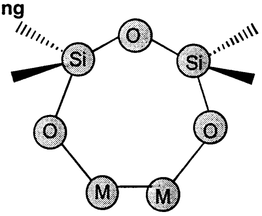
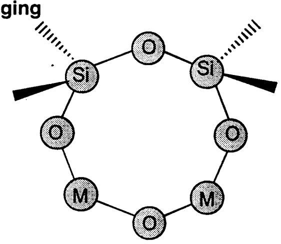
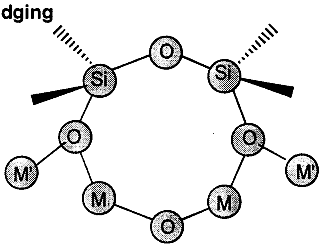
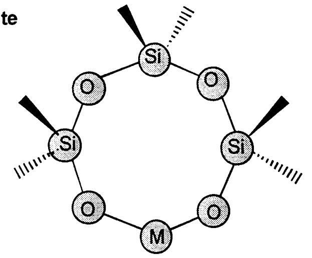
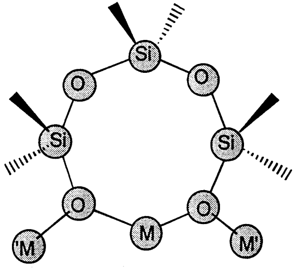
Coordination Mode	Example(s) – [Reference]
μ_2- bridging 	n) $[O(Ph_2SiOSnPh_3)_2]$ [15] (acyclic) o) $[Cp_2Zr\{O(OSiPh_2O)_2\}]$ [16] (12-membered ring) p) $[(t\text{-}BuN)Cr\{O(SiPh_2O)_2\}]_2$ [17] (12-membered ring)
μ_2- bridging 	q) $[(Ph_2Ge)_2\{O(Ph_2SiO)_2\}]$ [22] (7-membered ring)
μ_2- bridging 	r) $[Al(OH)\{O(Ph_2SiO)_2\}]_4.4Et_2O$ [23] (8-membered ring)
μ_4- bridging 	s) $[Al(OLi)\{O(Ph_2SiO)_2\}]_4$ [24] (8-membered ring)

Table 4
Coordination modes of α,ω-siloxanolate ligands $[O(R_2SiO)_n]^{2-}$. Ligand type: $[O(R_2SiO)_n]^{2-}$, $n = 3$

Coordination Mode	**Example(s) – [Reference]**
chelate 	**t) $[Ti\{Ph_2Si(OPh_2SiO)_2\}_2].2py$* [26]** **u) $[PhB\{Ph_2Si(OPh_2SiO)_2\}]$* [27]** **v) $[FB\{Me_2Si(Ot\text{-}Bu_2SiO)_2\}]$* [28]** **w) $[Cl_2Ge\{Me_2Si(Ot\text{-}Bu_2SiO)_2\}]$* [28]** * = 8-membered ring
μ3- chelate bridging 	**x) $[\{O(Ph_2SiO)_2\}Mg\{Ph_2Si(OPh_2SiO)_2\}$-μ-$(LiTHF_2)_2]$ [29]** (8-membered ring)

unknown. Despite this, the compound has been used effectively as a reagent in the synthesis of various metallasiloxane systems. Reactions involving metal halides with this source have yielded products containing the diolate moieties $(OSiPh_2O)^{2-}$, $(OSiPh_2OSiPh_2O)^{2-}$, and $(OSiPh_2OSiPh_2OSiPh_2O)^{2-}$, e.g. $[(Cp/Cp^*)_2ZrOSiPh_2\text{-}OLiOH]_2$ [10], $[Mg\{O(Ph_2SiO)_2\}_2]$-μ-(Lipy)-μ-$\{(Lipy)_3(OH)(Cl)\}]$ [34], incorporating two six-membered magnesiasiloxane rings and an $MgLi_3O_3Cl$ cubane fragment, $[Cr\{O(Ph_2SiO)_2\}_2$-μ-$(Lipy_2)_2]$ [34], with two six-membered chromiasiloxane rings, and $[Co\{O(Ph_2SiO)_2\}\{(OPh_2Si)_3O)_2$-μ-$(Lipy_2)_2]$ [34], with both six- and eight-membered rings.

2.3. *α,ω-Siloxane diols, $[HO(R_2SiO)_nH]$*

A variety of well-characterised disiloxanols are known, and some of these have been used for the synthesis of metallasiloxanes. The stability of these diols towards oligomerisation varies, but is unsurprisingly improved greatly by the presence of bulky organic substituents on the silicon atoms.

Attempts to transfer the disiloxanediolate, $O(Ph_2SiO)_2^{2-}$, to target metal centres using the parent diol $O(Ph_2SiOH)_2$ have been met with varying degrees of success. Some examples of intact transfer are given below:

$3[Mn\{N(SiMe_3)_2\}_2] + 4[O(Ph_2SiOH)_2]$

$\rightarrow [Mn\{O(Ph_2SiO)_2\}_2\text{-}\mu\text{-}\{MnN(SiMe_3)_2\}_2]\cdot 3THF$ [35]

$[Ph_3SnOH] + O(Ph_2SiOH)_2/\text{pyridine} \rightarrow [O(Ph_2SiOPh_3Sn)_2]$ [15]

$[(t\text{-}BuN)_2CrCl_2] + O(Ph_2SiOH)_2/\text{pyridine} \rightarrow [(t\text{-}BuN)(O)CrO(Ph_2SiO)_2]_2$ [17]

$[(t\text{-}BuN)_2MoCl_2] + [O(Ph_2SiOH)_2] \rightarrow [(t\text{-}BuN)Mo\{(O(Ph_2SiO)_2\}_2\cdot py]$ [17]

$[t\text{-}Bu_2SnCl_2] + [O(Ph_2SiOH)_2] \rightarrow [(t\text{-}Bu_2SnO)(Ph_2SiO)_2]_n$ [63]

This selection sees the ligand $[O(Ph_2SiO)_2]^{2-}$ in simple *chelate mode* in $[(t\text{-}BuN)Mo\{O(Ph_2SiO)_2\}_2\cdot py]$, in *bridging mode* in acyclic $[O(Ph_2SiOPh_3Sn)_2]$ polymeric $[(t\text{-}Bu_2SnO)(Ph_2SiO)_2]_n$ and cyclic $[(t\text{-}BuN)(O)CrO(Ph_2SiO)_2]_2$ and in *chelate-bridging mode* in spirocyclic $[Mn\{O(Ph_2SiO)_2\}_2\text{-}\mu\text{-}\{MnN(SiMe_3)_2\}_2]\cdot 3THF$. $[(t\text{-}Bu_2SnO)(Ph_2SiO)_2]_n$ reverts to monocyclic $[(t\text{-}Bu_2SnO(Ph_2SiO)_2]$ in solution. In other cases reactions involving $[O(Ph_2SiOH)_2]$ proceed with the formation of a metal oxide species and the elimination of a trisiloxane compound $(Ph_2SiO)_3$, e.g. in reactions with Me_3Al, $Zr(CH_2Ph)_4$, $Co\{N(SiMe_3)_2\}_2$ [36].

In general, the products obtained from reactions with the diol $[O(Ph_2SiOH)_2]$ are largely dependent on the nature of the target metal centre used.

Table 5
Coordination modes of α,ω-siloxanolate ligands $[O(R_2SiO)_n]^{2-}$. Ligand type: $[O(R_2SiO)_n]^{2-}$, $n = 4$

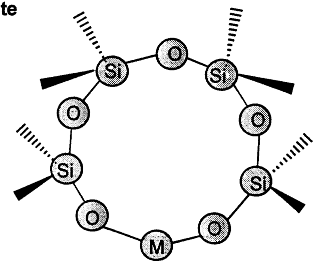
Coordination Mode	Example(s) - [Reference]
chelate 	**y) $[Ti\{O(Ph_2SiO)_4\}_2]$* [30]** **z) $[PhB\{O(Ph_2SiO)_4\}_2]$* [11]** * = 10-membered ring system

Table 6
Periodic group listings of compounds: selected details on synthesis and structure of metallasiloxanes having ligands $[R_2SiO_2]^{2-}$ or $[O(R_2SiO)_n]^{2-}$

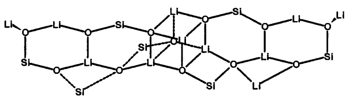
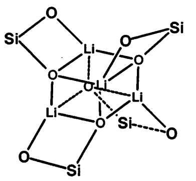
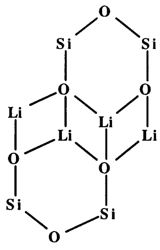
Main Group Metal Compounds **Group 1 compounds**		
Metallasiloxane	**Comments**	**Reference**
$[t\text{-}Bu_2Si(OLi)_2]_6.8THF$ 	$t\text{-}Bu_2Si(OH)_2$, BuLi **cryst struct:** polycyclic assembly of $(LiO)_2$ 4-membered rings and LiOSiOLiO 6-membered rings extending from edges of central $(LiO)_4$ cubane. Structural parameters not available	11
$[t\text{-}Bu_2Si(OH)OLi]_4$. 	$t\text{-}Bu_2Si(OH)_2$, BuLi **cryst struct:** polycyclic assembly of $(LiO)_2$ 4-membered rings and LiOSiOH 4-membered rings extending from edges of central $(LiO)_4$ cubane **Li-O(Si)** 1.905(25)-2.116(19) Å **Si-O(Li)** 1.567(7)-1.596(8) Å **Si-O(H)** 1.664(7)-1.683(7) Å	58
$[O(Ph_2SiOLi.py)_2]_2$ 	$O(Ph_2SiOH)_2$, BuLi, pyridine **cryst struct:** pentacyclic dimer with a central stepped group of three 4-membered lithiooxane rings bridged by two disiloxanediolate ligands giving two 6-membered lithiodisiloxane rings. **Li-O(Si)** 1.800(8)-2.011(7) Å **Si-O(Li)** in 6-rings 1.573(3) Å **Si-O(Si)** 1.644(3) Å **Si-O-Si** 138.86(2) ° **Li-O-Si** 111.8(2)-158.2(3) ° **O-Li-O** in 6-rings 111.53(4) ° ^{29}Si (toluene-d_8) δ -44.3	20

Table 7

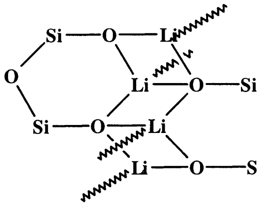
Group 1 compounds contd.		
$[O(Ph_2SiOLi)_2.(1,4\text{-dioxane})_3]_\infty$	$O(Ph_2SiOH)_2$, BuLi,1,4-dioxane **cryst struct:** dimeric units as for $[O(Ph_2SiOLi.py)_2]_2$ linked by single linear 1,4-dioxane bridges. **Li-O(Si)** 1.812(21)-1.981(17) Å **Si-O(Li)** 1.579(8)-1.602(8) Å **Si-O(Si)** 1.620(8)-1.648(8) Å **Si-O-Si** 140.2(4) ° **Li-O-Si** 115.8(5)-144.9(7)° **O-Li-O** in 6-rings 109.8(5) ° ^{29}Si(toluene-d_8) δ -39.6	36
$[\{O(Ph_2SiOLi)_2\}_2.2THF.DABCO]_\infty$	$O(Ph_2SiOH)_2$, BuLi, DABCO **cryst struct:** dimeric units as above linked by single linear 1,4-DABCO bridges **Li-O(Si)** 1.803(10)-2.094(7) Å **Si-O(Li)** 1.584(4) Å **Si-O(Si)** 1.635(3) Å **Si-O-Si** 140.05(2) ° **Li-O-Si** in 6-rings 117.6(3)-118.2(3) ° **O-Li-O** in 6-rings 110.6.(5), 113.2(6) °	38
$[\{O(Ph_2SiOLi)_2\}_2.2THF.24,4'\text{-bipyridine}]_\infty$ 	$O(Ph_2SiOH)_2$, BuLi, 4,4'-bipyridine **cryst struct:** dimeric units (with 6-membered lithiodisiloxane and 4-membered lithiooxane rings) linked by double linear 4,4'-bipyridine bridges **Li-O(Si)** 1.892(9)-2.050(8) Å **Si-O(Li)** 1.578(7) Å **Si-O(Si)** 1.635(3) Å **Si-O-Si** 141.9(2) ° **Li-O-Si** in 6-rings 115.8(4) ° **O-Li-O** in 6-rings 110.7(5) °	38
$[O(Me_2SiONa.)_2.4H_2O]_n$	$(Me_2SiO)_4$, NaOH **cryst struct:** double layer with hydrophillic, hydrated Na ions sandwiched between chains of hydrophobic siloxane **$Na\text{-}O_t(Si)$** 2.606(6) Å **$Na\text{-}O_b(Si)\text{-}Si$** 2.454(6) Å **Si-O(Si)** 1.640(7)-1.669(6) Å **Si-O-Si** 144.2(3)-146.7(3) °	37

Table 8

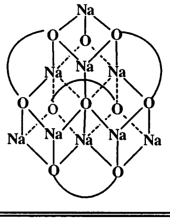
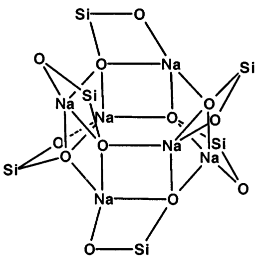
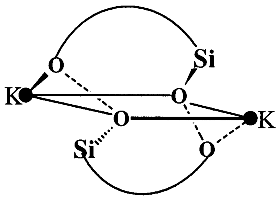
Group 1 compounds contd.		
[O(Ph$_2$SiONa.)$_2$py]$_2$	Na(s), O(Ph$_2$SiOH)$_2$, pyridine	21
[{O(Ph$_2$SiONa)$_2$}$_4$.(NaOH).7py(H$_2$O)]  	O(Ph$_2$SiOH)$_2$, Na(s), pyridine **cryst struct:** three edge-shared Na$_4$O$_4$ siloxane-bridged cubes, sharing one -μ_6-OH site, where one cube corner is occupied by a -μ_3 -OH$_2$ group. **Na-O(Si)** 2.239(2)-2.454(2) Å **Si-O(Na)$_{mean}$** 1.585(2) Å **Si-O(Si)$_{mean}$** 1.643(2) Å **Si-O-Si** 135.52(14)- 151.7(2) ° **O-Na-O** in 6-rings 97.80(8)-105.98(8) ° **Na-O-Si** in 6-rings 109.05(9)-124.65(9) °	21
[t-Bu$_2$Si(OH)ONa.THF]$_6$  	t-Bu$_2$Si(OH)$_2$, Na(s) **cryst struct:** central hexagonal prismatic (NaO)$_6$ assembly with (NaOSiOH) four membered rings extending from alternate edges of the 6-membered rings in the central hexagonal prism. **Na-O(Si)** 2.223(3)-2.422(3) Å **Na-OH** 2.321(3)-3.350(3) Å	11
[K{O(Ph$_2$SiO)$_2$SiPh$_2$OH}]$_2$. C$_6$H$_6$  	O(Ph$_2$SiOH)$_2$, KOBu^t **cryst struct:** dimeric units (with two 8-membered potassiotrisiloxanol rings fused along alternate edges of a central 4-membered potassiooxane ring) **K-O(Si)** 2.681(4), 2.812(4) Å **K-OH(Si)** 2.912(4) Å **Si-O(Si)** 1.584(4)-1.646(4) Å **Si-OH(Si)** 1.604(4) Å **Si-O-Si** 135.52(14)- 151.7(2) ° **K-O(Si)-K** 92.54(13) °	50

Table 9
Periodic group listings of compounds: selected details on synthesis and structure of metallasiloxanes having ligands $[R_2SiO_2]^{2-}$ or $[O(R_2SiO)_n]^{2-}$

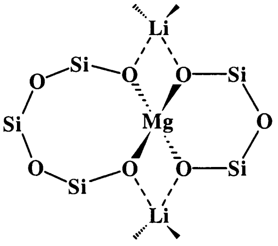
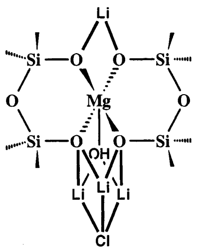
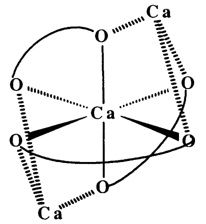
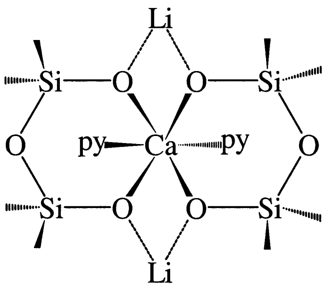
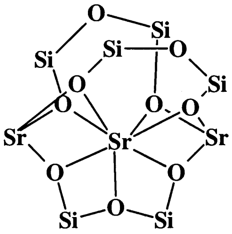
Group 2 compounds		
[{O(Ph$_2$SiO)$_2$}Mg{(OPh$_2$Si)$_3$O)$_2$}-μ-(LiTHF$_2$)$_2$] 	[O(Ph$_2$SiOLi.py)$_2$], MgCl$_2$.2THF, pyridine **cryst struct:** spirocyclic magnesiasiloxane with both 6- and 8-membered magnesiasiloxane rings and lithium bridges between the rings. **Mg-O(Si)** 1.923(3)-1.954(3) Å **Si-O(Mg)** 8-ring 1.586(3) Å **Si-O(Mg)** 6-ring 1.596(3),1.600(3) Å **Si-O(Si)** 8-ring 1.586(3)-1.641(3) Å **Si-O(Si)** 6-ring 1.596(3)-1.641(3) Å **Si-O-Si$_{mean}$** 8-ring 158.8(2) ° **Si-O-Si** 6-ring 133.2(3) ° **Si-O-Mg$_{mean}$** 8-ring 142.2(2) ° **Si-O-Mg$_{mean}$** 6-ring 123.5(2) ° **O-Mg-O** 6,8-ring 104.53(14), 114.85(14) °	29
[Mg{O(Ph$_2$SiO)$_2$}$_2$]-μ-(Lipy)-μ-{(Lipy)$_3$(OH)(Cl)} 	Ph$_2$Si(OH)$_2$, BuLi, MgCl$_2$.2THF, pyridine **cryst struct:** spirocyclic magnesiasiloxane with two 6-membered rings having a lithium bridge between the rings on one side and a fused MgLi$_3$O$_2$Cl(OH) cubane fragment on the other.	34
Ca$_3${O(Ph$_2$SiO)$_2$}$_3$(H$_2$O)$_2$py$_4$ 	[O(Ph$_2$SiONa)$_2$, CaCl$_2$, pyridine **cryst struct:** tris chelate octahedron with three calciadisiloxane rings, bicapped with solvated calcium. **Ca-O(Si)** 2.363(6)-2.390(6) Å **Si-O(Si)** 1.588(7)-1.653(8) Å **Si-O-Si** 135.8(4) - 141.3(4) ° **O-Ca-O** in 6-rings 90.0(2), 88.0(2), 89.3(2) °	59

Table 10

Group 2 compounds contd.		
[py$_2$Ca{O(Ph$_2$SiO)$_2$}$_2$-μ-(Lipy)$_2$] 	i) [O(Ph$_2$SiOLi.py)$_2$, CaCl$_2$,pyridine *or* ii) Ph$_2$Si(OH)$_2$, BuLi, CaCl$_2$, pyridine **cryst struct:** spirocyclic calciasiloxane with 6-membered rings and lithium bridges between the rings. **Ca-O(Si)** 2.363(6)-2.390(6) Å **Si-O(Si)** 1.588(7)-1.653(8) Å **Si-O-Si** 135.8(4)-141.3(4) ° **O-Ca-O** (in 6-rings) 90.0(2),88.0(2), 89.3(2) °	59
[Ca{O(Ph$_2$SiO)$_2$}(H$_2$O)(NH$_3$)$_{0.33}$]	Ca(s), NH$_3$, Ph$_2$Si(OH)$_2$ ^{29}Si (C$_5$D$_5$N) δ -46.9 ^{29}Si CP/MAS δ -44.4	31
[Sr{O(Ph$_2$SiO)$_2$}(H$_2$O)(NH$_3$)$_{0.33}$]	Sr(s), NH$_3$, Ph$_2$Si(OH)$_2$ ^{29}Si (C$_5$D$_5$N) δ -47.2 ppm ^{29}Si CP/MAS δ -43.2, -46.0, -48.1	31
[Sr$_3${O(Ph$_2$SiO)$_2$}$_3$(tetraglyme)$_2$] 0.5C$_6$H$_5$Me 	Sr{O(Ph$_2$SiO)$_2$}(H$_2$O)(NH$_3$)$_{0.33}$, tetraglyme **cryst struct:** distorted trigonal prism tris chelate with three strontiasiloxane rings; bicapped with solvated strontium **Sr-O(Si)** 2.414(6)-2.608(6) Å **Si-O-Si** 145.4(2)-163.7(7) ° **O-Sr-O** 6 rings 98.1(2), 88.7(2) ° **Sr-O-Si** 6 rings 117.2(3)-126.9(3) ° ^{29}Si (C$_5$D$_5$N) δ -47.9	31
[Sr$_3${O(Ph$_2$SiO)$_2$}$_3$(hmpa)$_5$] .C$_6$H$_5$Me	Sr{O(Ph$_2$SiO)$_2$}(H$_2$O)(NH$_3$)$_{0.33}$, hmpa ^{29}Si (C$_5$D$_5$N) δ -48.9 ^{29}Si CP/MAS δ -47.2, 49.6, -50.7 (1:4:1)	31
[Ba{O(Ph$_2$SiO)$_2$}(H$_2$O)(NH$_3$)$_{0.33}$]	Ba(s), NH$_3$, Ph$_2$Si(OH)$_2$ ^{29}Si (dmso-d$_6$) δ -51.3	25

The *t*-butyl substituted diol, $[O(t\text{-Bu}_2SiOH)_2]$, has been used for the preparation of the acyclic $[O(t\text{-Bu}_2SiOReO_3)_2]$ (from Re_2O_7) [35], and spirocyclic $[Sn\{O(t\text{-Bu}_2SiO)_2\}_2]$ (from $SnCl_4$) [14]. In both cases the diolate is transferred intact. A number of trisiloxanediols are available which can be readily converted to the corresponding alkali metal derivatives e.g. $[\{Me_2Si(Ot\text{-Bu}_2SiOH)_2\}]$ [28].

2.4. Alkalimetal α,ω-siloxane diolates, $[MO(R_2SiO)_nM]$; M = Li, Na

A relatively large number of metallasiloxanes are accessible from the alkalimetal α,ω-siloxane diolates, $[MO(R_2SiO)_nM]$ (M = Li, Na). The reagents themselves are

Table 11

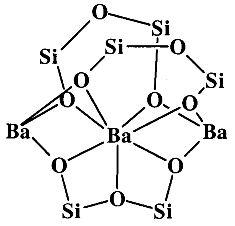
Group 2 compounds contd.		
$[Ba_3\{O(Ph_2SiO)_2\}_3(hmpa)_5(H_2O)]$ 	$Ba\{O(Ph_2SiO)_2\}(H_2O)(NH_3)_{0.33}$, hmpa **cryst struct:** distorted trigonal prism tris chelate with three bariasiloxane rings bicapped with solvated barium. **Ba-O(Si)** 2.671(19)-2.957(21) Å **Si-O(Ba)** 1.558(21)-1.594(23) Å **Si-O(Si)** 1.588(7)-1.653(8) Å **Si-O-Si** 146.2(14),153.0(15),164.3(14) ° **Ba-O-Si** in 6-rings 99.6(10)-119.9(10) ° **O-Ba-O** in 6-rings 86.0(6)-105.3(6) °	25
$[Ba_3\{O(Ph_2SiO)_2\}_3(tetragylme)_2]$	$Ba\{O(Ph_2SiO)_2\}(H_2O)(NH_3)_{0.33}$, tetraglyme **cryst struct:** distorted trigonal prism tris chelate with three bariasiloxane rings bicapped with solvated barium. **Ba-O(Si)** 2.69(1)-2.82(1) Å **Si-O(Si)** 1.588(7)-1.653(8) Å **Si-O-Si** 151(1) - 175(1) °	25
$[Ba\{O(Me_2SiO)_2\}\{O(Me_2SiO)_3\}(py)_3]$ **$\{Y(tmhd)_2\}_2$ (Htmhd = 2,2,6,6-tetramethylene-3,5-heptanedione**	Ba(s), $Y_5(O^iPr)_{13}$, siloxanes **cryst struct:** spirocyclic bariasiloxane with both 6- and 8-membered rings; solvated yttrium bridges between rings	60

Table 12
Periodic group listings of compounds: selected details on synthesis and structure of metallasiloxanes having ligands $[R_2SiO_2]^{2-}$ or $[O(R_2SiO)_n]^{2-}$

Group 13 compounds		
$[PhBO(Ph_2SiO)_2]$	$O(Ph_2SiCl)_2$, $PhB(OH)_2$, NEt_3, **cryst struct:** planar 6-membered ring **B-O(Si)** 1.3696(20) Å **Si-O(B)** 1.6388(13) Å **Si-O(Si)** 1.6363(9) Å **O-B-O** 120.79 ° **Si-O-Si** 127.13(10) ° **B-O-Si** 128.89(14) ° ^{29}Si ($CDCl_3$) δ -30.8 ^{29}Si (C_6D_6) δ -30	12,13
$[PhBO(Me_2SiO)_2]$	$O(SiMe_2Cl)_2$, $PhB(OH)_2$, NEt_3 ^{29}Si ($CDCl_3$) δ -3.3 ^{29}Si (C_6D_6) δ -3.0	27
$[PhBO(Ph_2SiO)_3]$	$[Cl(OSiPh_2)_2Ph_2SiCl]$, $PhB(OH)_2$, NEt_3 **cryst struct:** puckered 8-membered ring **B-O(Si)** 1.352(6), 1.366(6) Å **Si-O(B)** 1.626(3) Å **Si-O(Si)** 1.619(3)-1.630(3) Å **O-B-O** 122.1(4) ° **Si-O-Si** 144.7(1), 149.1(2) ° **B-O-Si** 148.6(3), 149.4(3) ° $^{29}Si(C_6D_6)$ δ $-40.3_{Si\beta}$, δ $-42.8_{Si\alpha}$	27
$[PhBO(Ph_2SiO)_4]$	$[Cl(OSiPh_2)_3Ph_2SiCl]$, $PhB(OH)_2$, NEt_3 $^{29}Si(C_6D_6)$ δ $-43.6_{Si\beta}$, δ $-45.0_{Si\alpha}$	27
$[PhBO(PhMeSiO)_2]$	$O(PhMeSiCl)_2$, $PhB(OH)_2$, NEt_3 ^{29}Si ($CDCl_3$) δ -16.5	27
$[PhBO(Me_2SiO)_3]$	$Me_2Si(OMe_2SiCl)_2$, $PhB(OH)_2$, NEt_3 ^{29}Si (C_6D_6) δ $-16.2_{Si\beta}$, $-17.3_{Si\alpha}$	27
$[Me_2Si(Ot\text{-}Bu_2SiO)_2BF]$	$[\{Me_2Si(Ot\text{-}Bu_2SiOH)_2\}]$, BuLi, BF_3 **cryst struct:** 8-membered ring **B-O(Si)** 1.320(3), 1.313(2) Å **Si-O(B)** 1.626(1),1.635(2) Å **Si-O(Si)** 1.612(1)-1.620(1) Å **O-B-O** 126.3(2) ° **Si-O-Si** 151.3(1), 163.6(1) ° **B-O-Si** 146.6(1) ° $^{29}Si(C_6D_6)$ δ -22.8	28

readily formed on treatment of the parent diol compounds with BuLi or sodium metal (the compound, $[O(Me_2SiONa)_2{\cdot}4H_2O]$ [37] however was synthesised by treatment of the tetrasiloxane $(Me_2SiO)_4$ with NaOH. Several of these compounds have been structurally characterised e.g. $[O(Ph_2SiOLi{\cdot}L)_2]_n$ L = py, 1.4-dioxan [36] DABCO, 4.4′-bipyridine [38]; $[O(Me_2SiONa)_2{\cdot}4H_2O]_n$ [37];

Table 13

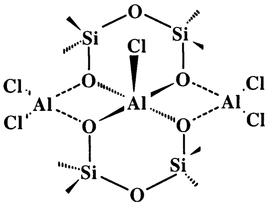
Group 13 compounds contd.		
$[PhBO(Me_2SiO)_4]$	$[Cl(OSiMe_2)_3Me_2SiCl]$, $PhB(OH)_2$, NEt_3, $^{29}Si(C_6D_6)$ δ -18.7$_{Si\beta}$, δ -19.7$_{Si\alpha}$	27
$[\{t\text{-}Bu_2SiO_2\}BPh]_2$	$t\text{-}Bu_2Si(OH)_2$, $PhBCl_2$, **cryst struct:** planar 8-membered ring **B-O(Si)** 1.350(4), 1.350(5) Å **Si-O(B)** 1.630(3)-1.631(2) Å **O-B-O** 122.8(3) ° **O-Si-O** 111.5(1) ° **B-O-Si** 149.1(3) ° $^{29}Si(CDCl_3)$ δ -23.6	7
$[Al_3\{O(Me_2SiO)_2\}_2Cl_5]$  	$(Me_2SiO)_4$, Al_2Cl_6 **cryst struct:** spirocyclic aluminasiloxane, with AlCl at the spiro site, and 6-membered aluminadisiloxane rings bridged by $AlCl_2$ groups. **Al-O(Si)** 1.872(2)-1.899(2) Å **Si-O(Al)** 1.628(1)-1.630(1) Å **Si-O(Si)** 1.683(1)-1.696(1) Å **Si-O-Si** 130.6(1), 136.4(4) ° **Al-O-Si** 130.50(7)-132.69(7) ° **O-Al-O** (in 6-rings) 94.5(1), 92.7(1) °	45
$[Al_3\{O(Me_2SiO)_2\}_2Br_5]$	$(Me_2SiO)_4$, $AlBr_3$ **cryst struct:** structure same as related chloro derivative above **Al-O(Si)** 1.72(4)-1.94(2) Å **Si-O(Al)** 1.66(3)-1.76(3) Å **Si-O(Si)** 1.60(3)-1.76(3) Å **Si-O-Si** 130.6(15) ,136.4(16) ° **Al-O-Si** 126.8(19)-133.9(15) ° **O-Al-O** in 6-rings 94.5, 92.7 °	19

Table 14

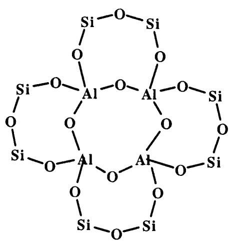
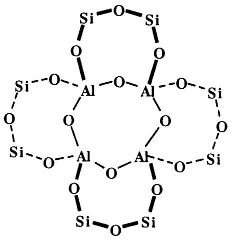
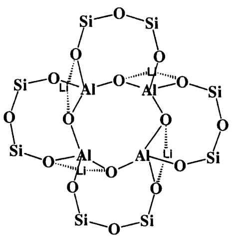
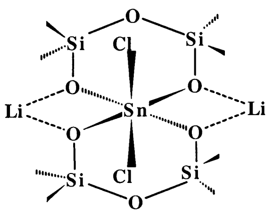
Group 13 compounds contd.		
$[Al(OH)\{O(Ph_2SiO)_2\}]_4.4Et_2O$ 	$AlH_2(Ot\text{-}Bu)$, $Ph_2Si(OH)_2$ **cryst struct:** pentacyclic molecule with central $(AlOH)_4$ eight membered ring with disiloxanediolate bridging adjacent AlOH Al edges **Al-O(Si)** mean, 1.604(3) Å **Si-O(Si)** mean 1.631(3) Å **Si-O-Si** 144.8(2) ° **Al-O-Si$_{mean}$** 157.6(2) ° $^{29}Si(C_6D_6)$ δ -44.1	23
$[Al_4O_2(OH)_2\{O(Ph_2SiO)_2\}_4]$. $2HNEt_3$ 	$[Al(OH)\{O(Ph_2SiO)_2\}]_4.4Et_2O$, NEt_3 **cryst struct:** pentacyclic structure with central $(AlOAl(OH))_2$ 8-membered ring cation $HNEt_3^+$ interacts with ring hydroxyls. **Al-O(Si)$_{mean}$** 1.604(4) Å **Si-O(Si)$_{mean}$** 1.625(5) Å **Si-O-Si** 147.2(3) ° **Al-O-Si$_{mean}$** 149.5(3) ° $^{29}Si(C_6D_6)$ δ -45.9 ^{29}Si CP/MAS δ -47	23
$[Al(OLi)\{O(Ph_2SiO)_2\}]_4$. $4Et_2O$ 	$[Al(OH)\{O(Ph_2SiO)_2\}]_4.4Et_2O$,PhLi **cryst struct:** pentacyclic molecule with central $(AlO)_4$ eight membered ring; disiloxanediolate bridging adjacent AlOAl fragments and lithium bridges between the oxygen in the$(AlO)_4$ ring and oxygens in the dialumina- tetrasiloxane rings. **Al-O(Si)** 1.736(4), 1.799(4) Å **Si-O(Al)** 1.605(4), 1.593(4) Å **Si-O(Si)** 1.630(5), 1.631(5) ° $^{29}Si(C_6D_6)$ δ -45.93	24
$[Al(OH)\{O(Ph_2SiO)_2\}]_4.4Py$	$[Al(OH)\{O(Ph_2SiO)_2\}]_4.4Et_2O$, Py **Cryst struct:** pentacyclic molecule with central $(Al(OH))_4$ 8-membered ring; disiloxanediolate bridging adjacent AlOAl fragments. **Al-O(Si)** 1.703(2) Å, **Si-O(Al)** 1.594(2), 1.586(2) Å **Si-O(Si)** 1.633(2), 1.632(2) Å **Si-O-Si** 147.23 ° **Al-O-Si** 154.4(1), 166.5(1) ° $^{29}Si(C_6D_6)$ δ -45.98	24

Table 15
Periodic group listings of compounds: selected details on synthesis and structure of metallasiloxanes having ligands $[R_2SiO_2]^{2-}$ or $[O(R_2SiO)_n]^{2-}$

Group 14 compounds		
$[Me_2GeOPh_2SiO]_2$	Me_2GeCl_2, $Ph_2Si(OH)_2$, NEt_3 **cryst struct:** puckered 8-membered rings **Ge-O(Si)** 1.758(1)-1.785(1) Å **Si-O(Ge)** 1.590(1), 1.615(1) Å **Ge-O-Si** 137.1, 141.1 °	61
$[Ph_2GeOPh_2SiO]_2$	Ph_2GeCl_2, $Ph_2Si(OH)_2$, NEt_3 **cryst struct:** puckered 8-membered ring. Si and Ge disordered	61
$[\{Ph_2Ge\}_2\{O(Ph_2SiO)_2\}]$	$(ClPh_2Ge)_2$, $Ph_2Si(OH)_2$,NEt_3, **cryst struct:** slightly puckered 7-membered ring with Ge-Ge bond. **Ge-O(Si)** 1.775(1)-1.779(1) Å **Si-O(Ge)** 1.612(1), 1.622(1) Å **Si-O(Si)** 1.607(1) Å **Si-O-Si** 157.9(2) ° **Ge-O-Si** 143.2(1), 145.3(1) °	22
$[Cl_2Ge(Ot\text{-}Bu_2SiO)]_2$	$t\text{-}Bu_2Si(OH)_2$, $GeCl_4$ **cryst struct:** planar 8-membered ring **Ge-O(Si)** 1.691(4), 1.704(3) Å **Si-O(Ge)** 1.648(4), 1.624(4) Å **Si-O-Si** 147.2(3) °	7
$[Me_2Si(Ot\text{-}Bu_2SiO)_2GeMe_2]$	$Me_2Si(Ot\text{-}BuSiOLi)_2$, Me_2GeCl_2 $^{29}Si(CDCl_3)$ δ -19.4($t\text{-}Bu_2Si$), -22.4(Me_2Si)	62
$[Me_2Si(Ot\text{-}Bu_2SiO)_2GeCl_2]$	$Me_2Si(Ot\text{-}BuOLi)_2$, $GeCl_4$	62
$[Me_2Sn(Ot\text{-}Bu_2SiO)]_2$	Me_2SnCl_2, $t\text{-}Bu_2Si(OLi)_2$ $^{29}Si(CDCl_3)$ δ -23.5	62

Table 16

Group 14 compounds contd.		
$[Cl_2Sn\{O(Ph_2SiO)_2\}_2)$-μ-$(Li(THF)_2)_2]$  	$SnCl_4$, $\{O(Ph_2SiOLi)_2\}$ **cryst struct:** spirocyclic stannasiloxane, $SnCl_2$ at the spiro site, with 6-membered stannadisiloxane rings bridged by solvated lithium groups. **Sn-O(Si)** 2.041(4),2.053(4) Å **Si-O(Sn)** 1.616(4), 1.622(4) Å **Si-O(Si)** 1.624(4), 1.625(4) Å **Si-O-Si** 141.8(3) ° **Sn-O-Si** 130.0(2), 131.1(2) ° **O-Sn-O** in 6-rings 98.1(2) ° ^{29}Si(toluene-d_8) δ -34.6	42
$[O(Ph_2SiOSn\ Ph_3)_2]$	Ph_3SnOH, $O(Ph_2SiOH)_2$, pyridine **cryst struct:** acyclic structure with disiloxane diolate bridging two Ph_3Sn groups **Sn-O(Si)** 1.96(1), 1.93(2) Å **Si-O(Sn)** 1.59(1) Å **Si-O(Si)** 1.61(1) Å **Si-O-Si** 165.4(10) ° **Sn-O-Si** 140.0(8), 142.7(9) ° $^{29}Si(CDCl_3)$ δ -43.0	15
$[O(Ph_2SiOSnBu_3)_2]$	Bu_3SnCl, $\{O(Ph_2SiONa)_2\}$ $^{29}Si(CDCl_3)$ δ -45.3	15
$[O(Me_2SiOSn\ Bu_3)_2]$	Bu_3SnCl, $\{O(Me_2SiONa)_2\}$ $^{29}Si(CDCl_3)$ δ -19.9	15
$[O(Me_2SiOSn\ Ph_3)_2]$	Ph_3SnCl, $\{O(Me_2SiONa)_2\}$ $^{29}Si(CDCl_3)$ δ -17.0	15
$[O(Ph_2SiOSnCy_3)_2]$	Cy_3SnCl, $O(Ph_2SiOH)_2$ $^{29}Si(CDCl_3)$ δ -19.0	15

[$\{O(Ph_2SiONa)_2\}_4\cdot(NaOH)\cdot7py(H_2O)$] [21]. Of the compounds within the class [$O(R_2SiOM)_2$] (M = Li, Na), the phenyl substituted analogue has received the most widespread attention. Studies involving these reagents with various precursor target metal compounds have led to a variety of interesting observations concerning ligand behaviour:

1. Intact transfer of the diolate ligand may occur to afford compounds with chelate-bridging coordination modes, e.g. [$Cr\{O(Ph_2SiO)_2\}_2$)-μ-($NaTHF_2)_2$] [18], [$Co\{O(Ph_2SiO)_2\}_2$-μ-$(LiTMEDA)_2$] [39], and [$Cu\{O(Ph_2SiO)_2\}_2$)-μ-$(Lipy)_2$] [40] (simple chelate [12] or bridging modes [15] were found in compounds derived from $O(Ph_2SiOH)_2$).
2. Transfer of the diolate ligand may occur with chain expansion to the trisiloxanenediolate $Ph_2Si(OSiPh_2O)_2{}^{2-}$ moiety; this in turn, may adopt a chelate or

Table 17

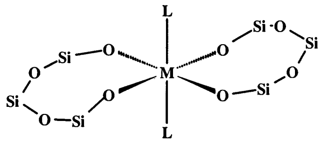
Group 14 compounds contd.		
[$t\text{-}Bu_2SnO(Ph_2SiO)_2]_n$	$t\text{-}Bu_2SnCl_2$, $O(Ph_2SiOH)_2$ **cryst struct**: polymeric chain **Sn-O(Si)** 1.952(2), 1.958(2) Å **Si-O(Sn)** 1.589(3), 1.1.594(3) Å **Si-O(Si)** 1.6089(9), 1.6111(9) Å **Si-O-Si** 180.0 ° **Sn-O-Si** 140.0(8), 142.7(9) ° $^{29}Si(CDCl_3)$ δ -35.9	64
[$(THF)_2Sn\{O(Ph_2SiO)_3\}_2$] 	$SnCl_4$, $\{O(Ph_2SiONa)_2\}$ **cryst struct**: THF solvated bis-chelate with 8-membered puckered stannasiloxane rings in trans- orientation. **Sn-O(Si)** 1.972(2) Å **Si-O(Sn)** 1.593(2), 1.597(2) Å **Si-O(Si)** 1.606(2)-1.635(2) Å **Si-O-Si** 149.09(12), 164.14(14) ° **Sn-O-Si** 153.2(7)-154.3(5) ° **O-Sn-O** in 8-rings 90.42(7) ° $^{29}Si(toluene\text{-}d_6)$ δ $-37.7_{Si\beta}$, $-40.6_{Si\alpha}$	42
[$Sn\{O(t\text{-}Bu_2SiO)_2\}$]	$SnBr_4$, $O(t\text{-}Bu_2SiOLi)_2$ $^{29}Si(C_6D_6)$ δ -8.36	11

Table 18
Periodic group listings of compounds: selected details on synthesis and structure of metallasiloxanes having ligands $[R_2SiO_2]^{2-}$ or $[O(R_2SiO)_n]^{2-}$

Transition Metal compounds

Group 4 compounds

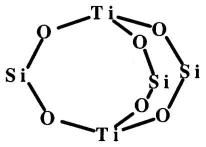
Metallasiloxane	Comments	Reference
$[Ti(acac)_2OSiPh_2O]_2$	$Ti(OPr^i)_4$,$Ph_2Si(OH)_2$,acetylacetone, dioxane **cryst struct:** near planar 8-membered ring **Ti-Si(O)** 1.821(5),1.806(5) Å **Si-O** 1.620(4),1.624(5) Å **Ti-O-Si** 154.9(2), 156.4(3) ° ^{29}Si NMR (thf) δ -48.8(solid state) δ -49.0	54
$Ti(acac)O_{1.5}]_2(OSiPh_2)_3]$. $2C_4H_8O$  	$Ti(OPr^i)_4$,$Ph_2Si(OH)_2$,acetylacetone, THF **cryst struct:** bicyclic with two 8-membered rings **Ti-Si(O)** 1.787(3)-1.836(4) Å **Si-O** 1.616(4)-1.631(4) Å **Ti-O-Si** 141.6(2)-161.9(2) ° ^{29}Si NMR (thf) δ -47.6	54
$[ClCp^*Ti\{OPh_2SiO\}]_2$	Cp^*TiCl_3, $Ph_2Si(OLi)_2$ **cryst struct:** non-planar 8-membered ring **Ti-O(Si)$_{mean}$** 1.809(4) Å **Si-O(Ti)** 1.625(4)-1.631(3) Å **Ti-O-Si** 155.6(2)-163.2(2) ° **O-Si-O** 109.5(2), 109.6(2) º **O-Ti-O** in 8-ring 108.3(1) 104.7(2) º	33
$[ClCpTi\{Ot\text{-}Bu_2SiO\}]_2$	i) $[Cl_2Ti\{Ot\text{-}Bu_2SiO\}]_2$, CpNa ii) $CpTiCl_3$, $t\text{-}Bu_2Si(OH)_2$ **cryst struct:** non-planar 8-membered ring, Cp substituents on opposite sides of ring **Ti-O(Si)$_{mean}$** 1.788(7) Å **Si-O(Ti)** 1.645(2)-1.642(2) Å **Ti-O-Si** 162.5(1), 163.4(1) ° **O-Si-O** 105.8(1) º **O-Ti-O** in 8-ring 103.0(1) º	33

Table 19

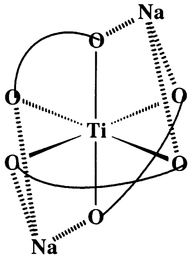
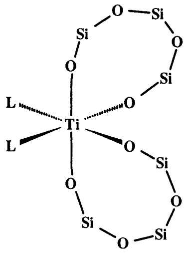
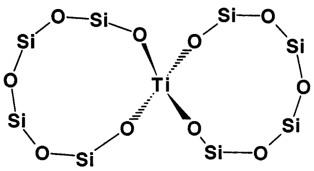
Group 4 compounds contd.		
$[Ti\{O(Ph_2SiO)_2\}_2]$	$TiCl_4$, $O(Ph_2SiOH)_2$, pyridine	53,54
$[Ti\{O(Ph_2SiO)_2\}_3)$-μ-$(Na(py))_2]$ 	$TiCl_4$, $O(Ph_2SiONa)_2$, pyridine **cryst struct:** near planar 6-membered titannasiloxane rings in solvated-Na-capped *tris* chelate **Ti-Si(O)** $_{\mathbf{mean}}$ 1.946(7) Å **Si-O(Ti)** 1.623(4)-1.653(4) Å **Si-O(Si)** 1.606(4)-1.616(4) Å **Ti-O-Si** 138.1(3), 138.4(3) ° **Si-O-Si** 131.4(3), 129.9(3) °, 129.7(3) °	41
$[Ti\{O(Ph_2SiO)\}_3Li_2].3py]$	$Ti\{O(Ph_2SiO)_2\}_3)$-μ-$(Na(py))_2]$, LiI	41
[*cis*-$(py)_2Ti\{O(Ph_2SiO)_3\}_2]$ 	$TiCl_4$, $O(Ph_2SiOLi)_2$, **cryst struct:** Py solvated bis-chelate with 8-membered puckered titanasiloxane rings in *cis*-orientation. - octahedral geometry at Ti **Ti-O(Si)** $_{\mathbf{mean}}$ 1.855(5)Å **Si-O(Ti)** 1.603(5)-1.630(6) Å **Si-O(Si)** 1.612(5)-1.623(6) Å **Ti-O-Si** 151.5(2), 158.2(2) ° **Si-O-Si** 146.4(3)°, 156.0(3) ° **O-Ti-O** in 8-rings 95.5(2) °	26
$[Ti\{O(Ph_2SiO)_4\}_2]$ 	i) $Ti(OPr^i)_4$, $Ph_2Si(OH)_2$ ii) $Ti(OBu^t)_4$, $Ph_2Si(OH)_2$ **cryst struct:** non-planar 10-membered rings; nr. tetrahedral geometry about Ti **Ti-O(Si)** $_{\mathbf{mean}}$ 1.782(1) Å **Si-O(Ti)** 1.621(5)-1.637(5) Å **Si-O(Si)** 1.608(5)-1.635(5) Å **O-Ti-O** in 10-rings 110.0(2), 111.0(2) °	30

Table 20

Group 4 compounds contd.		
$[Br_2Ti\{Ot\text{-}Bu_2SiO\}]_2$	$TiBr_4$, $t\text{-}Bu_2Si(OH)_2$, **cryst struct:** near planar 8-membered ring; **Ti-O(Si)** $_{\mathbf{mean}}$ 1.747(3) Å **Si-O(Ti)** 1.658(3)-1.660(3) Å **Ti-O-Si** 155.4(2), 169.2(2) ° **O-Si-O** 106.6(2) ° **O-Ti-O** in 8-ring 105.4(2) °	32
$[I_2Ti\{Ot\text{-}Bu_2SiO\}]_2$	TiI_4, $t\text{-}Bu_2Si(OH)_2$	32
$[(Me_3Si)_2NClTi\{(t\text{-}BuSiO)O\}]_2$	$[Cl_2Ti\{Ot\text{-}Bu_2SiO\}]_2$, $(Me_3Si)_2NLi$	33
$[(Et_2N)_2Ti\{Ot\text{-}Bu_2SiO\}]_2$	$Ti(NEt_2)_4$, $t\text{-}Bu_2Si(OH)_2$	33
$[(Ti(acac)_2O)(OSiPh_2)_3]$	$Ti(acac)O_{1.5}]_2(OSiPh_2)_3.2C_4H_8O$,thf, H_2O **cryst struct:** near planar 8-membered ring **Ti-O(Si)**1.807(2) 1.829(2) Å **Si-O(Ti)** 1.619(2),1.622(2) Å **Si-O(Si)** 1.621(2),1.631(2) Å **Si-O-Si** 139.5(1), 155.9(1) ° **Ti-O-Si** 142.7(1), 170.3(1) °	54

chelate-bridging coordination, e.g. $[(Py)_2Ti\{O(Ph_2SiO)_3\}_2]$, [26] and $[\{O(Ph_2SiO)_2\}Mg\{O(Ph_2SiO)_3\}\text{-}\mu\text{-}(LiTHF_2)_2]$ [29].

3. The diolate may function as an oxo transfer reagent—a process that is accompanied by elimination of the cyclic trisiloxane $(Ph_2SiO)_3$ [43], e.g.

$$VCl_4 + [O(Ph_2SiOLi{\cdot}L)_2] \rightarrow VOCl_2 + (Ph_2SiO)_3 + 2LiCl$$

$$VOCl_3 + [O(Ph_2SiOLi{\cdot}L)_2] \rightarrow VO_2Cl + (Ph_2SiO)_3 + 2LiCl$$

For reactions involving the *t*-butyl substituted compound, $[O(t\text{-}Bu_2SiOLi)_2]$, intact ligand transfer is invariably observed. Interestingly, the compounds [Me_2Si(OSi-*t*-

Table 21

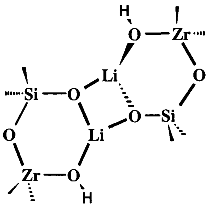
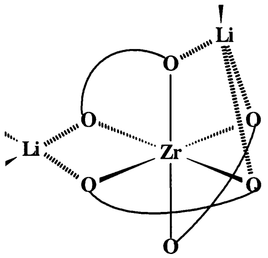
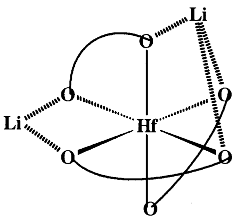
Group 4 compounds contd.		
[$Cp_2ZrOSiPh_2O]_2$	Cp_2ZrMe_2, $Ph_2Si(OH)_2$ **cryst struct:** non-planar 8-membered ring **Zr-O(Si)** $_{\text{mean}}$ 1.977(2) Å **Si-O(Zr)** 1.612(3)-1.614(3) Å **Zr-O-Si** 154.3(2)-155.4(2) ° **O-Si-O** 111.1(1), 118.8(1) ° **O-Zr-O** in 8-ring 98.5(1) °	16
$[(Cp)_2ZrOSiPh_2OLiOH]_2$	Cp_2ZrCl_2, $Ph_2Si(OLi)_2$	10
$[Cp^*{}_2ZrOSiPh_2OLiOH]_2$ 	$Cp^*{}_2ZrCl_2$, $Ph_2Si(OLi)_2$ **cryst struct:** tricyclic core consisting of two outer 6-membered rings, fused to an inner 4-membered lithiooxane ring **Zr-O(Si)$_{\text{mean}}$** 2.021(8) Å **Si-O(Zr)** 1.642(4) Å **Si-O(Li)** 1.574(4) Å **Zr-O-Si** 141.0(2) ° **O-Si-O** 112.4(2) °	10
$[Zr\{O(Ph_2SiO)_2\}_3)$-μ-$(Li)_2$.3py] 	$ZrCl_4$, $O(Ph_2SiOLi)_2$ **cryst struct:** near planar 6-membered zirconadisiloxane rings in solvated-Li-capped/bridged *tris* chelate; nr. Planar 6-membered rings; octahedral geometry at Zr **Zr-O(Si)** $_{\text{mean}}$ 2.089(2) Å **Si-O(Zr)** 1.607(7)-1.622(7) Å **Si-O(Si)** 1.615(7)-1.637(7) Å **Zr-O-Si** 132.7(3)-138.6(2) ° **Si-O-Si** 131.1(3), 132.2(3), 133.4(3) ° **O-Zr-O** in 6-rings 85.3(3)-88.1(3) °	26
$[Zr\{O(Ph_2SiO)_2\}_3)]$ $2[NEt_2H_2]$	$Zr(NEt_2)_4$, $Ph_2Si(OH)_2$ **cryst struct:** near planar 6-membered zirconasiloxane rings in dianionic *tris* chelate **Zr-O-Si** ~139 ° **Si-O-Si** ~132 ° **O-Zr-O** in 6 rings 85.9 °	14

Table 22

Group 4 compounds contd.		
$[Cl_2Zr\{Ot\text{-}Bu_2SiO\}]_2.2THF$	$ZrCl_4$, t-$Bu_2Si(OLi)_2$ **cryst struct:** Planar 8-membered ring; **Zr-O(Si)** $_{mean}$ 1.927(8) Å **Si-O(Zr)** 1.634(3)-1.635(3) Å **Zr-O-Si** 161.3(2), 169.2(2) ° **O-Si-O** 109.9(2) ° **O-Zr-O** in 8-ring 99.6(1) °	32
$[Br_2Zr\{Ot\text{-}Bu_2SiO\}]_2$	$ZrBr_4$, t-$Bu_2Si(OLi)_2$	32
$[(py)_2Zr\{O(Ph_2SiO)_3\}_2]$	$ZrCl_4$, $O(Ph_2SiONa)_2$, pyridine	41
$[Cp_2HfOSiPh_2O]_2$	Cp_2HfMe_2, $Ph_2Si(OH)_2$	16
$[Hf\{O(Ph_2SiO)_2\}_3)\text{-}\mu\text{-}Li_2.3py]$ 	$HfCl_4$, $O(Ph_2SiOLi)_2$, pyridine **cryst struct:** near planar 6-membered hafnasiloxane rings in solvated Li-capped or bridged *tris* chelate; octahedral geometry at Hf **Hf-Si(O)** $_{mean}$ 2.073(4) Å **Si-O(Hf)** 1.602(1)-1.642(1) Å **Si-O(Si)** 1.602(1)-1.663(1) Å **Hf-O-Si** 133.8(5)-141.1(5) ° **Si-O-Si** 131.9(5), 132.3(6), 133.7(7) ° **O-Hf-O** in 6-rings 85.9(4)-87.6(4) °	36
$[(py)_2Hf\{O(Ph_2SiO)_3\}_2]$	$HfCl_4$, $O(Ph_2SiONa)_2$ **cryst struct:** Py solvated bis-chelate with 8-membered puckered hafnasiloxane rings in *cis*-orientation. **Hf-Si(O)** $_{mean}$ 1.988(0) Å **Si-O(Hf)** 1.601(6)-1.606(5) Å **Si-O(Si)** 1.611(6)-1.631(6) Å **Hf-O-Si** 148.8(4), 158.9(4) ° **Si-O-Si** 129.7(3), 129.9(3), 131.4(3) ° **O-Hf-O** in 8 rings 94.4(3) °	41

$Bu_2O)_2GeCl_2$] and [{$Me_2Si(O$*t*-$Bu_2SiO)_2$}BF] are rare examples of metalla/hetero-tetrasiloxanes obtainable from an alkalimetal trisiloxanediolate source. The reagent used for these reactions, [$Me_2Si(OSi$-*t*-$Bu_2OLi)_2$], may be prepared conventionally from the parent diol and BuLi [28].

Table 23

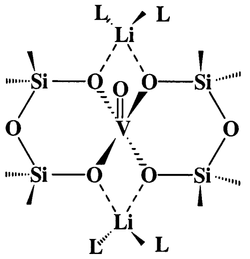
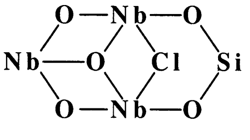
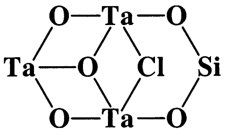
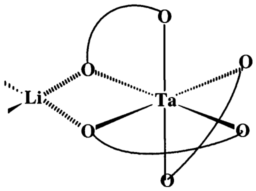
Group 5 compounds		
[VO{O($Ph_2SiO)_2$}$_2$)-μ-(LiTHF)$_2$]  	VCl_4, [O{$Ph_2SiOLi(THF)$}]$_2$ **cryst struct:** spirocyclic vanadasiloxane (VO at spiro-site) with two near planar 6-membered vanadasiloxane rings with solvated lithium bridges between the rings. **V-O(Si)$_{mean}$** 1.989(5) Å **Si-O(Si)** 1.630(5)-1.632(5) Å **Si-O(V)** 1.591(5)-1.601(5) Å **V-O-Si** 134.0(3), 135.6(3) ° **Si-O-Si** 130.1(3) ° **O-V-O** in 6-rings 90.1(2) °	57
[(t-Bu)$_2$SiO$_2$V(O)Cl]$_3$	$VOCl_3$, t-$Bu_2Si(OH)_2$ **cryst struct:** 12-membered non-planar (OVOSi)$_3$ ring **V-O(Si)$_{mean}$** 1.727(5) Å **Si-O(Si)$_{mean}$** 1.658(3) Å **V-O-Si** 141.4(2)-171.6(3) ° **O-V-O** in 6-rings 112.8(3) ° ^{29}Si ($CDCl_3$) δ -1.1(s), 0.3(s).	8
[Nb{O($Ph_2SiO)_2$}$_3$)-μ-(Lipy$_2$)]	$NbCl_5$, O($Ph_2SiOLi)_2$, pyridine	52
{t-Bu_2SiO_2[(t-Bu_2Si O(OH))$_2$ Nb] [[Cp_5H4Et NbCl]$_3$-(μ$_2$-Cl)-(μ$_2$-O)$_2$-(μ$_3$-O)-}.2C_7H_8  	$C_5Me_4EtNbCl_4$, t-$Bu_2Si(OLi)_2$ **cryst struct:** one (η^5-C_5Me_4Et}NbCl unit and two [NbO(t-BuSiOH)$_2$] units form a triangle with two sides bridged by oxygen atoms and one side bridged by a t-$BuSiO_2$ unit and Cl; additional oxygen atom covers trianglular core (as above) **Nb-O(Nb)$_{mean}$** 1.939(9) Å **Nb-O(Si)$_{mean}$** 1.882(2) Å **Si-O(Nb)** 1.654(8)-1.677(8) Å **Nb-O-Si** 141.0(5), 141.2(5) °	35

Table 24
Group 5 compounds cond.

Group 5 compounds		
[t-Bu_2SiO_2(Cp^*TaCl)$_3$-(μ_2-Cl)-(μ_2-O)$_2$-(μ_3-O)].2C_7H_8 	Cp^*TaCl_4, t-$Bu_2Si(OLi)_2$ **cryst struct:** three Cp^*TaCl units linked by two bridging oxygen atoms and bridging Cl and t-$BuSiO_2$; an additional oxygen atom 'covers' the triangular core. **Ta-O(Si)** 1.967(4) Å **Si-O(Ta)** 1.613(5) Å **Ta-O-Si** 143.1(3) °	35
[Ta{O(Ph_2SiO)$_2$}$_3$)-µ-(Lipy_2)] 	$TaCl_5$, O(Ph_2SiOLi)$_2$, pyridine **cryst struct:** near planar 6-membered tantalasiloxane rings in solvated-Li- bridged *tris* chelate; **Ta-O(Si)** $_{\mathbf{mean}}$ 1.947(3) Å **Ta-O(Li)** 2.027(4)-2.038(3) Å **Li-O(Ta)** 1.997(9)-1.999(1) Å **Si-O(Ta)** 1.604(4)-1.633(4) Å **Si-O(Si)** 1.618(4)-1.646(4) Å **Ta-O-Si** 133.9(2), 141.1(2) ° **Si-O-Si** 130.6(2), 131.6(2), 132.0(2) º **O-Ta-O** in 6-rings 85.13(14)-87.74(16) º	52

2.5. *α,ω-Siloxanedichlorides, Cl(R_2SiO)$_n$$R_2SiCl$*

α,ω-Siloxanedichloride, $Cl(R_2SiO)_nR_2SiCl$, reagents have proved particularly successful upon reaction with target element diols such as boric acids $XB(OH)_2$ (where, X = Ph, F). In these cases, simple examples of monocyclic heterosiloxane rings are usually observed, including a rare example of a monocyclic heterotrisiloxane [12,27].

2.6. *Cyclic and polysiloxanes*

α,ω-Siloxanediolate units may be abstracted by metal compounds from cyclic or polysiloxanes to give various metallasiloxanes. Several reports of compounds formed in this way have appeared in the literature, e.g.

Table 25

Group 6 compounds		
$[(t\text{-BuN})_2CrOSiPh_2O]_2$	$(t\text{-BuN})_2CrCl_2$, $Ph_2Si(OH)_2$, NEt_3 **cryst struct:** non-planar 8-membered ring; **Cr-O(Si)$_{mean}$** 1.808(4) Å **O-Si(Cr)** 1.628(5)-1.631(5) Å **Cr-O-Si** 125.2(8), 133.6(4) °	17
$[(t\text{-BuN})(O)CrOSiPh_2O]_2$	$(t\text{-BuN})_2CrCl_2$, $Ph_2Si(OH)_2$, pyridine **cryst struct:** non-planar 8-membered ring **Cr-O(Si)$_{mean}$** 1.775(4) Å **O-Si(Cr)** 1.632(4)-1.641(4) Å **Cr-O-Si** 132.2(9), 133.6(5) °	17
$[(t\text{-BuN})(O)CrO(Ph_2SiO)_2]_2$	$(t\text{-BuN})_2CrCl_2$, $O(Ph_2SiOH)_2$ **cryst struct:** non-planar 12-membered ring **Cr-O(Si)$_{mean}$** 1.768(5) Å **Si-O(Cr)** 1.629(5)-1.6306 Å **Si-O(Si)** 1.611(6)-1.623(5) Å **Cr-O-Si** 139.2(3)-141.0(3) ° **Si-O-Si** 151.8(4), 154.2(4) °	17
$[Cr(O(Ph_2SiO)_2)_2\text{-}\mu\text{-}(NaTHF_2)_2]$	$CrCl_2$, $O(Ph_2SiONa)_2$ **cryst struct:** spirocyclic chromiasiloxane with co-planar 6-membered chromiasiloxane rings solvated Na bridges between the rings; sq. planar geometry about Cr **Cr-O(Si)$_{mean}$** 1.986(6) Å **Si-O(Cr)** 1.589(6) Å **Si-O(Si)$_{mean}$** 1.637(7) Å **Cr-O-Si$_{mean}$** 131.3(3) ° **Si-O-Si** 128.0(4) ° **O-Cr-O** in 6-rings 93.2(3)	18
$[(t\text{-BuN})_2MoOSiPh_2O]_2$	$(t\text{-BuN})_2MoCl_2$, $Ph_2Si(OH)_2$, NEt_3	17

Table 26

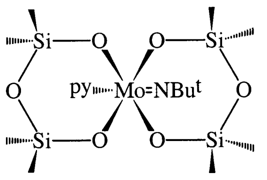
Group 6 compounds contd.		
$[(O)_2MoOSi(t\text{-}Bu)_2O]_2.2py$	MoO_2Br_2, t-$Bu_2Si(OLi)_2$, pyridine **cryst struct:** near planar 8-membered ring **Mo-O(Si)** 1.890(8) Å **Si-O(Si)** 1.631(3)-1.639(3) Å **Mo-O-Si** 147.9(2)-165.5(3) ° **O-Mo-O** 92.4(2) ° $^{29}Si(CDCl_3)$ δ -3.8	8
$[(t\text{-}BuN)Mo\{(O(Ph_2SiO)_2\}_2 .py]$ 	$(t\text{-}BuN)_2MoCl_2$, $O(Ph_2SiOH)_2$, pyridine **cryst struct:** bis-chelate with 6-membered molybdasiloxane rings	17
$[(t\text{-}BuNH)_2W[(O(Ph_2SiO)_2]_2$	i) $(t\text{-}BuNH)_2W(t\text{-}BuN)_2$, $Ph_2Si(OH)_2$ ii) $(t\text{-}BuNH)_2W(t\text{-}BuN)_2$, $O(Ph_2SiOH)_2$ **cryst struct:** bis-chelate with 6-membered tungstasiloxane rings in trans-orientation. **$W\text{-}O(Si)_{mean}$** 1.928(9) Å **Si-O(W)** 1.591(8)-1.648(2) Å **Si-O(Si)** 1.6042-1.642(2) Å **W-O-Si** 137.0(2), 137.5(4) ° **O-Si-O** 129.6(8)-133.0(6) °	17
$[(t\text{-}BuN)_2W\{Ot\text{-}Bu_2SiO\}]_2$	$(t\text{-}BuNH)_2W(t\text{-}BuN)_2$, t-$Bu_2Si(OH)_2$ **cryst struct:** near planar 8-membered $(WOSiO)_2$ tungstasiloxane ring. **$W\text{-}O(Si)_{mean}$** 1.889(3) Å **Si-O(W)** 1.606(1)- 1.626(8) Å **W-O-Si** 147.0(6) ° **O-W-O** 112.3(4) °	35

Table 27

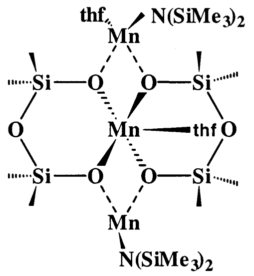
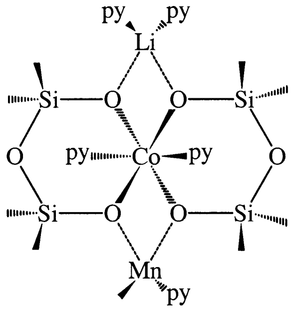
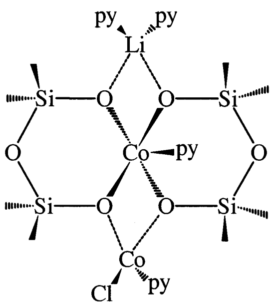
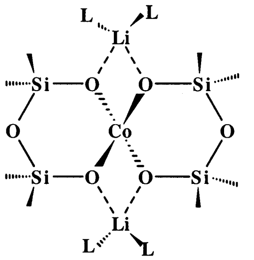
Group 7 compounds		
[Mn{O(Ph$_2$SiO)$_2$}$_2$-μ-(Mn{N(SiMe$_3$)$_2$.thf)$_2$}].thf 	[Mn{N(SiMe$_3$)$_2$}$_2$], [O(Ph$_2$SiOH)$_2$] **cryst struct:** spirocyclic cobaltasiloxane with 6-membered rings and solvated manganesesilylamide bridges between the rings. **Mn-O(Si)** in 6-rings 2.105(3)-2.155(3) Å **Si-O(Mn)** in 6-rings 1.616(2),1.621(4) Å **Si-O(Si)** 1.628(4),1.643(4) Å **Si-O-Si** 137.8(2),138.3(2) ° **Mn-O-Si** 125.3(2)-131.4(2) ° within 6-rings	35
[py$_2$Co{O(Ph$_2$SiO)$_2$}$_2$)-μ-{(Lipy$_2$)(MnClpy)}] 	1.CoCl$_2$, [O(Ph$_2$SiOLi.py)$_2$] 2.MnCl$_2$ **cryst struct:** spirocyclic cobaltasiloxane with 6-membered rings and solvated metal chloride bridges between the rings. **Co-O(Si)** in 6-rings 2.167(8), 2.17(1) Å **Si-O(Co)** in 6-rings 1.604(8), 1.593(9) Å **Si-O(Si)** 1.628(6), 1.633(7) Å **Si-O-Si** 144.7(8), 135.1(9) ° **Co-O-Si** in 6-rings 126.5(5), 126.8(6)° **O-Co-O** in 6-rings 99.2(4) °	52
[t-Bu$_2$Si(OReO$_3$)$_2$]	t-Bu$_2$Si(OH)$_2$,Re$_2$O$_7$ **cryst struct:**acyclic chain structure with bridging silane diolate **Re-O(Si)** 2.157(5)Å, **Si-O(Re)** 1.656(5), 1.674(6) Å **Re-O-Si** 168.4(5), 157.3(4)° ^{29}Si(CDCl$_3$):δ 2.9	9
[O(t-Bu$_2$SiOReO$_3$)$_2$]	O(t-Bu$_2$SiOH)$_2$, Re$_2$O$_7$ **cryst struct:**acyclic chain structure with siloxane diolate bridges between two ReO$_3$ groups. **Re-O(Si)** 1.787(8), 1.810(7) Å, **Si-O(Re)** 1.685(9), 1.680(8) Å **Re-O-Si** 165.7(6), 163.5(5) ° **Si-O-Si** 147.2(3) ° ^{29}Si(C$_6$D$_6$):δ -9.3	35

Table 28

Group 9 compounds		
$[Co\{O(Ph_2SiO)_2\}_2)\text{-}\mu\text{-}\{(Lipy)_2]$	$CoCl_2$, $[O(Ph_2SiOLi.py)_2]$	39
$[Co\{O(Ph_2SiO)_2\}_2)\text{-}\mu\text{-}\{(Lipy)\text{ -}\mu\text{-}\{(CoClpy)]$ 	$CoCl_2$, $[O(Ph_2SiOLi.py)_2]$ **cryst struct:**spirocyclic cobaltasiloxane with 6-membered rings and solvated cobalt chloride and lithium bridges between the rings. **Co-O(Si)** 1.982(7)-2.198(7) Å within 6-rings, **Si-O(Co)** 1.589(8)-1.620(8) Å within 6-rings **Si-O(Si)** 1.612(8)-1.648(8) Å **Si-O-Si** 130.3(3), 132.2(4) ° **Co-O-Si** in 6-rings 123.2(4)-130.2(3) ° **O-Co-O** in 6-rings	39
$[Co\{O(Ph_2SiO)_2\}_2)\text{-}\mu\text{-}\{(Li\ tmeda)_2]$ 	$CoCl_2$, $[O(Ph_2SiOLi.py)_2]$, tmeda **cryst struct:** spirocyclic cobaltasiloxane with 6-membered rings and solvated lithium bridges between the rings. **Co-O(Si)** 1.974(4) Å within 6-rings, **Si-O(Co)** 1.600(5) Å within 6-rings **Si-O(Si)** 1.641(4) Å **Si-O-Si** 132.7(2) ° **Co-O-Si** 120.2(2)° within 6-rings **O-Co-O** in 6-rings 91.3(2) °	39

$$(Me_2SiO)_4 + [(C_5Me_5)_2Sm(\mu\text{-}H)]_2THF]_2 \rightarrow [(C_5Me_5)_2SmTHF]_2\text{-}\mu\text{-}[O(Me_2SiO)_2]\ [44]$$

$$Al_2X_6 + (Me_2SiO)_4 \rightarrow \underset{X = Cl,\ Br}{[Al_3\{O(Me_2SiO)_2\}_2X_5]}\ [19,45]$$

$$NaOH/H_2O/EtOH + (Me_2SiO)_4 \rightarrow [O(Me_2SiONa)_2 \cdot 4H_2O]_n\ [37]$$

$$[Ag(C_6H_4CH_2NMe_2\text{-}2)]_4 + 2PPh_3/\text{silicone grease}$$

$$\rightarrow [Ag(PPh_3)(O(Me_2SiO)_2)]_2\ [46]$$

3. Features of $[R_2SiO_2]^{2-}$ and $[O(R_2SiO)_n]^{2-}$ ligand transfer with oligomerisation

Both silane diols and disiloxane diols are susceptible to oligomerisation under certain reaction conditions. This process will occur particularly in cases where the organic substituent (R) has a low steric demand. Oligomerisation may occur following prolonged storage of the diol compounds in solution (the dry, solid reagents are generally stable). Reactions utilising these reagents for the preparation of metallasiloxanes, even when conducted at low temperature, will often lead to

Table 29

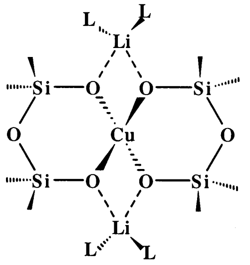
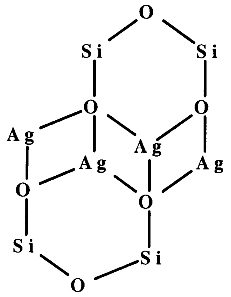
Group 10 compounds		
$[Cu\{O(Ph_2SiO)_2\}_2)$-μ-$(Lipy)_2]$ 	$CuCl_2$, $[O(Ph_2SiOLi.py)_2]$ **cryst struct:** spirocyclic cuprasiloxane with 6-membered rings and solvated metal chloride bridges between the rings. **Cu-O(Si)** within 6-rings 1.896(8)-1.944(8) Å **$Si\text{-}O(Cu)_{mean}$** within 6-rings 1.619(8) Å **$Si\text{-}O(Si)_{mean}$** 1.640(9) Å **Si-O-Si** 123.7(5) ° **Cu-O-Si** in 6-rings 123.7(5) ° **O-Cu-O** in 6-rings 95.6(4), 96.7(4) °	40
$[Ag(PPh_3)(O(Me_2SiO)_2)]_2$, 	$[Ag(C_6H_4CH_2NMe_2\text{-}2)]_4$,$PPh_3$, silicone grease **cryst struct:** pentacyclic dimer with a central stepped group of three 4-membered argentiooxane rings bridged by two disiloxanediolate ligands giving two 6-membered argentiodisiloxane rings. **Ag-O(Si)** 2.025(12)-2.376(12) Å **Si-O(Ag)** 1.564(8),1.578(8) Å **Si-O(Si)** 1.639(12),1.665(15) Å **Si-O-Si** 134.8(10) ° **Si-O-Ag** 113.0(6)-132.4(12) ° **O-Ag-O** in 6-rings 92.3(6) **Ag-O-Ag** 85.4(3)-98.3(5) ° $^{29}Si(CDCl_3$ - CH_2Cl_2-$Cr(acac)_3)$:δ -8.1, -18.9	46

Table 30

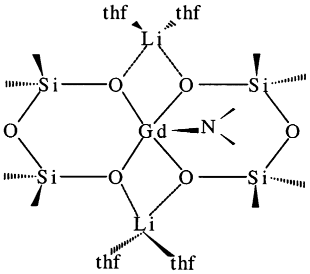
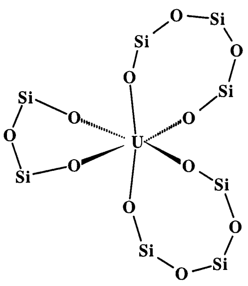
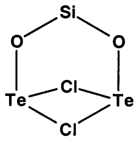
Lanthanides and others		
$[(C_5Me_5)_2SmTHF]_2$-μ-$[O(Me_2SiO)_2]$	$[(C_5Me_5)_2Sm(\mu\text{-}H)]_2THF]_2$, $(Me_2SiO)_3$ or silicone grease **cryst struct:** acyclic chain structure with disiloxane diolate bridges between two Cp*SmTHF groups. **Sm-O(Si)** 2.157(5) Å, **Si-O(Sm)** 1.601(5) Å **Si-O(Si)** 1.646(3) Å **Si-O-Si** 139.4(5) ° **Sm-O-Si** 173.6(3), 142.7(9)°	44
$[Sm\{O(Ph_2SiO)_2\}_2)$-μ-$(Li(dme))_2.(Cl)(dme)]$	$[Sm\{N(SiMe_3)_2\}_3\{LiCl(THF)_3\}_3]$, $2[O(Ph_2SiOH)_2]$ **cryst struct:** spirocyclic, disubstituted metallasiloxane comprising of two 6-membered rings (solvated Li bridges between the rings); the functional halide ligand is retained.	65
$[Gd\{O(Ph_2SiO)_2\}_2)$-μ-$(Li(THF)_2)_2$ $(N(SiMe_3)_2)]$  	$[Gd\{N(SiMe_3)_2\}_3\{LiCl(THF)_3\}_3]$, $2[O(Ph_2SiOH)_2]$ **cryst struct:** spirocyclic, disubstituted metallasiloxane comprising of two 6-membered rings (solvated Li bridges between the rings); the functional ligand $[N\{SiMe_3\}_2]$ is retained.	65
$[Eu\{O(Ph_2SiO)_2\}_3)$-μ-$\{Li(Et_2O)\}_3$	$[Eu\{N(SiMe_3)_2\}_3\{LiCl(THF)_3\}_3]$, $3[O(Ph_2SiOH)_2]$ **cryst struct:** Oh geometry at Eu centre; *tris* chelate structure with solvated metal ions between the three 6-membered siloxane rings in the manner of edge bridges in $[Zr\{O(Ph_2SiO)_2\}_3)$-μ-$(Li)_2.3py]$	65

Table 30 (Continued)

Lanthanides and others continued		
$[U\{Ph_2Si(OSiPh_2O)_2\}_2\{(Ph_2SiO)_2O\}]$ 	$[U(\eta^8\text{-}C_8H_8)_2]$, excess $[O(Ph_2SiOH)_2]$ **cryst struct:** Oh geometry at metal centre; *tris* chelate structure incorporating one $(OSiPh_2OSiPh_2O)$ ligand and two ring expanded trisiloxane diolate ligands.	65
$[t\text{-}Bu_2Si(OTeCl_3)_2]$ 	$t\text{-}Bu_2Si(OH)_2$,$TeCl_4$ **cryst struct:** cyclic structure with two chlorines and one silane diolate bridging two $TeCl_2$ centres. **Te-O(Si)** 1.880(2)Å, **Si-O(Te)** 1.709(2)Å **Te-O-Si** 147.1(1), 157.3(4)° $^{29}Si(CDCl_3)$: δ 6.5	9
$[MeSbO(Ph_2SiO)_2]_2$	$MeSb(OMe)_2$, $O(Ph_2SiOH)_2$	63
$[PhSbO(Ph_2SiO)_2]_2$	$PhSb(OMe)_2$, $O(Ph_2SiOH)_2$	63
$[PhSbO(Me_2SiO)_2]_2$	$PhSb(OMe)_2$, $O(Ph_2SiOH)_2$ $^{29}Si(CDCl_3)$: δ -13.7	63

products incorporating chain expanded siloxane units. The exact role of the target metal in promoting these oligomerisations is not easy to distinguish from oligomerisation that occurs away from the metal centre. Solutions of the siloxanediol, $[O(Ph_2SiOH)_2]$ alone or in the presence of pyridine, are stable to oligomerisation under the conditions generally employed for the preparation of the metallasiloxanes. It is noteworthy that the variable temperature (VT) NMR spectra of 1:1 mixtures of the diol compounds, $[O(Ph_2SiOH)_2]$ and $[O(C_6H_4CH_3\text{-}4)_2SiOH)_2]$ represent a direct combination of the VT spectra of the individual components [47]. Thus reversible Si–O cleavage is not observed on the NMR time-scale.

With regard to the role of the target metal in promoting ligand oligomerisation it is possible to highlight specific pairs of metal/diolate compounds that either give rise to intact transfer of a ligand or give chain expanded products. For example, the reagent combination which is employed in the following reaction will greatly affect the nature of the resulting metallasiloxane product:

$$[O(Ph_2SiOM')_2] + MCl_4 \rightarrow$$

$$M' = Li,\ Na;\ M = Ti,\ Zr,\ Hf,\ Sn$$

The dilithium reagent, $[O(Ph_2SiOLi)_2]$ gives products which result from intact transfer of ligands in reactions with MCl_4; M = Zr, Hf [41], Sn [42], but siloxane chain expanded products for M = Ti [26]. This situation is reversed when the disodium reagent is used. Furthermore, the product of the reaction with $MgCl_2$ and the dilithium reagent exhibits both intact transfer and chain expanded ligand in the same complex (both in chelate-bridging modes) which indicates that the pathways are not mutually exclusive [29]. All reactions employed similar conditions in terms of time, temperature, solvent, dilution and in each case only one compound is isolated. Relatively high isolated crystalline product yields (in terms of available silicon) can be obtained indicating a relatively high degree of product selectivity in each case. The product selectivity for specific reacting pairs $[O(Ph_2SiOLi)_2]/TiCl_4$, $[O(Ph_2SiOLi)_2]/MgCl_2$ and $[O(Ph_2SiONa)_2]/TiCl_4$ [41] persists with variations in reaction conditions like time, temperature, dilution, or solvent. Variation in reaction stoichiometry from the ideal stoichiometric precursor metal compound requirement (based on the products) does not alter the course of reactions. *Therefore, it is clear that for these cases, the observed reaction pathways are highly selective for specific reagent pairs.* These results suggest that the ligand oligomerisation which occurs *en route* to metallasiloxane compounds, depends on the combination of reagent and the target metal centre employed. However, no obvious trends associated with the reagent pairs have emerged from the observations to date which might allow us to predict the outcome for specific cases.

4. Spectroscopic properties of metallasiloxanes

4.1. Vibrational spectroscopy

Infra red data on many of the metallasiloxanes derived from α,ω-siloxane diolates, $[O(R_2SiO)_n]^{2-}$, are available. For the most part however, only tentative band assignments have been made. One particularly useful study reported the IR/Raman spectra of the compounds $[\{Ot\text{-}Bu_2SiO\}BPh]_2$, $[Cl_2Ge\{Ot\text{-}Bu_2SiO\}]_2$, $[Cl_2Ti\{Ot\text{-}Bu_2SiO\}]_2$, $[Br_2Ti\{Ot\text{-}Bu_2SiO\}]_2$, and $[I_2Ti\{Ot\text{-}Bu_2SiO\}]_2$ assigned with the aid of normal coordinate analysis of a model of the compound $t\text{-}Bu_2Si(OH)_2$ [48,49]. In these cases, strong bands in the region of 950 cm^{-1} are attributed to stretching and bending in the Si–O–M unit. In many other cases where there are $[MO(R_2SiO)_n]$ ligands present, it is common to observe additional overlapping bands in the region 1120–1000 cm^{-1} due to Si–O–Si stretching and bending vibrations; the patterns in this region vary considerably with changes in ligand coordination mode or metallasiloxane ring size. Isostructural analogues as expected usually have identical patterns in this region.

4.2. NMR spectroscopy

Solution phase NMR data is a useful structural probe for metallasiloxanes, which do not exhibit fluxional behaviour on the NMR timescale, and is an excellent tool for the detection and study of fluxionality. The available ambient temperature ^{29}Si-NMR chemical shift data for the compounds discussed within this review are given in the compound reference tables (as average values for fluxional compounds). These data are obtained for solutions of varying concentrations and solvent, which unfortunately rules out meaningful comparisons between chemical shift data. The majority of compounds containing the ligands $[O(Ph_2SiO)_2]$, $[Ph_2Si(OPh_2SiO)_2]$, or $[O(Ph_2SiO)_4]$, have chemical shift values in the range δ -40 to -50; compounds containing the ligands $[O(Me_2SiO)_2]$, $[Me_2Si(OMe_2SiO)_2]$, $[O(Me_2SiO)_4],]$, have chemical shift values in the range δ -16 to -20; and compounds containing the ligands $[Ot\text{-}Bu_2SiO]$, $[Me_2Si(Ot\text{-}Bu_2SiO)_2]$, have chemical shift values in the range δ -18 to -29. In general, the greater shielding at a given Si atom α to a metal centre (e. g. (M)O**Si**O(Si)), compared to a Si atom α to another silicon atom (e.g. (Si)O**Si**O(Si)) is reflected in the chemical shift data; with the former having the higher chemical shift values. This is anticipated from structural parameters where Si–O(M) distances are generally shorter than Si–O(Si) distances, an indication of greater electron density in the Si–O(M) bond.

Metallasiloxanes which exist as -ate- complexes with additional internally solvated cations, (particularly H^+, Li^+, or Na^+), e.g. $[K\{O(Ph_2SiO)_2SiPh_2OH\}]_2\text{-}C_6H_6$ [50], $[\{O(Ph_2SiO)_2\}Mg\{(OPh_2Si)_3O)_2\text{-}\mu\text{-}(LiTHF_2)_2]$ [29] and $[\{O(Ph_2\text{-}SiONa)_2\}_4\cdot(NaOH)\cdot 7py(H_2O)]$ [21] exhibit fluxional behaviour in solution. Lithium hopping and proton hopping processes have been invoked to explain the variable temperature spectra of the metallasiloxanes $[Hf\{O(Ph_2SiO)_2\}_3\text{-}\mu\text{-}(Li)_2\cdot 3py]$ [36], $[Ta\{O(Ph_2SiO)_2\}_3\text{-}\mu\text{-}(Lipy_2)]$ [51], and $[K\{O(Ph_2SiO)_2SiPh_2OH\}]_2C_6H_6$ [50] The Gibbs free energy of activation for the proposed two-site exchange processes is of the order of 40 kJ mol^{-1}.

5. Chemical and thermal properties

Some details on the reported chemical reactivity of the metallasiloxanes described in this review are outlined below. For metallasiloxanes derived from $[O(Ph_2SiOM)_2]$ ($M = Li$, Na), e.g. $[Co\{O(Ph_2SiO)_2\}_2\text{-}\mu\text{-}(Lipy_2)_2]$ [52], some of the metal sites are known to be substitutionally labile. Thus it is possible to exchange one of the lithium ions to give $[(Lipy_2)\text{-}\mu\text{-}pyCo\{O(Ph_2SiO)_2\}_2\text{-}\mu\text{-}(CoClpy)]$ [39] or $[(Lipy2)\text{-}\mu\text{-}py_2Co\{O(Ph_2SiO)_2\}_2\text{-}\mu\text{-}(MnClpy)]$ [52]. In addition the spiro cobalt atom in $[Co\{O(Ph_2SiO)_2\}_2)\text{-}\mu\text{-}\{(Lipy_2)_2]$ may be exchanged for copper to give $[Cu\{O(Ph_2SiO)_2\}_2)\text{-}\mu\text{-}(Lipy)_2]$.[40] Coordinating donor solvent molecules are readily exchanged with interesting consequences for structure, e.g. compare $[O(Ph_2SiOLi\cdot py)_2]_2$ with $[\{O(Ph_2SiOLi)_2\}_2\cdot 2THF\cdot 2(4,4'\text{-bipyridine})]_\infty$ [20,38], or $[Al(OH)\{O(Ph_2SiO)_2\}]_4\cdot 4Et_2O$ with $[Al_4O_2(OH)_2\{O(Ph_2SiO)_2\}_4]\cdot 2HNEt_3$, [23,24].

In general, M–O(Si) bonds in compounds described in this review are readily hydrolysed by water and the compounds are usually prepared and stored under anhydrous conditions. A ^{29}Si-NMR study on hydrolytic stability of some titanasiloxanes showed that the di-titanacylcotetrasiloxane $[Ti(acac)_2OSiPh_2O]_2$ is more stable than the spyrocyclic systems $[Ti\{O(Ph_2SiO)_2\}_2]$ [53], or $[Ti\{O(Ph_2SiO)_4\}_2]$ [30], which in turn are more stable than bicyclic systems $[Ti(acac)O_{1.5}]_2(OSiPh_2)_3\cdot 2C_4H_8O$ and $[Ti(acac)O_{1.5}]_2(OSiPh_2)_3\cdot 2C_4H_8O_2$. The parent silanols are among the hydrolysis products in each case [54].

Many of the lower molecular weight (< 1000 amu), generally monocyclic, hetero- and metallasiloxanes give molecular ions in their mass spectra. However, molecular ions are frequently not observed for metallasiloxanes with more complex polycyclic structures.

Thermal gravimetric analyses of the compounds $[Sr\{O(Ph_2SiO)_2\}(H_2O)(NH_3)_{0.33}$, and $[Sr_3\{O(Ph_2SiO)_2\}_3(\text{tetragylme})_2]$ [31], gave final residual weights much higher than expected for the metal oxide. Preparative scale pyrolysis studies on $[Co\{O(Ph_2SiO)_2\}_2)\text{-}\mu\text{-}\{(LiTMEDA)_2]$ afforded the volatile products $(Ph_2SiO)_n$, biphenyl and TMEDA. The non-volatile residue $\gamma\text{-}Co_2SiO_4$ was recovered and identified by powder diffraction. Interestingly, the compounds $[Li\{Nb\{O(Ph_2SiO)_2\}_3\}]\cdot 4LiCl\cdot 4THF$, and $[Li\{Ta\{O(Ph_2SiO)_2\}_3\}]\cdot 4LiCl\cdot 4THF$ yielded $LiMO_3$; M = Nb, and Ta as non-volatile residue when pyrolysed at temperatures between 200 and 500°C [50].

Newly developed metallocene catalyst technology for the polymerisation of α-olefins has been the focus of much attention in recent years. A wide variety of new compounds have been produced, and much emphasis placed on the production of tailor-made polymer materials. The catalysts themselves predominantly based on Group 4/6 metal centres, range from simple metallocene dichlorides to more complex chiral systems. Interestingly within this vein, the series of Group 4 cyclopentadienyl metallasiloxanes: $[Cp_2M(OSiPh_2O)]_2$, $[Cp_2M(OSiPh_2OSiPh_2O)]_2$, $[Cp_2M(OSiPh_2OSiPh_2O)]$ (where Cp = cyclopentadienyl and M = Zr) [55] have been cited, and are shown to be extremely active towards ethylene polymerisation. Catalytic activity is not restricted to metallocene systems alone. The mixtures $Zr(CH_2Ph)_4/[(O(Ph_2SiOH)_2]$ are also reported as catalysts in the patent literature

[56], and the complexes $[(py)_2Ti\{O(Ph_2SiO)_3\}]$ [26], $[VO\{O(Ph_2SiO)_2\}_2\text{-}\mu\text{-}(LiTHF)_2]$ [57], $[Cr\{O(Ph_2SiO)_2\}_2\text{-}\mu\text{-}(Lipy_2)_2]$, $[Cr\{O(Ph_2SiO)_2\}_2\text{-}\mu\text{-}(NaTHF_2)_2]$ [18] are known to catalyse ethylene polymerisation in conjunction with $AlMe_3$. Despite the reported activity nothing is known about active-cites within these systems. The design of more active/versatile metallasiloxanes for this type of application clearly depends upon a better understanding of the chemistry at the molecular level.

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