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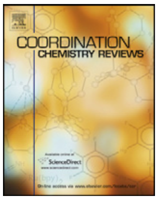

Review

Coordination complexes of silicon and germanium halides with neutral ligands

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Contents

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ABSTRACT

The coordination chemistry of silicon(IV) and (II) and germanium(IV) and (II) halides with neutral donor ligands from groups 15 (N, P or As) and 16 (O, S or Se) is reviewed; N-heterocyclic carbene complexes are also included. The focus is mainly on results published after 1990 and illustrates that significant recent developments have been made in the coordination chemistry of low-valent silicon and germanium halide complexes in particular; this is expected to pave the way for much new reaction chemistry both from a fundamental and application-driven perspective.

Abbreviations: 2,2′-bipy, 2,2′-bipyridine; 1,10-phen, 1,10-phenanthroline; Me_3-tacn, 1,4,7-trimethyl-1,4,7-triazacyclonane; Rpy, substituted pyridine; 3-Mepy, 3-methylpyridine; mi, 1-methylimidazole; vi, 1-vinylimidazole; dmi, 1,1′-dimethyl-2,2′-imidazole; hmpa, hexamethylphosphoramide; 12-crown-4, 1,4,7,10-tetraoxacyclododecane; 15-crown-5, 1,4,7,10,13-pentaoxacyclopentadecane; 18-crown-6, 1,4,7,10,13,16-hexaoxacyclooctadecane; dmso, dimethylsulfoxide; dmf, N,N-dimethylformamide; cyclam, 1,4,8,11-tetraazacyclotetradecane; Me_4-cyclam, 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane; [9]aneS_3, 1,4,7-trithiacyclononane; [14]aneS_4, 1,4,8,11-tetrathiacyclotetradecane; [18]aneS_6, 1,4,7,10,13,16-hexathiacyclooctadecane; [16]aneS_4, 1,5,9,13-tetrathiacyclohexadecane; [18]aneS_3O_3, 1,4,7-trithia-10,13,16-trioxacyclooctadecane; [15]aneS_2O_3, 14-dithia-7,10,13-trioxacyclopentadecane; [8]aneSe_2, 1,5-diselenacyclooctane; [16]aneSe_4, 1,5,9,13-tetraselenacyclohexadecane; [24]aneSe_6, 1,5,9,13,17,21-hexaselenacyclotetracosane;
NHC, N-heterocyclic carbene; pyNO, pyridine-N-oxide.

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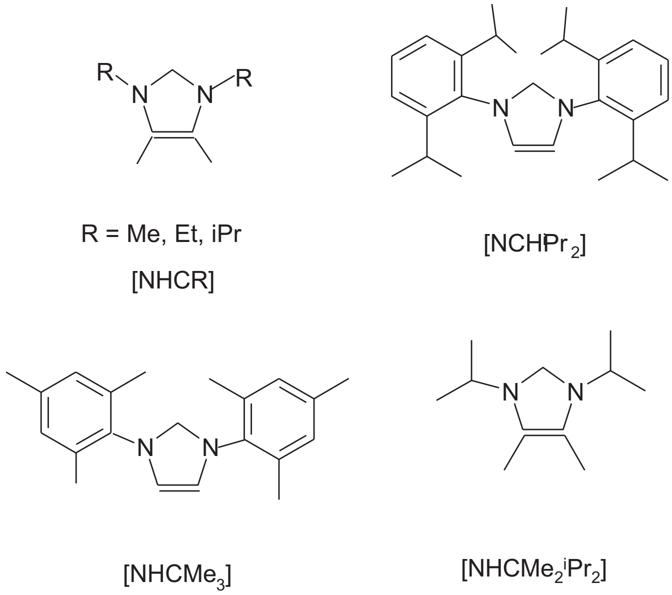
1. Introduction and scope

This review focuses on complexes of silicon and germanium Lewis acids with neutral Lewis bases, which mostly means ligands with donor atoms drawn from groups 15 (N, P, As, Sb and Bi) and 16 (O, S, Se and Te). N-heterocyclic carbene (NHC) ligands (neutral C donor ligands) are included, and an overview of haloanions (in which the Lewis base is a charged halide anion) is also provided for completeness. Organo-silicon and -germanium species, defined as compounds containing at least one Si–C or Ge–C bond, are excluded, unless of particular interest from the point of view of the Lewis base complex. In practice, the chemistry is dominated by complexes of the di- or tetra-halides, and there is a growing chemistry of divalent germanium cations, although silicon(II) complexes remain very rare.


R = Me, Et, iPr

[NHCR]

[NCH^{i}Pr$_2$]

[NHCMe$_3$]

[NHCMe$_2$^{i}Pr$_2$]

NHC = N-heterocyclic carbene (specific formulae)

The vast organic chemistry of silicon and germanium which falls outside this article has been covered in multiple reviews, for example in the three series of *Comprehensive Organometallic Chemistry* [1], in several volumes in the Patai series, *The Chemistry of Organic Functional Groups* [2,3], and other recent reviews [4,5]. The coordination chemistry of silicon and germanium has also featured in chapters in *Comprehensive Coordination Chemistry* [6] and a number of reviews [4,7–10].

The present review contains detailed coverage of silicon and germanium complexes with neutral donor ligands taken from the literature ~1990 until mid-2010, with selected earlier literature included where it contains key results or where the systems have not been revisited more recently. Whilst we have not attempted comprehensive literature citation, the aim has been to provide reasonably complete descriptions of relevant chemistry.

2. Overview of inorganic silicon and germanium chemistry

The inorganic chemistry of these two elements is dominated by compounds in formal oxidation states IV and (to a lesser extent) II, the former having a closed shell configuration, the latter a formal lone pair [11–13]. There are also a substantial number of compounds with Si–Si or Ge–Ge bonds, ranging from “sub-halides” such as Si_2Cl_6 to clusters and Zintl anions. However, such species have little or no Lewis acid/base chemistry, and indeed are often cleaved by donor ligands, and thus mostly fall outside of the scope of this review. The M(IV) state is the most important for both elements and is associated with coordination numbers 4, 5 or 6. Germanium(II) is represented by a variety of compounds often of rather limited stability, and the coordination numbers range from two in $Ge(NBu^t{}_2)_2$, through to eight in some macrocyclic complexes, and often the stereochemistry is highly distorted. Silicon(II) is found in very few compounds stable at room temperature, and compounds such as SiF_2 or $SiCl_2$ exist in low pressure vapours at high temperatures, and polymerise on condensation. It is notable that single bond energies involving silicon are often the highest in group 14 (e.g. C–F ~490, Si–F ~596, Ge–F ~471, C–Cl ~325, Si–Cl ~400 and Ge–Cl ~340 kJ mol^{-1}), although values can vary substantially with the compound, and do not simply reflect reactivities—Si–F and Si–Cl bonds are usually much more reactive than C–F or C–Cl. The electronegativities of Si and Ge are similar (Pauling scale ~1.9) as are the covalent radii, Si ~1.17 Å and Ge ~1.22 Å.

3. Halides and haloanions of silicon and germanium

The majority of compounds discussed in this review are complexes of, or prepared from, the binary halides and thus a brief account of the latter provides an appropriate starting point. The eight tetrahalides (Table 1) are well known compounds, and are commercially available. All are tetrahedral monomers in gas, solid and liquid phases, and key physical and structural data are given in Table 1. The four dihalides of germanium are well established, although GeF_2 has been little studied. The structure is a fluorine bridged polymer based upon a distorted trigonal bipyramidal GeF_4 unit with a vacant equatorial vertex, whilst the structures of GeX_2 (X = Br or I) have the germanium in distorted octahedral environments; the structure of solid $GeCl_2$ has not been determined. The SiX_2 are highly unstable and only exist in high temperature vapours at low pressures, and polymerise on condensation. There is a considerable number of other halides, either mixed oxidation state (M(II)–M(IV)) species including Ge_5F_{12}, Ge_7F_{16}, or with direct E–E bonds Si_2F_6, Si_2Cl_6 and Ge_5Cl_{12} [14–16]. Mixed $SiH_{4-x}X_x$ (X = halide) also form a limited number of complexes.

Haloanions are important only for the fluorides. The well known octahedral $[SiF_6]^{2-}$ is formed by incomplete hydrolysis of SiF_4 in water or from SiO_2 and aqueous HF, and is stable even at quite high pH. Many hexafluorosilicate(IV) structures have been determined and show near regular octahedra with d(Si–F) ~1.70 Å (see for example $[Ph_4P]_2[SiF_6]$ [17]). The $[SiF_5]^-$ ion is also well known, and is a discrete trigonal bipyramid with $d(Si–F_{ax}) > d(Si–F_{eq})$, usually isolated with large $[R_4N]^+$ cations. It is fluxional in solution at room temperature [18–21]. Both fluorosilicate anions have been observed as unexpected by-products from reactions of aggressive fluorine reagents in glass vessels [22,23]. The $[SiCl_6]^{2-}$ ion does not exist, and evidence for $[SiCl_5]^-$ is limited to some vibrational spectra attributed to this ion in mixtures of $SiCl_4$ and Et_4NCl in $MeNO_2$ solution [24], although calculations have suggested it may be thermodynamically stable [25]. The hexafluorogermanate(IV) anion is well established, and may be isolated by adding an appropriate cation to a solution of GeO_2 in aqueous HF, and many examples with non-metal cations are known, resulting from fluoride abstraction reactions of GeF_4. The anion is less stable to hydrolysis than $[SiF_6]^{2-}$, but has the expected octahedral structure (d(Ge–F) ~1.80 Å [26]). The structural chemistry of the pentafluorogermanate(1−) anion is more complicated; in $[R_4N][GeF_5]$ the anions are trigonal bipyramidal [27], but in other cases chains of fluorine bridged GeF_6 octahedra are present; and the bridging fluorines may be disposed either *cis* (as in $[ClO_2][GeF_5]$) or *trans* (as in $[XeF_5][GeF_5]$) [28]. The readily hydrolysed $[A]_2[GeCl_6]$ ([A] = Cs, Rb, R_4N, *etc.*) are made by combination of $GeCl_4$ and ACl either in concentrated aqueous HCl

Table 1
Silicon and germanium tetra- and di-halides.

	M.P. °C	B.P. °C	Structure[a]	d(M–X) Å[b]	Refs.
SiF_4		Sub −95.7	I−43m $Z = 2$ T_d molecule	1.56(1)	[c]
$SiCl_4$	−70	57.6	$P2_1/c$ $Z = 4$ T_d molecule	2.006–2.010	[d]
$SiBr_4$	5.4	154	Not known		
SiI_4	120.5	287	Pa−3 $Z = 8$ T_d molecule	2.427(2), 2.416(4)	[e]
GeF_4	−15 (4 atm)	Sub −37	I−43m $Z = 2$ T_d molecule	1.689(1)	[f]
$GeCl_4$	−49.5	83	$P2_1/c$ $Z = 4$ T_d molecule	2.093(1)–2.098(1)	[g]
$GeBr_4$	26	186	$P2_1/c$ $Z = 4$ T_d molecule	2.264–2.269	[h]
			Pa−3 $Z = 8$ T_d molecule	2.262(2), 2.267(1)	[i]
GeI_4	146	350	Pa−3 $Z = 8$ T_d molecule	2.495–2.500	[j]
GeF_2	110		$P2_12_12_1$ polymer $Z = 4$ GeF_3 pyramids	1.79, 1.91 and 2.09	[k]
$GeCl_2$	Decomposes		Not known		
$GeBr_2$	122		$P2_1/c$ $Z = 8$ distorted $GeBr_6$ octahedra	2.479–2.739	[l]
GeI_2	Decomposes		P−3m1 GeI_6 octahedra	2.811–2.865	[m]

[a] X-ray crystal structure—space group and approximate geometry stated.
[b] X-ray data from a; for many of the tetrahalides gas phase electron diffraction data also exist.
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solution or in non-aqueous media [29,30]. The anion is a near regular octahedron in $[Ph_4P]_2[GeCl_6]$ (d(Ge–Cl) = 2.283–2.298 Å [31]). The $[GeCl_5]^-$ ion was identified spectroscopically in $MeNO_2$ solutions containing $[Et_4N]Cl$ and $GeCl_4$, and subsequently $[A][GeCl_5]$ ($A = R_4N$, Ph_3C) were isolated from the constituents in $SOCl_2$ solution. The anion is trigonal bipyramidal [32,33]. Neither silicon nor germanium tetrabromide or tetraiodide appear able to form haloanions, even the crystalline solid of stoichiometry $[Et_4N]I{\cdot}2GeI_4$ contains $[Et_4N]^+$, tetrahedral GeI_4 and I^- anions [34].

Germanium(II) anions are of type $[GeX_3]^-$. The $[GeF_3]^-$ is readily obtained from GeF_2 and alkali metal fluorides in aqueous solution. In neutral or mildly basic solution it slowly air-oxidises to Ge(IV), and in strongly acidic solution hydrogen is evolved and Ge(IV) again forms [35]. The $[GeX_3]^-$ (X = Cl or Br) are obtained from $Ge(OH)_2$ and MX in aqueous HX [36], and often result from disproportionation reactions of GeX_2 with neutral ligands (L) to give $[GeX(L)_n][GeX_3]$ [37]. In the latter cases the anions are pyramidal with three Ge–X bonds and often much longer Ge···X contacts to the cations or neighbouring anions. However, in $MGeX_3$ (M = Cs, Rb, K, *etc.*) the structures are distorted perovskite with the Ge in a distorted octahedral environment. Many are polymorphic and the germanium environments exhibit quite a range of bond lengths and distortions in the different forms [36,38].

4. Bonding models and geometries

The bonding in hypervalent main group compounds remains an area of considerable debate. The problems are not specific to the silicon and germanium compounds in this review, but are much the same for any species which formally exceeds the octet of electrons around the central atom [2,4,39–43]. Earlier work simply invoked the nd orbitals on the central atom, so that in $[SiF_6]^{2-}$ the silicon was described as sp^3d^2 hybridised and forming six 2c–2e bonds to the fluorines. Whilst this model is still used by some workers and appears widely in standard undergraduate texts, recent years have seen it fall out of favour, as calculations showed the inability of the higher energy d-orbitals to make a major contribution to the bonding. A convenient alternative model invokes the electron rich 3c–4e approach. For a linear X–M–X unit, the central M uses one empty p-orbital, and combining this with one filled donor orbital on each X, one generates three molecular orbitals; bonding, nonbonding and antibonding in order of increasing energy, with the two electron pairs occupying the first two (Fig. 1).

Thus, it is possible to produce a trigonal bipyramid by using sp^2 hybrids for the equatorial MX_3 donors (2c–2e) and the p_z orbital for the axial X–M–X unit (3c–4e). An octahedron on this model uses three orthogonal p orbitals on M to form three 3c–4e bonds. When the groups around the central M are different (X–M–Y), the model can be adapted so that with the primary M–X bond with the bonding orbital polarised towards X, and the M–X antibonding orbital polarised towards M (and empty) can then behave as an acceptor orbital towards an electron pair from Y. If the X–M bonding dominates and M–Y is weak the latter is often termed "secondary bonding". Hoffmann has shown that these variants all result from the same basic model and are easily brought into correspondence [42]. For the Ge(II) and Si(II) compounds there is the extra problem of the "lone pair". The irregular coordination geometries of Ge(II) compounds do not lend themselves to simple descriptions, but a core geometry of pyramidal three-coordination is often found, which could be rationalised as due to sp^3 hybridised Ge with a stereochemically active lone pair. An alternative explanation is that the GeX_3 unit uses the three 3p orbitals and the "lone

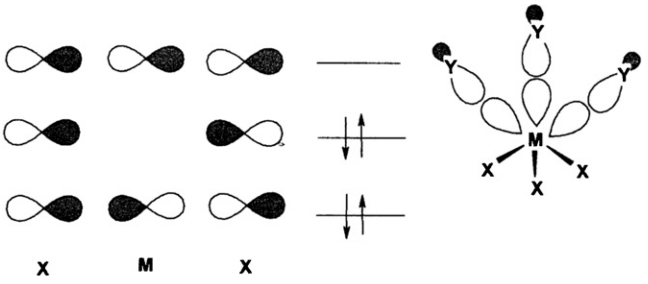

Fig. 1. 3c–4e bonding model (left) and the use of M–X σ* orbitals as acceptor orbital for M–Y bonding (right).

pair" is in the 3s orbital. Since many of the germanium(II) complexes show weaker interactions to other donors (X or Y) *trans* to X, this model is also consistent with asymmetric 3c–4e bonding, primary M–X bonding and secondary weaker M–Y(X) interaction. The central atom s–p orbital energies become increasingly disparate as group 14 is descended, and whilst the differences at silicon are relatively small, at germanium they may be becoming significant [4]. At present the bonding in germanium(II) compounds, particularly those with higher coordination numbers, is not easily rationalised and certainly merits further study.

5. Structural and spectroscopic techniques

The majority of the Ge(IV) and Si(IV) complexes described below are discrete molecular species, whereas the structures of Ge(II) complexes, although often containing a pyramidal GeL_3 unit, have irregular environments completed by long, secondary bonds. In all cases single crystal X-ray diffraction is the pre-eminent characterisation technique in the solid state. For the five- and six-coordinate complexes of the tetrahalides, IR and Raman spectroscopy focused on the M–X stretching modes usually provide reliable fingerprints and distinguish geometric isomers. In contrast, the irregular geometries and significant secondary coordination in many Ge(II) complexes, make vibrational spectroscopy of limited value, other than in special cases, e.g. for distinguishing $[GeX_3]^-$ anions. In solution, multinuclear NMR spectroscopy is the most useful technique, although often data must be acquired at low temperatures due to exchange processes, such as reversible ligand dissociation, which occur for many of the complexes at ambient temperatures. The application of ^{1}H, ^{13}C or ^{19}F NMR spectroscopy is straightforward, but in addition, both Si and Ge have NMR active isotopes, which deserve comment [44]. Silicon-29 ($I = 1/2$, 4.67%, $\Xi = 19.87$ MHz, $\gamma = -5.315 \times 10^7$ rad T^{-1} s^{-1}, $D_c = 2.09$), although of modest sensitivity is readily observed in organosilicon compounds, the major problems being the negative magnetogyric ratio, which results in signal diminution (or even nulling) in proton decoupled spectra, and the long T_1's. Use of relaxation agents such as $[Cr(acac)_3]$ or TEMPO (2,2,6,6-tetramethylpiperidine-N-oxyl) can address both problems [45]. However, in labile systems, including many of the compounds covered by the present article, it is necessary to be sure that the relaxation agent does not interact chemically with the sample. Solution lability also means that spectra will usually need to be recorded over a temperature range, or at least at low temperatures, to slow exchange processes, and as a result, ^{29}Si NMR data on coordination complexes are rather sparse. The problems of studying ^{73}Ge NMR spectra ($I = 9/2$, 7.8%, $\Xi = 3.488$ MHz, $\gamma = -0.933 \times 10^7$ rad T^{-1} s^{-1}, $Q = -0.2 \times 10^{-28}$ m^2, $D_c = 0.617$), are much greater. The nuclear properties place ^{73}Ge in the "difficult" category, the low frequency produces experimental problems such as acoustic ringing and baseline roll (which can be at least partially overcome by appropriate pulse sequences), but the quadrupolar nature and insensitivity remain as major barriers [44,46]. Thus whilst four-coordinate germanium compounds with cubic symmetry such as GeX_4 or GeR_4 are readily observed, quite small lowering of the symmetry (and hence increasing electric field gradients) can result of loss of the signal due to fast quadrupolar relaxation (resulting in extreme line-broadening). In labile coordination complexes, such problems are exacerbated and usually low temperature studies (to slow dynamic processes) will be necessary, although quadrupolar relaxation rates may also be adversely affected by temperature changes. One should also remember that for labile systems containing quadrupolar nuclei, only some of the species present in solution may give an observable resonance, and there are a number of cases in the literature where this has resulted in wrongly identified/attributed resonances. Thus it seems likely that for coordination compounds, whilst ^{29}Si NMR spectra should be observable at least at low temperatures if sufficient instrument time and concentrated solutions are available, ^{73}Ge NMR spectra will be obtainable only in a limited number of systems, and it is doubtful if they will often provide sufficiently useful data to repay the experimental effort required.

^{29}Si MAS NMR spectra of solid silicates, zeolites, *etc.* are routinely used to characterise the species present and to establish connectivities, but the technique has more rarely been applied to coordination compounds, although a number of examples will be found in subsequent sections. Studying ^{73}Ge NMR spectra of molecular compounds in the solid state is extremely challenging, and although spectra have been successfully recorded in a few cases [47,48], the effort involved almost certainly means it will not become routine in coordination chemistry.

6. Modeling of donor–acceptor bonding in group 14

Major advances in computational chemistry in the last 15 years have made it possible for DFT calculations to reliably optimise the geometries of medium-sized molecules, compare isomer stabilities, calculate bond lengths, and model vibrational and NMR spectroscopic data. There is now a considerable body of data on hypervalent silicon(IV) and to a lesser extent germanium(IV) complexes [49–61]. Much of the fine detail falls outside the scope of the present article which is focused on the synthesis and characterisation of solid complexes (the calculations are based upon gas phase molecules and ignore solvation effects in solution or intramolecular interactions in solids). Although in many cases the effects of phase on the geometries and energies will be a relatively small energy term, it can make a very significant contribution when other factors largely cancel out. Generally the calculations have predicted that five-coordinate $[SiX_4L]$ will have an axial L ligand, that the six-coordinate $[SiF_4L_2]$ are more stable than the five-coordinate $[SiX_4L]$, and that for monodentate L the $[SiF_4L_2]$ will favour *trans* geometry over *cis*, although the calculated energy differences between the isomers (gas phase) are not large. These results are generally in good agreement with experimental observations. The most important conclusions to arise from this work concern the nature of the donor–acceptor bonds and the insights into the major factors affecting "observed" Lewis acidity of silicon and germanium halides and hydrides. Whilst there are a number of factors involved in adduct formation, the two major ones are the inherent donor–acceptor bond strength and the reorganisation energy of the MX_4 unit. The reorganisation energy (molecular "floppiness") needed to convert the tetrahedral MX_4 molecule into the four-coordinate fragment of either a TBP or an octahedron in the complexes is significant, and is larger for Si than Ge for a common X. Despite the fact that the Lewis acid–Lewis base bond energies also fall from Si to Ge, this is a rather smaller fall, and the overall effect is that the germanium complexes are more stable. The stability with halide is $F > Cl > Br$, and the instability of SiH_4 adducts is believed to be significantly affected by the large reorganisation energy. In addition to rationalising the observed results with hard N-donors (the calculations are mostly focused on N-donors), these studies offer an explanation for the reluctance of hard acceptors like SiF_4 to bond to softer donors; the mismatch in orbital size and energy in these cases means that bond formation (which may still be inherently favourable, albeit much smaller in energy terms) would not pay back the high reorganisation energy of SiF_4. As reorganisation energies fall $Si > Ge$, complex formation becomes more likely.

There is very little modeling work on Ge(II) halide adducts, but the often irregular geometries, the presence of long "secondary bonding" interactions, indicative of shallow and rather flat potential wells, and the possibility of a stereochemically active lone pair, provide a very substantial challenge to the theoretician. The diffi-

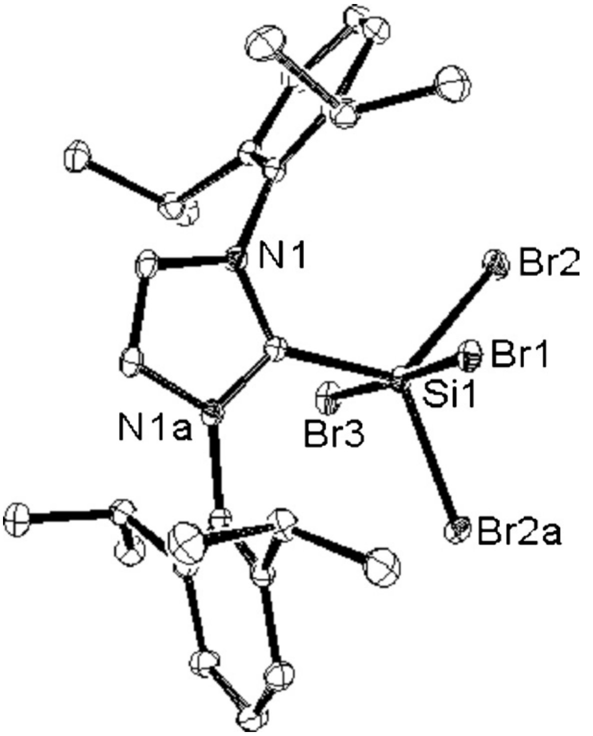

Fig. 2. Crystal structure of [$SiBr_4(NHC^iPr_2)$] [65].

culties of modeling even simple N-base adducts are discussed in Section 9, and it seems that intramolecular interactions and crystal packing may play a role in controlling the structures involved. These will be very difficult to model, not least due to the time and cost of the computational resource involved.

7. Silicon(IV) complexes

7.1. Carbon donor ligands

In keeping with the scope outlined in the Introduction, this section is limited to a discussion of Lewis base carbene ligands. Kuhn et al. [62] obtained three examples of [$SiCl_4$(NHCR)] by reaction of $SiCl_4$ and the imidazol-2-ylidenes in thf, followed by recrystallisation from pentane. They formed colourless crystals, and for R = ^iPr, the crystal structure showed a trigonal bipyramidal molecule with an equatorial carbene. Subsequently the carbene analogues with the bulky R groups 2,6-$^iPr_2C_6H_3$– were prepared (NHC^iPr_2) [63,64], and these could be reduced by KC_8 to Si(II) carbenes or compounds with Si–Si or Si=Si bonds, depending upon the reaction conditions. Reaction of $SiBr_4$ with NHC^iPr_2 in toluene gave [$SiBr_4(NHC^iPr_2)$], a trigonal bipyramidal monomer, whereas reaction in hexane gave the ionic form [$SiBr_3(NHC^iPr_2)$]Br, indicating very little difference in energy between the two structures [65,66]. The two structures are shown in Figs. 2 and 3 with significantly shorter Si–Br and Si–C distances in the cation. The chemistry of NHC^iPr_2 with SiF_4 is different again in that both the five- and six-coordinate complexes [$SiF_4(NHC^iPr_2)_x$] (x = 1,2) can be isolated, depending upon the reaction conditions [65]. Whilst the 1:1 complex has the expected TBP geometry the carbene occupies an axial rather than equatorial position found with the heavier halides, and the 2:1 complex is *trans* octahedral. Computational studies [67] predict the stabilities to lie in the order F > Cl > Br for five-coordinate complexes, but suggest little difference for six-coordination, and also that the stabilities of the carbene complexes are higher than amine or phosphine analogues, which is borne out by the experimental results.

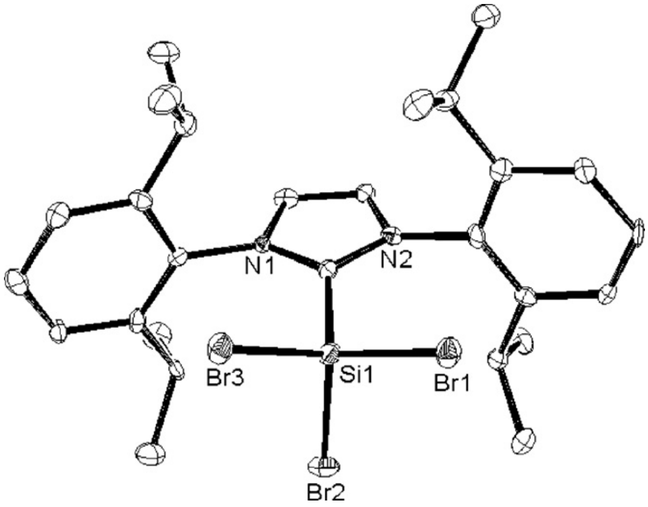

Fig. 3. Crystal structure of [$SiBr_3(NHC^iPr_2)$]$^+$ [66].

7.2. Nitrogen donor ligands

Complexes of silicon(IV) halides with neutral N-donor ligands are well known and many examples were described in the older literature [6,10]. The complexes of SiF_4 are the most stable, those with heavier halides being more dissociated in solution. The majority of complexes of SiF_4 are neutral adducts of types [SiF_4L], [SiF_4L_2] or [SiF_4(L–L)] which retain the four Si–F bonds, and examples of anions or cations are very rare. The anionic type, [SiF_5L]$^-$ (L = NH_3, Et_2NH, Me_3N, *etc.*), are made by reaction of [R_4N][SiF_5] with the amine and easily lose the amine in vacuum or in solution [27,68,69]. Crystals of [NH_4][$SiF_5(NH_3)$] were obtained by heating silicon powder with NH_4HF_2 in a sealed Monel ampoule, the structure confirming the identity of the octahedral anion [70]. Given the strength of the Si–F bond (~580 kJ mol^{-1}) it is not surprising that cleavage of a Si–F bond in SiF_4 on reaction with neutral ligands does not usually occur. However, the unique cation [$SiF_3(Me_3$-tacn)]$^+$ (Me_3-tacn = 1,4,7-trimethyl-1,4,7-triazacyclononane) as its [SiF_5]$^-$ salt, is formed by reaction of SiF_4 with Me_3-tacn in CH_2Cl_2 or toluene solution at room temperature [71]. The structure (Fig. 4) reveals the expected octahedral geometry with a facially coordinated aza-macrocycle. The solid is air stable and the anion can be exchanged for [B{3,5-$(CF_3)_2C_6H_3$}$_4$]$^-$. The driving force for this reaction appears to be the strong tendency of the aza-macrocycle to coordinate κ^3 to the silicon. The corresponding reaction of $Me_2N(CH_2)_2N(Me)(CH_2)_2NMe_2$, which is the nearest acyclic analogue to Me_3tacn, in CH_2Cl_2 solution gives [$SiF_4\{\kappa^2$-$Me_2N(CH_2)_2N(Me)(CH_2)_2NMe_2(CH_2Cl)\}$][$SiF_5$], in which only two of the amine donors are coordinated to silicon, and the third has been quaternised by the chlorocarbon solvent (Fig. 5) [71].

The study of adducts of SiF_4 with monodentate nitrogen donor ligands stretches back to $SiF_4{\cdot}2NH_3$ in 1812 (!), with many reports of [SiF_4L], [SiF_4L_2] and occasionally other stoichiometries (L = NH_3, RNH_2, R_2NH, substituted pyridine and aniline derivatives, *etc.*). Considerable uncertainty surrounds some of the earlier work due to the often very limited characterisation methods available (vapour pressure measurements, dipole moments, partial microanalytical data, sometimes IR spectra), and to the sensitivity of the systems to water. Even compounds which are relatively robust as solids must be prepared under anhydrous conditions to avoid formation of ammonium fluorosilicates [10]. In the last 20 years thorough re-examination of several of these systems has been undertaken both for their fundamental interest, and their possible use as pre-

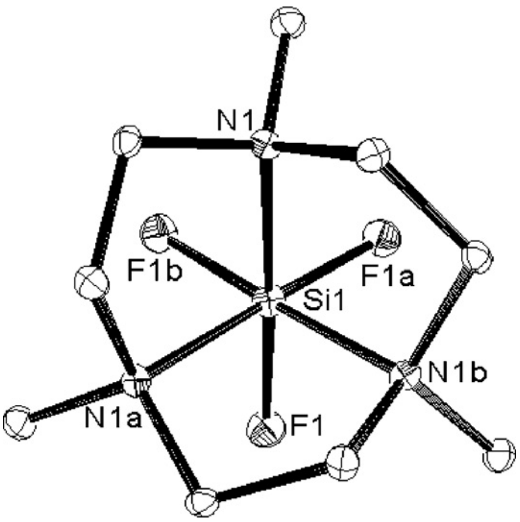

Fig. 4. Crystal structure of $[SiF_3(Me_3\text{-tacn})]^+$ [71].

cursors to silicon nitride materials. The systems have also proved popular with theoreticians, testing developments in computational methods (Section 6).

The simplest system SiF_4/NH_3 was reported to form both $[SiF_4(NH_3)]$ and $[SiF_4(NH_3)_2]$ (variously described as the *cis* or *trans* isomer) complexes. Detailed studies showed that $[SiF_4(NH_3)]$ was only stable $<-50\,^{\circ}C$ and had a trigonal bipyramidal structure with axial ammonia [72,73]. Matrix-isolation studies in noble gas matrices confirmed the formation of this 1:1 adduct at low temperatures. On warming it disproportionates into SiF_4 and $[SiF_4(NH_3)_2]$; the latter is stable at ambient temperatures and has been shown both by X-ray crystallography and IR spectroscopy to be the *trans* isomer [70,72,74,75]. More recently the reaction of SiF_4 with liquid ammonia has been shown to afford $[SiF_4(NH_3)_2]\cdot 2NH_3$, which again is the *trans* isomer with strongly hydrogen bonded (N–H···N and N–H···F) ammonia molecules [76]. The structure of $[SiF_4(ND_3)_2]$ has also been determined; it is the expected *trans* isomer, but the H-bonding network differs from that of $[SiF_4(NH_3)_2]$ [77]. Similar 1:1 complexes have been prepared $[SiF_4L]$ ($L = Me_{3-n}H_nN$, $n = 0, 1, 2$) and have C_{3v} geometries based upon their vibrational spectra [72,78,79]. The $[SiF_4L_2]$ ($L = Me_3N$, EtH_2N, various substituted anilines, *etc.*) are *trans* isomers, confirmed by the X-ray structure for $L = EtH_2N$ [72,78–83]. Pyridine and substituted pyridines, piperidine and pyrrolidine mostly form *trans*-$[SiF_4L_2]$ complexes, although the 1:1 $[SiF_4(py)]$ has been identified in noble gas matrices [84–86]. Complexes with various substituted imidazoles and thiazoles have also been reported [87,88], although their structures are less clear. A wide range of diamines and diimines afford stable *cis*-$[SiF_4(L\text{–}L)]$ including $H_2N(CH_2)_2NH_2$, $H_2NCH_2CH(Me)NH_2$, $MeHN(CH_2)_2NH_2$, $Me_2N(CH_2)_2NH_2$, $MeHN(CH_2)_2NHMe$, $Me_2N(CH_2)_2NMe_2$, 2,2′-bipy, 1,10-phen, and *o*-phenylenediamine [71,72,84,89–98]. The *cis* geometry is easily established by the IR spectra, the presence of two triplets in the ^{19}F NMR spectra ($^2J_{FF}$ ~20 Hz) and by X-ray structures for the complexes with 2,2′-bipy, 1,10-phen and $Me_2N(CH_2)_2NMe_2$ (Fig. 6). Bidentate ligands incapable of chelation, including triethylenediamine, afford *trans*-$[SiF_4(L\text{–}L)]$, presumably ligand-bridged polymers [99].

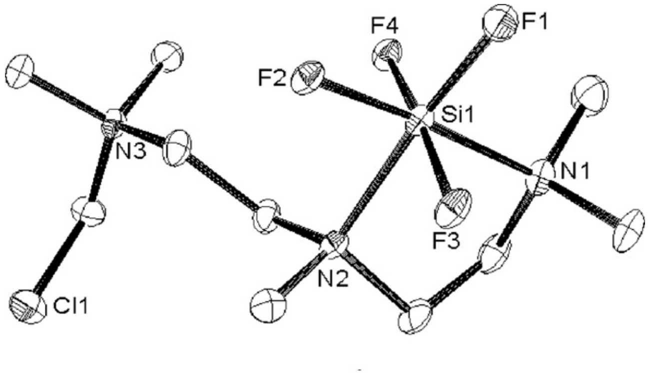

Fig. 5. Crystal structure of $[SiF_4\{\kappa^2\text{-}Me_2N(CH_2)_2N(Me)(CH_2)_2NMe_2(CH_2Cl)\}]^+$ [71].

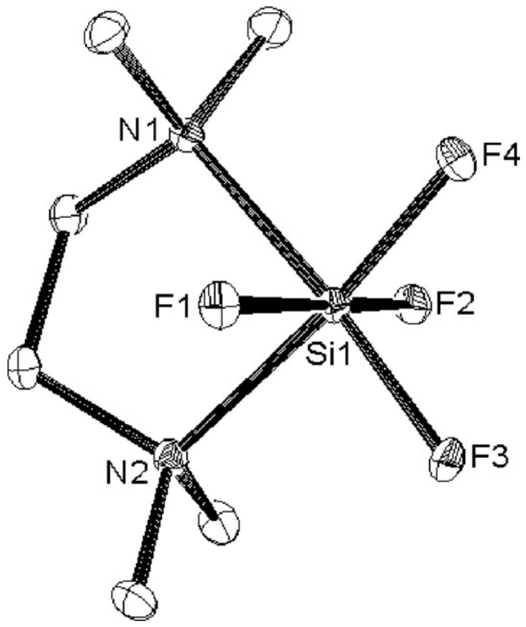

Fig. 6. Crystal structure of $[SiF_4\{Me_2N(CH_2)_2NMe_2\}]$ [71].

The affinity of the heavier silicon halides for aliphatic amines is small. White $[SiCl_4(NMe_3)]$, with C_{3v} symmetry, was identified by vibrational spectroscopy at low temperatures, but there seems to be no 2:1 adduct (*cf* SiF_4 above) nor any complexation at all between NMe_3 and $SiBr_4$ [79,100–102]. The octahedral $[SiCl_4\{Me_2N(CH_2)_2NMe_2\}]$ is known [101]. Complexes with nitrogen heterocycles are much better established and include the structurally authenticated *trans*-$[SiCl_4(py)_2]$ [103] and *trans*-$[SiBr_4L_2]$ ($L = py$, 3,5-Me_2py, 3,4-Me_2py, 4-Mepy) [104–106]. Mixed halide adducts $[SiCl_{4-x}Br_xL_2]$ ($L = py$, 4-MePy, 3,4-Me_2py) have also been prepared and the structures of the (disordered) complexes reported [105–107].

There is an extensive chemistry of diimine complexes with silicon halides, in addition to the long known $[SiX_4(L\text{–}L)]$ ($X = Cl$, Br; L–L = 2,2′-bipy, 1,10-phen), there are dications $[SiX_2(L\text{–}L)_2]^{2+}$, and the halide free $[Si(L\text{–}L)_3]^{4+}$ [108–116]. The simple $[SiX_4(L\text{–}L)]$ [108,109] are unexceptional, although structural authentication was lacking until very recently when the structure of $[SiCl_4(1,10\text{-phen})]$ was reported (Fig. 7) [110]. Silicon iodide affords the $[SiI_4(L\text{–}L)]$ complexes, but also $[SiI_2(L\text{–}L)_2]I_2$ [108,109,111]. The *bis*(ligand) cations *cis*-$[SiX_2(L\text{–}L)_2]I_2$ ($X_2 = I_2$, Cl_2, ClH, ClMe, *etc.*) are prepared by reaction of the diimine with SiI_2X_2, and the iodide anions can be exchanged easily with ClO_4^-, NO_3^-, *etc.* [112,113]. The structure of *cis*-$[SiCl_2(L\text{–}L)_2]I_2$ has been reported [114] (Fig. 8). An alternative route to the dications *cis*-$[SiX_2(2,2'\text{-bipy})_2]Y_2$ ($X = F$ or Cl) is from halogen oxidation of $[SiX_2(2,2'\text{-bipy})_2]$[1] (see Sec-

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[1] These complexes are best viewed as Si(IV) complexes with radical anion ($bipy^-$) ligands.

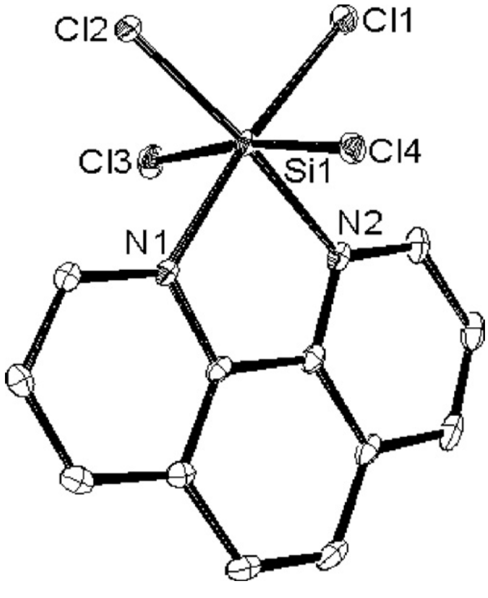


Fig. 7. Crystal structure of [$SiCl_4$(1,10-phen)] [110].

tion 10) [115]. Melting SiI_4 with the diimines results in complete displacement of the iodide to form [$Si(L–L)_3$]I_4 (L–L = 2,2′-bipy, 1,10-phen), also made by iodine oxidation of [$Si(2,2'\text{-bipy})_3$],[1] and the iodide anions may be exchanged for a wide variety of others without affecting the cations, which are stable even in aqueous solution [116]. The enantiomers have been resolved and show no racemisation even after 1 month in aqueous solution at ambient temperatures [117,118]. In similar chemistry to that shown by silicon iodide and pyridine, 1-methylimidazole (mi), 1-vinylimidazole (vi) and 1,1′-dimethyl-2,2′-imidazole (dmi) produced [$SiI_2(py)_4$]I_2, [SiL_6]I_4 (L = mi, vi) or [$Si(dmi)_3$]I_4, although the products are less robust and easily hydrolysed [108,109,116]. Surprisingly, N-methylimidazole (mi) gave very moisture sensitive silicon chloride cations [$SiCl_2(mi)_4$]X_2 (X = Cl or Br) directly on reaction with $SiCl_4$ or $SiCl_2Br_2$ [119]. The structures of both were determined and show a *trans*-geometry (Fig. 9).

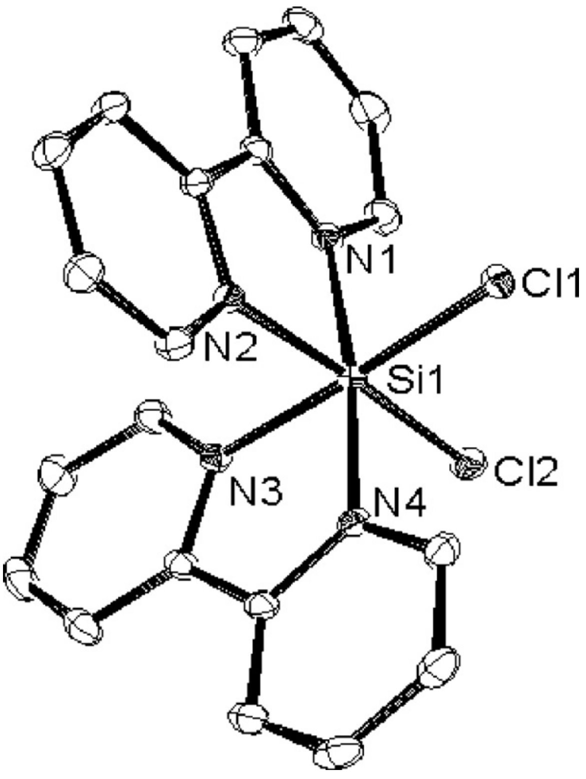


Fig. 8. Crystal structure of *cis*-[$SiCl_2(2,2'\text{-bipy})_2$]$^{2+}$ [114].

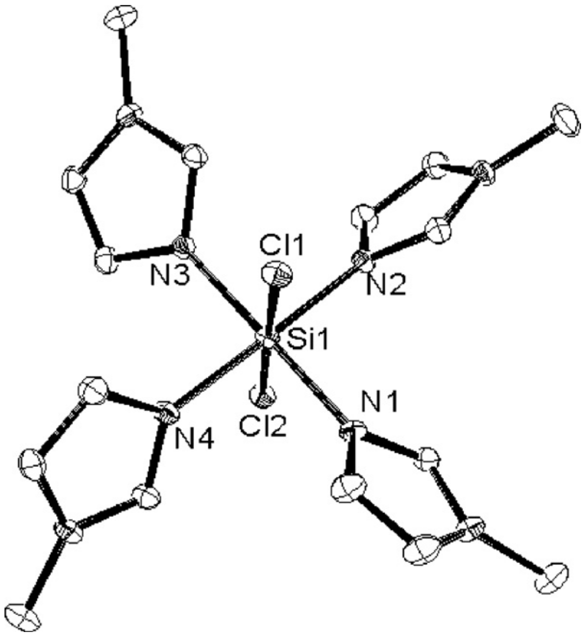


Fig. 9. Crystal structure of [$SiCl_2(mi)_4$]$^{2+}$ (mi = N-methylimidazole) [119].

Although SiH_4 does not form nitrogen base complexes, it has been known for many years that most halosilanes SiH_nX_{4-n} (X = F, Cl, Br, I) give adducts with pyridine and related ligands, the stability depending markedly upon X and *n*. In some cases disproportionation of the halosilane occurs, and partial replacement of X by alkyl groups reduces the Lewis acidity [120,121]. Whilst 1:1 complexes are best established with NMe_3, pyridine usually forms 1:2 adducts, and with SiH_2X_2 and $SiHX_3$ (X = Br or I) 4:1 adducts form [120]. The importance of halosilanes in organic synthesis and in the production of electronic materials (especially ultrapure silicon) has led to detailed re-examination of the halosilane adducts. A matrix isolation IR spectroscopic study of $SiHCl_3$ adducts with NH_3, NMe_3 and $NHMe_2$ obtained spectra consistent with the formation of 1:1 adducts, although with excess base other products, possibly H-bonded species rather than ones with new Si–N linkages were also formed [122]. Detailed studies of [$SiHCl_3(Rpy)_2$] (Rpy = py, 4-Mepy, 3-Brpy, 4-Phpy, 4-^{t}Bupy, 4-vinylpy, 4-Etpy) found the complexes to be stable solids at room temperature in the absence of dioxygen, but at elevated temperatures in polar solvents they disproportionated into [$SiH_2Cl_2(Rpy)_2$] and [$SiCl_4(Rpy)_2$] [123,124]. The unpredictability of these diproportionation reactions is shown by the reaction of $SiHCl_3$ with $Me_2N(CH_2)_2NMe_2$ which gives the expected [$SiHCl_3\{Me_2N(CH_2)_2NMe_2\}$], whereas $Et_2N(CH_2)_2NEt_2$ forms $SiCl_4$ and [$SiH_2Cl_2\{Et_2N(CH_2)_2NEt_2\}$]; both complexes were characterised by X-ray crystallography [125]. 2,2′-bipy and 1,10-phen give adducts with $SiHCl_3$, $MeSiCl_3$ and $PhSiCl_3$ [110]. Dichlorosilane, SiH_2Cl_2, reacts with a wide range of substituted pyridine-type ligands to form *all-trans*-[$SiH_2Cl_2(Rpy)_2$] or *trans*-[$SiH_2(Rpy)_4$]Cl_2 depending upon the conditions [126–128], and with some bidentate nitrogen ligands [SiH_2Cl_2(L–L)] forms [110]. A wealth of ^{29}Si CPMAS NMR spectroscopic and X-ray crystallographic data (Figs. 10 and 11) is available on these compounds and detailed comparisons have revealed the subtle chemistry involved and, along with DFT calculations, have led to an understanding of the relative Lewis acidity of the silanes and insight into their dispro-

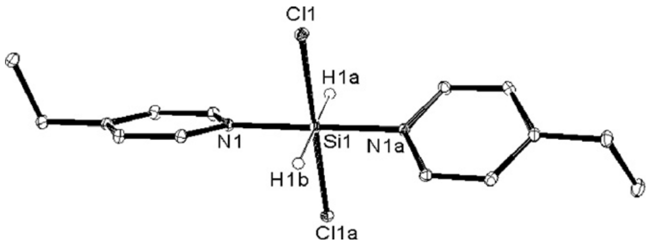


Fig. 10. Crystal structure of [SiH_2Cl_2(4-Etpyridine)$_2$] [126].

portionation reactions [110,119,122,125–129]. The linear triamine, $Me_2N(CH_2)_2N(Me)(CH_2)_2NMe_2$, reacts with $SiHCl_3$ and SiH_2Cl_2 to give the cations [$SiHCl_2\{Me_2N(CH_2)_2N(Me)(CH_2)_2NMe_2\}$]Cl and [$SiH_2Cl\{Me_2N(CH_2)_2N(Me)(CH_2)_2NMe_2\}$]Cl, respectively, both containing a *mer* arrangement of the nitrogen donor atoms, however, $Et_2N(CH_2)_2N(Et)(CH_2)_2NEt_2$ reacts with either $SiHCl_3$ or SiH_2Cl_2 to form only [$SiH_2Cl\{Et_2N(CH_2)_2N(Et)(CH_2)_2NEt_2\}$]Cl [130]. The tetramine, $Me_2N(CH_2)_2N(Me)(CH_2)_2N(Me)(CH_2)_2NMe_2$, coordinates κ^3 to the silicon in similar complexes [130].

Although all the complexes described in this section have been based upon silicon halides, silicon pseudohalides can also behave as Lewis acids, exemplified by the [$Si(NCO)_4$(L–L)] (L–L = 2,2′-bipy or 1,10-phen) described recently [131].

7.3. Phosphorus and arsenic donor ligands

In marked contrast to the current effort devoted to silicon complexes of N-donor ligands, little new work with phosphorus ligands has been reported in the last 30 years. Although some of the early work on adducts of SiX_4 with tertiary phosphines incorrectly identified the phosphine oxides as phosphine adducts, Beattie and Ozin [79,102,132] established that $SiCl_4$ and $SiBr_4$ react with PMe_3 under rigorously anhydrous and oxygen free conditions and in the absence of a solvent, to form [$SiX_4(PMe_3)_2$], which were identified as *trans* isomers by vibrational spectroscopy. The crystal structure of *trans*-[$SiCl_4(PMe_3)_2$] was subsequently determined [133]. In a marked reversal of the trends found with N-donors, SiF_4 adducts of PMe_3 were much less stable than those with the heavier silicon halides, and only identified by vibrational spectroscopy and tensimetric studies at low temperatures (−78 °C). These studies suggested the formation of 1:1 and 1:2 adducts, although neither was obtained free from the other [79,102]. Following on from the recent characterisation of GeF_4 adducts of phosphine ligands (Section 8), attempts were made to react PMe_3, o-$C_6H_4(PMe_2)_2$ and $R_2P(CH_2)_2PR_2$ (R = Me or Et) with SiF_4 in solution in CH_2Cl_2 or toluene [134]. Although trace amounts of phosphine oxide adducts or phosphonium salts were sometimes found, no doubt due to trace adventitious oxygen or water, removal of the solvent left only the "free" phosphine. ^{31}P and ^{19}F NMR studies found no evidence for complexes in these systems down to −95 °C in CD_2Cl_2 solution [134]. The system SiF_4/PMe_3 would seem well suited to a matrix isolation study to confirm the original results. There is no evidence for interaction of arsenic donor ligands with SiX_4 [134].

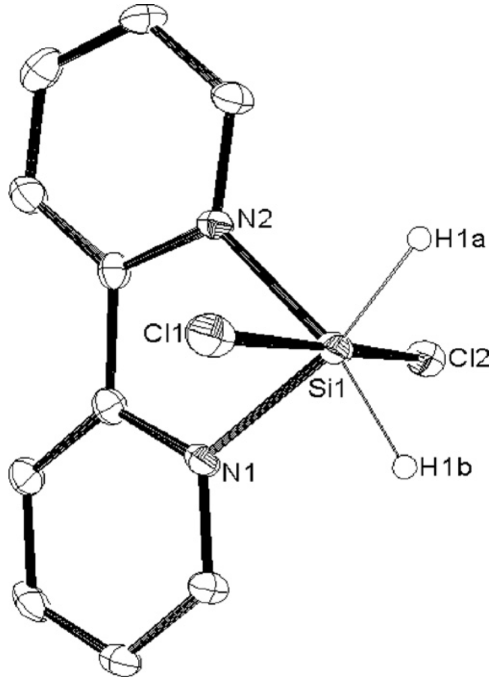


Fig. 11. Crystal structure of [SiH_2Cl_2(2,2′-bipy)] [110].

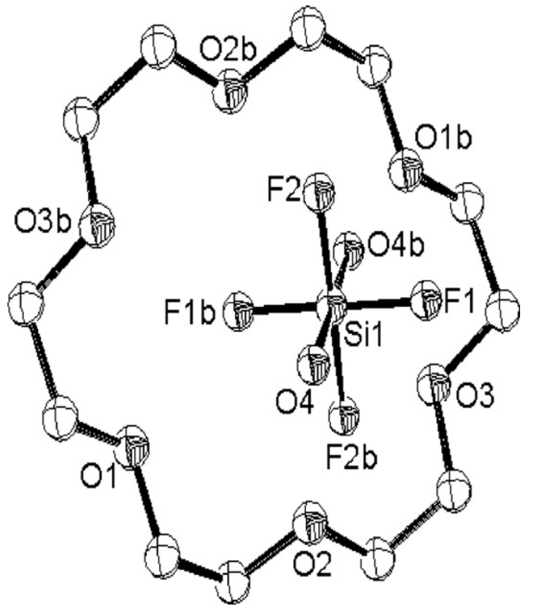


Fig. 12. Crystal structure of [$SiF_4(H_2O)_2$]·(18-crown-6) [138].

7.4. Oxygen and sulfur donor ligands

In general, oxygen donor ligands form weaker adducts with silicon halides than do nitrogen donor ligands, and most complexes are partially or completely dissociated in solution at room temperature.

IR spectroscopic studies identified 1:1 adducts between SiF_4 and H_2O, MeOH and a range of ethers in low temperature matrices; all appear to be axially substituted trigonal bipyramids [135,136]. Although [$SiF_4(H_2O)_2$] has been suggested to be present (along with fluorosilicic acids) in aqueous solutions of SiF_4, it has not been isolated. However, this unit is present in the supramolecular adducts [$SiF_4(H_2O)_2$]·2(12-crown-4) and [$SiF_4(H_2O)_2$]·(crown)·$2H_2O$ (crown = 15-crown-5, 18-crown-6). The structure of [$SiF_4(H_2O)_2$]·(18-crown-6)·$2H_2O$ reveals (Fig. 12) *trans*-[$SiF_4(H_2O)_2$] units hydrogen-bonded to the other water molecules and the crown [137–139]. The result conflicts with *ab initio* MO calculations, which predict [$SiF_4(H_2O)_2$] would be a *cis* isomer (albeit in the gas phase) [140]. Alcohols form adducts with SiF_4, probably of type [$SiF_4(ROH)_2$]·nROH, although the proposed structure is based only on spectroscopic data [72,141,142]. Ethers, including Me_2O, thf, $(CH_2)_2O$, also form highly

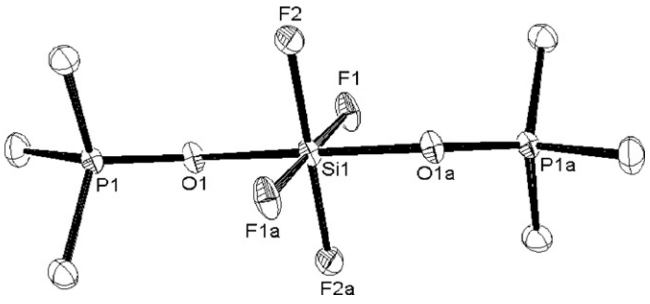


Fig. 13. Crystal structure of [$SiF_4(Me_3PO)_2$] [134].

unstable 2:1 adducts with SiF_4, identified tensimetrically at low temperatures [143], and ^{19}F NMR studies of solutions of ethers and SiF_4 in CD_2Cl_2 indicate fast dissociative exchange is still present even at −90 °C [134].

Pnictogen and chalcogen oxides form much more stable adducts with SiF_4, although even these are hygroscopic and readily hydrolyse to fluorosilicates, often with protonated ligand cations [134]. The former include [$SiF_4(Me_3NO)_2$] [144], [$SiF_4(pyNO)_2$] [134,144] and [$SiF_4(R_3PO)_2$] (R = Me, Et, Ph) [134,145]. The crystal structures of the [$SiF_4(R_3PO)_2$] (Fig. 13) showed them to be *trans* isomers in the solid state, but in CH_2Cl_2 solution ^{19}F and ^{31}P NMR studies reveal mixtures of *cis* and *trans* isomers present at low temperatures, and extensive dissociation/fast exchange above ∼−50 °C [134]. Two diphosphine dioxide complexes, [$SiF_4\{R_2P(O)CH_2P(O)R_2\}$] (R = Ph or Me), which are as expected *cis* isomers, have also been isolated [134]. Phosphine oxide complexes of stoichiometry [$SiCl_4(R_3PO)_2$] (R = Ph, Et, Pr, cyclohexyl), $SiCl_4(Me_3PO)_4$ and $SiBr_4(Ph_3PO)_x$ (x = 2 or 4), have been reported [144,145] but are characterised only by analysis and limited IR spectroscopic data, and need structural authentication. In contrast, reaction of R_3AsO with SiF_4, fails to give simple adducts; the mixture of products formed including [R_3AsOH]$^+$, [SiF_5]$^-$ and [SiF_6]$^{2-}$, and for R = Ph, Ph_3AsF_2 was also identified [134]. Complexes of 2,2′-bipyridyl-N-monoxide (bipyO) and 1,10-phenathroline-N-monoxide (phenO) are of stoichiometry [SiF_4(L–L)] (L–L = bipyO, phenO), [$SiCl_4$(L–L)], [SiX_2(L–L)$_2$]X_2 (X = Cl, Br or I), [Si(L–L)$_3$]I_4—all are assumed to contain six-coordinate silicon with chelating diimine monoxides (*cf* the diimine complexes in Section 7.2), although no structural data are available [146,147].

The white, hygroscopic complex [$SiF_4(dmso)_2$] is formed from the constituents [134,148], and also in the unusual reaction of $RSiF_3$ with dmso (R_2SiF_2 is the other product) [149]. The IR spectrum suggest O-coordination to silicon, and at low temperatures in solution both *cis* and *trans* isomers are present [134,149]. N,N-Dimethylformamide also decomposes $RSiF_3$ to form [$SiF_4(dmf)_2$] [149]. As usual, SiI_4 behaves differently in forming [$Si(dmf)_6$]I_4, the identity being confirmed by a structure determination which showed a regular octahedral (SiO_6) cation geometry [150]. There is an early report of SiX_4 (X = Cl, Br or I) adducts of Ph_2SO made at low temperature, which decompose with O-atom transfer from S to Si at room temperature [151], and $SiCl_4$ deoxygenates dmso [152]. Oxygen/halogen exchange between chalcogen- and pnictogen-oxides and the heavier silicon halides (but not SiF_4) seems very likely under some conditions and these systems are in need of re-examination.

The system hexamethylphosphoramide/$SiCl_4$ has been studied in detail by VTNMR (^{31}P and ^{29}Si) which identified *mer*- and *fac*-[$SiCl_3(hmpa)_3$]$^+$, *cis*- and *trans*-[$SiCl_4(hmpa)_2$] and the five-coordinate [$SiCl_3(hmpa)_2$]$^+$ [153]. X-ray structures were reported for *mer*-[$SiCl_3(hmpa)_3$]HCl_2 and *trans*-[$SiCl_4(hmpa)_2$].

There is no evidence for complex formation between SiF_4 or $SiCl_4$ and neutral sulfur ligands such as Me_2S or $MeS(CH_2)_2SMe$ [134,154].

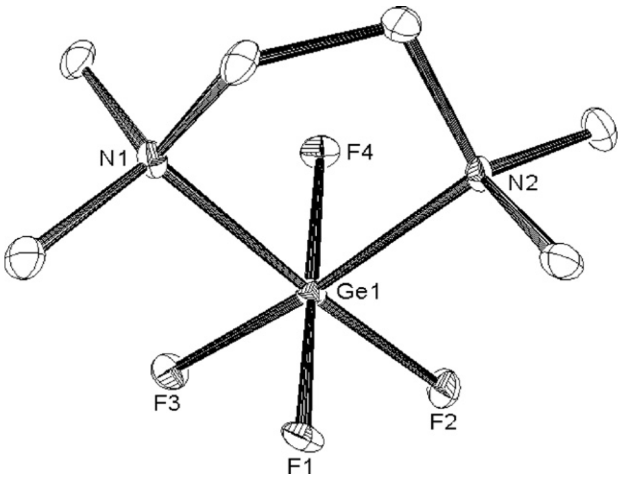


Fig. 14. Crystal structure of [$GeF_4\{Me_2N(CH_2)_2NMe_2\}$] [157].

8. Germanium(IV) complexes

Exploratory studies of Ge(IV) complexes were carried out in the 1960s but in succeeding years relatively little new work was reported, until the last 10 years or so which have seen intense interest in germanium chemistry in general.

8.1. Nitrogen donor ligands

Lewis base complexes of germanium anions are very rare, but [$GeF_5(H_2O)$]$^-$ and [$GeF_5(NH_3)$]$^-$ are both known and have silicon analogues [27]. Matrix-isolation–IR spectroscopy has been used to identify [GeF_4L] (L = NH_3, NMe_3, $NMeH_2$, MeCN) complexes in noble gas matrices; like the silicon analogues the amines were assigned a tbp structure with axial amine [74,86,155]. In contrast to silicon tetrafluoride which does not give an acetonitrile adduct at room temperature, GeF_4 forms white [$GeF_4(MeCN)_2$], which is a useful synthon for other GeF_4 adducts [156]. The solid is stable for months in a closed system, although it vapourises in vacuum, and in CH_2Cl_2 solution is a mixture of *cis* and *trans* isomers [156,157]. Nitrogen heterocycle adducts of GeF_4 are air-stable solids and stable in solution in dry CH_2Cl_2 or MeCN. X-Ray structures have been determined for *trans*-[$GeF_4(py)_2$], *cis*-[GeF_4(L–L)] (L–L = 2,2′-bipy, 1,10-phen) and for a typical diamine, *cis*-[$GeF_4\{Me_2N(CH_2)_2NMe_2\}$] [92,157,158] (Fig. 14). The formation of complexes between a variety of alkyl substituted diaminoethanes and aminoalcohols and GeF_4 has been studied in solution by ^{19}F NMR spectroscopy [159].

Displacement of F^- from GeF_4 by neutral ligands is very rare, but like the SiF_4 case, it is achieved by Me_3-tacn (1,4,7-trimethyl-1,4,7-triazacyclononane), which forms [$GeF_3(Me_3\text{-tacn})$]$_2$[GeF_6] upon reaction with [$GeF_4(MeCN)_2$] in CH_2Cl_2 solution. This salt is insoluble in common solvents, but the structure of [$GeF_3(Me_3\text{-tacn})$]Cl, obtained as a minor by-product, shows the *facially* coordinated aza-macrocycle (Fig. 15) [157]. The tetra-azamacrocycles, 1,4,8,11-tetraazacyclotetradecane (cyclam) and 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (Me_4-cyclam) form 2:1 complexes with excess GeF_4 which are believed to be [$(GeF_4)_2(\kappa^2\kappa'^2$-tetraazamacrocycle)]; a minor by-product with Me_4-cyclam, was identified by its X-ray structure as [$GeF_4(\kappa^2$-Me_4-cyclam)] (Fig. 16). The different behaviour of the tri- and tetra-azamacrocycles is rationalised as whilst the former are pre-organised for tridentate coordination the latter are not, and coordinate as bidentates or *bis*(bidentates)—presumably the breaking of a second Ge–F bond to form [$GeF_2(Me_4\text{-cyclam})$]$^{2+}$ is not thermodymanically favoured [157]. 2,2′,2″-terpyridyl (terpy)

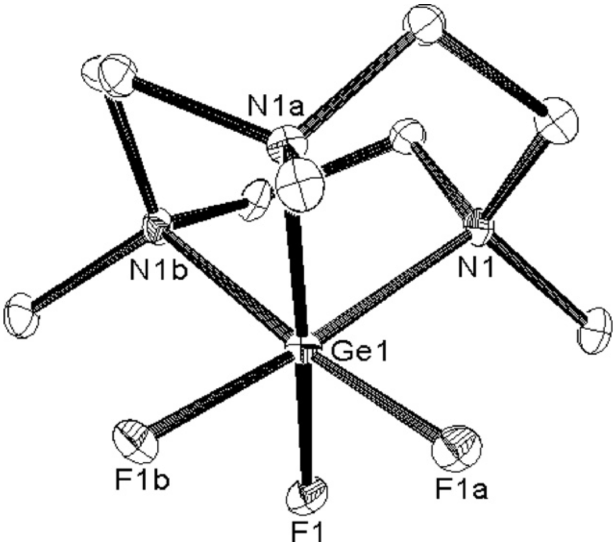


Fig. 15. Crystal structure of [$GeF_3(Me_3$-tacn)]$^+$ [157].

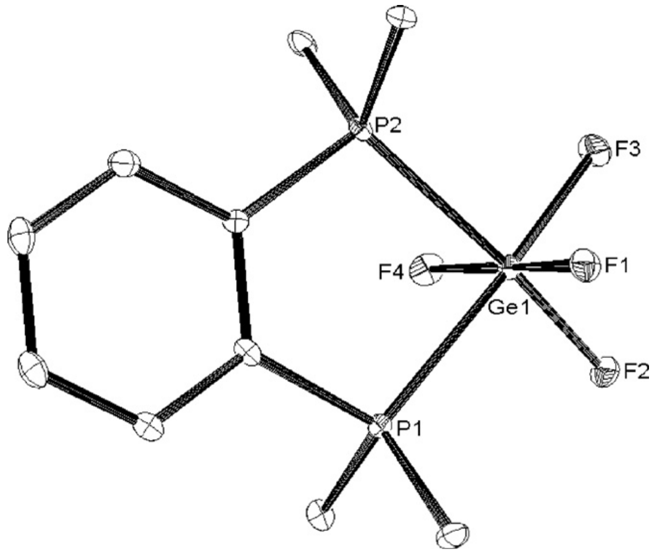


Fig. 17. Crystal structure of [$GeF_4\{o\text{-}C_6H_4(PMe_2)_2\}$] [175].

forms an insoluble [$(GeF_4)_3(terpy)_2$] complex of unknown structure [157].

In contrast to the hydrolytically stable fluoride adducts, nitrogen donor complexes of $GeCl_4$ or $GeBr_4$ hydrolyse easily both as solids and in solution, and in solution are often partially dissociated at room temperature. The long known [$GeCl_4(NMe_3)$] is a tbp molecule with axial amine [79,160,161]. A large number of [$GeX_4(Rpy)_2$] (X = Cl sometimes Br; Rpy = py, 4-Mepy, 3,4-Me_2py, *etc.*) have been prepared and all examples X-ray structurally characterised are *trans*-isomers [157,161–164]. The report of *cis*-isomers with 3-Mepy and 4-MePy based upon their IR spectra is probably in error [165]. Pyrimidine forms both 1:1 and 1:2 complexes with $GeCl_4$ suggested to be a *trans* polymer (with bridging pyrimidine) and *trans* monomer, respectively [166]. X-Ray structures are also available for [$GeX_4\{Me_2N(CH_2)_2NMe_2\}$], [$GeX_4$(2,2′-bipy)] and [$GeX_4$(1,10-phen)] (X = Cl or Br) and comparison of the Ge–N bond lengths with those in the corresponding fluoride adducts (above) show the Ge–N bond length, and hence Lewis acidity decreases $F > Cl \geq Br$, as expected. The dissociation of the neutral ligand in solution in non-coordinating solvents also increases in the same order [157,167,168]. The X-ray structure of the citric acid adduct [GeCl(2,2′-bipy)(Hcit)] has also been reported, with the citrate a tridentate trianionic ligand [168]. Tridentate (N_3) coordination is present in the crystal structures of [$GeCl_3(Me_3$-tacn)]$_2[H_3O]_2Cl_3$·MeCN and [$GeBr_3(L)]_2[MeNH_3]Br_3$·MeCN (L = 1,3,5-trimethyl-1,3,5-triazacyclohexane) [169].

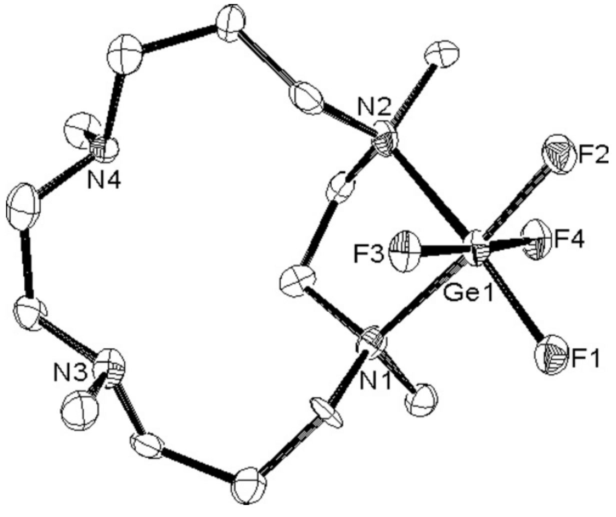


Fig. 16. Crystal structure of [$GeF_4(\kappa^2$-Me_4-cyclam)] [157].

The complexes derived from GeI_4 are less clearly identified. They include $GeI_4(L)_4$ (L = $Et_2NC_6H_5$, N-methylmorpholine, Et^iPr_2N, 3-Mepy) [170], GeI_4(2,2′-bipy)$_2$ [171] and GeI_4(2,2′,2″-terpyridyl) [171]. Comparison with the SiI_4 derivatives, which have been more thoroughly studied, would suggest six-coordination with N_4I_2 or N_3I_3 donor sets, respectively, with ionic iodides balancing the charge, but these compounds require re-examination and especially crystallographic authentication. Notably, red crystals derived from the GeI_4/1,10-phenathroline system were identified by an X-ray study as [1,10-phenanthrolinium]$_3I_3$·GeI_4 [157].

In contrast to the substitution chemistry of $SiH_{4-x}Cl_x$ with nitrogen bases (q.v.), $GeHCl_3$ is deprotonated by NMe_3 or pyridine to form the trichlorogermanate(II) anion [172].

A few complexes of germanium pseudohalides are also known, including the structurally characterised [$Ge(N_3)_4$(L–L)] (L–L = 2,2′-bipy, 1,10-phen) [173], [$GeCl_2(N_3)_2$(2,2′-bipy)] [167], and a number of thiocyanate derivatives of uncertain structure [174].

8.2. Phosphorus and arsenic donor ligands

In contrast to the SiF_4 adducts reported over 40 years ago, the first phosphine complexes of GeF_4 were described in 2008 [175]. The white *trans*-[$GeF_4(PR_3)_2$] (R = Me or Ph) and *cis*-[GeF_4(L–L)] (L–L = $R_2P(CH_2)_2PR_2$, R = Me, Et, Ph; o-$C_6H_4(PR_2)_2$, R = Me, Ph) are made from [$GeF_4(MeCN)_2$] and the ligands and characterised by ^{19}F and ^{31}P NMR spectroscopy and by X-ray structures for [GeF_4(L–L)] (L–L = $Ph_2P(CH_2)_2PPh_2$, and o-$C_6H_4(PMe_2)_2$) [175] (Fig. 17). In solution in CH_2Cl_2, dry O_2 slowly converts them into the corresponding phosphine oxide complexes, but they are stable with respect to reduction at germanium [175]. In contrast, whilst *trans*-[$GeCl_4(PMe_3)_2$] can be made by reaction of $GeCl_4$ with PMe_3 at low temperatures and without a solvent, in solution this rapidly undergoes a redox reaction to form [PR_3Cl][$GeCl_3$] [79,132,175]. Similar trichlorogermanate(II) products are formed by reaction of $GeCl_4$ with PR_3 (R = ^tBu, Et, Me, ^nPr, cyclohexyl, 2,6-$(MeO)_2C_6H_3$, *etc.*), in diethyl ether solution [175–177]. With $GeBr_4$ the redox reaction occurs without evidence for a Ge(IV) intermediate [175,179], and the reported [$GeX_4(PMe_3)$] (X = Cl or Br) [178] are almost certainly [PMe_3X][GeX_3] [175]. Primary (PRH_2) and secondary (PR_2H)

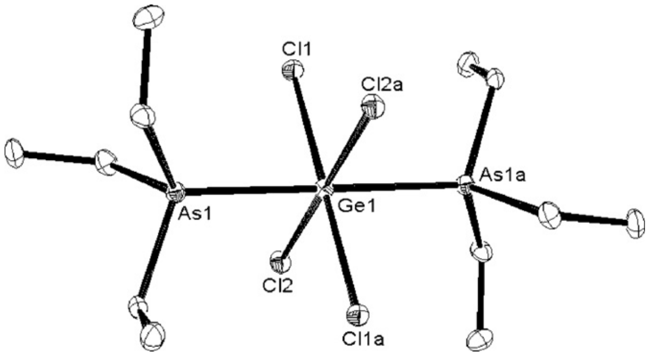


Fig. 18. Crystal structure of [$GeCl_4(AsEt_3)_2$] [175].

phosphines also reduce $GeCl_4$ to Ge(II), but further reactions are complex, involving loss of HCl to form the trichlorogermylphosphines $RHPGeCl_3$ or R_2PGeCl_3 [180,181]. The recent report of the ^{73}Ge NMR spectrum of $GeCl_4/Bu_3P$ attributed to the Ge(IV) complex [182] is in error, since the ^{31}P NMR spectrum shows the phosphorus present as [Bu_3PCl]$^+$ [176].

The direct reaction of $GeCl_4$ with AsR_3 (R = Me or Et) readily forms *trans*-[$GeCl_4(AsR_3)_2$] both of which have been structurally characterised [175,176] (Fig. 18) but these decompose over a few days in solution to produce R_3AsCl_2. There was no reaction between $GeCl_4$ and $AsPh_3$ or *o*-$C_6H_4(AsMe_2)_2$ [175,176] and whilst some complexation occurs between GeF_4 and tertiary arsines, the products were too unstable to isolate or characterise [175].

8.3. Oxygen and sulfur donor ligands

The adducts of oxygen donor ligands with GeF_4 are rather more stable than their SiF_4 analogues, but often moisture sensitive and extensively dissociated in solution in non-donor solvents at ambient temperatures. IR spectroscopic studies of mixtures of GeF_4 and oxygen Lewis bases including H_2O, Me_2O, MeOH, thf, $(CH_2)_2O$, and Me_2CO trapped in noble gas matrices at low temperatures, identified 1:1 adducts with tbp geometries and axial oxygen ligands [135,136,183]. [$GeF_4(Et_2O)_2$] was isolated as very sensitive colourless crystals from reaction of $GeCl_4$ and SbF_3 in Et_2O solution, and its crystal structure revealed the expected *trans* isomer [184]. *Cis*-[$GeF_4\{MeO(CH_2)_2OMe\}$] and [$GeF_4(thf)_2$] are hygroscopic solids at ambient temperatures, and extensively dissociated in solution at 295 K, but at low temperatures in CH_2Cl_2 solution the latter is a mixture of *cis* and *trans* isomers [156]. GeF_4 adducts of alcohols and esters have been studied in solution by ^{19}F NMR spectroscopy [185–187].

The reaction of GeF_4 and 18-crown-6 in aqueous solution produced crystals of [$GeF_4(OH_2)_2$]·(18-crown-6)·$2H_2O$ which are isostructural with the SiF_4 analogue [188].

Phosphine- and arsine-oxides react with [$GeF_4(MeCN)_2$] to give [GeF_4L_2] (L = Me_3PO, Et_3PO, Ph_3PO, Ph_3AsO), which are only slightly moisture sensitive in the solid state. X-ray structures of the three phosphine oxides reveal *trans* octahedral geometries, but in solution varying amounts of *cis* isomers are also present, the *cis*:*trans* ratio in CH_2Cl_2 solution at ambient temperatures varies from ~1:20 (Me_3PO) to ~1:1 (Ph_3PO) [156]. GeF_4 also forms *cis* isomers with the diphosphine dioxides, $R_2P(O)CH_2P(O)R_2$ (R = Me or Ph), and [$GeF_4\{Ph_2P(O)(CH_2)_2P(O)Ph_2\}$] shows a *cis* geometry, confirmed by X-ray crystal structure determinations [134]. The reactions of phosphine oxides with $GeCl_4$ and $GeBr_4$ proved unexpectedly more complicated. Depending upon the reaction conditions and the solvent, crystals of *fac*-[$GeCl_3(Me_3PO)_3$]$_2$[$GeCl_6$], *cis*-[$GeCl_2(Me_3PO)_4$]Cl_2 and *cis*-[$GeBr_2(Me_3PO)_4$]Br_2 were isolated and all characterised by X-ray crystallographic studies (Figs. 19 and 20) [156]. Variable temperature NMR spectroscopic studies show the species undergo fast exchange at ambient temperatures in non-donor solvents, but that the different complexes can be identified at 200 K when exchange processes have slowed. *Fac*-[$GeCl_3(Me_3PO)_3$]$_2$[$GeCl_6$] is the correct formulation for the complex reported as [$GeCl_4(Me_3PO)_2$] in older literature [189]. The assignments of ^{73}Ge NMR resonances in solutions of $GeCl_4/R_3PO$ [182] do not take into account the complexity of the speciation and should be viewed with suspicion. Attempts to isolate GeI_4-phosphine oxide adducts were unsuccessful, and only polyiodide salts of protonated phosphine oxides were identified [156]. The reactions between GeX_4 (X = Cl or Br) and R_3AsO (R = Me or Ph) are different again; no adducts were identified (*cf.* GeF_4 complexes above), instead clean conversion to the organoarsenic(V) dihalides (R_3AsX_2) was found [156].

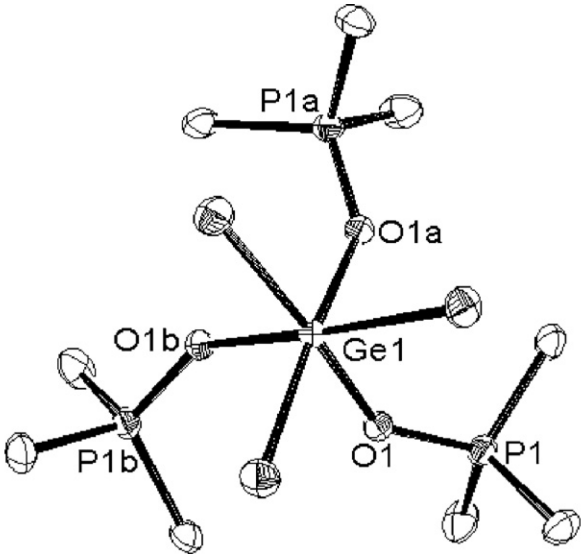


Fig. 19. Crystal structure of *fac*-[$GeCl_3(Me_3PO)_3$]$^+$ [156].

The *trans*-[$GeCl_4(dmso)_2$] adduct has been fully characterised spectroscopically and by a crystal structure [190,191]; its formation contrasts with the deoxygenation of the ligand achieved by $SiCl_4$ [152].

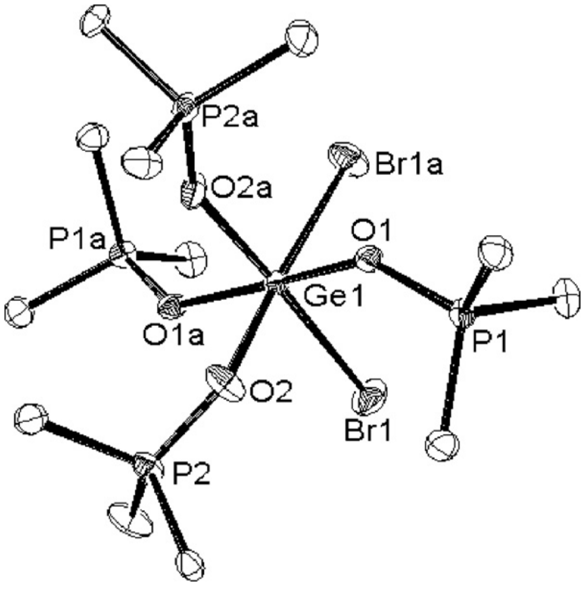


Fig. 20. Crystal structure of *cis*-[$GeBr_2(Me_3PO)_4$]$^{2+}$ [156].

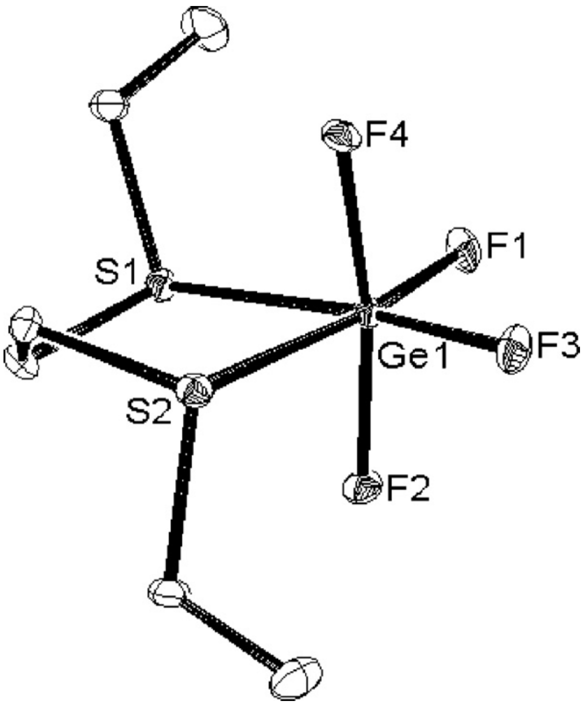


Fig. 21. Crystal structure of [$GeF_4\{EtS(CH_2)_2SEt\}$] [192].

The extremely moisture sensitive [$GeF_4(RS(CH_2)_2SR)$] (R = Me, Et) are formed from [$GeF_4(MeCN)_2$] and the dithioethers in anhydrous CH_2Cl_2 [192]. Both were characterised by X-rays studies (Fig. 21), showing the expected *cis*-octahedral geometries. ^{19}F NMR spectroscopic evidence was reported for the formation of *cis*- and *trans*-[$GeF_4(SMe_2)_2$] and [$GeF_4(\kappa^2$-[9]ane$S_3)$] in solution at low temperatures, but neither was stable enough to be isolated [192]. Similar studies suggested [$GeF_4\{MeSe(CH_2)_2SeMe\}$] was present in solution of [$GeF_4(MeCN)_2$] and $MeSe(CH_2)_2SeMe$ in CH_2Cl_2 at low temperatures, although attempts to isolate the complex failed [134]. In marked contrast, there is no evidence for interaction between $GeCl_4$ and thio- or seleno-ethers [154], although $SnCl_4$ complexes are well established [193].

9. Germanium(II) complexes

The presence of a Ge-based lone pair in Ge(II) complexes has led to significant interest in the structural chemistry of Ge(II), whilst the organo-germanium(II) (germylene) compounds have received intense study, although the latter fall outside the scope of this particular review. Complexes of Ge(II) frequently exhibit highly distorted coordination environments based upon a combination of (normal) primary and (long) secondary bonding interactions.

9.1. Carbon donor ligands

Arduengo et al. reported the first preparation of an NHC complex with Ge(II), [$GeI_2\{NHCMe\}$], by direct reaction of the NHC with GeI_2 in thf [194]. Reaction of a diethylether suspension of [$GeCl_2$(dioxane)] with one equivalent of the NHC$^iPr_2$ gives [$GeCl_2(NHC^iPr_2)$] in high yield. This complex undergoes reduction with potassium graphite to give the very unusual, formally Ge(0) dimer [$(NHC^iPr_2)Ge{=}Ge(NHC^iPr_2)$] [195]. The structure of [$GeCl_2(NHC^iPr_2)$] shows discrete molecules with pyramidal coordination at Ge (with a stereochemically active Ge-based lone pair) and an almost planar carbene C atom [195]. Structurally this complex is very similar to its Si analogues [$SiX_2(NHC^iPr_2)$] (Section 10). The Ge–Cl and Ge–C bond distances are comparable to those in the related Ge(II) NHC complex [$GeCl_2\{NHCMe_2{}^iPr_2\}$], which is obtained by direct substitution of the ether ligand in [$GeCl_2$(dioxane)] by the NHC in thf [196]. The latter undergoes halide exchange via Me_3SiI in thf solution to give the yellow [$GeI_2\{NHCMe_2{}^iPr_2\}$] which is also pyramidal [196]. Addition of excess NHC to this diiodo complex gives the colourless, three-coordinate Ge(II) dication, [$Ge(NHCMe_2{}^iPr_2\})_3]^{2+}$, isolated as its diiodide salt. The structure of this dication shows a pyramidal, C_3 symmetric unit, with Ge–C = 2.070(6) Å [196] (Fig. 22). [$GeCl_2\{NHCMe_2{}^iPr_2\}$] undergoes a range of halide substitution reactions, to give for example [$GeX_2\{NHCMe_2{}^iPr_2\}$] (X = F, Br, NCS, O^{t}Bu, mesityl), whilst addition of $Me_3SiCF_3SO_3$ to [$GeCl_2\{NHCMe_2{}^iPr_2\}$] affords [$GeCl\{NHCMe_2{}^iPr_2\}(CF_3SO_3)$] which incorporates covalently bonded triflate [197,198].

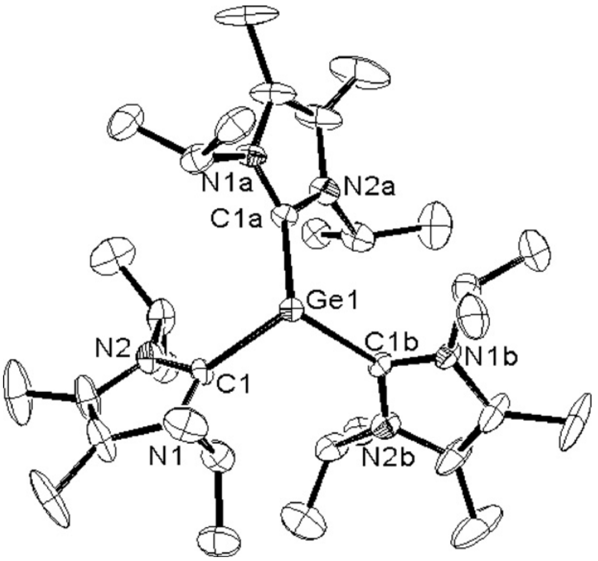


Fig. 22. Crystal structure of [$Ge(NHCMe_2{}^iPr_2)_3]^{2+}$ [196].

X-ray structural studies on the Ge(II) NHC complexes [$GeX_2\{NHCMe_2{}^iPr_2\}$] show a decrease in the carbenic C–Ge bond distance with decreasing π-donating ability of other ligands on germanium, e.g. d(Ge–C) shortens when the Cl ligands in [$GeCl_2$(NHC)] are replaced by mesityl groups [197,198]. However, for the related series [$GeX_2\{NHCMe_2{}^iPr_2\}$] d(Ge–C) does not vary significantly with X [199], and computational studies indicate that the electronic NHC substituent effect is negligible in these compounds, suggesting that the trend in Ge–C observed in [$GeX_2\{NHCMe_2{}^iPr_2\}$] may be a consequence of crystal packing.

9.2. Nitrogen donor ligands

[$GeCl_2$(dioxane)] reacts with $Me_2N(CH_2)_2NMe_2$ to give [$GeCl_2\{Me_2N(CH_2)_2NMe_2\}$] as a white solid. The structure of this compound shows a very distorted environment at Ge(II) through an asymmetrically chelating diamine and two Cl ligands. The [$GeCl_2\{Me_2N(CH_2)_2NMe_2\}$] molecules are weakly associated into dimers through weak Cl-bridges, giving a very distorted square-pyramidal environment at each Ge(II) centre. The asymmetric diamine coordination (Δ(Ge–N) ~0.30 Å) evident in this complex is particularly unusual (Fig. 23) [37].

Using the linear triamine pmdta ($MeN\{(CH_2)_2NMe_2\}_2$) with [$GeCl_2$(dioxane)] or $GeBr_2$ gives [GeX(pmdta)][GeX_3] (X = Cl or Br), the structures of which are similar, with discrete [$GeX(pmdta)]^+$ cations and [$GeX_3]^-$ anions. The cations show tridentate triamine coordination, the neutral N-base leading to displacement of one halide from the Ge(II) precursors, giving nearly planar GeN_3 units,

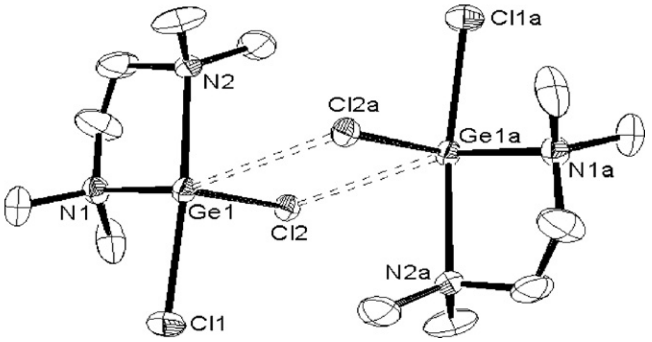


Fig. 23. Crystal structure [$GeCl_2\{Me_2N(CH_2)_2NMe_2\}$] [37].

and a terminal halide ligand occupies a fourth coordination site (Fig. 24) [37]. In contrast, using the macrocyclic triamine Me_3-tacn with one molar equivalent of $GeBr_2$ in anhydrous MeCN solution, gives [$Ge(Me_3$-tacn)]Br[$GeBr_3$], unusually containing a formally Ge(II) dication [200]. The crystal structure shows the only significant interactions to Ge(II) are through a tridentate Me_3-tacn coordinated *facially* to the Ge atom, giving a very unusual pyramidal, three-coordinate dication (Fig. 25), with the Br^- and $[GeBr_3]^-$ present as anions. The Ge–N separations lie in the range 2.124(3)–2.156(3) Å; considerably longer than the sum of the covalent radii for Ge and N, indicative of weak interactions.

Using the tetra-azamacrocycle Me_4-cyclam with [$GeCl_2$(dioxane)] gives [$Ge(Me_4$-cyclam)][$GeCl_3$]$_2$, the crystal structure which shows *endocyclic* coordination giving a distorted N_4 donor set within the dication, with two shorter (~2.16 Å) and two slightly longer (~2.32 Å) Ge–N bonds [200]. The Ge atom lies ~0.8 Å above the approximate N_4 plane, and the four Me groups are directed to the same side of the plane as the Ge ion (Fig. 26). Two pyramidal $[GeCl_3]^-$ anions balance the charge.

These azamacrocycle complexes of Ge(II) present two extremely unusual examples of halide-free dicationic Ge(II) complexes stabilised by a neutral donor ligand and it is likely that the macrocyclic structures play an important role in stabilising the dications. It is also significant that the related thioether macrocycles do not give halide-free cations.

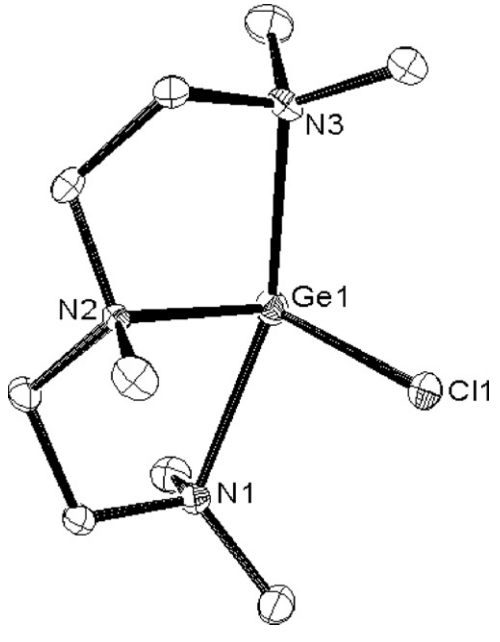


Fig. 24. Crystal structure of [GeCl(pmdta)]$^+$ [37].

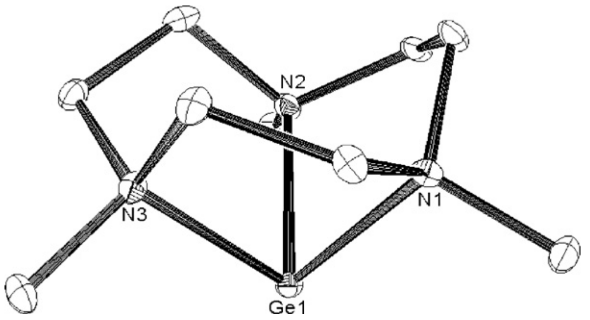


Fig. 25. Crystal structure of [$Ge(Me_3$-tacn)]$^{2+}$ [200].

Early work described the preparation of Ge(II) halide complexes incorporating nitrogen heterocycles [201,202]. These and related compounds have been re-examined recently to allow their structures to be determined [37]. Thus [$GeCl_2$(dioxane)] reacts with neutral N-heterocycles 2,2′-bipy or 1,10-phen in CH_2Cl_2 solution to give [$GeCl_2$(L–L)]. The structure of [$GeCl_2$(2,2′-bipy)] shows the coordination to be through a symmetrically chelating 2,2′-bipy, and two *trans* Cl ligands. Monomer units are linked via weak, intermolecular Ge···Cl bridges to form a zig-zag chain (Fig. 27), based on very distorted six-coordinate Ge [37]. There is also evidence for some π-stacking interactions between the aromatic rings of the 2,2′-bipy. DFT calculations indicate that the bonding in the [$GeCl_2$(2,2′-bipy)] system can be described as covalent, with longer range interactions to other ligands involving the 4p orbitals of Ge [37]. The calculations also show that the geometry of the monomer unit in the experimental crystal structure does not correspond to the global minimum determined for the isolated molecule, but to a higher energy minimum, and that the structure calculated for a [$GeCl_2$(2,2′-bipy)]$_4$ tetramer shows some of the main structural characteristics observed in the crystal structure [37].

[$GeCl_2$(1,10-phen)] adopts a weakly associated dimeric structure similar to [$GeCl_2\{Me_2N(CH_2)_2NMe_2\}$], but with the two Ge–N distances similar [37]. The dimers are based upon a distorted five-coordinate square pyramidal geometry at Ge. The Ge···Ge distances in both [$GeCl_2$(2,2′-bipy)] and [$GeCl_2$(1,10-phen)] are less than 2× the van der Waals radius of Ge (4.0 Å), suggesting a weak interaction.

The related bromo complexes of Ge(II) were prepared by direct reaction of $GeBr_2$ with the ligand in anhydrous MeCN, giv-

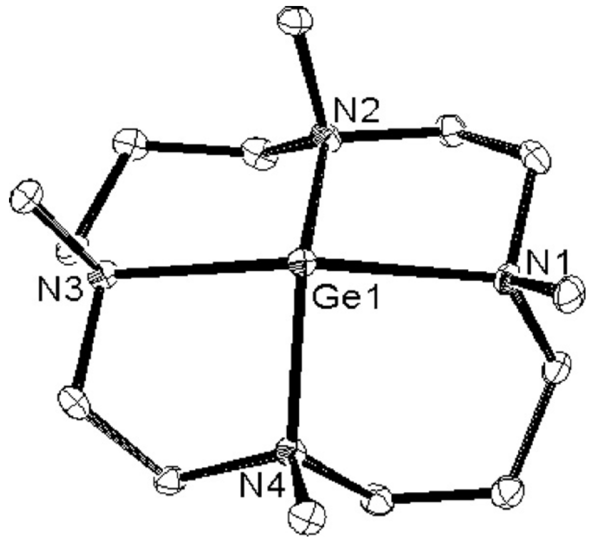


Fig. 26. Crystal structure of [$Ge(Me_4$-cyclam)]$^{2+}$ [200].

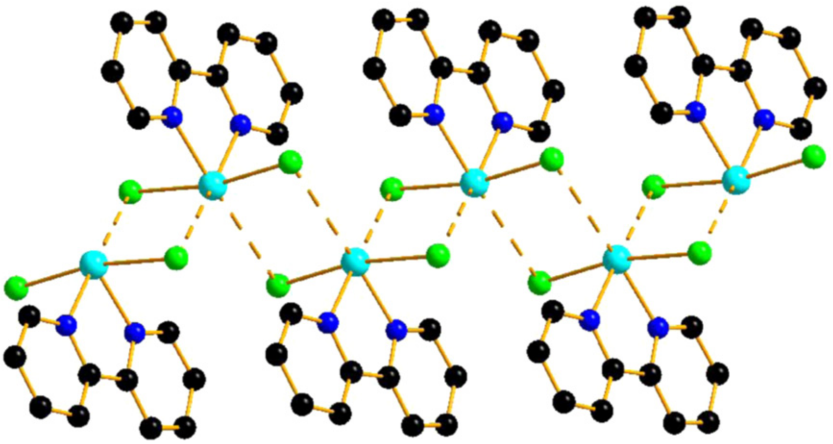


Fig. 27. Crystal structure of [$GeCl_2$(2,2′-bipy)] (turquoise = Ge; green = Cl; blue = N; black = C) [37].

ing neutral [$GeBr_2$(L–L)] [37]. The zig-zag polymer structure of [$GeBr_2$(1,10-phen)] is similar to [$GeCl_2$(2,2′-bipy)], and bridging Ge···Br contacts of ~3.6 Å.

Recrystallisation of [$GeBr_2$(2,2′-bipy)] from MeCN gave crystals of [GeBr(2,2′-bipy)][$GeBr_3$], which was characterised structurally and shows (Fig. 28) a pyramidal cation with symmetrically chelating 2,2′-bipy, and a terminal Br [37]. Three Br atoms in the anion form secondary contacts to Ge in the cation, completing the distorted octahedral coordination at Ge.

9.3. *Phosphorus and arsenic donor ligands*

Early work from King [203] reported the preparation of [$GeI_2(PPh_3)$], along with several other secondary and tertiary phosphine complexes, from GeI_2 and phosphine in refluxing ethylcyclohexane/xylene. Subsequently, the structures of [$GeX_2(PPh_3)$] (X = Cl, I) were determined, showing discrete pyramidal structures, with Ge–P = ~2.50 Å [204–206]. Du Mont and co-workers [207] have described the preparation of [$GeCl_2\{Ph_2P(CH_2)_2PPh_2\}$], the structure of which is a very distorted monomer, with one short Ge–P bond (2.314(2) Å) and one much longer long Ge···P distance (3.340(2) Å). Very recent work has involved a systematic study of the synthesis and structural properties of Ge(II) halide (chloride, bromide and iodide) complexes with neutral diphosphine and diarsine ligands, all of which can form five-membered chelate rings, but have different steric and electronic properties [208]. The moisture sensitive complexes are obtained by reaction of [$GeCl_2$(dioxane)], $GeBr_2$ or GeI_2 with the appropriate diphosphine in dry CH_2Cl_2 (Cl) or MeCN (Br or I).

[$GeX_2\{o\text{-}C_6H_4(PPh_2)_2\}$] (X = Cl, Br or I) adopt very similar structures involving discrete monomers with two halide ligands and the $o\text{-}C_6H_4(PPh_2)_2$ ligand essentially monodentate giving a pyramidal primary coordination sphere, with the second P-donor atom interacting very weakly (d(Ge–P) differ by *ca.* 0.6 Å) giving [3 + 1] coordination overall (Fig. 29). The very asymmetric chelation (or *pseudo*-monodentate) coordination mode is very unusual for $o\text{-}C_6H_4(PPh_2)_2$, but is similar to the structure of [$GeCl_2\{Ph_2P(CH_2)_2PPh_2\}$] [208].

The $o\text{-}C_6H_4(PMe_2)_2$ ligand in [$GeCl_2\{o\text{-}C_6H_4(PMe_2)_2\}$] is sterically less demanding and also a stronger σ-donor than $o\text{-}C_6H_4(PPh_2)_2$. Unlike the $o\text{-}C_6H_4(PPh_2)_2$ complexes above, the $o\text{-}C_6H_4(PMe_2)_2$ is symmetrically chelating to Ge(II), with one terminal and two asymmetrically bridging Cl atoms completing the

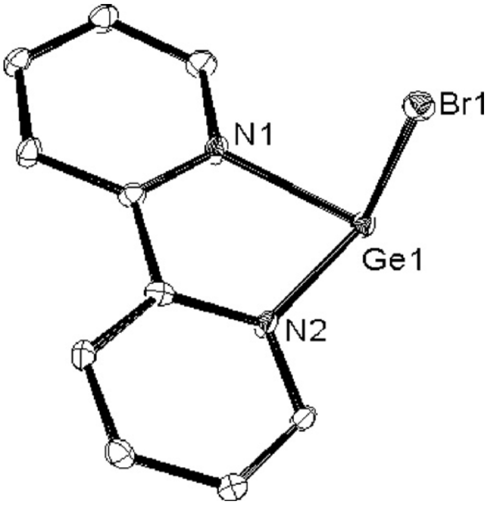


Fig. 28. Crystal structure of [GeBr(2,2′-bipy)]$^+$ [37].

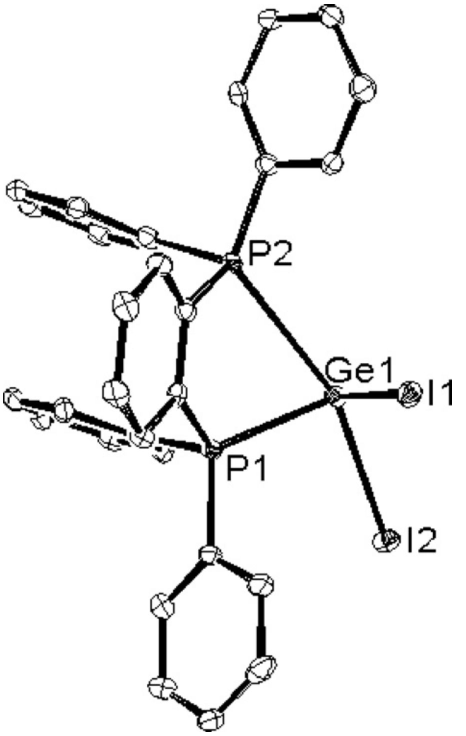


Fig. 29. Crystal structure of [$GeI_2\{o\text{-}C_6H_4(PPh_2)_2\}$] [208].

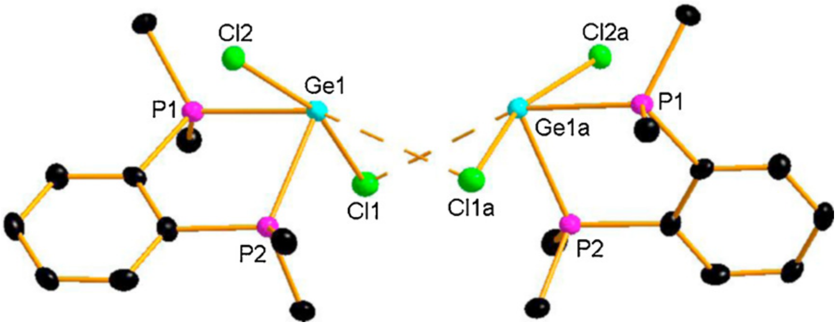


Fig. 30. Crystal structure of [$GeCl_2\{o\text{-}C_6H_4(PMe_2)_2\}$] [208].

coordination environment. Curiously, the Ge···Ge distance across the dimer unit (3.64 Å) is considerably shorter than twice the van der Waals radius for Ge (4.0 Å), and the Ge_2Cl_2 unit is not planar (Fig. 30) [208]. The bromo analogue, [$GeBr_2\{o\text{-}C_6H_4(PMe_2)_2\}$], is isomorphous [208]. [$GeI_2\{o\text{-}C_6H_4(PMe_2)_2\}$] forms a similar monomer unit [208] with the $o\text{-}C_6H_4(PMe_2)_2$ chelating and the GeI_2 unit essentially linear, however, adjacent monomers align to give a precisely planar rhombic Ge_2I_2 arrangement (Fig. 31), although the intermolecular Ge1···I1a distance (3.92 Å) is only marginally within the sum of the van der Waals radii for the elements.

Within the complexes [$GeX_2\{R_2P(CH_2)_2PR_2\}$] (X = Cl or Br; R = Me or Et), for a given phosphine, each pair of halide derivatives is isomorphous. All four species form discrete monomers with 2-fold crystallographic symmetry, in which the diphosphine chelates and the GeX_2 units are linear [208] (Fig. 32). [$GeI_2\{Me_2P(CH_2)_2PMe_2\}$] adopts a similar structure, although there is some evidence for weak intermolecular Ge···I contacts to form very weakly associated centrosymmetric dimers [208] (Fig. 33).

Notable features in these series of compounds are that for a given diphosphine the Ge–P distances are independent of the halide; within the [$GeX_2\{o\text{-}C_6H_4(PPh_2)_2\}$] monomers the X–Ge–X unit is bent, whereas in the four-coordinate [$GeX_2\{R_2P(CH_2)_2PR_2\}$] they are linear; the Ge–P distances are dependent on the terminal substituent on P, i.e. comparing [$GeX_2\{o\text{-}C_6H_4(PPh_2)_2$] with [$GeX_2\{o\text{-}C_6H_4(PMe_2)_2\}$] shows that Ge–P is shorter by ~0.05 Å in the latter, consistent with the increased σ-donor power of the $o\text{-}C_6H_4(PMe_2)_2$ [208].

The variable temperature $^{31}P\{^1H\}$ NMR data suggest that for L–L = $o\text{-}C_6H_4(PMe_2)_2$, $Me_2P(CH_2)_2PMe_2$ and $Et_2P(CH_2)_2PEt_2$ the [GeX_2(L–L)] involve chelating phosphine in solution, whereas for the $o\text{-}C_6H_4(PPh_2)_2$ complexes the phosphine is probably monodentate in solution, undergoing rapid exchange of the 'free' and coordinated P atoms even at 200 K [208].

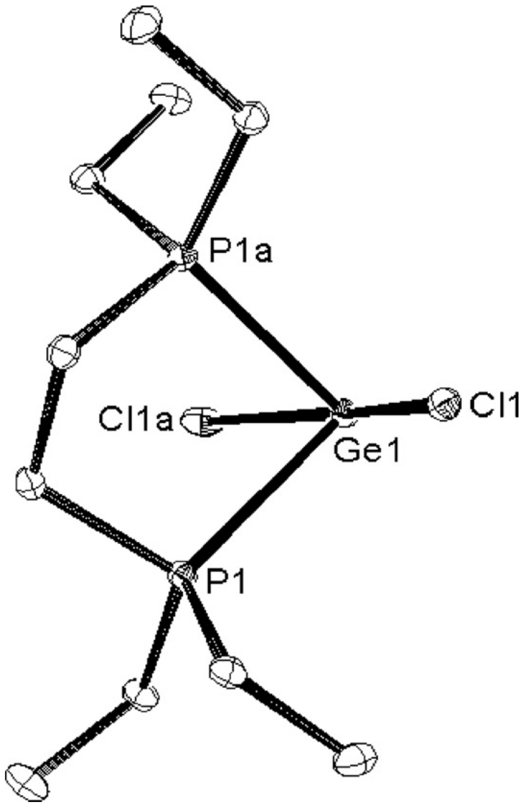


Fig. 32. Crystal structure of [$GeCl_2\{Et_2P(CH_2)_2PEt_2\}$] [208].

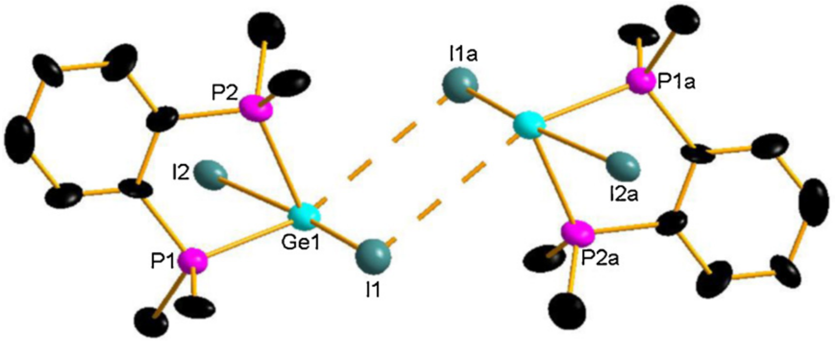


Fig. 31. Crystal structure of [$GeI_2\{o\text{-}C_6H_4(PMe_2)_2\}$] [208].

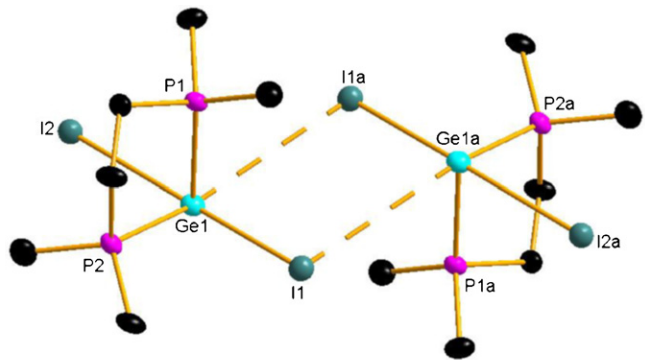


Fig. 33. Crystal structure of [$GeI_2\{Me_2P(CH_2)_2PMe_2\}$] [208].

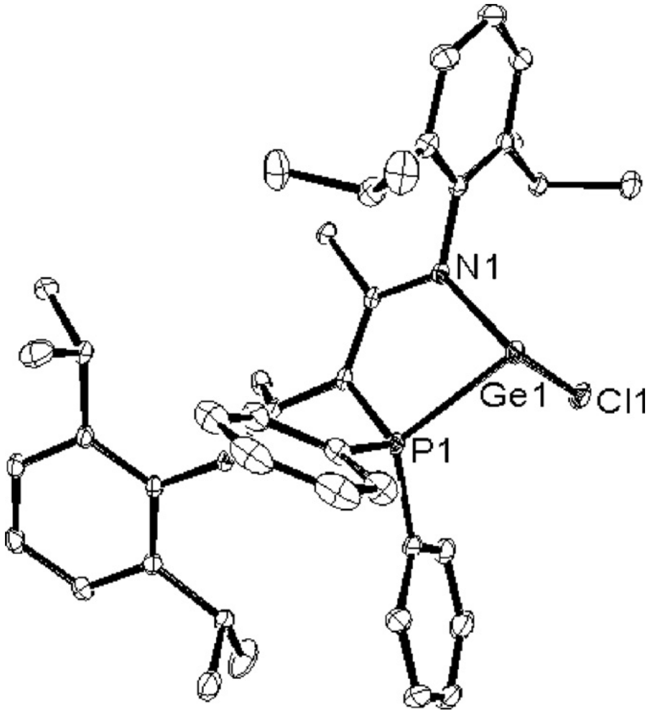
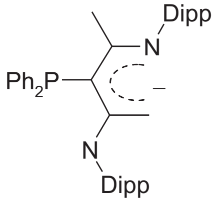
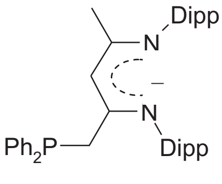


Fig. 34. [$Ph_2PC\{C(Me)N(Dipp)\}_2GeCl$] (Dipp = 2,6-$^iPr_2C_6H_3$) [209].

Recent work from Roesky and co-workers [209] has reported the Ge(II) complexes with two isomeric β-diketiminates which incorporate neutral phosphine functions, I and II, proposed as means of building heterometallic species.



(I)



(II)

However, ligand I reacts with [$GeCl_2$(dioxane)] in diethyl ether at −30 °C to form a five-membered *N*,*P* chelate complex, [$Ph_2PC\{C(Me)N(Dipp)\}_2GeCl$] (Dipp = 2,6-$^iPr_2C_6H_3$) [209] (Fig. 34), the structure of which is based upon pyramidal coordination at Ge, with Ge–P = 2.4300(11) Å—in line with the other phosphine complexes above. Phosphorus-31 NMR data confirm retention of the Ge–P coordination in solution. On the other hand, in $CH\{[C(CH_2PPh_2)N(Dipp)][C(Me)N(Dipp)]\}GeCl$, ligand II coordinates to Ge(II) as expected via the N-atoms, leaving the phosphine moiety free [209].

The only Ge(II) complexes with monoarsines are with $AsPh_3$ and As^tBu_3, however, these lack structural authentication [210]. There are only two structural reports concerning Ge(II) arsines: the crystal structure of [$GeI_2\{o\text{-}C_6H_4(AsMe_2)_2\}$], formed from reaction of GeI_2 with the diarsine in MeCN, shows a weakly associated zigzag chain polymer formed through long Ge···I contacts, with the diarsine chelating, and based upon very distorted [$As_2I_2 + I_2$] coordination at Ge(II) [208] (Fig. 35); in contrast, the ionic complex [$GeCl\{o\text{-}C_6H_4(AsMe_2)_2\}$][$GeCl_3$] is the product obtained from reaction of [$GeCl_2$(dioxane)] with the diarsine in CH_2Cl_2. Its structure shows pyramidal cations and anions, both with crystallographic mirror symmetry, and with the diarsine symmetrically chelating (Ge–As = 2.5847(5) Å). Cl atoms in the anion form long contacts with the Ge atoms in the cation giving a loosely associated chain polymer with alternating cations and anions [208] (Fig. 36). Both the Ge–As and Ge–Cl distances are slightly longer than in the Ge(IV) complexes *trans*-[$GeCl_4(AsR_3)_2$] (R = Me or Et) (Section 8.2).

$Ph_2As(CH_2)_2AsPh_2$ does not displace dioxan from [$GeCl_2$(dioxane)] under similar reaction conditions in CH_2Cl_2 [208]. There are no reports of Ge(II) complexes involving either stibine (SbR_3) or bismuthine (BiR_3) ligands, the heavier analogues of the phosphines and arsines described in this section.

9.4. Oxygen, sulfur and selenium donor ligands

The complex [$GeCl_2$(dioxane)], prepared by reduction of $GeCl_4$ with triethylsilane [211], has been used very widely as a soluble Ge(II) source in the preparation of inorganic and organometallic compounds of Ge(II), since the dioxane can be substituted by a wide range of other ligands, and the compound is stable indefinitely in the absence of air or moisture. Its structure was originally refined in space group Cc [212], but a reinvestigation led to re-refinement in C2/c, revealing the structure consists of molecules of $GeCl_2$ coordinated to 1,4-dioxane ligands which bridge to adjacent $GeCl_2$ units, giving a polymeric chain structure, Ge–O = 2.3989(12), Ge–Cl = 2.2813(5) Å [213] (an independent structure determination shows slightly different distances [204]). There are two further secondary Ge···Cl contacts of 3.463(1) Å which cross-link the chains into a 2D sheet. The corresponding [$GeBr_2$(dioxane)] is isostructural [214].

The very unstable [$GeCl_2(thf)_2$] can be prepared by refluxing a solution of [$GeCl_2$(dioxane)] in thf and then cooling the solution to −78 °C. The compound decomposes above −30 °C. Its structure reveals each Ge atom is bonded to two *cis* Cl ligands and two trans thf molecules, and further weak association of monomers through a long Ge···Cl bridge, giving a chain polymer structure [215] (Fig. 37).

Independent studies have shown that both [$GeCl_2$(dioxane)] and $GeBr_2$ react with 12-crown-4 to give the very moisture sensitive, eight-coordinate, square antiprismatic [$Ge(12\text{-crown-}4)_2]^{2+}$ dication, with complete displacement of the halide ligands by the neutral crown ether [200,216] (Fig. 38). The Ge–O distances are around 2.3–2.4 Å. The same dication was also isolated from reaction of $GeCl_4$ and 12-crown-4 in the presence of Et_3SiH and $LiAlH_4$ [200]. Using larger 15- and 18-membered ring crown ethers gives the monocationic complexes [GeCl(L)]Y (L = 15-crown-5; Y = [$GeCl_3$] or [CF_3SO_3]; L = 18-crown-6; Y = [$GeCl_3$]) [216]. The structures of the two 15-crown-5 complexes show some anion dependence affecting the Ge–O distances [216]. The structure of [GeCl(18-crown-6)][$GeCl_3$] involves planar *endocyclic* coordination to Ge via four weakly interacting ether O atoms (Ge–O = 2.195(3), 2.359(4), 2.640(4), 2.869(5) Å), with the Cl axial [216].

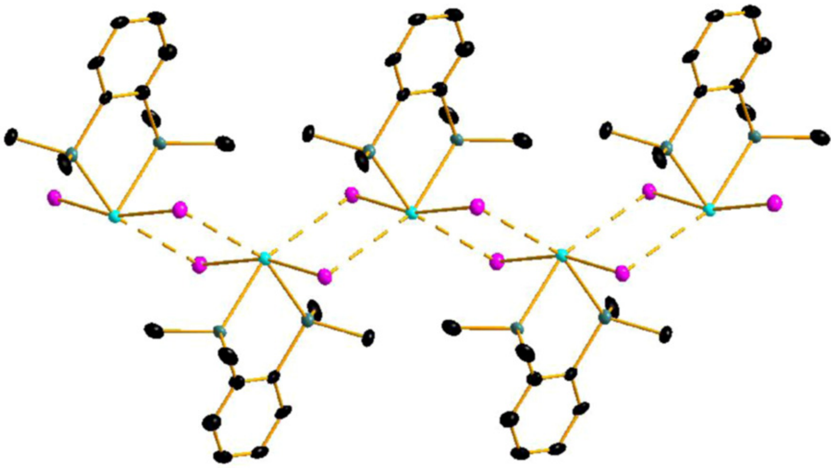


Fig. 35. Crystal structure of [$GeI_2\{o\text{-}C_6H_4(AsMe_2)_2\}$] (turquoise = Ge; teal = As; pink = I; black = C) [208].

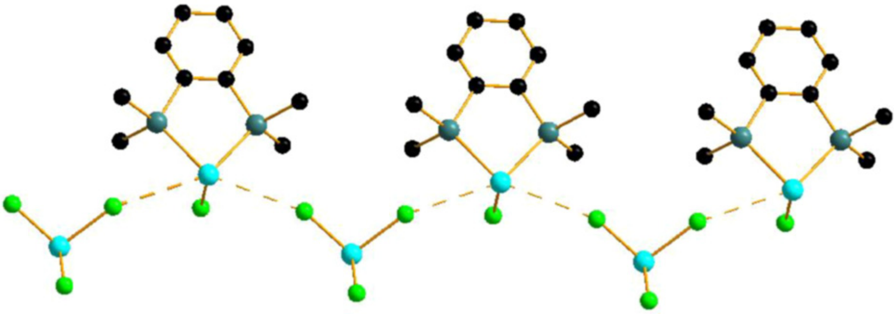


Fig. 36. Crystal structure of [$GeCl\{o\text{-}C_6H_4(AsMe_2)_2\}$][$GeCl_3$] (turquoise = Ge; teal = As; green = Cl; black = C) [208].

Addition of two mol. equivs. of $Me_3SiCF_3SO_3$ to [$GeCl_2$(dioxane)] and 18-crown-6 gives [Ge(18-crown-6)][CF_3SO_3]$_2$ in which four O-donor atoms from the crown (Ge–O = 2.218(3), 2.673(3) Å) and both triflate anions (Ge–O = 2.204(5) Å) coordinate weakly to the Ge [216] (Fig. 39).

Baines and co-workers have also described the preparation and structure of the dicationic cryptand-encapsulated complex [Ge(2.2.2-crypt)][CF_3SO_3]$_2$, obtained by reaction of 2.2.2-crypt with [$GeCl(NHCMe_2{}^iPr_2)(CF_3SO_3)$] in thf solution [217]. The D_3 symmetric dication (Fig. 40) shows a Ge–N distance of 2.524(3) Å and a Ge–O distance of 2.4856(16) Å, indicating very weak bonding interactions.

[$GeCl_2$(dioxan)] reacts with the macrocyclic thioethers [9]aneS_3 (1,4,7-trithiacyclononane) or [14]aneS_4 (1,4,8,11-tetrathiacyclotetradecane) in anhydrous CH_2Cl_2 to afford [$GeCl_2$([9]aneS_3)] and [$GeCl_2$([14]aneS_4)] as colourless, moisture sensitive solids in good yield [218]. Unlike the vast majority of complexes of [9]aneS_3 with other Lewis acids which show *fac* tridentate coordination of the crown, the structure of [$GeCl_2$([9]aneS_3)] shows the trithia macrocycle coordinated in a

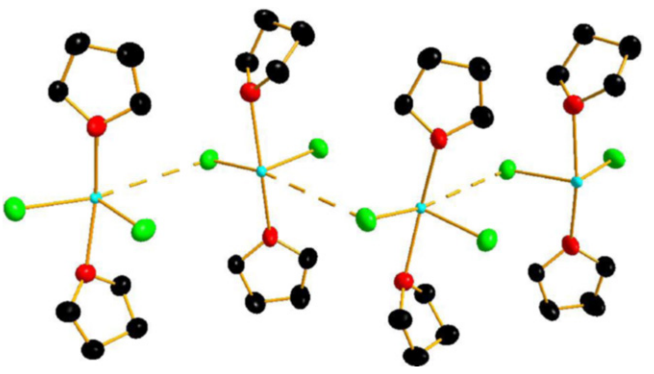


Fig. 37. Crystal structure of [$GeCl_2(thf)_2$] [215].

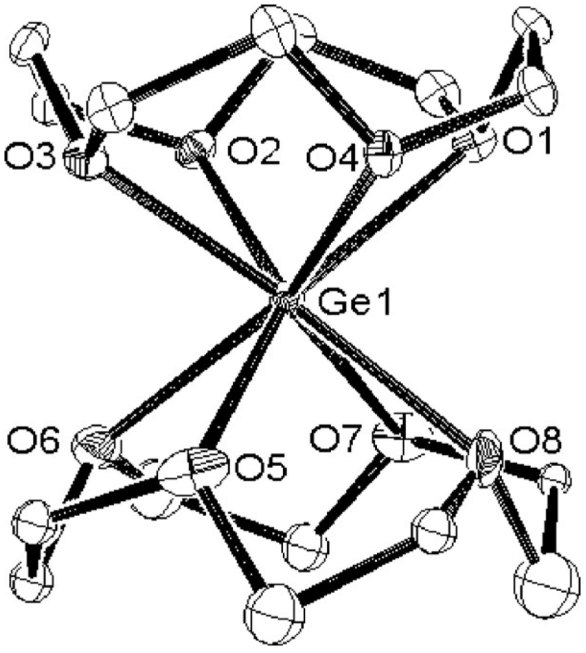


Fig. 38. Crystal structure of [Ge(12-crown-4)$_2$]$^{2+}$ [200].

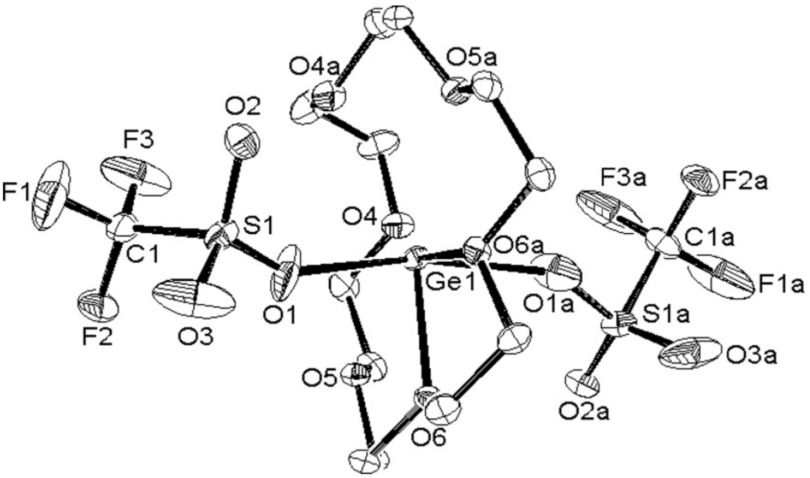


Fig. 39. Crystal structure of [Ge([18]crown-6)] $(CF_3SO_3)_2$ [216].

μ_2-κ^1 mode forming infinite zig-zag chains of $GeCl_2$ units bridged by *exocyclic* [9]aneS_3 ligands. The coordination at Ge(II) is via two primary Ge–Cl bonds (*ca.* 2.29 Å) and two long, mutually *trans* Ge–S bonds (*ca.* 2.74 Å), giving a saw-horse environment at Ge, with the lone pair of electrons assumed to occupy the vacant equatorial site of a distorted *pseudo*-trigonal bipyramid [218]. Two further long (secondary) Ge$\cdots$Cl interactions (*ca.* 3.7 Å) to Cl ligands on an adjacent chain lead to a highly distorted octahedron, $[S_2Cl_2 + Cl_2]$ donor set (Fig. 41).

Concentration of the CH_2Cl_2 from the filtrate from the preparation of $[GeCl_2([14]aneS_4)]$ gave crystals of the 2:1 compound $[(GeCl_2)_2([14]aneS_4)]\cdot 0.7CH_2Cl_2$ whose structure shows a $GeCl_2$ unit bound weakly to each of the four S-donor atoms of an *exocyclic* [14]aneS_4 molecule, and the μ_4-κ^1-coordinated tetrathiacrown units bridge $GeCl_2$ units to form infinite 2D sheets (Fig. 42) [218]. The coordination environment and bond lengths at Ge are similar to those for $[GeCl_2([9]aneS_3)]$. Using the hexathiacrown [18]aneS_6 (1,4,7,10,13,16-hexathiacyclooctadecane) gives the 1:1 complex $[GeCl_2([18]aneS_6)]$, again forming chains through *exocyclic* coordination of the S atoms in the 1- and 10-positions to $GeCl_2$ units (Fig. 43) [219].

Similarly, direct reaction of $GeBr_2$ with the tetrathioethers [14]aneS_4 or [16]aneS_4 (1,5,9.13-tetrathiacyclohexadecane) in

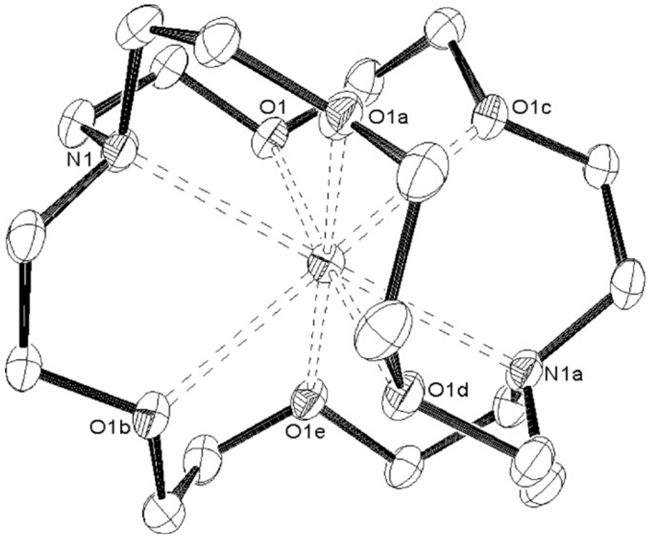


Fig. 40. Crystal structure of [Ge(2.2.2-crypt)]$^{2+}$ [217].

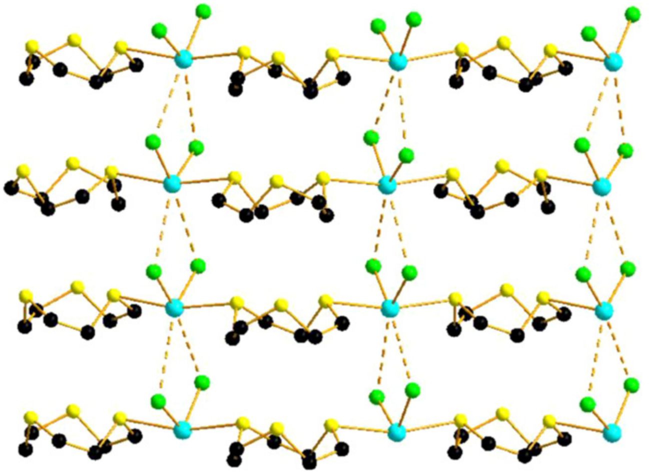


Fig. 41. Crystal structure of $[GeCl_2([9]aneS_3)]$ (turquoise = Ge; yellow = S; green = Cl; black = C) [219].

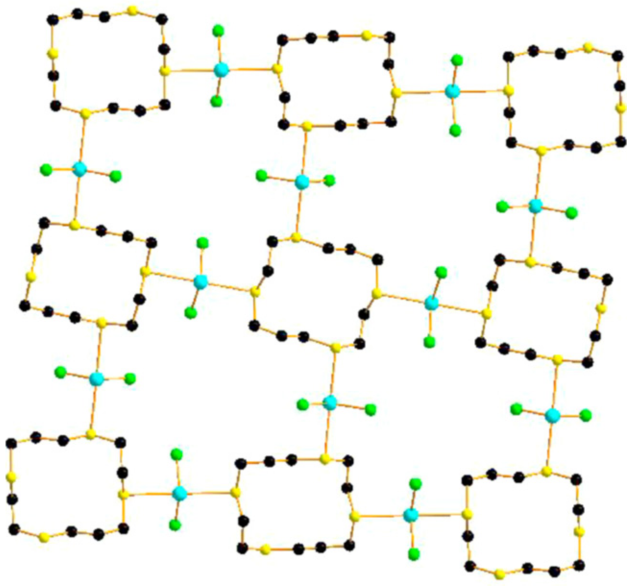


Fig. 42. Crystal structure of $[GeCl_2([14]aneS_4)]$ (turquoise = Ge; yellow = S; green = Cl; black = C) [219].

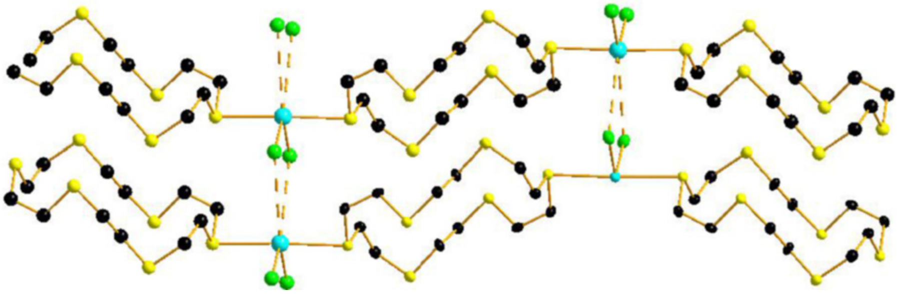


Fig. 43. Crystal structure of $[GeCl_2([18]aneS_6)]$ (turquoise = Ge; yellow = S; green = Cl; black = C) [219].

anhydrous MeCN gives $[GeBr_2([14]aneS_4)]$ and $[GeBr_2([16]aneS_4)]$, respectively [218]. Crystal structures show that both species adopt infinite chain structures like those in $[GeCl_2([9]aneS_3)]$ and $[GeCl_2([18]aneS_6)]$ above, through *exocyclic* μ_2-κ^1-coordination of the macrocycles to $GeBr_2$ units. Every alternate S atom from the macrocycles is coordinated, giving the linear chains. The Ge atoms are coordinated to two primary (*cis*) Ge–Br bonds (*ca.* 2.65 Å), two long, mutually *trans* Ge–S bonds of *ca.* 2.74 Å, giving a sawhorse geometry with the Ge-based lone pair assumed to occupy an equatorial site of a *pseudo*-trigonal bipyramid. As in the chloro complexes above, two weak, secondary Ge···halogen interactions (~3.9 Å) occur between the chains. The coordination environments at Ge(II) and the extended structures in these Ge(II) thioether complexes, show strong similarities, and the Ge–S bond distances do not differ significantly, suggesting that the Lewis acidity of $GeCl_2$ and $GeBr_2$ are rather similar [218].

The Ge–S bond distances in these Ge(II) complexes are significantly longer than those observed in the Ge(IV) species $[GeF_4\{RS(CH_2)_2SR\}]$ (R = Me, Et) (Section 8.3), d(Ge–S) = 2.43–2.49 Å. Attempts to isolate complexes of GeX_2 with these dithioethers were not successful [218].

In contrast, to these thiamacrocyclic systems, using the mixed thia-oxa macrocycle $[18]aneS_3O_3$ (1,4,7-trithia-10,13,16-trioxacyclooctadecane) and $[GeCl_2(dioxane)]$ gives the ionic $[GeCl([18]aneS_3O_3)][GeCl_3]$, comprising discrete $[GeCl([18]aneS_3O_3)]^+$ cations and $[GeCl_3]^-$ anions [219]. Within the cation the Ge is coordinated to one axial Cl ligand (2.252(2) Å), with three weak Ge–O bonds (~2.5 Å) and two weak Ge–S contacts (2.770(2), 2.802(2) Å), giving a distorted pentagonal pyramid (Fig. 44). It is clear that introducing O-donor atoms into the macrocyclic ring leads to *endocyclic* coordination, giving a structure quite similar to that of $[GeCl(18\text{-crown-}6)]^+$ (above). Addition of excess $Me_3SiCF_3SO_3$ to the reaction mixture gives $[GeCl([18]aneS_3O_3)][CF_3SO_3]$, containing the same cation structure, whereas no reaction was apparent with the $[GeCl_2(dioxane)]/[18]aneS_6$ system [219].

Similar *endocyclic* coordination occurs with the smaller ring $[15]aneS_2O_3$ (1,4-dithia-7,10,13-trioxacyclopentadecane), giving $[GeCl([15]aneS_2O_3)][GeCl_3]$. The crystal structure of the cation in this compound (Fig. 45) is also a distorted pentagonal pyramid, with Ge coordinated to all of the macrocyclic donor atoms and the remaining Cl ligand. The ligand conformation is, however, significantly different, occupying four equatorial coordination sites (O_3S donor set), with the Cl also equatorial, and the second S atom axial, possibly a result of the smaller 'hole-size' available. One Cl atom from the $[GeCl_3]^-$ anion interacts weakly in the sixth coordination site (Ge1···Cl3a = 3.2650(9) Å) [219]. The bond lengths around Ge are also quite different from those in $[GeCl([18]aneS_3O_3)]^+$; the Ge–S distances in $[GeCl([15]aneS_2O_3)]^+$ are ~0.1–0.2 Å shorter and the Ge–O distances are 0.1–0.5 Å longer [219].

There are no reported examples of Ge(IV) chloro complexes with neutral selenoether ligands, and earlier ^{77}Se NMR studies showed no interaction of $GeCl_4$ with Me_2Se and $RSe(CH_2)_2SeR$ in solution [154]. However, it has been shown very recently [219] that reaction of $[GeCl_2(dioxane)]$ with $[8]aneSe_2$ (1,5-diselenacyclooctane), $[16]aneSe_4$ (1,5,9,13-tetraselenacyclohexadecane) or $[24]aneSe_6$ (1,5,9,13,17,21-hexaselenacyclotetracosane) in anhydrous CH_2Cl_2 solution affords the complexes $[GeCl_2([8]aneSe_2)]$, $[(GeCl_2)_2([16]aneSe_4)]$ and $[GeCl_2([24]aneSe_6)]$, respectively, as white moisture sensitive solids. The crystal structure of $[GeCl_2([8]aneSe_2)]$ shows the Ge atom coordinated to two *cis* Cl ligands (~2.3 Å), and two mutually *trans* Se donor atoms from

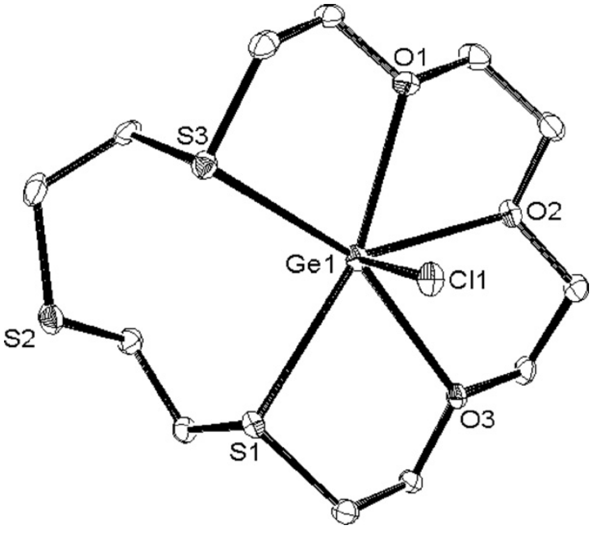


Fig. 44. Crystal structure of $[GeCl([18]aneS_3O_3)]^+$ [219].

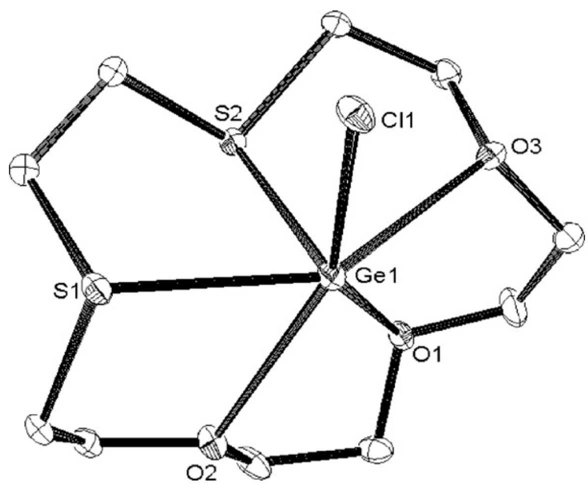


Fig. 45. Crystal structure of $[GeCl([15]aneS_2O_3)]^+$ [219].

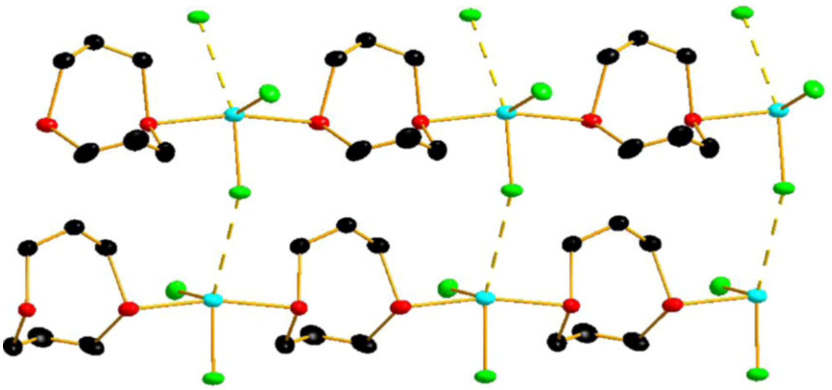


Fig. 46. Crystal structure of [$GeCl_2$([8]aneSe_2)] (turquoise = Ge; green = Cl; red = Se; black = C) [219].

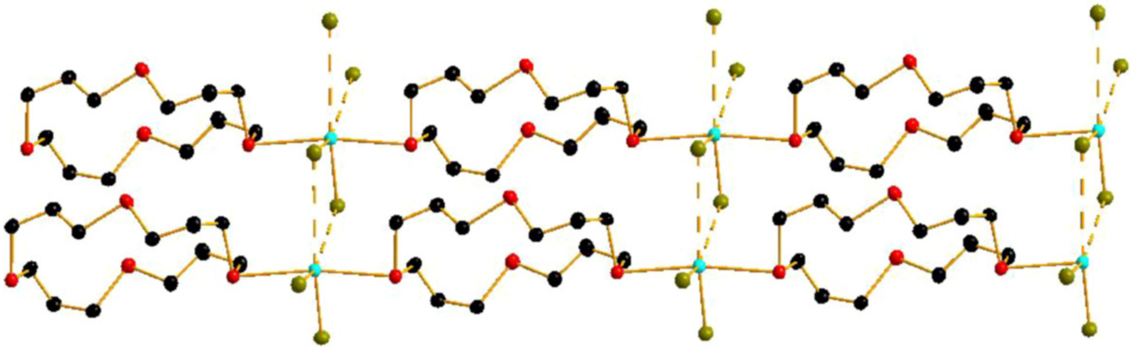


Fig. 47. Crystal structure of [$GeBr_2$([16]aneSe_4)] (turquoise = Ge; gold = Br; red = Se; black = C) [219].

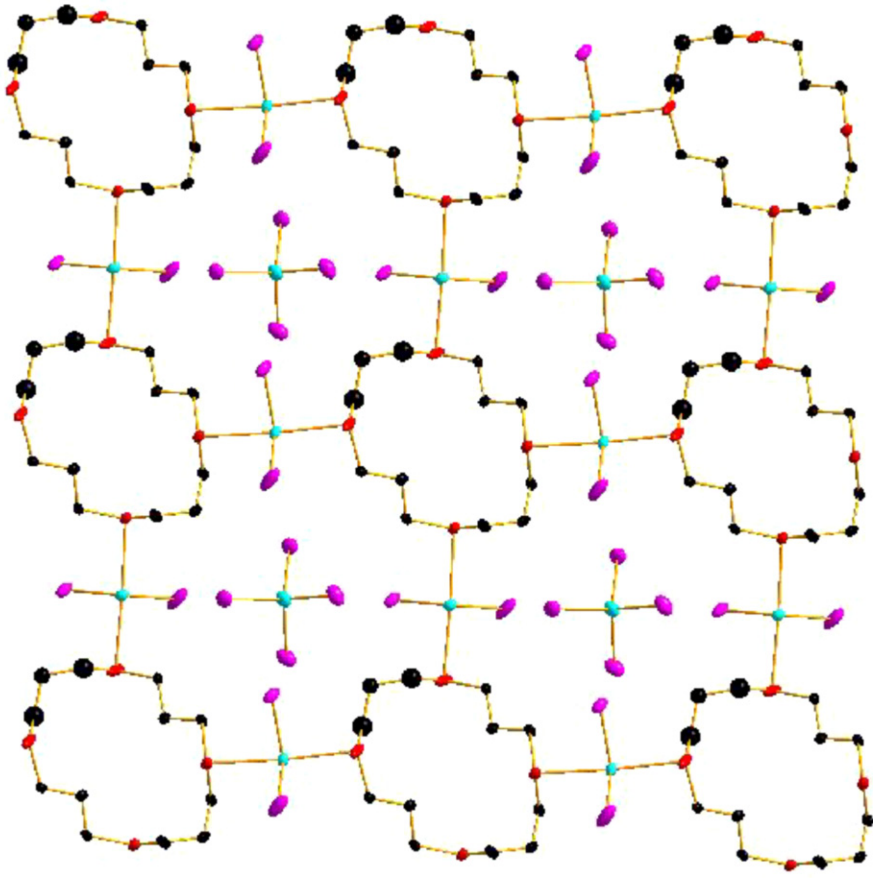


Fig. 48. Crystal structure of [$(GeI_2)_2$([16]aneSe_4)]·GeI_4 (turquoise = Ge; pink = I; red = Se; black = C) [219].

[8]aneSe_2 molecules (Ge–Se = 2.8467(8) Å), giving a distorted saw-horse geometry for the $GeCl_2Se_2$ units. The selenoethers bridge to the next Ge atom to form infinite chains, whilst each Ge forms one further (weak) Ge···Cl interaction (3.589(2) Å) to a Cl on an adjacent chain, cross-linking them into a 2D sheet (Fig. 46) [219].

The tetraselena crown, [16]aneSe_4, apparently gives the 2:1 Ge:macrocycle complex, $[(GeCl_2)_2([16]aneSe_4)]$ irrespective of whether the ratio of Ge:selenoether ligand used in the reaction is 1:1 or 2:1 [219]. The structure of this species shows the macrocyclic ligand has 4-fold symmetry and the complex is also a 2D sheet polymer, with each Ge atom coordinated to two *cis* Cl atoms and two mutually *trans* Se atoms, giving a *pseudo* trigonal bipyramidal geometry at Ge with the lone pair assumed to be in the equatorial void. The other Se atoms coordinate to other $GeCl_2$ units to give the sheet network, similar to the structure of $[(GeCl_2)_2([14]aneS_4)]$ above. Using $GeBr_2$ gives the 1:1 complex $[GeBr_2([16]aneSe_4)]$ which is a chain polymer structure (Fig. 47) with *exocyclic* selenoether coordination (Ge–Se = 2.824(1) Å) and weak Ge···Br contacts (∼3.96 Å) between the chains to form a network similar to that for $[GeCl_2([18]aneS_6)]$, $[GeCl_2([9]aneS_3)]$ and $[GeBr_2([14]aneS_4)]$ [219].

The different stoichiometries observed for these GeX_2/[16]aneSe_4 systems illustrate the sensitivity of this chemistry to subtle changes in the reaction constituents, and is further exemplified by the isolation of a few orange crystals of $[(GeI_2)_2([16]aneSe_4)]\cdot GeI_4$ from reaction of GeI_2 with the macrocycle in anhydrous MeCN. The structure comprises a very similar arrangement to that in $[(GeCl_2)_2([16]aneSe_4)]$ above. The Ge–Se bond distances are 2.792(2) and 2.8364(19) Å. The presence of molecular GeI_4 co-crystallised within the voids of the Ge(II) network is unexpected, and weak long-range I···I contacts between the network and the GeI_4 may contribute to stabilising this arrangement (Fig. 48). The GeI_4 is thought to arise from either oxidation or disproportionation of GeI_2 in the presence of the selenoether [219].

10. Silicon(II) complexes

Coordination complexes of formally silicon(II) halides are extremely rare. A report on $[SiCl_2(2,2'\text{-bipy})_2]$ which was assigned as Si(II) is most probably erroneous. Given the intense colour of the compound, it is more likely to be a Si(IV) complex involving 2,2′-bipy radical anions [115].

Very recent work has enabled preparation and structural authentication of the first two stable silicon dihalide complexes involving N-heterocyclic carbene ligands [63,66]. Thus the complex $[SiCl_2(NHC^iPr_2)]$ (Fig. 49) formed in high yield under mild reaction conditions by reductive elimination of HCl from $HSiCl_3$ in the presence of the NHC^iPr_2 [66]. This compound can also be obtained by reduction (with two molar equivalents of KC_8 at room temperature in toluene) of the Si(IV) complex $[SiCl_4(NHC^iPr_2)]$, and the analogous $[SiCl_2(NHCMe_3)]$ ($NHCMe_3$ = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene) has been obtained similarly [63]. Earlier work has shown that the same $[SiCl_4(NHC^iPr_2)]$ is reduced by excess KC_8 to produce the zero-valent $[(NHC^iPr_2)Si{=}Si(NHC^iPr_2)]$ [64]. Although strictly species of this type fall outside the scope of this review, it serves to illustrate the sensitivity of this chemistry to the precise reaction conditions and the prospects for diverse new silicon chemistry.

These dichlorosilylene compounds are unusually stable at room temperature and have been characterised spectroscopically in solution, whilst the crystal structure of $[SiCl_2(NHC^iPr_2)]$ shows a pyramidal coordination environment via the two Cl atoms and the C atom of the N-heterocyclic carbene NHC^iPr_2; the Si-based lone pair is assumed to occupy the void in the pyramidal structure. $[SiCl_2(NHC^iPr_2)]$ reacts with diphenylacetylene to form an unusual trisilacyclopentene species, accompanied by liberation of the NHC. The NHC ligands clearly play an important role in stabilising the otherwise very reactive dichlorosilylene unit [63].

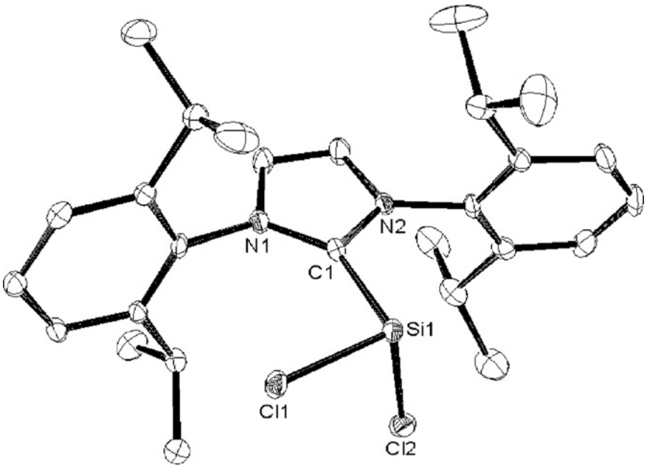


Fig. 49. Crystal structure of $[SiCl_2(NHC^iPr_2)]$ [66].

The dibromo analogue, $[SiBr_2(NHC^iPr_2)]$ [66] was prepared independently by first reacting $SiBr_4$ with one equivalent of NHC^iPr_2 at room temperature to give the ionic $[SiBr_3(NHC^iPr_2)]Br$. This compound is then reduced using 2.5 equiv. of KC_8 in THF at room temperature to give $[SiBr_2(NHC^iPr_2)]$, whose structure is very similar to its chloro analogue above [66]. The Si–C bond distances of 1.985(4) (X = Cl) and 1.989(3) Å (X = Br) indicate a strong bonding interaction with the NHC. DFT calculations have been conducted to probe the electronic structure of $[SiX_2(NHC^iPr_2)]$ (X = Cl or Br) [63,66]. Given the importance of silicon species in the electronic industry, and the exceptional ability of the NHC ligands to moderate the reactivity of the SiX_2 unit, it seems highly probable that these Si(II) NHC complexes will lead to discovery of a rich and new chemistry of low valent silicon.

11. Conclusions

The literature surveyed in the previous sections shows that in addition to classical Lewis acid–Lewis base complexes of silicon and germanium tetrahalides with neutral, hard N- and O-donor ligands, there is also a significant developing chemistry with softer donor ligands (P, As, S and Se). Recent studies have demonstrated a rich coordination chemistry of germanium(II), and that these complexes can adopt very variable coordination numbers, and irregular geometries. Understanding the structures and properties of these new types of complex presents a challenge to theoreticians, and DFT calculations are likely to contribute significantly to future research in this area. The very recent characterisation of the first stable molecular silicon(II) complexes with NHC ligands is a very notable development. In addition to their inherent interest, they present potentially very useful synthons for new low-valent silicon chemistry which will drive both coordination and organo-silicon chemistry. The continued importance of silicon and germanium in the manufacture of semi-conductor films, nanowires or nanoparticles, as well as the application of silicon and germanium nitrides in ceramics, will undoubtedly ensure continued research activity.

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