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Recent developments in the chemistry of selenoethers and telluroethers

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Abstract

The synthesis, properties and structures of complexes of mono-, bi-, poly-dentate and macrocyclic seleno- and telluro-ethers with both d-block and p-block elements reported in the last 10 years are described. Sections also describe the synthesis of new polydentate and macrocyclic ligands, the uses of their complexes, applications of ^{77}Se- and ^{125}Te-NMR spectroscopy, and current theories of bonding between d-block metals and neutral Group 16 donor ligands.

Keywords: Selenoether; Telluroether; Metal complexes; Macrocycles; ^{77}Se- and ^{125}Te-NMR spectroscopy

Nomenclature

naphtho-[8]aneSe$_2$	3,4-dihydro-2H-naphtho[1,8-*bc*]-1,5-diselenacyclooctane
[8]aneSe$_2$	1,5-diselenacyclooctane
[8]aneSe$_2$(OH)	1,5-diselenacyclooctane-3-ol
Me$_4$[8]aneSe$_2$	3,3,7,7-tetramethyl-1,5-diselenacyclooctane
sebc	3*H*-1,4,5,7-tetrahydro-2,6-benzodiselenonine
[9]aneS$_2$Te	1,4-dithia-7-telluracyclononane
[11]aneS$_2$Te	1,4-dithia-8-telluracycloundecane
[12]aneS$_2$Te	1,5-dithia-9-telluracyclododecane
[14]aneS$_3$Te	1,4,7-trithia-11-telluracyclotetradecane
naphtho-[12]aneSe$_3$	3,4,7,8-tetrahydro-2H; 6H-[1,8-*bc*]-1,5,9-triselenacyclododecane
[12]aneSe$_3$	1,5,9-triselenacyclododecane
Me$_6$[12]aneSe$_3$	3,3,7,7,11,11-hexamethyl-1,5,9-triselenacyclododecane
[14]aneSe$_4$	1,4,8,11-tetraselenacyclotetradecane
dibenzo-[14]aneSe$_4$	6,7,13,14-dibenzo-1,5,8,12-tetraselenacyclotetradecane
[16]aneN$_4$	1,5,9,13-tetraazacyclohexadecane
[16]aneS$_4$	1,5,9,13-tetrathiacyclohexadecane
[16]aneS$_2$Se$_2$	1,5-diselena-9,13-dithiacyclohexadecane
dinaphtho-[16]aneSe$_4$	8,9,19,20-tetrahydrodinaphtho[1′,8′-*jk*;1,8-*bc*]-1,5,9,13-tetraselenacyclohexadecane
[16]aneSe$_4$	1,5,9,13-tetraselenacyclohexadecane
[16]aneSe$_4$(OH)	1,5,9,13-tetraselenacyclohexadecane-3-ol
[16]aneSe$_4$(OH)$_2$	1,5,9,13-tetraselenacyclohexadecane-3,11-diol
Me$_8$[16]aneSe$_4$	3,3,7,7,11,11,15,15-octamethyl-1,5,9,13-tetraselenacyclohexadecane
benzo-[15]aneSe$_2$O$_3$	11,12-benzo-1,4,7-trioxa-10,13-diselenacyclopentadecane
[20]aneSe$_5$	1,5,9,13,17-pentaselenacycloicosane
[24]aneSe$_6$	1,5,9,13,17,21-hexaselenacyclotetracosane
[8]aneTe$_2$	1,5-ditelluracyclooctane
[12]aneTe$_3$	1,5,9-tritelluracyclododecane

1. Introduction

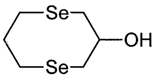
Selenium and tellurium chemistry has developed rapidly over the past 30 years or so. It is not the intention of this article to present a comprehensive review of all of this chemistry, but rather to review the significant developments in the chemistry of selenoether and telluroether ligands. The last review of this topic covered the literature up to 1992 [1]. This article brings coverage of literature available to us up to the end of 2000. The growing interest in these systems over the last decade may be attributed, in part, to the availability of reliable synthetic routes to the ligands, increasing availability of FT-NMR to study their solution behaviour and increasing evidence of enhanced ligating properties of the heavier telluroether and selenoether ligands compared to the previously much more widely explored thioethers. The main focus of this review will be to consider their role as ligands, and as such will detail their coordination and organometallic chemistry with transition metal and main group elements. We also illustrate recent developments on the synthesis of new ligands, although our treatment of the organoselenium and -tellurium chemistry does not aim to be comprehensive.

There are no reported compounds involving elements from Groups 1 or 2, nor are there any lanthanide or actinide compounds; hence their exclusion from the present discussion. The review will include discussion of structural aspects of the compounds, as well as their spectroscopic properties. Although thioether chemistry is not specifically included, it will be discussed for comparison where relevant. Selenide (selenolate) and telluride (tellurolate) compounds are not included. These topics have been reviewed previously by Smith and Ibers [2], Arnold [3] and Singh and Sharma [4]. Selenium-77-NMR spectroscopy is the subject of a recent review by Duddeck [5].

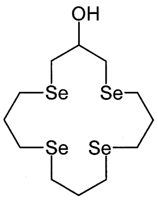
2. Ligands

The synthetic methods used for the preparation of monodentate, bidentate and hybrid selenoether and telluroether ligands have been reviewed previously and there have been no significant developments recently, the new ligands being prepared largely by variations of known methods. Therefore, in this review we shall focus on the preparation of macrocyclic and polydentate selenoether and telluroether ligands.

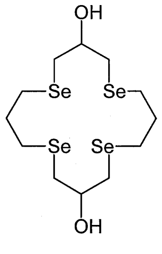
In 1989 Pinto and co-workers described the preparation of the cyclic selenoethers [8]aneSe_2, [14]aneSe_4, [16]aneSe_4 and [24]aneSe_6, formed via Na/NH_{3liq} reduction of the appropriate $NCSe(CH_2)_nSeCN$ ($n = 2$ or 3) and subsequent treatment of the resulting disodium salt with $Br(CH_2)_3Br$ at low temperature [6]. More recently, Pinto and co-workers have obtained the hydroxyl-functionalised di- and tetra-selenoether macrocycles [8]aneSe_2(OH), [16]aneSe_4(OH) and [16]ane$Se_4(OH)_2$ which are obtained by a modification of this method, using the appropriate hydroxy-functionalised bis-selenocyanate precursor [7].



[8]aneSe_2-OH



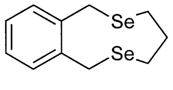
[16]aneSe_4-OH



[16]aneSe_4-$(OH)_2$

Reaction of o-$C_6H_4(CH_2SeCN)_2$ with $Br(CH_2)_3Br$ under similar conditions affords the cyclic diselenoether sebc in high yield [8].

The preparations of [12]aneSe_3 and [20]aneSe_5 involve stepwise introduction of the Se atoms, with ring closure occurring via a high dilution cyclisation of $NaSe(CH_2)_3SeNa$ (generated in situ) with TsO-$(CH_2)_3\{Se(CH_2)_3\}_nOTs$, $n = 1$ or 3, respectively, according to Scheme 1 [9]. Dibenzo-[14]aneSe_4 is synthesised by a similar approach (Scheme 2) [10]. The mixed thiaselena macrocycle [16]aneS_2Se_2 [10] is obtained by a [1 + 1] cyclisation of the appropriate α,ω-dithiol with $Br(CH_2)_3Br$ under high dilution conditions with Cs_2CO_3 in dmf, analogous to the route used for the preparation of [16]aneS_4 [11].

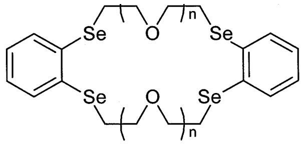


sebc

Adams and co-workers have demonstrated a new route to cyclic selenoether ligands. Thus, the catalytic cyclo-oligomerisation of 3,3-dimethylselenetane to Me_4[8]aneSe_2, Me_6[12]aneSe_3 and Me_8[16]aneSe_4 occurs effectively using $[Re_2(CO)_9(\overline{SeCH_2CMe_2CH_2})]$ or $[Re_2(CO)_9(NCMe)]$ at 115 °C (Scheme 3) [12].

The naphthalene-derivatised selenoether macrocycles dinaphtho-[16]aneSe_4, naphtho-[8]aneSe_2 and naphtho-[12]aneSe_3 have been isolated from reactions depicted in Scheme 4. Hydrolysis of dinaphtho-[16]aneSe_4 with sulphuric acid leads to formation of the ring contracted species naphtho-[8]aneSe_2 [13,14].

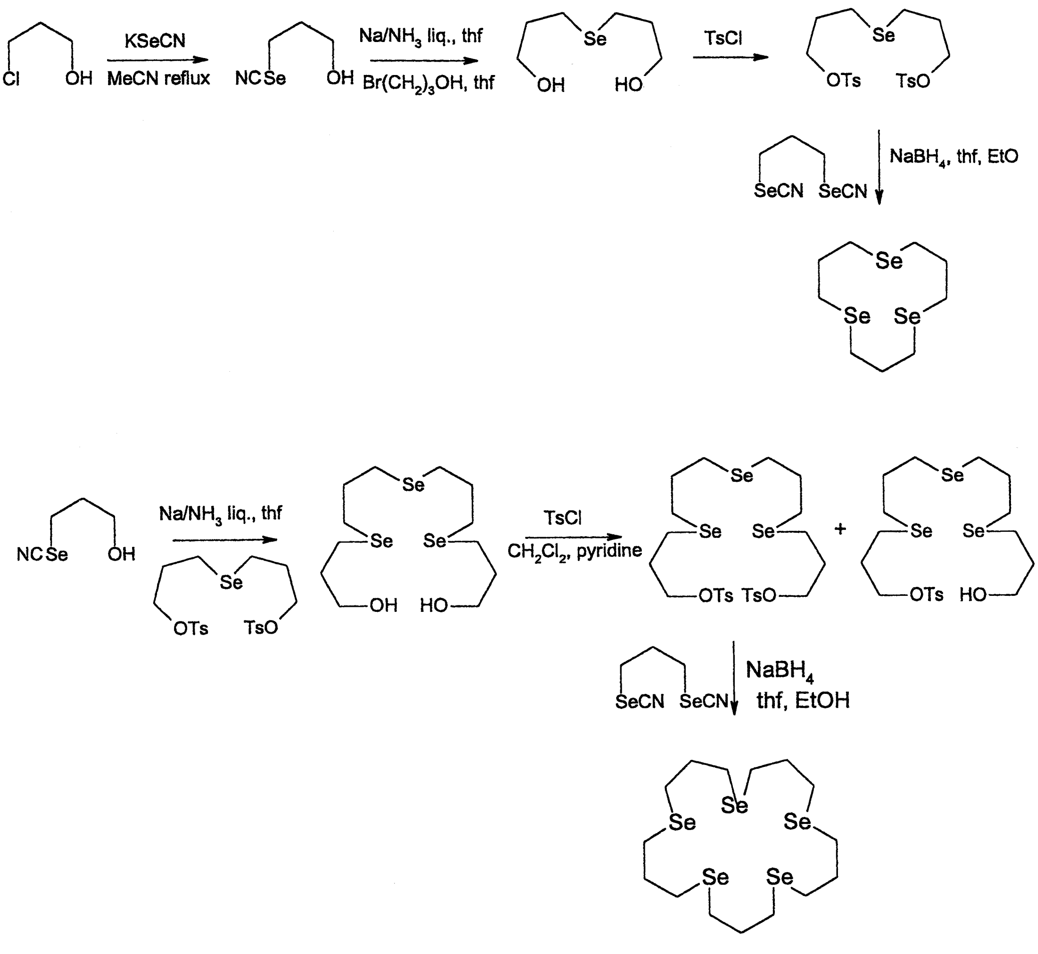
The mixed Se_4O_2-donor macrocycles I–III, Se-containing crown ethers, have been obtained in moderate yield (10–20%) via reaction of o-$C_6H_4(SeK)_2$ with o-$C_6H_4\{SeCH_2(CH_2OCH_2)_nCH_2X\}_2$ (X = Cl, $n = 1$–3 or X = Br, $n = 3$, 4) in a [1 + 1] cyclisation process [15]. The yield is increased to between 18 and 40% if o-$C_6H_4(SeH)_2$ is treated with the dichloroselenoether in Cs_2CO_3/dmf, utilising the 'caesium effect' [15]. The corresponding benzo-[15]aneSe_2O_3 crown is obtained via a similar methodology [16]. A series of crown ether derivatives incorporating one Se or Te atom within the ring has been reported [17].



n = 1, 2, 3

I - III

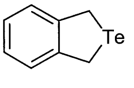
Se_4O_x ligands



Scheme 1.

The cyclic ditelluroether [8]aneTe$_2$ is prepared by treatment of Na$_2$Te with 0.5 molar equivalents of 1,3-dibromopropane in ethanol, followed by addition of NaBH$_4$ and a further equivalent of 1,3-dibromopropane [18]. The first example of a macrocyclic tritelluroether, [12]aneTe$_3$ has been isolated as a product from the pyrolysis of ditellurane in dmf at 160 °C, followed by reduction (Scheme 5) [19].

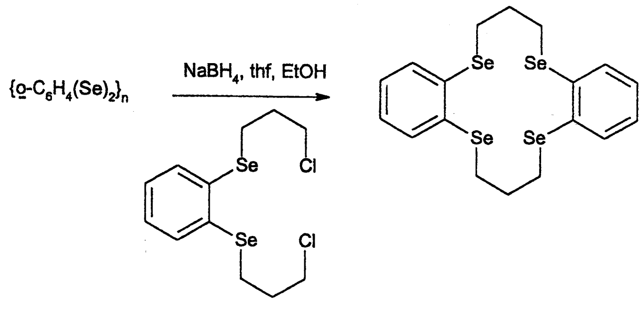
1,3-Dihydrobenzo[*c*]tellurophene has been isolated as a by-product of an unsuccessful attempt to prepare 2,11-ditellura[3.3]orthocyclophane, via treatment of α,ω-dichloro-*o*-xylene with two molar equivalents of KTeCN and subsequent reaction with a further equivalent of dichloro-*o*-xylene in EtOH/NaBH$_4$ [20].



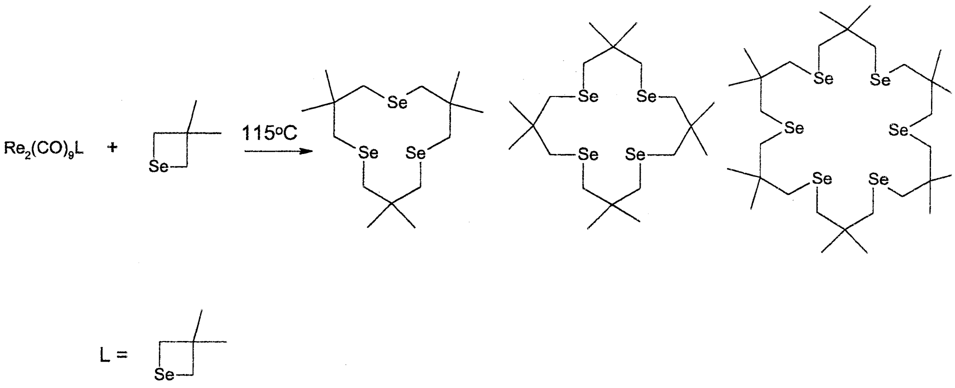
1,3-dihydrobenzo[c]tellurophene

A small number of mixed donor Te-containing macrocyclic ligands has been reported. The synthesis of the first series of mixed thia/tellura macrocycles, [9]aneS$_2$Te, [11]aneS$_2$Te, [12]aneS$_2$Te and [14]aneS$_3$Te, has been reported. These are obtained according to Scheme 6, in which Na$_2$Te in liquid NH$_3$ is treated with the appropriate α,ϖ-dichlorothioalkane. Following work-up, the macrocyclic ligands were obtained as light yellow poorly soluble solids in moderate yields [21].

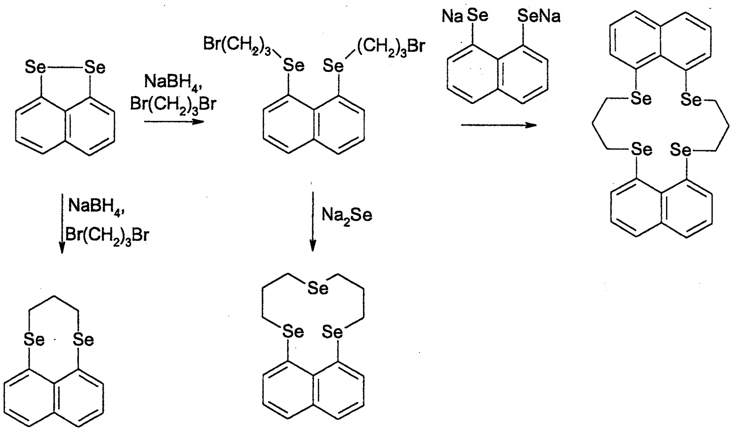
The telluroether Schiff base macrocycle IV has been obtained by condensation of bis(2-formylphenyl)-telluride with 1,2-diaminoethane [22].



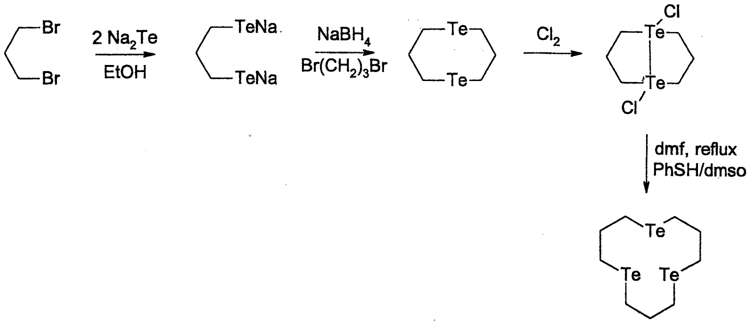
Scheme 2. Dibenzo[14]aneSe$_4$.



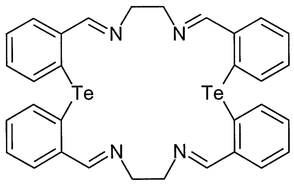
Scheme 3.



Scheme 4.



Scheme 5.

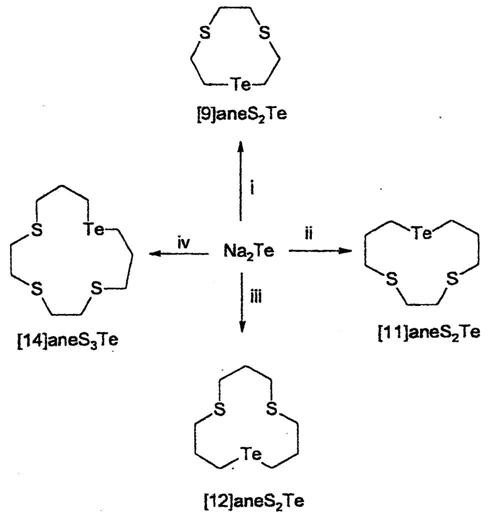


Te-containing Schiff base macrocycle

The synthesis of the tripod telluroether $MeC(CH_2TeMe)_3$ has been reported previously [23]. This method has been modified to produce the Ph-substituted derivative, $MeC(CH_2TePh)_3$ [24]. The preparations of the first facultative tritelluroethers, $RTe(CH_2)_3Te(CH_2)_3TeR$ ($R = Me$ or Ph) are achieved in good yield via the reaction of $RTe(CH_2)_3Cl$ with Na_2Te according to Scheme 7 [25].

3. Bonding

The bonding of Group 15 ligands, especially phosphines, but also arsines, stibines and even bismuthines, to transition metals, has been discussed at great length and investigated intensively for nearly 50 years [26]. Steric effects, usually qualitatively discussed via the Cone Angle model, are also important in Group 15, but for Group 16 ligands with only two substituent R-



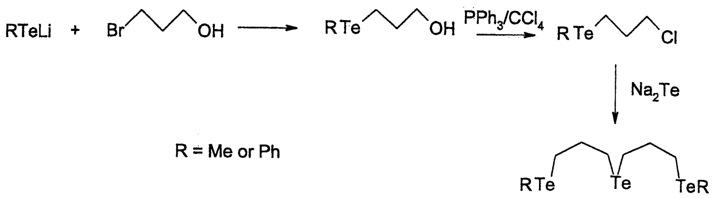
***Reagents and conditions*: i, $Cl(CH_2)_2S(CH_2)_2S(CH_2)_2Cl$, THF/$NH_3$(liq); ii, $Cl(CH_2)_3S(CH_2)_2S(CH_2)_3Cl$, THF/$NH_3$(liq); iii, $Cl(CH_2)_3S(CH_2)_3S(CH_2)_3Cl$, THF/$NH_3$(liq); iv, $Cl(CH_2)_3S(CH_2)_2$-$S(CH_2)_2S(CH_2)_3Cl$, THF/NH_3(liq); *T* = −78 °C, reagents added dropwise over 30 min.**

Scheme 6.

for Group 16 ligands with only two substituent R-groups, steric effects are not usually of importance, although interdonor linkages and resulting ring sizes will influence the coordination of polydentates and macrocycles in the usual way. Whilst data on seleno- or telluro-ethers have been far too limited and fragmented until recently, the almost complete absence of similar studies on bonding in thioether complexes is astonishing. At the simplest level, neutral chalcogenoethers R_2E, have two lone pairs on each chalcogen atom, one of which may form a σ-bond to a metal acceptor. The second lone pair may form a σ-bond to a second metal, resulting in a bridging R_2E group, and examples of such behaviour are well established via single crystal X-ray studies for all three R_2E (E = S, Se or Te). The second lone pair on the R_2E could also behave as a π-donor to a suitable metal d-orbital, particularly to electron poor metals, although there seems no good evidence that this is a significant component of the bonding. For R_2E, exactly like the well known PR_3 case, the E atom could behave as a π-acceptor either into the lowest empty d-orbital as in the original Chatt model [27] (3d for S, 4d for Se, etc.), or more likely as proposed for Group 15 donors [28] into the E–C σ* orbitals which are of more suitable energy. It is possible that to electron-rich metal centres the second lone pair will be a source of π-repulsion in M–ER_2.

Although there have been occasional suggestions for some weak π-back-bonding, usually based upon M–E distances being slightly less than the sum of the appropriate covalent radii, these effects have been of borderline statistical significance, and consensus has been that thioethers are weak σ-donors with little or no π-component to the bonding [29–31]. However, it has recently been suggested that π-acceptor behaviour may be significant for some macrocyclic thioether complexes [32].

Detailed experimental studies by Schumann and co-workers on $[(\eta^5\text{-}C_5H_5)Fe(CO)_2L]^+$ cations where L was a Group 15 or 16 donor ligand, subsequently extended to a theoretical study using extended Huckel MO theory by Schumann and Hoffmann [33], showed that within Group 16, both the inertness and the stability of the Fe–E bond increased Te ≫ Se > S > O. The study concluded that π-effects are insignificant, and that the unusually strong binding of telluroethers is due to enhanced σ-donation. More recently, our own studies [34,35] have shown that for $[Mn(CO)_3X(L\text{–}L)]$ (L–L = dithioether, diselenoether or ditelluroether) and $[Mn(CO)_3(tripod)]^+$ (tripod = $MeC(CH_2EMe)_3$, E = S, Se or Te), analysis of the force constants resulting from the IR spectra of the $Mn(CO)_3$ groups and the magnitude of the NMR chemical shifts (^{55}Mn, ^{77}Se, ^{125}Te) show similar trends, with increased electron density at the manganese centre S < Se ≪ Te. There are hints in both the Fe and Mn systems, that M–Te bonds may be slightly shorter than expected by comparison with data on the lighter analogues. Similar trends within Group 16 are also present in $[M(CO)_4(L\text{–}L)]$ complexes of Group 6 carbonyls [36]. For these low valent metal acceptors, the data were interpreted as due to increased σ-donation as Group 16 is descended, resulting from decreased electronegativity of the donors. For low valent metals the spatial extension of the d-orbitals will be such that good overlap with the large Te σ-orbital is not a problem. As the metal oxidation state increases, the metal becomes harder and the orbitals contract, which would decrease bonding to the large soft tellurium. This effect is clearly manifested in the inability of telluroethers to bond to high oxidation states of the platinum metals (see Section 4), whereas thio- and



Scheme 7.

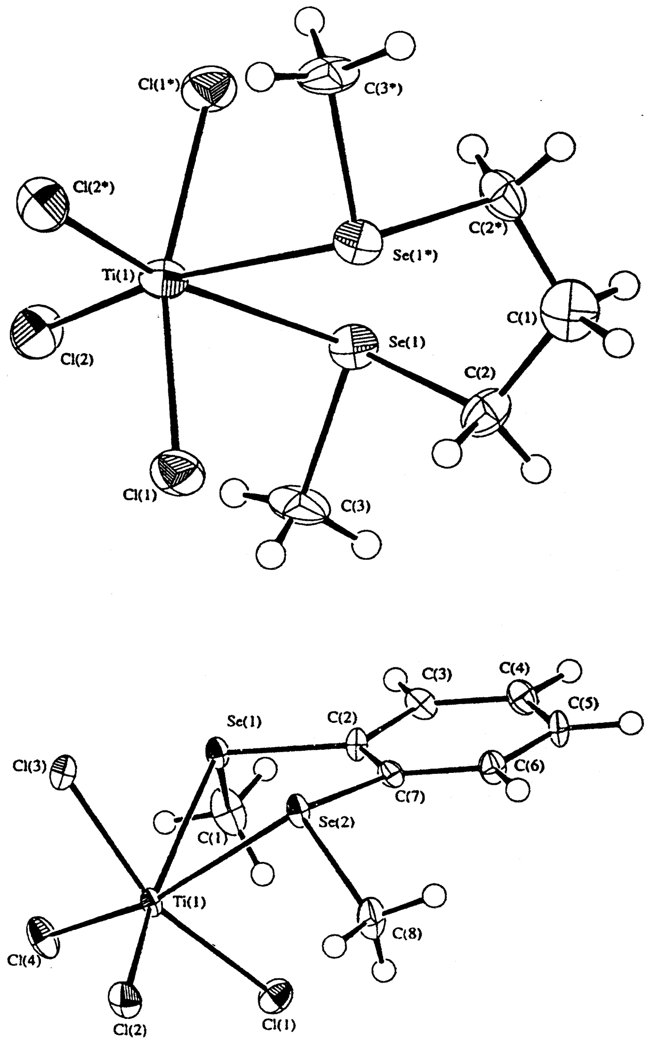


Fig. 1. Crystal structures of [$TiCl_4$(*DL*-MeSe$(CH_2)_3$SeMe)] and [$TiCl_4$(*meso*-*o*-$C_6H_4$$(SeMe)_2$], taken from Ref. [42] with permission from the Royal Society of Chemistry.

selenoether complexes of Pt(IV), Ru(III), and Os(IV) are all known. Recently we have compared [37] the ^{77}Se- and ^{125}Te-NMR coordination shifts on M(I) and M(III) centres (M = Rh or Ir). In complexes [M(COD){MeC$(CH_2EMe)_3$}]$^+$, the evidence is for strongest donation Te > Se, but for the higher oxidation states in [(η^5-C_5Me_5)M{MeC$(CH_2EMe)_3$}]$(PF_6)_2$ the interaction appears to be Se > Te (more details of the NMR parameters are in Section 5). Further studies on a much wider range of metal centres are required to explore the factors involved and refine the model, but it appears that within Group 16 the relative donor strength varies with the metal acceptor—to high or medium oxidation state metals it is S < Se > Te, whereas to low valent centres it is S < Se ≪ Te. This should be contrasted with Group 15 where the donation always appears to be P > As > Sb.

Theoretical studies to establish whether π-acceptor ability is important in the M–ER_2 bond have also continued. For example Ziegler and co-workers [38] using density functional theory, examined a series of [$(CO)_5$Cr–L] species where L = CO, NR_3, PR_3, SR_2, SeR_2 and R = H, Me or F. Of relevance to the present article, they concluded that thio- and selenoethers (telluroethers were not considered) were moderate σ-donors and weak π-acceptors. It was also concluded that SF_2 and SeF_2 (both are highly unstable in the free state) would be strong π-acceptors and, more surprisingly, good σ-donors.

4. Selenoether and telluroether complexes

4.1. Group 3

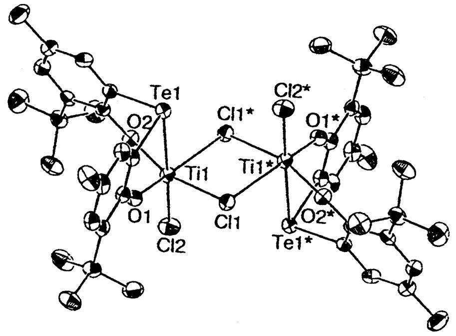
No complexes of scandium, yttrium or lanthanum have been reported. Scandium tellurolates including [(η^5-C_5Me_5)$_2$Sc(TeR)] [39] and [(β-diketiminate)Sc-$(TeR)_2$] [40] form TeR_2 on thermal decomposition, but the telluroether is expelled from the metal's coordination sphere in the process.

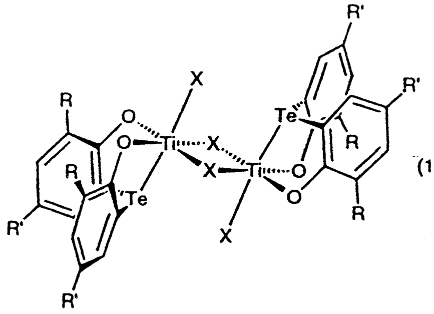
4.2. Group 4

New work is limited to titanium complexes. Deep red, very moisture-sensitive *cis*-[$TiCl_4(SeR_2)_2$] (R = Me or Et) were prepared by reaction of $TiCl_4$ with SeR_2 in hexane, and the [$TiCl_4(SeMe_2)_2$] is also produced by thermal decomposition of the diselenide [Ti_2Cl_8(Se_2-Me_2)] [41]. Both complexes have been characterised by single-crystal X-ray studies which confirmed the *cis* geometry, and revealed distorted octahedral environments about the Ti centre, with Cl–Ti–Cl angles > 90° and long Ti–Se bonds [2.740(2)–2.777(4) Å]. The diselenoethers, MeSe$(CH_2)_n$SeMe ($n = 2$ or 3), PhSe-$(CH_2)_2$SePh or *o*-$C_6H_4(SeMe)_2$ form deep orange or red [$TiCl_4$(diselenoether)] on reaction of the constituents in hexane. X-ray structures of [$TiCl_4$(*DL*-MeSe$(CH_2)_2$-SeMe)] and [$TiCl_4$(*meso*-*o*-$C_6H_4(SeMe)_2$] reveal similar geometries to the monodentate analogues, including the distorted octahedral geometry (Fig. 1) [42]. Intensely coloured [$TiBr_4$(L–L)] (L–L = MeSe$(CH_2)_n$SeMe ($n = 2$ or 3), *o*-$C_6H_4(SeMe)_2$) and [TiI_4(L–L)] (L–L = MeSe-$(CH_2)_2$SeMe or *o*-$C_6H_4(SeMe)_2$) were prepared similarly, the latter being very rare examples of complexes containing TiI_4.

Variable temperature solution NMR (^{1}H, ^{13}C{^{1}H}, ^{77}Se) studies of these complexes and their dithioether analogues show that for the chloro complexes, pyramidal inversion is fast at ambient temperatures but slow at 220 K, when resonances of the *meso* and *DL* invertomers are easily identified. In solution at low temperatures the bromo complexes are partially dissociated into mixtures of [$TiBr_4$(L–L)], $TiBr_4$ and free ligand, whilst the iodo complexes are still undergoing fast exchange even at 200 K.

The triselenoether $MeC(CH_2SeMe)_3$ forms $[TiX_4\{MeC(CH_2SeMe)_3\}]$ (X = Cl or Br), which are poorly soluble in non-coordinating solvents. Low temperature NMR spectra are consistent with the selenium ligand bound as a bidentate (and hence a six- rather than seven-coordinate Ti centre), exchange between the 'free' and 'bound' arms becoming rapid in solution below room temperature [43]. Generally, a comparison of the analogous thio- and seleno-ether complexes of Ti(IV) shows that dissociation is greater with Se than S donors consistent with weaker binding of the softer selenium to the hard Lewis acid Ti(IV), and dissociation also increases $TiCl_4 < TiBr_4 < TiI_4$ for a fixed Group 16 donor ligand [42,43]. Ditelluroethers react with TiX_4 to give intractible solids which have not yet been identified [44]. However, Ti(IV)–TeR_2 bonds are present in the complexes of some aryloxo ligands $[Ti_2Cl_4(L_3)_2]$ where L_3 are shown in Fig. 2. The Ti–Te distance is quite long, ca. 3 Å, which suggests a simple σ-bond. Similarly $[Ti(\eta^5\text{-}C_5R_5)Cl(L_3)]$ (R = Me or H) were also prepared, although these are mononuclear (Fig. 3) [45]. The complexes polymerise ethylene in the presence of MAO, the activity of the tellurium-containing complexes being significantly greater than for analogues containing methylene bridged aryloxides, but less than that of complexes of thioether bridged ligands, which conflicts with theoretical predictions [46].





(1)

5b: X = Cl, R = ᵗBu, R' = Me
6a: X = OⁱPr, R = R' = H
6b: X = OⁱPr, R = ᵗBu, R' = Me

Fig. 2. Crystal structure of $[Ti_2Cl_4(L_3)_2]$, taken from Ref. [45] with permission from the American Chemical Society.

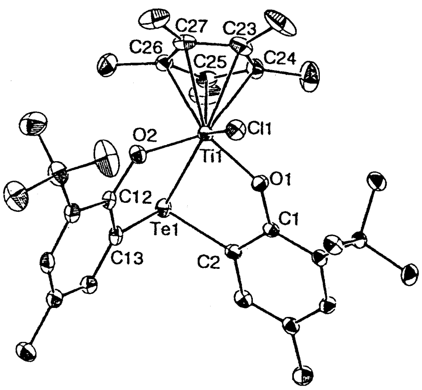


Fig. 3. Crystal structure of $[Ti(\eta^5\text{-}C_5R_5)Cl(L_3)]$ (R = Me or H), taken from Ref. [45] with permission from the American Chemical Society.

4.3. Group 5

No new work on SeR_2 or TeR_2 complexes of these three elements has been reported, and their Group 16 chemistry remains little known.

4.4. Group 6

There are a number of new reports on monodentate seleno- or telluroether complexes of Group 6 carbonyls. Examples include $[W(CO)_5(TePh_2)]$ made from $[W(CO)_5(thf)]$ and $[Fe(CO)_3I_2(TePh_2)]$, which has the expected octahedral structure with W–Te = 2.784(1) Å [47], and $[M(CO)_5L]$ (M = Mo or W; L = $(p\text{-}MeOC_6H_4)_2Te$) obtained by reaction of $[M(CO)_6]$ and the telluroxide $(p\text{-}MeOC_6H_4)_2TeO$ in thf [48]. The mechanism of the latter reactions, which involves *O*-atom transfer from Te to CO, and the kinetics were studied [48]. The synthesis of $[W(CO)_5\{Me(C_5Me_5)Se\}]$ [49], its unstable chromium analogue, and $[W(CO)_5\{((Me_3Si)_3C_5H_2)_2Te\}]$ [50] have been reported. The 1,3-dihydrobenzo[*c*]tellurophene (L) behaves as a simple Te-donor ligand in $[Mo(CO)_5(L)]$, *cis*-$[Mo(CO)_4(L)_2]$ and *fac*-$[Mo(CO)_3(L)_3]$ confirmed by multinuclear NMR studies and the crystal structure of the tetracarbonyl (Fig. 4) [20]. There are also several reports [51–53] of $[W(CO)_5L]$ compounds where L are selenetane or selenete ligands made in situ from tungsten carbonyl selenobenzaldehyde complexes.

A series of $[M(CO)_4(L\text{–}L)]$ (M = Cr, Mo or W; L–L = $MeSe(CH_2)_nSeMe$ ($n = 2$ or 3), $o\text{-}C_6H_4(SeMe)_2$, $MeTe(CH_2)_3TeMe$, $PhTe(CH_2)_3TePh$, $o\text{-}C_6H_4(TeMe)_2$ and some dithioether analogues) have been prepared from $[Cr(CO)_4(norbornadiene)]$, $[Mo(CO)_4(norbornadiene)]$ and $[W(CO)_4(Me_2N(CH_2)_3NMe_2)]$, respectively [36]. The structure of $[Cr(CO)_4(\mathit{DL}\text{-}MeSe(CH_2)_2SeMe)]$ was determined. Detailed IR and multinuclear NMR

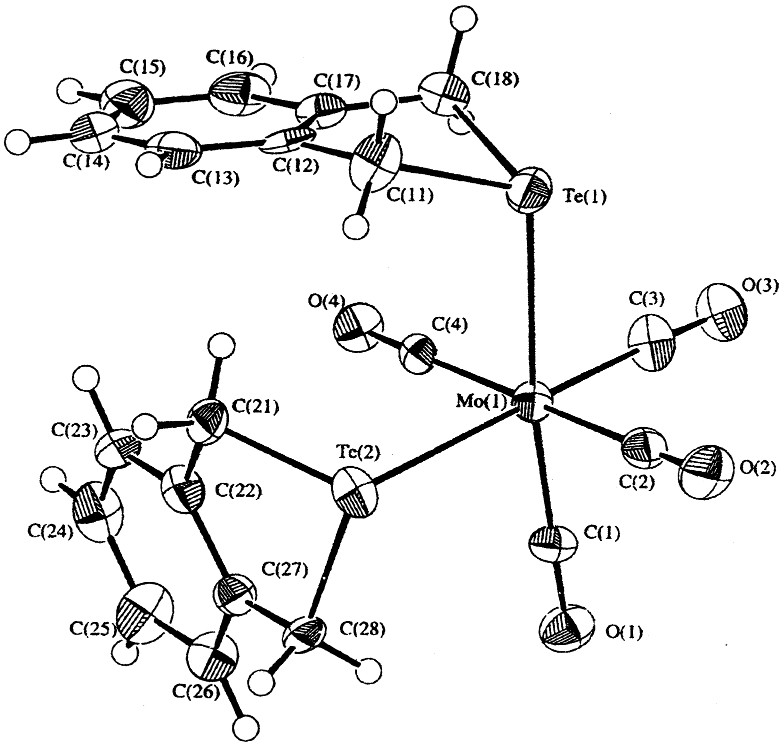


Fig. 4. Crystal structure of *cis*-[Mo(CO)$_4$(L)$_2$], taken from Ref. [20] with permission from the Royal Society of Chemistry.

(^{1}H, ^{13}C{^{1}H}, ^{77}Se, ^{125}Te and ^{95}Mo) studies on these systems were reported and reveal that σ-donation to the metal increases down Group 16 (see also Section 3) [36]. The ditelluroether, 1,2-bis(methyltelluromethyl)-benzene, forms [M(CO)$_4$(L–L)] (M = Mo or W), which are the first examples of 7-membered chelate ring telluroether complexes [54]. The structure of the W complex was determined by X-ray crystallography.

Similar studies have been carried out on *fac*-[M(CO)$_3$(tripod)] (M = Mo or W, tripod = MeC-(CH$_2$SMe)$_3$, MeC(CH$_2$SeMe)$_3$ or MeC(CH$_2$TeMe)$_3$) [55]. The complexes were made from [M(CO)$_3$(MeCN)$_3$] and the tripod ligands, and are surprisingly unstable in solution decomposing to [M(CO)$_4$(tripod)] and other products. Although [Cr(CO)$_3$(tripod)] was made in solution and identified spectroscopically, they were even less stable and have not been isolated. The [M(CO)$_3$-(tripod)] complexes show only a single invertomer in solution, the *syn* form (with a propeller-like arrangement of Me groups). *cis*-[Mo(CO)$_4${η^2-MeC(CH$_2$-SeMe)$_3$}] was isolated and fully characterised [55].

The linear tritelluroether {MeTe(CH$_2$)$_3$}$_2$Te forms *fac*-[Mo(CO)$_3${MeTe(CH$_2$)$_3$}$_2$Te}], but this is less stable than the tripod telluroether analogue and decomposes very rapidly in solution [25]. The cyclic selenoether [8]aneSe$_2$ forms [M(CO)$_4${[8]aneSe$_2$}] with all three metals, and the structure of the tungsten complex reveals the ligand in a chair–boat conformation (Fig. 5) [56].

Carbonyl halide complexes of Mo and W have been reported with the macrocyclic selenoethers [16]aneSe$_4$ and 1,6-diselena-3,4-benzocyclononane (sebc) of types [M(CO)$_3$X(L)] (M = Mo, X = Br or I, L = sebc; M = W, X = I, L = [16]aneSe$_4$ or sebc) and [{Mo(CO)$_3$-

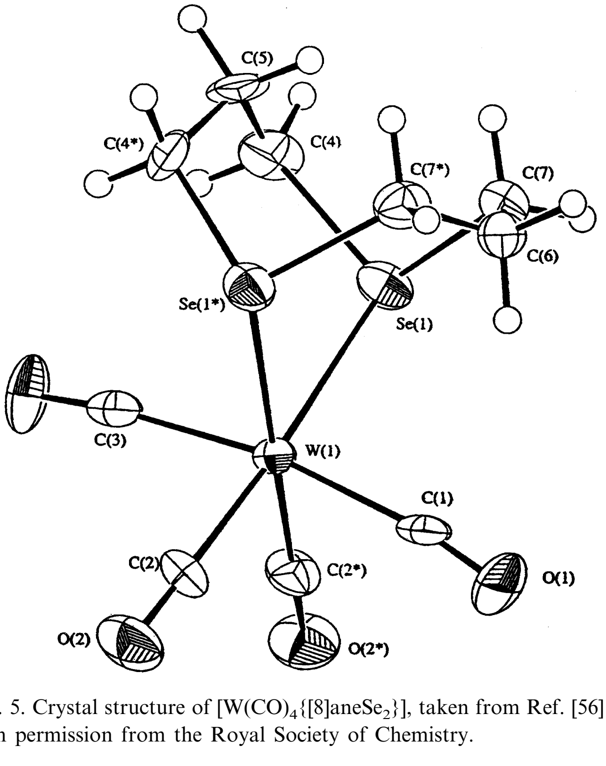


Fig. 5. Crystal structure of [W(CO)$_4${[8]aneSe$_2$}], taken from Ref. [56] with permission from the Royal Society of Chemistry.

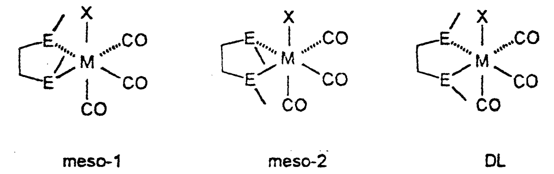


Fig. 6. NMR distinguishable isomers possible for *fac*-[MX(CO)$_3$(E–E)], E–E = dithio-, diseleno- or ditelluroether.

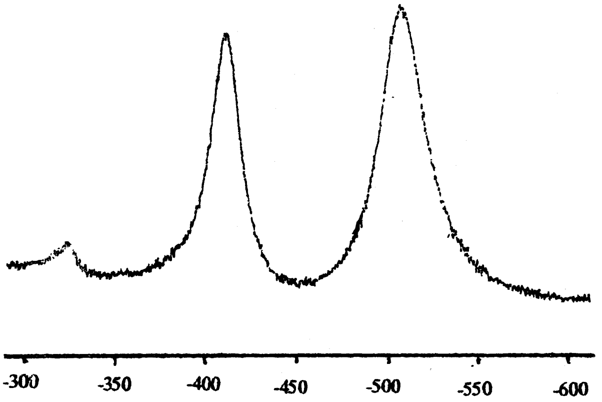


Fig. 7. ^{55}Mn-NMR spectrum of [MnBr(CO)$_3${*o*-C$_6$H$_4$(SeMe)$_2$}], taken from Ref. [64] with permission from the Royal Society of Chemistry.

X}$_2$([16]aneSe$_4$)] (X = Br or I) [56]. The complexes are poorly soluble in chlorocarbons and decomposed by other solvents which hindered characterisation, but are probably 7-coordinate, with bridging [16]aneSe$_4$ in the case of the dinuclear compounds.

The hybrid tridentate (2-Me$_2$NCH$_2$C$_6$H$_4$)$_2$Te coordinates only via the Te in [Cr(CO)$_5$(L)] [57].

Hydrolytically unstable Cr(III) complexes [CrX$_3$(L)] (X = Cl or Br) of the isomeric triselenoethers MeC(CH$_2$SeMe)$_3$ and (MeSeCH$_2$CH$_2$CH$_2$)$_2$Se have been prepared under anhydrous conditions from [CrX$_3$(thf)$_3$] in CH$_2$Cl$_2$ [58]. Similar reactions of [CrX$_3$(thf)$_3$] with [16]aneSe$_4$ and TlPF$_6$ gave [CrX$_2$([16]aneSe$_4$)]PF$_6$. The UV–vis spectra suggest that the selenium ligands exert weak ligand fields on the hard Cr(III) centre [58].

4.5. Group 7

No new data on Tc complexes have been reported, but there has been considerable interest in manganese and rhenium carbonyls.

The reactions of OTe(4-MeOC$_6$H$_4$)$_2$ with [M$_2$(CO)$_{10}$] (M = Mn or Re) results in the formation of [M$_2$(CO)$_8$(TeR$_2$)$_2$] via oxygen atom transfer, which on the basis of IR, ^{1}H- and ^{13}C-NMR spectra were identified as the diaxial isomers [59]. An unusual carbonyl cluster anion is [PPN][(TeMe$_2$)Mn(CO)$_4$(μ^5-Te)(μ^4-Te)Mn$_4$(CO)$_{12}$] made by alkylation of [(μ^4-Te)$_2$Mn$_4$(CO)$_{12}$]$^-$ with MeSO$_3$CF$_3$. The structure reveals a (TeMe$_2$)Mn(CO)$_4$ fragment bonded via Mn to the μ^5-Te group in the Mn$_4$Te$_2$ cluster [60]. Methylation of [(PhTe)Re(CO)$_5$] with [Me$_3$O]BF$_4$ gave the octahedral cation [Re(CO)$_5$(TePhMe)]BF$_4$ [61]. Several manganese halocarbonyl derivatives have been examined including [Mn(CO)$_4$Br(TeR$_2$)] (R = Me or Et) [62], [Mn(CO)$_3$Br(TeEt$_2$)$_2$] [62], [Mn(CO)$_3$Cl(SeMe$_2$)$_2$], [Mn(CO)$_3$Cl(TeMe$_2$)$_2$] [34] and [Mn(CO)$_3$Cl{1,3-dihydrobenzo(*c*)tellurophene}] [20]. Spectroscopic studies show that the [Mn(CO)$_3$X(L)$_2$] complexes have *fac* geometries, except for [Mn(CO)$_3$Cl(TeMe$_2$)$_2$] for which ^{55}Mn- and ^{125}Te-NMR spectra showed two species present, the second being the *mer,trans* isomer [34].

Treatment of [MeMn(CO)$_5$] with TeR$_2$ (R = Me, Et or ^{i}Pr) gave good yields of the acyls [(MeCO)Mn(CO)$_4$(TeR$_2$)], and the corresponding [(EtCO)Mn(CO)$_4$(TeR$_2$)] were prepared from [(EtCO)Mn(CO)$_5$] [62]. With [(PhCH$_2$)Mn(CO)$_5$] the acyls [(PhCH$_2$CO)Mn(CO)$_4$(TeR$_2$)] form initially, but on heating in pentane these decomposed to [(PhCH$_2$)Mn(CO)$_4$(TeR$_2$)]. All the complexes appear to be *cis* isomers [62].

Detailed structural and spectroscopic studies have been carried out on a substantial series of complexes of the form *fac*-[Mn(CO)$_3$X(L–L)] (X = Cl, Br or I, L–L = dithioether [63], MeSe(CH$_2$)$_n$SeMe (n = 2 or 3), PhSe(CH$_2$)$_2$SePh, *o*-C$_6$H$_4$(SeMe)$_2$ [64], [8]aneSe$_2$ [56], RTe(CH$_2$)$_3$TeR (R = Me or Ph), and *o*-C$_6$H$_4$(TeMe)$_2$ [34]. The [Mn(CO)$_3$X{PhTe(CH$_2$)$_3$TePh}] are unstable in solution, but the other complexes are reasonably stable as solids, although both light and oxygen sensitive in solution. Only one isomer is possible for the [8]aneSe$_2$ complexes, but for the acyclic ligands three invertomers are possible (Fig. 6) and if pyramidal inversion is slow on the appropriate NMR timescale, these are readily detected by ^{55}Mn-, ^{77}Se- or ^{125}Te-NMR spectroscopy (Fig. 7 shows a typical example). Interpretation of the spectroscopic data in terms of the bonding trends within Group 16 is discussed further in Section 3. X-ray structures were determined for [Mn(CO)$_3$Cl{*DL*-MeSe(CH$_2$)$_n$SeMe}] (n = 2 or 3) (Fig. 8), [Mn(CO)$_3$Br{*meso*-2-*o*-C$_6$H$_4$(SeMe)$_2$}], [Mn(CO)$_3$Br([8]aneSe$_2$)], and [Mn(CO)$_3$Cl{*meso*-2-*o*-C$_6$H$_4$(TeMe)$_2$}] [34,56,64]. The X-ray structure of [Mn(CO)$_3$Cl{*meso*-2-*o*-C$_6$H$_4$(CH$_2$TeMe)$_2$}] shows significantly longer Mn–Te bonds than those found in complexes with smaller chelate rings, but is spectroscopically similar to the other ditelluroether complexes [54].

A more restricted range of rhenium analogues has been reported, viz. [Re(CO)$_3$X([8]aneSe$_2$)] (X = Cl or Br) [56], [Re(CO)$_3$X{MeTe(CH$_2$)$_3$TeMe}] and [Re(CO)$_3$X{*o*-C$_6$H$_4$(TeMe)$_2$}] [34]. Structures were determined for [Re(CO)$_3$Br([8]aneSe$_2$)] [56], [Re(CO)$_3$Cl{*meso*-2-*o*-C$_6$H$_4$(TeMe)$_2$}] [34] and [Re(CO)$_3$Br{*meso*-2-PhTe(CH$_2$)$_3$TePh}] [61]. The macrocycle [16]aneSe$_4$ behaves as a bidentate in [Re(CO)$_3$Cl([16]aneSe$_4$)] and as a bis(bidentate) in [{Mn(CO)$_3$Cl}$_2$([16]aneSe$_4$)] [56].

A series of cationic *fac*-[Mn(CO)$_3$(tridentate)]CF$_3$SO$_3$ (tridentate = MeC(CH$_2$EMe)$_3$, E = S, Se or Te; MeC(CH$_2$TePh)$_3$, Se{(CH$_2$)$_3$SeMe}$_2$, some phosphorus and arsenic analogues) have been synthesised from [Mn(CO)$_3$(Me$_2$CO)$_3$]$^+$ and the ligands [24,35]. The *fac*-[Re(CO)$_3${MeC(CH$_2$SeMe)$_3$}]$^+$ is also known [24]. For the tripodal Group 16 donor ligands two invertomers are possible with either *syn* or *anti* Me groups. Interestingly, only one invertomer, (the *syn*) is found in solution in appreciable amounts, and this is also the form present in the solids for which X-ray structures are available—[Re(CO)$_3${MeC(CH$_2$SeMe)$_3$}]$^+$, [Mn(CO)$_3${MeC(CH$_2$EMe)$_3$}]$^+$ (E = S or Se), [Mn(CO)$_3${MeC(CH$_2$TePh)$_3$}]$^+$ (Fig. 9). ([Mn(CO)$_3${MeC(CH$_2$TeMe)$_3$}]$^+$ is disordered across a mirror plane in the crystal and hence the invertomer(s) cannot be distinguished.) Comparison of the spectroscopic and structural data suggest that, as expected, MeC(CH$_2$TePh)$_3$ is a weaker σ-donor than MeC(CH$_2$TeMe)$_3$ [24]. Similar *fac*-[Mn(CO)$_3$(tritelluroether)]CF$_3$SO$_3$ have been prepared with the linear tritelluroether ligands (RTe(CH$_2$)$_3$)$_2$Te (R = Me or Ph) and contain a mixture of invertomers [25].

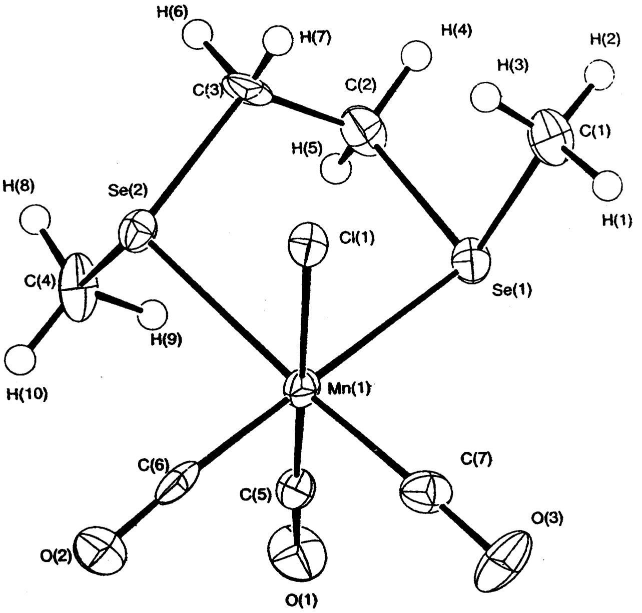


Fig. 8. Crystal structure of [Mn(CO)$_3$Cl{*DL*-MeSe(CH$_2$)$_2$SeMe}], taken from Ref. [64] with permission from the Royal Society of Chemistry.

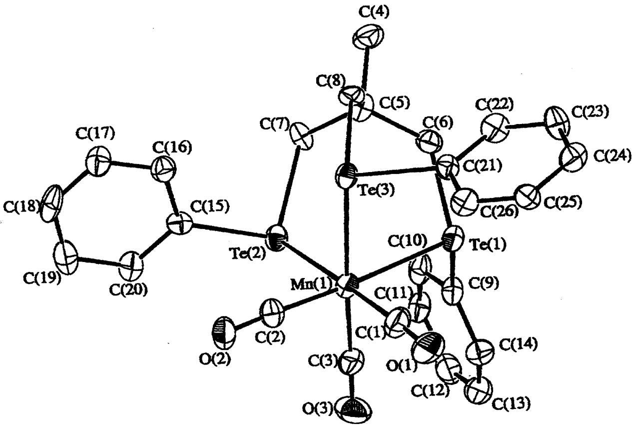


Fig. 9. Crystal structure of [Mn(CO)$_3${MeC(CH$_2$TePh)$_3$}]$^+$, taken from Ref. [24] with permission from the Royal Society of Chemistry.

Interestingly, [16]aneSe$_4$ also forms a *fac*-tricarbonylmanganese(I) complex (and hence behaves as a tridentate) on reaction with [Mn(CO)$_3$(Me$_2$CO)$_3$]$^+$ [56]. Treatment of this complex with Me$_3$NO [65] converts it into *cis*-[Mn(CO)$_2$([16]aneSe$_4$)]$^+$ (ν_{CO} = 1945, 1877 cm^{-1}) (compare [Mn(CO)$_2$([16]aneS$_4$)]$^+$ (ν_{CO} = 1956, 1885 cm^{-1}) [66].

Adams et al. [12,67] have shown that [Re$_2$(CO)$_9$(MeCN)] reacts with 3,3-dimethylselenetane ($\overline{\mathrm{SeCH_2CMe_2CH_2}}$) to form eq-[Re$_2(CO)_9$($\overline{\mathrm{SeCH_2CMe_2CH_2}}$)] which catalyses cyclo-oligomerisation of the selenetane to mixtures of 8-, 12- and 16-membered ring macrocycles (see Section 2) and large amounts of polymer. All three macrocycles have been structurally characterised, as have [Re$_2$(CO)$_9$($\overline{\mathrm{SeCH_2CMe_2CH_2}}$)] and [Re$_2(CO)_9$(η^1-Me$_6$[12]aneSe$_3$)].

4.6. Group 8

4.6.1. Iron

Alkylation of [Fe(CO)$_4$(PhTe)]$^-$ produced [Fe(CO)$_4$(PhMeTe)] [68], which reacted with I$_2$ in thf to form [Fe(CO)$_3$I$_2$(PhMeTe)] [47]. The corresponding [Fe(CO)$_3$I$_2$(Ph$_2$Te)] is made from [Fe(CO)$_5$] and Ph$_2$TeI$_2$, and an X-ray structure revealed *fac* tricarbonyls and *cis* iodines [47]. Schumann and co-workers have described studies on an extensive series of [(C$_5$H$_5$)Fe(L)$_2$L′]$^+$ complexes where L and L′ are combinations of CO, Group 15 or 16 donor ligands (see Section 3), most of which has been covered by previous reviews. More recent studies include the X-ray crystal structure of [(C$_5$H$_5$)Fe{P(OPh)$_3$}$_2$(TeMe$_2$)]BF$_4$ [69] and ^{13}C CP-MAS-NMR studies of [(C$_5$H$_5$)Fe(CO)$_2$L]BF$_4$ (L = SMe$_2$, SeMe$_2$ or TeMe$_2$) [70]. In contrast to its behaviour as a simple monodentate Te donor ligand with many metals, 1,3-dihydrobenzo[*c*]tellurophene reacts with Fe$_3$(CO)$_{12}$ with loss of Te (as Fe$_3$Te$_2$(CO)$_9$) and formation of a Te-free organoiron complex [71,72]. Similar loss of Te occurs on reaction of Fe$_3$(CO)$_{12}$ with tellurophenes and benzotellurophenes [72].

4.6.2. Ruthenium

The reaction of the mixed metal clusters [HRuCo$_3$(CO)$_{11}$(L)] (L = SMe$_2$, SeMe$_2$ or TeMe$_2$) with PMe$_2$Ph resulted in simple replacement of the Ru-bound chalcogen with the phosphine. In contrast, [HRuCo$_3$(CO)$_{11}$-

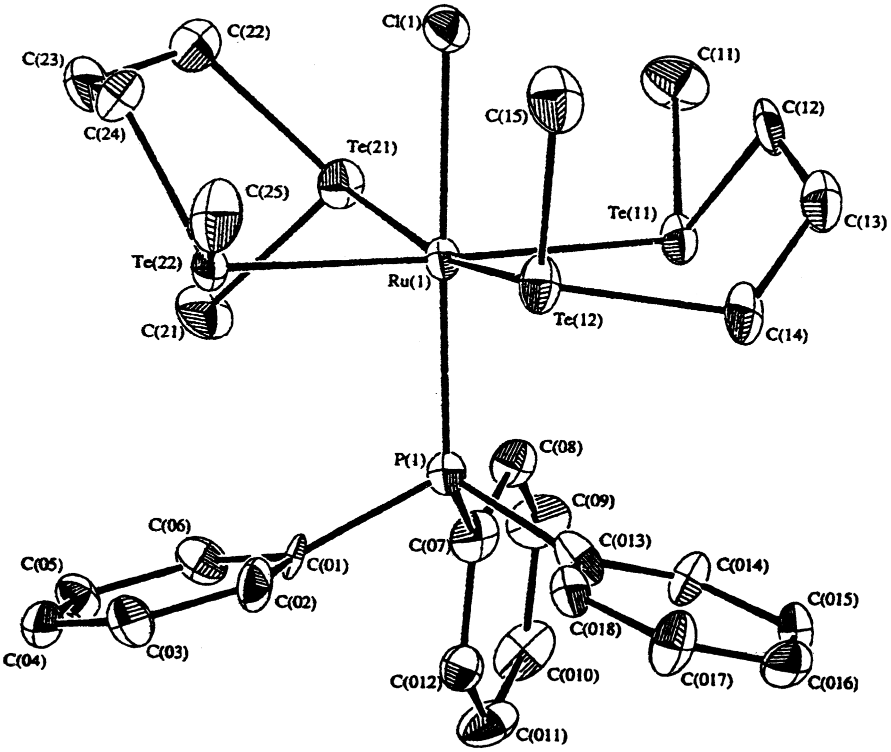


Fig. 10. Crystal structure of $[RuCl(PPh_3)\{MeTe(CH_2)_3TeMe\}_2]^+$, taken from Ref. [78] with permission from the Royal Society of Chemistry.

$(PMe_2Ph)]$ with $TeMe_2$ produced $[HRuCo(CO)_{10}(PMe_2Ph)(TeMe_2)]$ [73]. The $[Ru(CO)_2Cl_2(TePh_2)_2]$ previously prepared from $RuCl_3{\cdot}nH_2O$, $TePh_2$ and CO, has been prepared in improved yield from $[\{Ru(CO)_3Cl_2\}_2]$ and the ligand as a single isomer, shown by an X-ray crystal structure to contain octahedral Ru with *trans* $TePh_2$, *cis* CO and *cis* Cl [74]. The reaction of $[\{Ru(CO)_3Cl_2\}_2]$ with $(4\text{-}EtOC_6H_4Te)_2CH_2$, various hybrid telluroethers, including $PhTeCH_2CH_2SMe$ and $\{2\text{-}(4\text{-}MeOC_6H_4Te)_2C_2H_4\}_2NH$, has been reported [75]. Various oligomeric structures were suggested, although none of the complexes has been characterised by X-ray crystallography and most fail to give parent ions in the FAB mass spectra; the structures are thus speculative.

Reduction of $RuCl_3{\cdot}nH_2O$ with H_3PO_2 in ethanol in the presence of 1,3-dihydrobenzo[*c*]tellurophene forms yellow–brown *trans*-$[RuCl_2L_4]$ [20]. Ruthenium(II) diselenoether complexes, *trans*-$[RuCl_2(L\text{–}L)_2]$ (L–L = $MeSe(CH_2)_2SeMe$ or $PhSe(CH_2)_2SePh$), are readily obtained by reaction of $RuCl_3{\cdot}nH_2O$ with the ligand in ethanol using either Zn/Hg or H_3PO_2 as a reducing agent [76]. The corresponding bromides and iodides were obtained by prolonged reflux of the chloro-complex with LiX in ethanol. ^{77}Se-NMR spectra, the UV–vis spectra and an X-ray structure of $[RuCl_2\{$*DL*$PhSe(CH_2)_2SePh\}_2]$ all confirm the *trans* geometry. Cyclic voltammetry reveals reversible 1e oxidations at less positive potentials than the dithioether analogues, although changing the halide has little effect [76]. The complexes where X = Cl or Br are chemically oxidised in suspension in 40% aqueous HBF_4 by HNO_3 to green or blue *trans*-$[RuX_2(L\text{–}L)_2]BF_4$ [77]. The reaction of *o*-$C_6H_4(TeMe)_2$ with $RuCl_3{\cdot}nH_2O$ or $[Ru(dmso)_4Cl_2]$ gave $[RuCl_2\{o\text{-}C_6H_4(TeMe)_2\}_2]$, but a more general route to ditelluroether complexes, *trans*-$[RuX_2(L\text{–}L)_2]$ (X = Cl, Br or I; L–L = $RTe(CH_2)_3TeR$; R = Me or Ph, or *o*-$C_6H_4(TeMe)_2$; L–L = *o*-$C_6H_4(CH_2TeMe)_2$; X = Cl), is combination of $[Ru(dmf)_6][CF_3SO_3]_3$ with the ditelluroether and LiX in ethanol [54,78]. The products are orange or brown powders, poorly soluble in organic solvents, which showed irreversible or quasi-reversible oxidations in the cyclic voltammograms, and attempted chemical oxidation to Ru(III) brought about decomposition. The differing abilities of diseleno- and ditelluroethers to stabilise higher oxidation states of the platinum metals is notable. An X-ray crystal structure of *trans*-$[RuCl_2\{PhTe(CH_2)_3TePh\}_2]$ showed both ligands present as *meso* invertomers which may correlate with the major invertomer identified in solution by ^{125}Te-NMR spectroscopy [78]. The reaction of the same ditelluroethers with $[RuCl_2(PPh_3)_3]$ gave yellow $[RuCl(PPh_3)(L\text{–}L)_2]PF_6$ complexes which were much more soluble in organic solvents although slow decomposition with oxidation of the PPh_3 to $OPPh_3$ occurred in air [78]. The structure of $[RuCl(PPh_3)\{MeTe(CH_2)_3TeMe\}_2]PF_6$ (Fig. 10) showed a *trans* cation with one *DL* and one *meso* ditelluroether, whilst ^{125}Te-NMR studies showed several invertomers were present in solution.

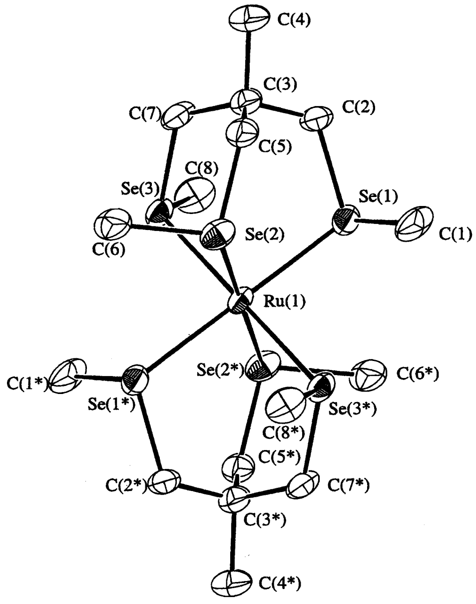


Fig. 11. Crystal structure of $[Ru\{MeC(CH_2SeMe)_3\}_2]^{2+}$, taken from Ref. [80] with permission from the Royal Society of Chemistry.

The C_1 backboned ditelluroether $(4\text{-}MeOC_6H_4Te)_2CH_2$ reacts with $[RuCl_2(dmso)_4]$ to form *cis*-$[Ru(dmso)_2Cl_2(L–L)]$ which contains a chelating ditelluroether with a rather strained 4-membered ring (Te–Ru–Te = 78°) [79]. The same ligand reacts with $[\{RuCl_2(p\text{-cymene})\}_2]$ to give orange–red crystals of $[\{RuCl_2(p\text{-cymene})\}_2(L–L)]$ where the ligand bridges the 6-coordinate Ru centres [79].

The tripodal ligands $MeC(CH_2EMe)_3$ (E = S, Se or Te) and $MeC(CH_2TePh)_3$ react with $[Ru(dmf)_6][CF_3SO_3]_3$ in refluxing MeOH to give homoleptic cations $[Ru^{II}(tripod)_2][CF_3SO_3]_2$ [80,81]. The structure of $[Ru\{MeC(CH_2SeMe)_3\}_2][CF_3SO_3]_2$ reveals (Fig. 11) an octahedral Ru centre coordinated to *syn* tripodal ligands, and NMR studies have identified this invertomer as the major solution form for all four complexes. Analysis of the UV–vis spectra shows the ligands exert strong fields on the d^6 metal centre, and this correlates with electrochemical data which show irreversible reduction or oxidation.

The reaction of these tripodal tridentates with $[RuCl_2(PPh_3)_3]$ produces the 'piano stool' $[RuCl_2(PPh_3)(tripod)]$, which are unstable in solution especially in the case of those containing the telluroethers, which decompose to paramagnetic species even with rigorous exclusion of air [82]. The X-ray structure of $[RuCl_2(PPh_3)\{MeC(CH_2SeMe)_3\}]$ (Fig. 12) shows the expected 6-coordinate ruthenium centre. The corresponding $[RuCl_2(dmso)(tripod)]$ made from the ligands and $[RuCl_2(dmso)_4]$ are much more stable in solution, suggesting that the instability of the phosphine complexes is associated with the presence of the PPh_3 [82]. The X-ray structure of $[RuCl_2(dmso)\{MeC(CH_2SeMe)_3\}]$ was reported [82]. The chlorine may be removed from $[RuCl_2(dmso)(tripod)]$ with $AgCF_3SO_3$ in MeCN to give $[Ru(MeCN)_3(tripod)]^{2+}$ as yellow or orange solids. The MeCN is readily displaced, for example, treatment of $[Ru(MeCN)_3\{MeC(CH_2SeMe)_3\}]^{2+}$ with $MeC(CH_2SMe)_3$ gave the mixed complex $[Ru\{MeC(CH_2SeMe)_3\}\{MeC(CH_2SMe)_3\}]^{2+}$ which was characterised by an X-ray structure, although the tripod ligands are disordered across the crystallographic inversion centre [82].

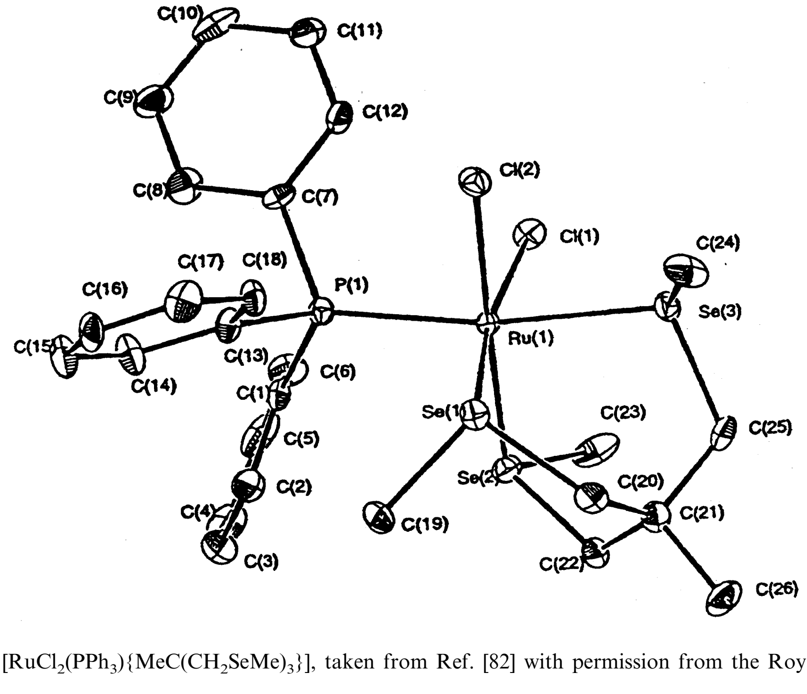


Fig. 12. Crystal structure of $[RuCl_2(PPh_3)\{MeC(CH_2SeMe)_3\}]$, taken from Ref. [82] with permission from the Royal Society of Chemistry.

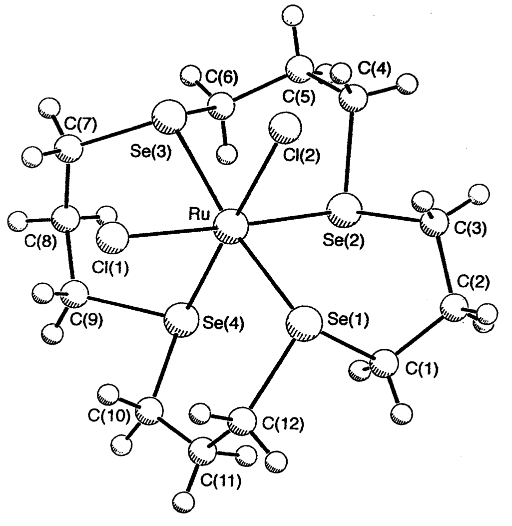
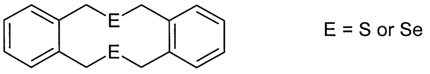


Fig. 13. Crystal structure of *cis*-[$RuCl_2$([16]aneSe_4)], taken from Ref. [84] with permission from the Royal Society of Chemistry.

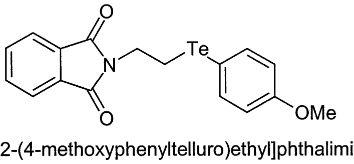
There have been significant studies of macrocyclic thio- and selenoether ligands with ruthenium. The cyclophanes 2,11-dithia- and 2,11-diselena[3,3]orthocyclophane bond as bidentate Group 16 donors in [(η^6-C_6H_6)Ru(cyclophane)(RCN)][BF_4]$_2$ and [(η^6-C_6H_6)Ru(cyclophane)X]X (X = Cl or Br) [83].



cyclophanes

Reaction of [Ru(dmf)$_6$]Cl_3 with [8]aneSe_2 or [16]aneSe_4 in boiling ethanol gave good yields of *cis*-[$RuCl_2$([8]aneSe_2)$_2$] or *cis*-[$RuCl_2$([16]aneSe_4)] (Fig. 13) [84]. Refluxing the *cis*-[$RuCl_2$([16]aneSe_4)] in nitromethane caused clean conversion to the corresponding *trans*-[$RuCl_2$([16]aneSe_4)]. Also, *cis* and *trans* dibromo-complexes were characterised, and the *trans*-[$RuBr_2$([16]aneSe_4)]Br was isolated by bromine oxidation. The reaction of [$RuCl_2$(PPh_3)$_3$] with [16]aneSe_4 gave yellow *trans*-[RuCl(PPh_3)([16]aneSe_4)]PF_6 which was shown by an X-ray crystal structure to contain the macrocycle in the rare *all up* conformation [84].

N-[2-(4-Methoxyphenyltelluro)ethyl]phthalimide behaves as a monodentate Te donor in [$RuCl_2$(*p*-cymene)L] [85].



N-[2-(4-methoxyphenyltelluro)ethyl]phthalimide

4.6.3. Osmium

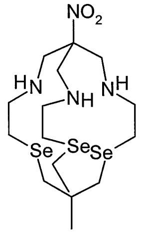
Although Os halo complexes of dithio- or diselenoether ligands have been made by reaction of the ligands with OsO_4–HX or [OsX_6]$^{2-}$, similar routes fail with ditelluroethers [86]. Orange or red *trans*-[$OsCl_2$(L–L)$_2$] (L–L = RTe(CH_2)$_3$TeR or *o*-C_6H_4(TeMe)$_2$, *o*-C_6H_4(CH_2TeMe)$_2$) were successfully made from [$OsCl_2$(dmso)$_4$] and the ligands and the structure of *trans*-[$OsCl_2${PhTe(CH_2)$_3$TePh}$_2$] determined [54,86]. In contrast to the ruthenium analogues, the osmium(II) complexes exhibit reversible one electron oxidations by cyclic voltammetry. Curiously, the reaction of [$OsCl_2$(dmso)$_4$] with dithioethers or diselenoethers is not a clean route to the corresponding [$OsCl_2$(L–L)$_2$]; instead, complex mixtures of the latter, [$OsCl_2$(dmso)$_2$(L–L)] and [OsCl(dmso)(L–L)$_2$]$^+$, are produced. However, [$OsCl_2$(PPh_3)$_3$] with MeS(CH_2)$_2$SMe, MeSe(CH_2)$_3$SeMe or RTe(CH_2)$_3$TeR, all gave yellow or brown *trans*-[OsCl(PPh_3)(L–L)$_2$]PF_6 [86]. The yellow *trans*-[OsCl(PPh_3)([16]aneSe_4)]PF_6 has also been obtained and is spectroscopically very similar to the ruthenium analogue [84].

4.7. Group 9

4.7.1. Cobalt

The [Co(CO)$_3$(NO)] reacted with $TeMe_2$ or $TeEt_2$ in the absence of solvent to form [Co(CO)$_2$(NO)(TeR_2)], and [(C_5H_5)Co(CO)$_2$$TeMe_2$] was made similarly from [(C_5H_5)Co(CO)$_3$] [87]. Air oxidation of a mixture of CoX_2 and [16]aneSe_4 in $MeNO_2$ followed by addition of NH_4PF_6 gave orange cobalt(III) complexes *trans*-[CoX_2([16]aneSe_4)]PF_6 (X = Cl or Br) [88]. The purple [CoI_2([16]aneSe_4)]PF_6 obtained similarly appears to be a mixture of *cis* and *trans* isomers and is unstable in solution. All three complexes were characterised by ^{77}Se- and ^{59}Co-NMR spectroscopy and an X-ray structure of the complex with X = Br confirms the *trans* structure (Fig. 14) [88].

A cobalt(III) complex of the sarcophagine ligand has been prepared by treating [Co{MeC(CH_2Se(CH_2)$_2$-NH_2)$_3$}]Cl_3 with HCHO and $MeNO_2$. The structure (Fig. 15) shows the cobalt encapsulated in a N_3Se_3 cage [89].



sarcophagine ligand

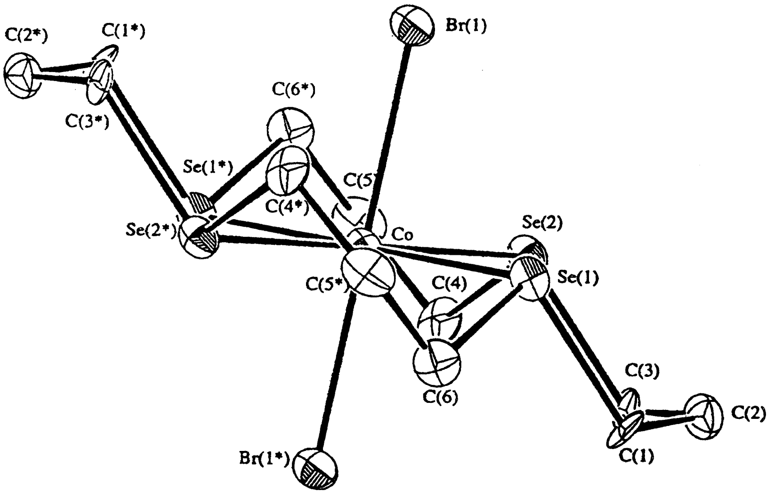
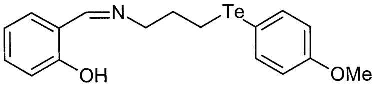


Fig. 14. Crystal structure of $[CoBr_2([16]aneSe_4)]^+$, taken from Ref. [88] with permission from the Royal Society of Chemistry.

Rather unstable cobalt(II) bromide complexes of hybrid Te–N donors have been reported with 4-$MeC_6H_4(NMe_2)(TeC_6H_4OEt$-4), 2-$C_5H_4NCH_2CH_2TeR$ (R = Ph, 4-$MeOC_6H_4$) [90–92]. The structures are unknown. Green cobalt(II) bromide complexes of the tellurium containing Schiff base (L) $CoBr_2L$, $CoBr_2L_2$, and CoBr(L–H) have been reported [93].



TeNO-donor Schiff base ligand

In the presence of air, nitromethane solutions of $CoBr_2$ and the N–Te hybrids 4-$MeC_6H_4(NMe_2)$-(TeC_6H_4OEt-4), 2-$C_5H_4NCH_2CH_2TeR$ (R = Ph, 4-$MeOC_6H_4$), 4-$MeOC_6H_4TeCH_2NH_2$ afford diamagnetic $[Co(N\text{–}Te)_2Br_2]BPh_4$ [90–93]. The isomer(s) present in these Co(III) products are not clear.

4.7.2. Rhodium

Little new work on rhodium complexes of simple seleno- or telluroether monodentates has been reported. 1:1 Adducts of $TeMe_2$ and $TeEt_2$ with the metallocycle $[(C_5H_5)_2Rh_2(\mu\text{-CO})(CF_3CCCF_2)]$ where the added TeR_2 bonds to one Rh and the carbonyl group is now bonded η^1 to the other have been described [94]. Me_2Se forms a similar complex in solution. Telluracyclopentane, $(CH_2)_4Te$, behaves similarly to $TeMe_2$ and the adduct has been characterised by an X-ray crystal structure [94]. Telluracyclopentane reacts with $RhCl_3 \cdot 3H_2O$ in ethanol to form red–brown $[RhCl_3L_3]$, which contains three doublets (^1J(Rh–Te) ca. 70–95 Hz) in the ^{125}Te-NMR spectrum consistent with a mixture of *mer* and *fac* isomers [95]. The $[RhCl_3L_3]$ (L = 1,3-dihydrobenzo[*c*]tellurophene) also contains a mixture of *fac* and *mer* isomers with the ligand bonded only via Te [20]. Coordination of this ligand through the Te only is also found in $[(\eta^5\text{-}C_5Me_5)RhL][CF_3SO_3]_2$ (as formulated the complex contains 4-coordinate Rh and coordination of the triflates is quite likely to give the much more common 6-coordination at the d^6 centre) and $[(\eta^5\text{-}C_5Me_5)RhCl_2L]$ [96,97]. Examples of dibenzotellurophene coordinated η^1 to Rh are also

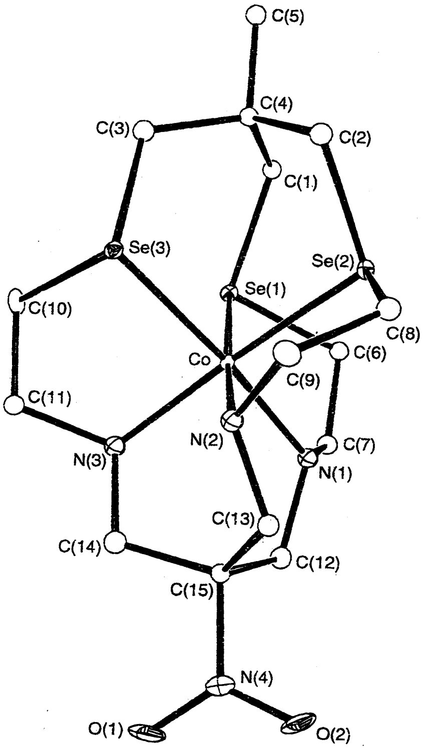


Fig. 15. Crystal structure of $[Co(L)]^{3+}$, taken from Ref. [89] with permission from the Royal Society of Chemistry.

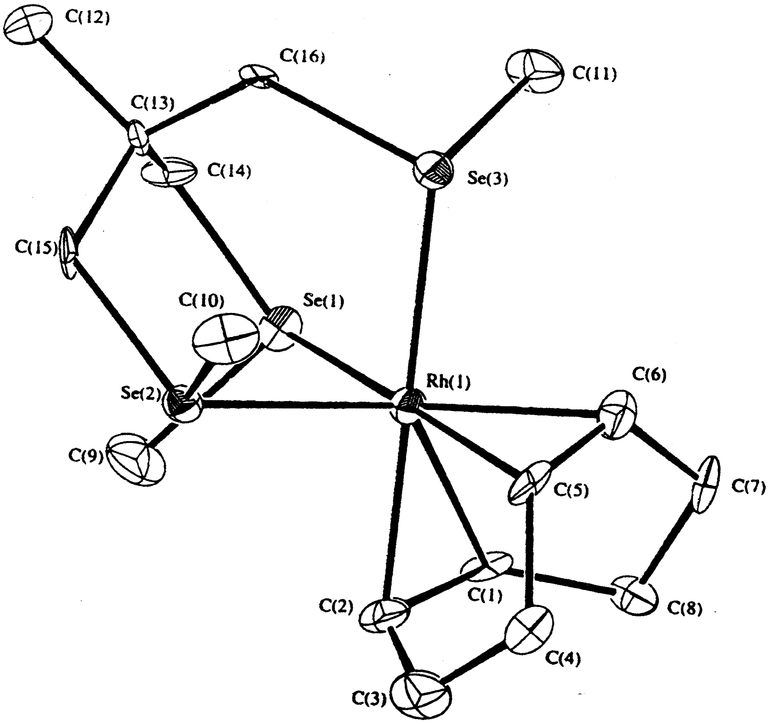


Fig. 16. Crystal structure of $[Rh(COD)\{MeC(CH_2SeMe)_3\}]^+$, taken from Ref. [37] with permission from the Royal Society of Chemistry.

known, although simple tellurophenes usually coordinate η^5 [96].

The ditelluroethers $RTe(CH_2)_3TeR$ (R = Me or Ph) and o-$C_6H_4(TeMe)_2$ react with $RhCl_3·3H_2O$ and NH_4PF_6 in ethanol to form deep orange $[RhCl_2(L–L)_2]PF_6$ complexes [78]. Although not subjected to X-ray studies, the presence of several doublets over a small frequency range in the ^{125}Te-NMR spectra and the UV–vis spectra are convincing evidence that these are predominantly *trans* isomers and that inversion at Te is slow. Deep-red $[Rh\{MeC(CH_2SeMe)_3\}_2][PF_6]_3$ is produced by reaction of the triselenoether with $[Rh(H_2O)_6]^{3+}$ and NH_4PF_6 in MeOH–H_2O, and is clearly an example of a $RhSe_6$ species [81]. Attempts to prepare analogues with $MeC(CH_2TeR)_3$ failed, probably due to Te–C bond cleavage under the harsh synthesis conditions rather than to inherent instability of the target $RhTe_6$ species [81]. Organometallic complexes of the tripodal seleno- and telluroethers have been prepared by reaction of $[\{Rh(COD)Cl\}_2]$ (COD = cyclooctadiene) with $MeC(CH_2ER)_3$ (E = Se, R = Me; E = Te, R = Me or Ph) [37]. The X-ray crystal structures of two of the complexes $[Rh(COD)\{MeC(CH_2SeMe)_3\}]PF_6$ and $[Rh(COD)\{MeC(CH_2TeMe)_3\}]PF_6$ show a 5-coordinate Rh(I) centre with a distorted square pyramidal geometry and a long apical Rh–Se(Te) bond. The structure of the former is shown in Fig. 16.

The ^{1}H-, ^{13}C-, ^{77}Se- or ^{125}Te-NMR spectra do not reflect the low symmetry shown in the solids and the complexes are no doubt fluxional in solution. Rh(III) complexes $[Rh(\eta^5\text{-}C_5Me_5)\{MeC(CH_2ER)_3\}][PF_6]_2$ of the same tripods are formed by the reaction of $[\{(\eta^5\text{-}C_5Me_5)RhCl_2\}_2]$, $TlPF_6$ and the ligands in refluxing methanol [37]. Comparison of the spectroscopic data on the $[Rh(COD)\{MeC(CH_2ER)_3\}]PF_6$ and $[Rh(\eta^5\text{-}C_5Me_5)\{MeC(CH_2ER)_3\}][PF_6]_2$ show that the tellurium ligands are superior σ-donors to Rh(I), but that to Rh(III) the donor ability is reversed, Se > Te (see Section 3). Complexes of linear tritelluroethers $Te\{(CH_2)_3TeR\}_2$ (R = Me or Ph) with Rh(III) have been obtained similarly and include $[Rh(\eta^5\text{-}C_5Me_5)\{Te\{(CH_2)_3TePh\}_2\}][PF_6]_2$ whose structure is shown in Fig. 17 [25].

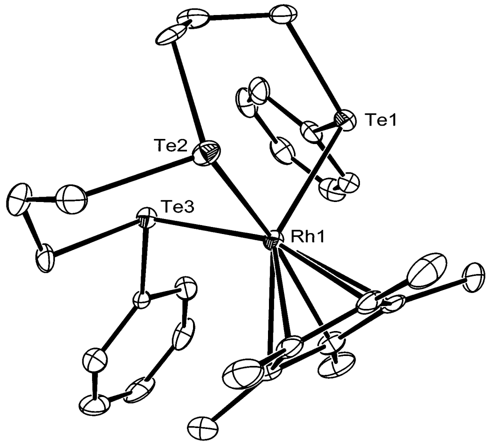


Fig. 17. Crystal structure of $[Rh(\eta^5\text{-}C_5Me_5)\{Te\{(CH_2)_3TePh\}_2\}][PF_6]_2$.

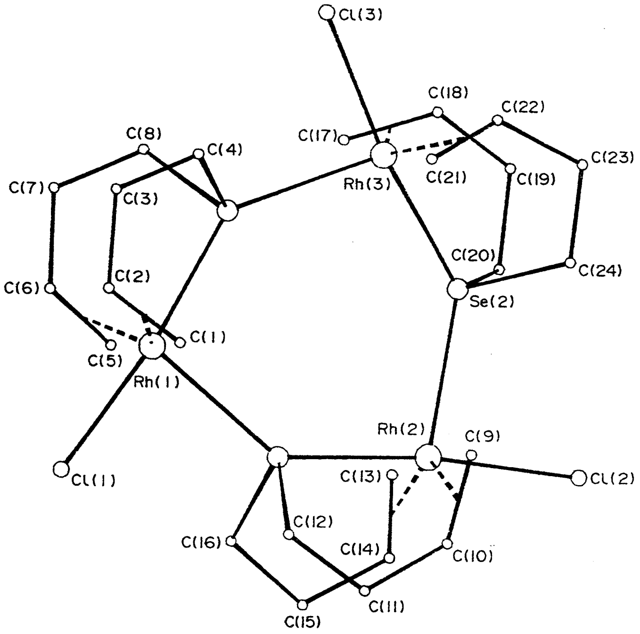


Fig. 18. Crystal structure of the [RhCl{Se($CH_2CH_2CH{=}CH_2)_2$}] trimer, taken from Ref. [100] with permission from Elsevier.

Rhodium trichloride complexes of both tripodal and linear tritelluroethers [$RhCl_3L$] have been prepared, but proved very poorly soluble in organic solvents, which has hindered spectroscopic studies [98].

The tetraselenoether [16]aneSe_4 forms very stable [RhX_2([16]aneSe_4)]PF_6 and a related [$RhCl_2$([8]-aneSe)$_2$]PF_6 is also known [88,99]. The structure of *trans*-[$RhCl_2$([16]aneSe_4)]PF_6 is very similar to those of the Co and Ir analogues (q.v.) even down to the conformation of the macrocyclic ring (*up*, *up*, *down*, *down*), a relatively rare example where structural data are available for all three metals in a triad of identical complexes [88]. In *N*,*N*-dimethylformamide solution, multinuclear NMR studies show both *cis* (minor) and *trans* (major) geometric isomers are present in both the chloro- and bromo-complexes, and partial separation may be achieved by recrystallisation from $MeNO_2$ in which the *cis* isomers are poorly soluble [88].

Rhodium(I) complexes of the dialkenylselenoether Se($CH_2CH_2CH{=}CH_2)_2$ and its sulphur analogue are formed as red crystals by reaction of [{RhCl($C_2H_4)_2$}$_2$] with the ligands at low temperatures in CH_2Cl_2 [100]. The X-ray crystal structure (Fig. 18) shows a trimeric unit with trigonal bipyramidal Rh(I) bonded to a terminal chloride (axial), the selenium (axial) and the two olefin groups of one ligand, whilst each selenium bonds to a second Rh centre via a longer (ca. 0.2 Å) bond to an equatorial position.

The work has been extended to the dialkenyltelluroether Te($CH_2SiMe_2CH{=}CH_2)_2$ which forms red [RhCl{Te($CH_2SiMe_2CH{=}CH_2)_2$}] possibly dimeric with chloride bridges like its thioether analogue, although the solution NMR spectra indicate some complex dynamic processes are occurring [101].

Hybrid N–Te ligands 4-$MeC_6H_4(NMe_2)(TeC_6H_4OR)$ (R = Me or Et) or HN{$CH_2CH_2Te(4\text{-}C_6H_4OR)$}$_2$ form brown [RhClL] complexes on reaction with [{RhCl(COD)}$_2$], which appear to be chloride-bridged dimers in the solid state, although in solution broad ^{1}H-NMR spectral lines suggest some exchange processes are present [102]. The trichloro-rhodium(III) complexes of the same ligands are also known [102].

4.7.3. Iridium

Considerably less work on iridium complexes has been reported, and all have rhodium analogues discussed in Section 4.7.2. Thus, pale yellow [Ir{MeC($CH_2SeMe)_3$}$_2$][PF_6]$_3$ is made from reaction of the ligand with [{IrCl(cycloctene)$_2$}$_2$] in H_2O–MeOH, followed by oxidation with HBF_4 and precipitation with NH_4PF_6 [81]. As with rhodium, attempts to isolate the telluroether analogue failed. The organometallic complexes [Ir(COD){MeC($CH_2ER)_3$}]PF_6 (ER = SeMe, TeMe, TePh) have similar properties to their Rh analogues described in Section 4.7.2 [37], and similar square pyramidal geometries were confirmed by X-ray crystal structures of [Ir(COD){MeC($CH_2TePh)_3$}]PF_6 and [Ir(COD){MeC($CH_2SeMe)_3$}]PF_6. The [Ir(η^5-C_5Me_5){MeC($CH_2ER)_3$}][PF_6]$_2$ were also isolated and show parallel spectroscopic properties to the Rh(III) analogues [37]. Boiling $IrX_3 \cdot nH_2O$ (X = Cl or Br) with [16]aneSe_4 in H_2O–EtOH followed by addition of $NaBPh_4$ gave yellow [IrX_2([16]aneSe_4)]BPh_4 [88]. An X-ray crystal structure of [$IrBr_2$([16]aneSe_4)]BPh_4 showed it to be the *trans* geometric isomer, but ^{77}Se-NMR spectroscopy show that both *cis* and *trans* isomers are present in solution.

4.8. Group 10

4.8.1. Nickel

Few examples of nickel selenoethers and no telluroethers have been reported. The previously known [$NiX_2(MeSeCH_2CH_2SeMe)_2$] produced by reaction of 2,5-diselenahexane with NiX_2 in *n*-BuOH under anhydrous conditions have been re-examined [103]. Attempts to isolate analogues with MeSe($CH_2)_3$SeMe or *o*-$C_6H_4(SeMe)_2$ failed, showing that both alkyl substituents and 5-membered chelate rings are necessary to stabilise complexes with the hard Ni(II). The X-ray crystal structure of [$NiCl_2(MeSeCH_2CH_2SeMe)_2$] (Fig. 19) shows a *trans* tetragonal octahedral geometry.

Macrocyclic analogues are the [NiX_2([16]aneSe_4)] (X = Cl, Br or I) which were too poorly soluble to grow crystals for an X-ray study, but nickel K-edge EXAFS data provided Ni–Se and Ni–X bond lengths. Analysis of the ligand field spectra of [NiX_2([16]aneSe_4)], [NiX_2([16]aneS_4)] and [NiX_2([16]aneN_4)] showed that on the hard Ni(II) centre the ligand field strength of these 16-membered ring macrocycles is [16]aneN$_4$ > [16]aneS$_4$ > [16]aneSe$_4$, with MeSeCH$_2$CH$_2$SeMe generating a larger ligand field than [16]aneSe$_4$, attributable to the smaller chelate ring size [103]. Attempts to oxidise the [16]aneSe$_4$ complexes to nickel(III) were unsuccessful. The reaction of [NiCl$_2${Ph$_2$PCH$_2$CH$_2$PPh$_2$}] with *o*-C$_6$H$_4$(CH$_2$ER)$_2$ (E = Se or Te, R = *p*-C$_6$H$_4$OR) is reported to give brown products formulated as octahedral [NiCl$_2${Ph$_2$PCH$_2$CH$_2$PPh$_2$}L] [104]. However, these materials give sharp ^{1}H- and ^{31}P-NMR resonances in the 'normal' range, whereas one would expect the paramagnetic Ni(II) ion to produce substantial shifts or possibly broaden the resonances so much they are not seen. The identity of these materials needs further study.

4.8.2. Palladium and platinum

A substantial amount of work on Pd(II) and Pt(II) complexes has been reported along with a small number of studies of Pt(IV). Since many papers reported parallel studies of the complexes of the two metals, these are treated together. The work will be covered in the order monodentate ligands, bidentates, polydentates, macrocycles, and then hybrid donor ligands.

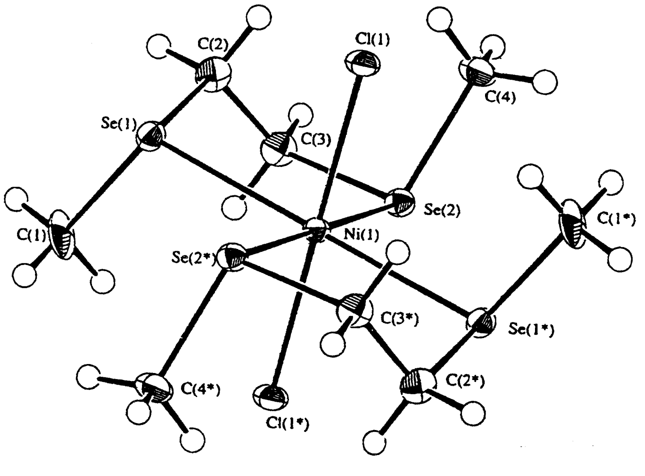


Fig. 19. Crystal structure of [NiCl$_2$(MeSeCH$_2$CH$_2$SeMe)$_2$], taken from Ref. [103] with permission from the Royal Society of Chemistry.

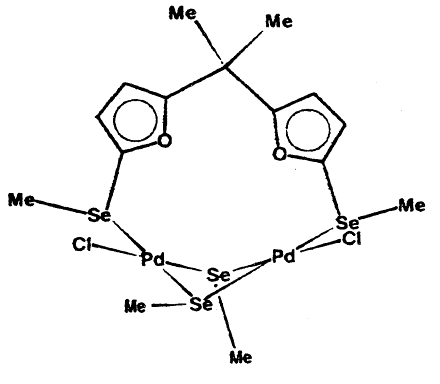
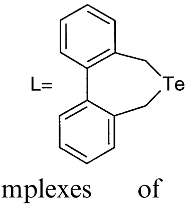


Fig. 20. Structure of [Pd$_2$Cl$_2$(μ-MeSe)$_2${(MeSe(C$_4$H$_3$O)}$_2$CMe$_2$] [108].

Relatively little new work with simple R$_2$Se or R$_2$Te has been reported. The system palladium(II) acetate–^{i}Pr$_2$Se activates arenes to produce arylpalladium(II) complexes [105]. The thienyl, MeE(C$_4$H$_3$S) and furyl, MeE(C$_4$H$_3$O) (E = Se or Te) substituted ligands bond only via the E donors to both metals in [MCl$_2${MeE(C$_4$H$_3$Y)}$_2$] (M = Pd or Pt, Y = O or S) [106,107]. X-ray structures show that in the solid state [PdCl$_2${MeTe(C$_4$H$_3$Y)}$_2$] are *cis* isomers, whereas [MCl$_2${MeSe(C$_4$H$_3$Y)}$_2$] are *trans*. It was also noted that in these and several other telluroether complexes, crystal packing appeared to produce short Te···X-(halide) contacts between neighbouring molecules, an effect absent in the selenoethers [107]. In solution, NMR studies show that the telluroethers exist as *cis*/*trans* mixtures, but the selenoethers exhibit only one isomer, believed to be the *trans*. Most unusually the [PdCl$_2${MeSe(C$_4$H$_3$O)}$_2$] on crystallisation from acetone gave small amounts of red crystals (in addition to the orange starting material) which were identified by an X-ray study as the rearrangement product [Pd$_2$Cl$_2$(μ-MeSe)$_2${MeSe(C$_4$H$_3$O)}$_2$CMe$_2$] where acetone has coupled two of the furyl groups and two MeSe bridges have been generated (Fig. 20) [108].

Telluracyclopentane, $\overline{\mathrm{Te(C}}\mathrm{H_2)_4}$ forms [MX$_2${$\overline{\mathrm{Te(C}}\mathrm{H_2)_4}$}$_2$] (M = Pd or Pt; X = Cl, Br or I) with both metals [95]. The [PtCl$_2${$\overline{\mathrm{Te(C}}\mathrm{H_2)_4}$}$_2$] exists as a mixture of *cis* and *trans* isomers both in solution and the solid, but for the other complexes only one isomer, probably the *trans* is found, and this was confirmed for [PdCl$_2${$\overline{\mathrm{Te(C}}\mathrm{H_2)_4}$}$_2$] by an X-ray structure [95]. The crystal structure of [PtCl$_2$(1,4-oxatellurane)$_2$] shows a *trans* square planar geometry, with Te-coordinated ligands [109]. Both metal dichlorides form [MCl$_2$(L)$_2$] complexes with 1,3-dihydrobenzo(*c*)tellurophene, the Pd appearing to be the *trans*, the platinum the *cis* isomer [20]. The unusual 2,7-dihydro-1*H*-dibenzo(*c*,*e*)tellurepin (L) forms both [PdCl$_2$(L)$_2$] and [Pd$_2$Cl$_4$(L)$_2$] complexes [110].



Platinum(II) complexes of unstable (2-bromovinyl)selenide ligands [PtCl$_2${RSeR′}$_2$] (R = 2-bromocyclooctenyl, 2-bromocyclohexenyl, R′ = Me, Et or Bz) and [PdCl$_2${2-bromocyclohexenyl(benzyl)selenide}$_2$] have been synthesised and the diastereoisomers present probed by solution NMR spectroscopy [111].

Ferrocenyl selenoethers have been immobilised on silica and their platinum(II) chlorocomplexes investigated as hydrosilylation catalysts [112]. A comparison of the chemistries of RECH$_2$ER (R = Me or Ph; E = S, Se or Te) with Pd(II) and Pt(II) [113] showed that whilst PhSCH$_2$SPh gave only [MCl$_2$(η^1-PhSCH$_2$SPh)$_2$] which are stable in solution, for MeSCH$_2$SMe, or

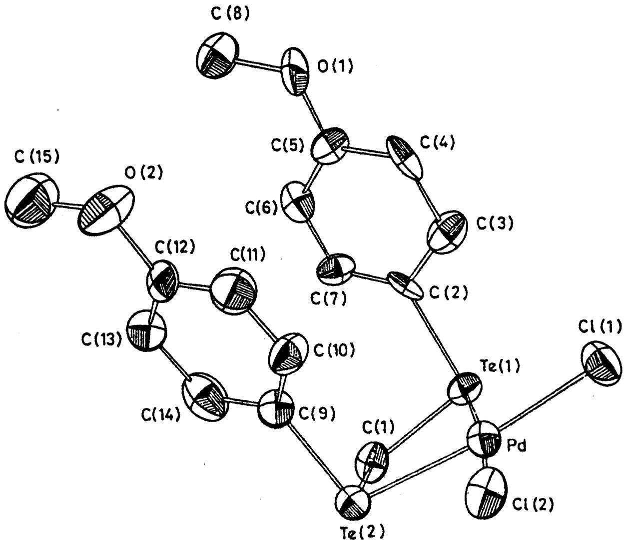


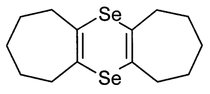
Fig. 21. Crystal structure of [PdCl$_2${(4-MeOC$_6$H$_4$Te)$_2$CH$_2$}], taken from Ref. [114] with permission from Elsevier.

RSeCH$_2$SeR, the [MCl$_2${η^1-RECH$_2$ER)$_2$] slowly decompose in solution into [{MCl$_2$(RECH$_2$ER)}$_n$] and free ligand. For RTeCH$_2$TeR only the [{MCl$_2$(RTeCH$_2$TeR)}$_n$] are formed. Detailed solution NMR studies identified both *cis* and *trans* geometric isomers and the diastereoisomers of the chiral coordinated RECH$_2$ER centres. The 1:1 complexes were suggested to be oligo- or polymeric with bridging RECH$_2$ER. The related (4-MeOC$_6$H$_4$Te)$_2$CH$_2$ however forms monomeric [MCl$_2$(L–L)], the structure of the Pd complex is shown in Fig. 21 [114,115] and reveals a strained 4-membered ring Te–Pd–Te = 81°. The related [Pd(Ph$_2$PCH$_2$CH$_2$PPh$_2$){(4-MeOC$_6$H$_4$Te)$_2$CH$_2$}](ClO$_4$)$_2$ also contains a 4-membered Te–C–Te–Pd ring with the *meso* invertomer of the ligand [115]. The ^{125}Te-NMR spectrum of the latter reveals a low frequency coordination shift of -62 ppm, described as 'anomalous' [115], whereas comparison with the similar effects in the ^{31}P-NMR spectra of the much studied Ph$_2$PCH$_2$PPh$_2$ complexes shows this low frequency shift is expected in 4-membered rings. Platinum(IV) complexes of types [{PtMe$_3$I}$_2${(4-MeOC$_6$H$_4$Te)$_2$CH$_2$}], [PtMe$_3$I(PhTeCH$_2$TePh)] and [PtMe$_3$I(PhTeCH$_2$TePh)$_2$] have been described [116], probably containing bridging, chelating and monodentate ditelluroether, respectively.

The reactions of MCl$_2$ (M = Pd or Pt), MeSe(CH$_2$)$_3$SeMe and TlPF$_6$ in MeCN produce [M{MeSe(CH$_2$)$_3$SeMe}$_2$](PF$_6$)$_2$ [117]. Multinuclear NMR studies show the presence of invertomers in solution below room temperature, but simpler or broadened resonances are observed at ambient temperatures, due to the onset of rapid pyramidal inversion. On addition of Cl$^-$ ions to the solutions, the complexes are converted into the corresponding [MCl$_2${MeSe(CH$_2$)$_3$SeMe}]. The X-ray structure of [Pt{*DL*-MeSe(CH$_2$)$_3$SeMe}$_2$](PF$_6$)$_2$·2MeCN shows the expected planar geometry [118]. Complexes [MX$_2$(L–L)] of 5- and 6-membered ring ditelluroethers were reported over 10 years ago, and now the homoleptic analogues [M(L–L)$_2$](PF$_6$)$_2$ (M = Pd or Pt; L–L = RTe(CH$_2$)$_3$TeR, R = Me or Ph; *o*-C$_6$H$_4$(TeMe)$_2$, *o*-C$_6$H$_4$(CH$_2$TeMe)$_2$) have been obtained from [MCl$_2$(MeCN)$_2$], TlPF$_6$ and the ligands in MeCN [78,54]. The NMR spectra show broad features probably due to inversion processes (the *trans*-Te–M–Te geometry will have lower inversion barriers). The structure of [Pd{*meso*-*o*-C$_6$H$_4$(TeMe)$_2$}$_2$](PF$_6$)$_2$ has been determined. Attempts to oxidise the platinum complexes to Pt(IV) failed, again a demonstration of the inability of tellurium ligands to stabilise higher oxidation states. The [MCl$_2${*o*-C$_6$H$_4$(CH$_2$TeMe)$_2$}] have also been described [54].

The tripods MeC(CH$_2$EMe)$_3$ (E = S or Se) form [MCl$_2$(tripod)] complexes with both metals where the tripod is coordinated as a bidentate, and the diastereoisomers present have been identified by VT-NMR methods [119]. The [MCl$_2${MeC(CH$_2$TeMe)$_3$}] are poorly soluble restricting NMR studies [120]. The homoleptic complexes [M(tripod)$_2$](PF$_6$)$_2$ (M = Pd or Pt, tripod = MeC(CH$_2$SeMe)$_3$, MeC(CH$_2$TeMe)$_3$, and MeC(CH$_2$TePh)$_3$) are made from [MCl$_2$(MeCN)$_2$], TlPF$_6$, and the ligands in MeCN, and the structure of the [Pt{MeC(CH$_2$SeMe)$_3$}$_2$](PF$_6$)$_2$ (Fig. 22) shows the ligands coordinated as bidentates with the 'free' arm of the tripod bent away from the metal [81]. NMR studies show the complexes undergo various dynamic processes in solution including exchange of the free and bound arms of the tripod and pyramidal inversion.

The cyclic diselenoether [8]aneSe$_2$ forms [MCl$_2$([8]aneSe$_2$)] and [M{[8]aneSe$_2$}$_2$](PF$_6$)$_2$, which differ from analogues containing MeSe(CH$_2$)$_3$SeMe in that the higher symmetry cyclic ligand does not produce diastereoisomers. ^{77}Se-NMR data on [MCl$_2$([8]aneSe$_2$)] show small high frequency coordination shifts typical of 6-membered chelate rings [118]. The X-ray structure of [PdCl$_2$([8]aneSe$_2$)] was reported [118]. Complexes of other cyclic diselenoethers include [MCl$_2$(sebc)] [8]; the structure of the palladium dichloride complex was reported, and unusually for complexes of these two metals low frequency coordination shifts were seen in the ^{77}Se-NMR spectra. Cyclohepteno-1,4-diselenin (L) reacted with [PdCl$_2$(MeCN)$_2$] to form *trans*-[PdCl$_2$(L)$_2$] with the diselenin bonded via one selenium only [121]. In contrast, on reaction with [PtCl$_2$(MeCN)$_2$] the ligand oxidatively adds to the metal to give the Pt(IV) complex shown in Fig. 23 [121].



cycloheptano-1,4-diselenin

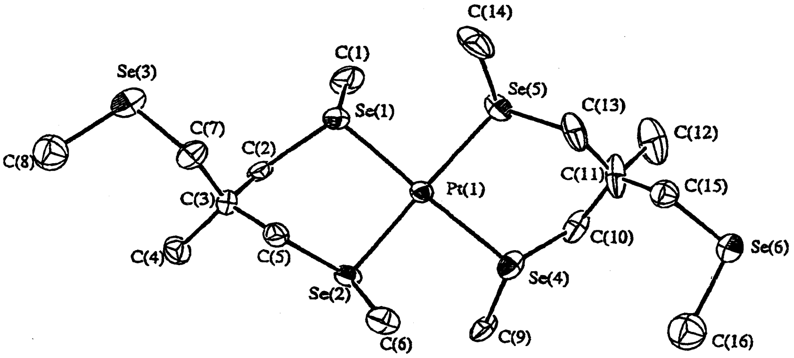


Fig. 22. Crystal structure of [Pt{MeC(CH$_2$SeMe)$_3$}$_2$]$^{2+}$, taken from Ref. [81] with permission from the American Chemical Society.

Whilst Pt(IV) is much more easily obtained than Pd(IV), this is a rare reaction where these two metals react differently with Group 16 donor ligands. The tetraselenoether [16]aneSe$_4$ forms [M([16]aneSe$_4$)](PF$_6$)$_2$, both of which have been characterised by single crystal X-ray studies, revealing the expected planar metal geometry and with the ligand in the *up*, *up*, *down*, *down* conformation (Fig. 24) [117]. Neither complex shows any evidence for oxidative processes in the cyclic voltammograms, although irreversible reductions are evident.

In contrast, an X-ray structure of [Pd([16]aneSe$_4$)](BF$_4$)$_2$ shows the macrocycle in the *all up* conformation (Fig. 25), which has been rationalised as due to the presence of smaller more polarising anions [122]. The red complex [Pd([16]aneSe$_4$)]Cl(BF$_4$) also contains the *all up* conformation of the ligand, and there is a very long Pd···Cl contact (3.07 Å) [122]. NMR studies are consistent with the two conformations identified being the major forms present in solution. The [Pt([16]aneSe$_4$)](PF$_6$)$_2$ complex is oxidised by Cl$_2$ or Br$_2$ to Pt(IV) in *trans*-[PtX$_2$([16]aneSe$_4$)](PF$_6$)$_2$, and the X-ray structure of the chloro complex shows the same ligand conformation as in the Pt(II) starting material [123]. In contrast to the planar M(II) complexes, the Pt(IV) show NMR evidence for only one macrocycle conformation in solution (*up*, *up*, *down*, *down*). Attempts to isolate a Pd(IV) complex were unsuccessful.

The potentially hexadentate [24]aneSe$_6$ reacts with PdCl$_2$ in MeCN to form [Pd$_2$Cl$_2$([24]aneSe$_6$)](BF$_4$)$_2$ which contains two planar PdSe$_3$Cl units (Fig. 26) [122].

A number of studies have used hybrid selenium donor ligands, and there is a substantial number of mixed Te-Group 15 or 16 donor ligands. The variety of ligand architectures makes it difficult to draw clear comparisons of the effects of different donors. In a number of these studies identification of the structures present is largely speculative, since neither X-ray crystallographic nor thorough spectroscopic studies have been conducted.

The reaction of [PtMe$_2$(SMe$_2$)$_2$] with Se(CH$_2$CH$_2$CH=CH$_2$)$_2$ in a 1:1 ratio gave [PtMe$_2${Se(CH$_2$CH$_2$CH=CH$_2$)$_2$}] which is fluxional in solution at ambient temperatures due to exchange between bound and free alkene groups, but at − 90 °C the NMR spectra show two distinct sets of alkene resonances showing exchange is slow [124]. The same reaction, using a 2:1 Pt:ligand ratio, gave the dinuclear [Pt$_2$Me$_4${Se(CH$_2$CH$_2$CH=CH$_2$)$_2$}]. The S(CH$_2$CH$_2$CH=CH$_2$)$_2$ behaves similarly and the structure shown in Fig. 27 has been established by an X-ray study. The NMR spectra of the dinuclear complexes are invariant with temperature since both alkenes are coordinated and the S(Se) bridge

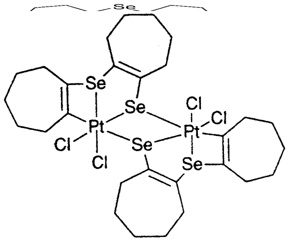


Fig. 23. Structure of the ring-opened product derived from cycloheptane-1,4-diselenin [121].

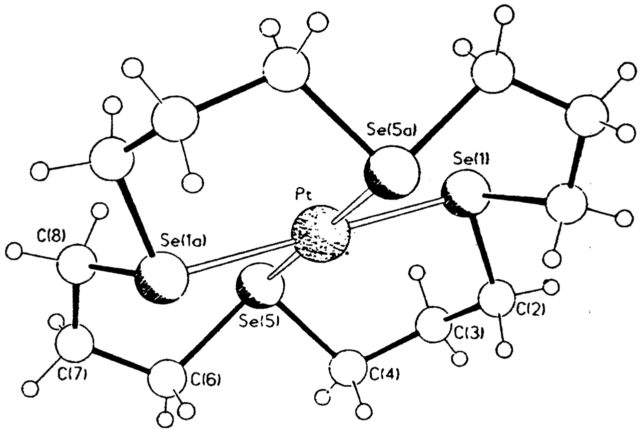


Fig. 24. Crystal structure of [Pt([16]aneSe$_4$)]$^{2+}$ (PF$_6^-$ salt), taken from Ref. [117] with permission from the American Chemical Society.

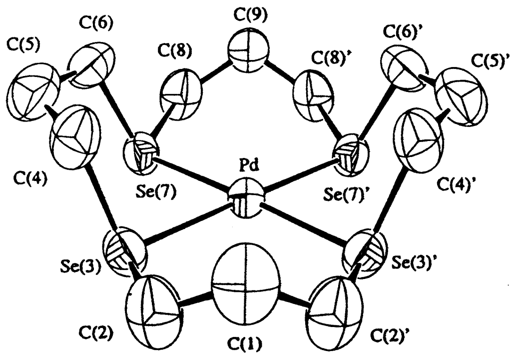


Fig. 25. Crystal structure of [Pd([16]aneSe$_4$)]$^{2+}$ (BF$_4^-$ salt), taken from Ref. [122] with permission from the American Chemical Society.

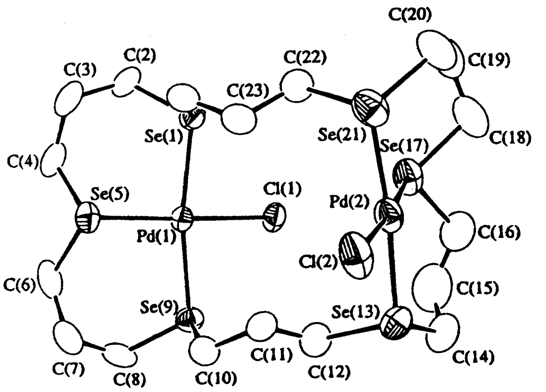


Fig. 26. Crystal structure of [Pd$_2$Cl$_2$([24]aneSe$_6$)](BF$_4$)$_2$, taken from Ref. [122] with permission from the American Chemical Society.

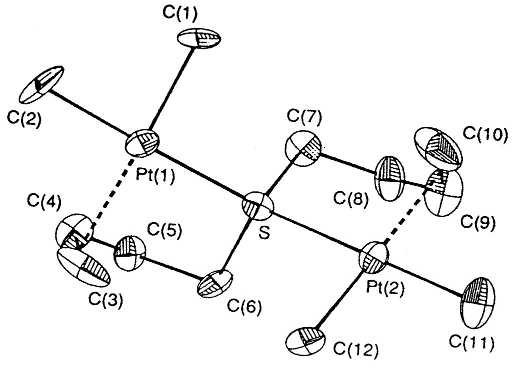


Fig. 27. Crystal structure of [Pt$_2$Me$_4${S(CH$_2$CH$_2$CH=CH$_2$)$_2$}], taken from Ref. [124] with permission from the Royal Society of Chemistry.

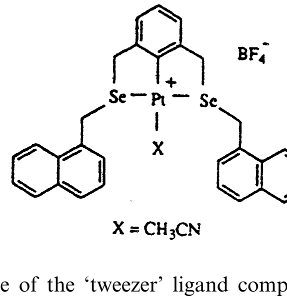


Fig. 28. Structure of the 'tweezer' ligand complex with Pt(II) [126].

results in both lone pairs coordinated precluding pyramidal inversion. Platinum(II) halide complexes of E(CH$_2$SiMe$_2$CH=CH$_2$)$_2$ (E = S, Se or Te) and Te(CH$_2$CH$_2$CH=CH$_2$)$_2$ have been reported [101,125] and again are planar with the Group 16 and one alkene group coordinated to the metal, confirmed by X-ray crystal structures of [PtI$_2${S(CH$_2$SiMe$_2$CH=CH$_2$)$_2$}] and [PtBr$_2${Te(CH$_2$SiMe$_2$CH=CH$_2$)$_2$}]. The energetics of exchange between the alkene groups have been studied in detail by multinuclear NMR spectroscopy. A Se$_2$C donor ligand with a 'tweezer-like' geometry has been complexed with PtCl$_2$ (Fig. 28) [126], whilst an SeNC donor set is present in the complex shown in Fig. 29 [127].

Several ligands containing Te in combination with possible oxygen donors have been described, including 1,3-(4-MeOC$_6$H$_4$TeCH$_2$)$_2$CHOH [128], 4-MeOC$_6$H$_4$TeCH$_2$CH(OH)CH$_2$OH [129], 2-(phenyltelluromethyl)tetrahydro-2-pyran [130], and 2-(phenyltelluromethyl)tetrahydrofuran [131]. Not surprisingly they mostly appear to bond to Pd or Pt only via Te, with little evidence for interaction of the oxygen function.

The 4-MeOC$_6$H$_4$TeCH$_2$CH$_2$SMe behaves as a chelating S,Te donor in [Pd(L–L)$_2$](ClO$_4$)$_2$ or [Pd(L–L)(Ph$_2$PCH$_2$CH$_2$PPh$_2$)](ClO$_4$)$_2$ [132]. X-ray crystal structures of [PtCl$_2${MeSCH$_2$CH$_2$Te(4-EtOC$_6$H$_4$)}] [133] and [PdCl$_2${EtSCH$_2$CH$_2$Te(4-MeOC$_6$H$_4$)}] [134] reveal the expected square planar geometries and that the *trans* influence of RTeR′ is greater than that of RSR′ groups.

The syntheses of [MCl$_2$(RECH$_2$CH$_2$NMe$_2$)] (M = Pd, Pt, RE = SBu, PhS, PhSe) have been reported, and the crystal structure of [PtCl$_2$(PhSeCH$_2$CH$_2$NMe$_2$)]·H$_2$O determined [135]. The three carbon backboned NH$_2$CH$_2$CH$_2$CH$_2$ER (ER = TePh, 4-MeOC$_6$H$_4$Te, SePh) behave as chelates in [MCl$_2$(L–L)] (M = Pd or Pt) and in [PdMeCl{NH$_2$CH$_2$CH$_2$CH$_2$Te(4-MeOC$_6$H$_4$)}] the arrangement is probably Te–*trans*-Cl [136]. The mixed ligand complex [Pd(MeSCH$_2$CH$_2$TeR){Me$_2$NCH$_2$CH$_2$Te(4-MeOC$_6$H$_4$)}](ClO$_4$)$_2$ is also known [132]. The structure of [PdCl$_2${1-(4-EtOC$_6$H$_4$Te)2-(NH$_2$)C$_6$H$_4$}], erroneously claimed [137] to be the first Te,N donor complex of Pd(II), is planar with Pd–Cl$_{trans\text{-Te}}$ 0.07 Å longer than Pd–Cl$_{trans\text{-N}}$. Bimetallic complexes (Pd/Pt, Pd/Ni) based upon the ligand 4-MeC$_6$H$_3$(1-NMe$_2$)(2-TeC$_6$H$_4$OEt) have been described [138].

The Te(CH$_2$CH$_2$CH$_2$NH$_2$)$_2$ behaves as a tridentate N$_2$Te donor in [PtLCl]Cl, [PdLCl]Cl and [PdLMe]Cl [139], and the X-ray crystal structure of [PtL′Cl]Cl·CHCl$_3$ where L′ is the related Te$_2$N donor N{CH$_2$CH$_2$Te(4-EtOC$_6$H$_4$)}$_2$ has been determined [140]. Ligands containing RTe and pyridyl nitrogen donors, (4-RC$_6$H$_4$)TeCH$_2$CH$_2$(2-C$_5$H$_4$N) (R = H, Me or MeO) and Te{CH$_2$CH$_2$(2-C$_5$H$_4$N)$_2$} form planar complexes with TeNCl$_2$ or TeN$_2$Cl donor sets with Pd(II) or Pt(II) chloride [141–143]. X-ray crystal structures of $[PdCl_2\{(4\text{-}MeC_6H_4)TeCH_2CH_2(2\text{-}C_5H_4N)\}]$ [142], and $[MCl_2\{(4\text{-}MeOC_6H_4)TeCH_2CH_2(2\text{-}C_5H_4N)\}]$ (M = Pd or Pt) [141] confirm the geometries proposed. A more unusual Te,N donor is 1-(dimethylaminomethyl)-2-(phenyltelluro)ferrocene which has given a 1:1 complex with $PdCl_2$ [144].

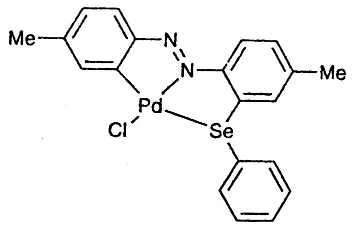


Fig. 29. Structure of SeNC-donor ligand on Pd(II) [127].

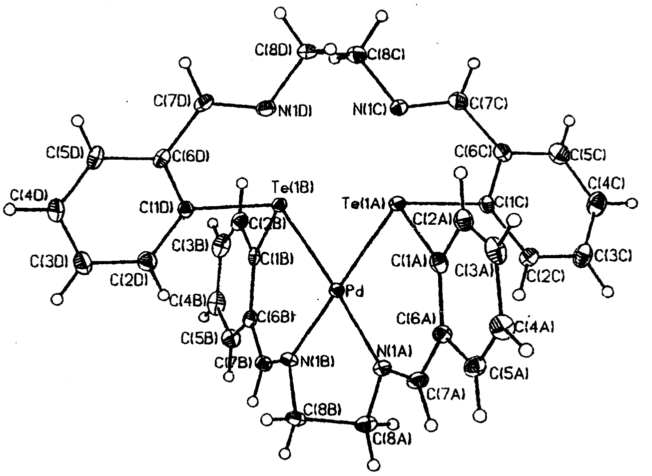


Fig. 30. Crystal structure of $[PdL]^{2+}$, taken from Ref. [147] with permission from the Royal Society of Chemistry.

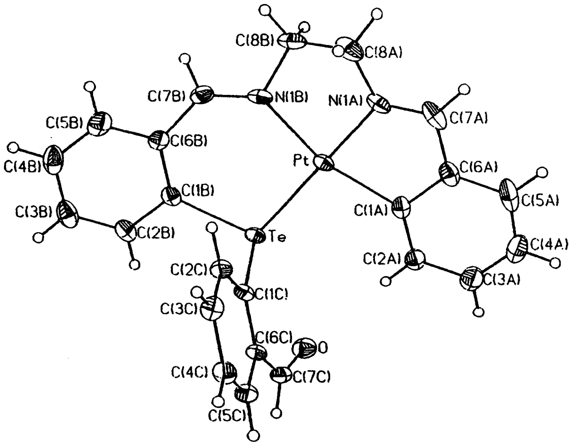
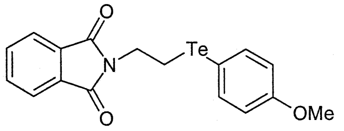


Fig. 31. Crystal structure of the ring-opened Pt(II) complex, taken from Ref. [147] with permission from the Royal Society of Chemistry.

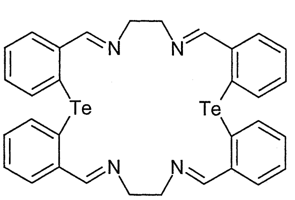
The ligand *N*-$\{2\text{-}(4\text{-}MeOC_6H_4Te)CH_2CH_2\}$-phthalimide has been reported as a potential Te,O,N donor [145], although sterically it would seem highly unlikely that the O-donor could bind to the same metal as the Te,N donor set. It is certainly bidentate (Te,N) in $[PdCl_2L]$ and $[Pd(PPh_3)_2L](ClO_4)_2$, and suggestions for O-coordination in other complexes are unconvincing.



N-[2-(4-methoxyphenyltelluro)ethyl]phthalimide

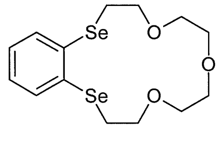
A series of Pt(IV) complexes $[PtMe_3X\{Me_2NCH_2\text{-}CH_2ER\}]$ (ER = SBu_t, SC_6H_4Me, SPh, SePh or TePh; X = Cl, Br or I) has been synthesised and the structure of one example, $[PtMe_3Br\{Me_2NCH_2CH_2S(4\text{-}MeC_6H_4)\}]$, determined [146].

Tellurium has been incorporated into a macrocyclic Schiff base (L) and this ligand reacts with $[PdCl_2(PhCN)_2]$ to form $[\{PdCl_2\}_2L]$ where each palladium is believed to be coordinated to one Te and one azomethine nitrogen [22]. Using a 1:1 Pd:L ratio with added NH_4PF_6 the product is $[PdL](PF_6)_2$ (Fig. 30) in which the palladium is coordinated to a Te_2N_2 donor set, leaving two uncoordinated *N*-donors [147]. However, on reaction of the same ligand with $[PtCl_2(COD)]$, the ligand is ring-opened to give the complex shown in Fig. 31 [147].



Te-containing Schiff base macrocycle

Selenium and tellurium donors have also been incorporated into crown ether ligands. The benzo-[15]aneSe_2O_3 ligand reacts with $[PdCl_4]^{2-}$ to form $[PdCl_2(\text{benzo-[15]ane}Se_2O_3)]$ in which the palladium is probably bonded to an Se_2Cl_2 set. In the 1:2 complex, $[Pd(\text{benzo-[15]ane}Se_2O_3)_2](PF_6)_2$ (Fig. 32) there is a planar $PdSe_4$ core; again the ether oxygens remain uncoordinated [148].



benzo-[15]aneSe_2O_3

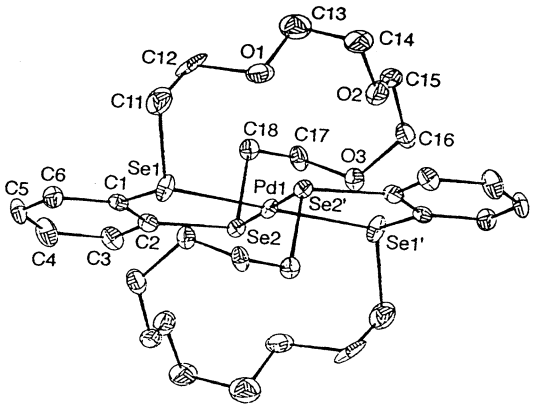


Fig. 32. Crystal structure of [Pd(benzo-[15]aneSe_2O_3)$_2$]$^{2+}$, taken from Ref. [148] with permission from the Royal Society of Chemistry.

Chinese workers have described a series of crown ethers of varying ring size and number of oxygens, containing one or two selenoether groups which bond to Pd or Pt only via the selenium [149]. Several of the complexes are efficient hydrosilylation catalysts. A smaller range of crown ethers containing one or two telluroether groups have been prepared by the same workers [150] and some complexes with $PtCl_2$ isolated. Preliminary studies indicated they were less effective hydrosilylation catalysts than the selenium analogues.

4.9. Group 11

4.9.1. Copper

The Cu(I) selenoether and telluroether complexes, $[CuL_4](CF_3SO_3)$ (L = $SeMe_2$, $SePh_2$, $TeMe_2$, $TePh_2$) and $[Cu(L–L)_2]PF_6$ (L–L = $RSe(CH_2)_2SeR$, $RE(CH_2)_3ER$, R = Me or Ph, E = Se or Te) are obtained by treatment of $[\{Cu(CF_3SO_3)\}_2(C_6H_6)]$ with L in anhydrous benzene, or by reaction of L–L with $[Cu(NCMe)_4]PF_6$ in dry methanol or CH_2Cl_2 [151]. Reaction of $[Cu(NCMe)_4]^+$ salts with $SePh_2$ or $TePh_2$ also gives $[Cu(EPh_2)_4]^+$, although this method does not work for EMe_2 (E = Se or Te) [151]. The products are readily decomposed in moist air and are extensively dissociated in solution. Variable temperature multinuclear (^1H, ^{77}Se, ^{125}Te, ^{63}Cu) NMR studies have been utilised to probe exchange processes in solution and demonstrate that the $[CuL_4](CF_3SO_3)$ are undergoing rapid exchange even at the lowest temperature accessible, although for the bidentate ligand systems, $[Cu(L–L)_2]PF_6$, rapid exchange occurs at r.t., but this is slow at low temperature. In all cases $\delta^{77}Se$ and $\delta^{125}Te$ shift to low frequency upon coordination of L or L–L to Cu(I). Upon addition of excess L or L–L, ^{63}Cu-NMR spectroscopy reveals a signal in the range -153 to $+21$ ppm, indicative of pseudo-tetrahedral Se_4 or Te_4 coordination under these conditions [151]. Reaction of $[Cu(NCMe)_4]PF_6$ with four equivalents of 1,3-dihydrobenzo[*c*]tellurophene, L gives $[CuL_4]PF_6$ in high yield [20].

The complexes $[Cu\{o\text{-}C_6H_4(EMe)_2\}_2]BF_4$ have been synthesised from $[Cu(NCMe)_4]BF_4$ and two molar equivalents of ligand in CH_2Cl_2. The structures of $[Cu\{meso\text{-}o\text{-}C_6H_4(EMe)_2\}_2]BF_4$ (E = Se or Te) both exhibit flattened tetrahedral coordination environments at Cu(I) (Fig. 33), with d(Cu–Se) = 2.379(2), 2.419(2) Å and d(Cu–Te) = 2.5299(8), 2.5598(7) Å. The latter species represented the first structurally characterised example of a telluroether complex involving a five-membered chelate ring and in solution this complex exhibits a resonance at -109 ppm in the ^{63}Cu-NMR spectrum [152]. The tetrahedral $[Cu\{o\text{-}C_6H_4(CH_2TeMe)_2\}_2]PF_6$ was prepared similarly and isolated as a yellow solid [54].

In an effort to promote the formation of infinite coordination polymers involving selenoether and telluroether coordination, $[Cu(NCMe)_4]BF_4$ was treated with two molar equivalents of the methylene bridged $MeECH_2EMe$ (E = Se or Te) in CH_2Cl_2 to give $[Cu(MeECH_2EMe)_2]BF_4$. The crystal structure of $[Cu(MeSeCH_2SeMe)_2]^+$ shows (Fig. 34) a 3-dimensional cationic polymer assembled by tetrahedral coordination of the Cu(I) ions to four Se atoms from bridging ligands, d(Cu–Se) = 2.399(3)–2.442(3) Å. The cation adopts an open structure, generating large channels which host the PF_6^- anions [153].

Copper(I) complexes involving the cyclic diselenoethers [8]aneSe_2 and sebc are obtained from $[Cu(NCMe)_4]Y$ (Y = BF_4 or PF_6) and two molar equivalents of the ligand in acetone. The structure of $[Cu(sebc)_2]^+$ shows a flattened tetrahedral coordination environment at Cu(I) arising from bidentate coordination of sebc, d(Cu–Se) = 2.403(6)–2.436(6) Å [8]. With the tripodal $MeC(CH_2EMe)_3$ (E = S or Se) the bis tripod complexes $[Cu\{MeC(CH_2EMe)_3\}_2]^+$ are obtained [81].

Reaction of CuI with Me_6[12]aneSe_3 in MeCN yields the polymeric $Cu_4I_4(\mu\text{-}\eta^2\text{-}Me_6[12]aneSe_3)_2$. The crystal structure of this compound shows (Fig. 35) a 3-dimensional network of cubane-like Cu_4I_4 units linked by four bridging triselena crowns. Each Cu(I) ion links to one η^1 selenoether and the Me_6[12]aneSe_3 units use one more Se atom to bridge to an adjacent Cu(I), leaving the third Se atom uncoordinated, d(Cu–Se) = 2.432(3)–2.485(3) Å [12].

$Cu(CF_3SO_3)_2$ reacts with [16]aneSe_4 in anhydrous acetone under N_2 to afford the Cu(II) species $[Cu([16]aneSe_4)](CF_3SO_3)_2$ as a dark red solid which is unstable in the presence of coordinating solvents and is readily reduced to the Cu(I) species under prolonged reaction. The crystal structure of the centrosymmetric Cu(II) species shows a tetragonally distorted octahedral coordination environment arising from tetradentate binding to [16]aneSe_4 which occupies the equatorial coordination sites, with O atoms from weakly bound triflate anions occupying the apical sites, d(Cu–Se) = 2.4553(9), 2.4592(9) Å (Fig. 36) [154]. The mechanism of electron transfer of this Cu(II) species has been investigated in detail and cyclic voltammetry shows that the reduction involves a two step reduction, firstly to $[Cu^{II}([16]aneSe_4)]^+$ and then to $[Cu^{I}([16]aneSe_4)]^+$. The reaction between $[Cu([16]aneSe_4)](CF_3SO_3)_2$ and [16]aneSe_4 has been found to be first order in each of these species, second order overall [154]. Dissolution of $[Cu([16]aneSe_4)](CF_3SO_3)_2$ in CH_2Cl_2/MeCN gave the dication $([16]aneSe_4)(CF_3SO_3)_2$ which has also been structurally characterised [10,154].

The mixed dithia/diselena macrocyclic complex $[Cu([16]aneS_2Se_2)](CF_3SO_3)_2$ adopts the same structure as $[Cu([16]aneSe_4)](CF_3SO_3)_2$ above (with the Se and S atoms disordered in a 50:50 ratio) and was prepared similarly [10]. The Cu(I) derivative of this ligand also exhibits disorder of the S and Se atoms, with a discrete flattened tetrahedral $[Cu([16]aneS_2Se_2)]^+$ cation (Fig. 37) [10].

Like the Cu(II) species above, the crystal structures of the Cu(II) complexes of the hydroxyl-derivatised crowns, $[Cu\{[16]aneSe_4(OH)_2\}](CF_3SO_3)_2$ and $[Cu\{[8]aneSe_2(OH)\}_2](CF_3SO_3)_2$ (Fig. 38) also adopted tetragonally distorted octahedral geometries. Although the former is severely disordered, it clearly shows one hydroxyl group coordinated to Cu(II) leading to pentadentate coordination from the crown, with one $CF_3SO_3^-$ anion occupying the sixth coordination site [10].

The structure of $[Cu\{[8]aneSe_2(OH)\}_2](CF_3SO_3)_2$ shows each selenacrown functioning as a tridentate ligand to Cu(II), with the hydroxyl functions ligating weakly in the apical positions. The $CF_3SO_3^-$ anions in this species are hydrogen bonded to the hydroxyl groups. The structure of the Cu(I) species $[Cu\{[16]aneSe_4(OH)\}](CF_3SO_3)$ reveals a distorted tetrahedral Se_4 donor set at Cu(I), with no hydroxyl coordination (H-bonds to the anion) [10]. Electrochemical studies on $[Cu([16]aneS_2Se_2)](CF_3SO_3)_2$, $[Cu\{[16]aneSe_4(OH)_2\}](CF_3SO_3)_2$ and $[Cu\{[8]aneSe_2(OH)\}_2](CF_3SO_3)_2$ indicate the presence of two different conformational isomers of the Cu(I) species which are oxidised at different potentials [10].

Red–brown Cu(II) complexes involving acyclic bidentate selenoethers, $[Cu(L\text{–}L)_2](BF_4)_2$ (L–L = $MeSe(CH_2)_3SeMe$ or $PhSe(CH_2)_2SePh$) are obtained from $Cu(BF_4)_2$ and L–L in anhydrous CH_2Cl_2, while a dark green mixed species involving both Cu(I) and Cu(II), $[Cu(L\text{–}L)_2](BF_4)_x$ is obtained with L–L = $MeSe(CH_2)_2SeMe$. The redox properties of these compounds have been studied by cyclic voltammetry and Cu K-edge EXAFS measurements have been used to obtain structural data for both the Cu(I) and Cu(II) complexes. The Cu(II) selenoether complexes are much more susceptible to reduction to Cu(I) compared to the

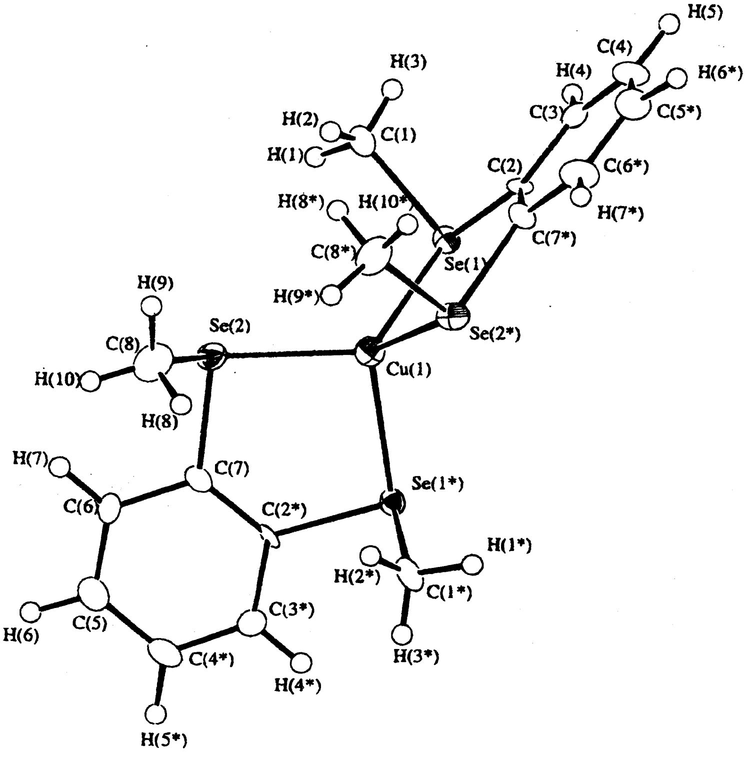


Fig. 33. Crystal structure of $[Cu\{o\text{-}C_6H_4(SeMe)_2\}_2]^+$, taken from Ref. [152] with permission from the American Chemical Society.

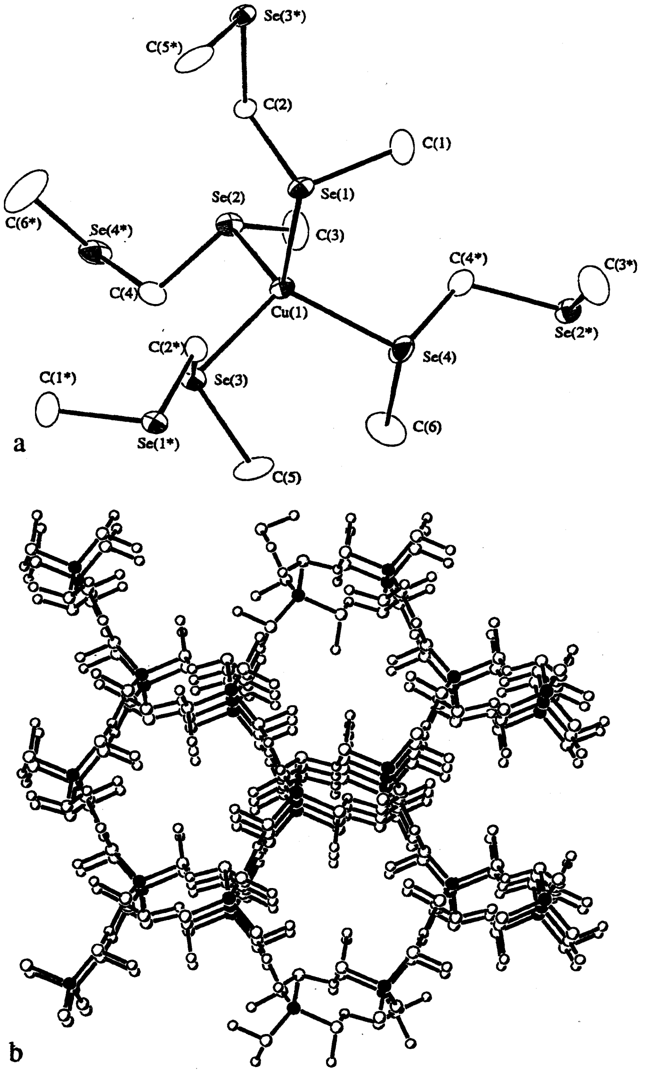


Fig. 34. Crystal structure of $[Cu(MeSeCH_2SeMe)_2]^+$ (Cu atoms shaded), taken from Ref. [153] with permission from the American Chemical Society.

thioether analogues [155,157]. Similar reactions of $Cu(BF_4)_2$ with the ditelluroethers $RTe(CH_2)_3TeR$ (R = Me or Ph) produced only the Cu(I) species $[Cu\{RTe(CH_2)_3TeR\}_2]BF_4$ [155]. Reaction of $CuCl_2{\cdot}2H_2O$ with $o\text{-}C_6H_4(CH_2EAr)_2$ (E = Se or Te; Ar = Ph, C_6H_4Me-4, C_6H_4OMe-4, C_6H_4OEt-4) in EtOH is reported to give the red–brown Cu(II) species $[CuCl_2\{o\text{-}C_6H_4(CH_2EAr)_2\}]{\cdot}2H_2O$ which have been assigned square planar geometries on the basis of UV–vis and EPR spectroscopic measurements, although no structural data are available [156]. Their assignment as square planar compounds contrasts with the tetragonally distorted geometry established crystallographically by Pinto and co-workers for the series of macrocyclic selenoethers discussed above.

Copper(I) complexes involving hybrid telluroamine [90] and telluropyridine [91,92] ligands have been reported and their air oxidation to Cu(II) is claimed, although no structural data are available. The assignment of a tetrahedral $BrNTe_2$ donor set for the Cu(II) telluroamine species is questionable [90].

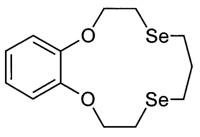
4.9.2. Silver

Light sensitive homoleptic Ag(I) selenoether and telluroether complexes of formula $[Ag(L\text{–}L)_2]BF_4$ (L–L = $RE(CH_2)_nER$ [R = Me: E = S, Se, n = 1, 2 or 3; E = Te, n = 1 or 3; R = Ph: E = S or Se, n = 2 or 3, E = Te, n = 3], $o\text{-}C_6H_4(EMe)_2$ (E = S, Se or Te)), are readily obtained as white to light yellow coloured solids by treatment of $AgBF_4$ with two molar equivalents of L–L in acetone or CH_2Cl_2. Multinuclear (^1H, ^{77}Se, ^{109}Ag) VTNMR spectroscopic studies reveal rapid ligand exchange processes occur at room temperature and that these slow upon cooling [152,158]. ^{77}Se-NMR shows a shift to low frequency upon coordination of the diselenoether ligands to the electron-rich d^{10} Ag(I). In the presence of excess L–L, these complexes reveal ^{109}Ag-NMR shifts at ca. 1000 ppm, indicative of AgL_4 species [158]. $[Ag\{MeSe(CH_2)_2SeMe\}_2]BF_4$ has been crystallographically characterised. The structure shows a discrete mononuclear cation comprising two chelating diselenoether ligands coordinated to Ag(I) giving a distorted tetrahedral stereochemistry, d(Ag–Se) = 2.610(1)–2.638(1) Å. The crystal structure of $[Ag\{PhSe(CH_2)_3SePh\}_2]^+$ on the other hand reveals (Fig. 39) an infinite 3-dimensional sheet derived from tetrahedrally coordinated Ag(I) ions bound to one Se atom of each of four diselenoethers. The second Se atom from each ligand serves to generate the 3-dimensional array by cross-linking to adjacent Ag(I) ions. The Ag–Se bond lengths lie in the range 2.643(1)–2.695(1) Å. This species is isostructural with its thioether analogue [158].

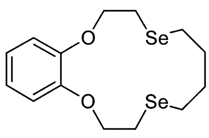
The structure of the o-phenylene ligand derivative $[Ag\{o\text{-}C_6H_4(SeMe)_2\}_2]BF_4$ reveals a very different structure from the discrete mononuclear cation seen for the Cu(I) analogue (above). In this case the structure shows (Fig. 40) infinite chains of $[Ag\{\mu\text{-}o\text{-}C_6H_4(SeMe)_2\}_2\{o\text{-}C_6H_4(SeMe)_2\}]^+$ cations. Each Ag(I) ion coordinates to both Se-donor atoms from one chelating diselenoether and to one Se-donor of each of two bridging diselenoethers. The second Se on these ligands then links to adjacent Ag ions to generate the polymer, giving a distorted tetrahedral geometry at each Ag ion, with d(Ag–Se) in the range 2.587(1)–2.861(1) Å [152]. $[Ag\{o\text{-}C_6H_4(CH_2TeMe)_2\}_2]BF_4$ has been prepared similarly [54].

The cyclic diselenoethers [8]aneSe_2 and sebc both form complexes with a 2:1 L:Ag ratio. The structure of $[Ag([8]aneSe_2)_2]^+$ (Fig. 41) reveals a discrete mononuclear species with two bidentate [8]aneSe_2 ligands generating a distorted tetrahedral stereochemistry at Ag(I), d(Ag–Se) = 2.636(4)–2.695(4) Å [8].

$[Ag(sebc)_2]^+$ also exhibits a discrete mononuclear structure, with the sebc units functioning as chelating ligands and with similar bond length and angle distributions [8]. A white solid with formula $[Ag([16]aneSe_4)]BF_4$ was prepared similarly through the reaction of $AgBF_4$ with the tetraselenoether in acetone, although this species has not been structurally characterised [159]. Ion selective electrodes for Ag(I) have been prepared which contain the mixed selena-oxa crowns, L^1 and L^2, in a PVC membrane. These exhibit excellent selectivity for Ag^+ over other metal ions [160].



L¹



L²

Silver(I) complexes of the methylene bridged ligands $MeECH_2EMe$ have been synthesised in an effort to promote the construction of polymeric complexes due to the mismatch of the tetrahedral geometry at Ag(I) and the small chelate bite angle from the bidentate ligand [153]. The crystal structure of $[Ag\{MeSeCH_2SeMe\}_2]BF_4$ reveals (Fig. 42) tetrahedrally coordinated Ag(I) ions, linked through one Se-donor atom from each of four diselenoethers. A 3-dimensional array is formed through coordination of the second Se atom on each ligand to adjacent Ag(I) centres which generates an open structure with large channels containing the BF_4^- anions [153].

Treatment of $AgBF_4$ with four molar equivalents of 1,3-dihydrobenzo[*c*]tellurophene, L affords the distorted tetrahedral $[Ag(L)_4]BF_4$, involving tetratelluroether coordination at Ag(I), $d(Ag–Te) = 2.7676(7)–2.8104(8)$ Å. Solution ^{125}Te-NMR spectroscopy shows a low frequency shift upon coordination of L to Cu(I) or Ag(I) compared to 'free' L. This species serves to stabilise L and provides a good source of L through transmetallation reactions [20]. The structure of an orange, light-sensitive crystal of $[Ag\{MeTe(CH_2)_3TeMe\}_2]^+$ reveals (Fig. 43) an infinite coordination polymer containing tetrahedral $AgTe_4^+$ units connected through ditelluroether bridges, $d(Ag–Te) = 2.785(2)–2.837(2)$ Å [161].

Reaction of the tripodal ligands $MeC(CH_2SeMe)_3$ or $MeC(CH_2TeR)_3$ (R = Me or Ph) with $Ag(CF_3SO_3)$ yields the 1:1 Ag:ligand species $[Ag\{MeC(CH_2SeMe)_3\}](CF_3SO_3)$ or $[Ag\{MeC(CH_2TeR)_3\}](CF_3SO_3)$ in good yield [81]. The crystal structure of the selenoether derivative shows that the $[Ag\{MeC(CH_2SeMe)_3\}]^+$ cation adopts an infinite 1-dimensional coordination chain polymer. This is assembled through

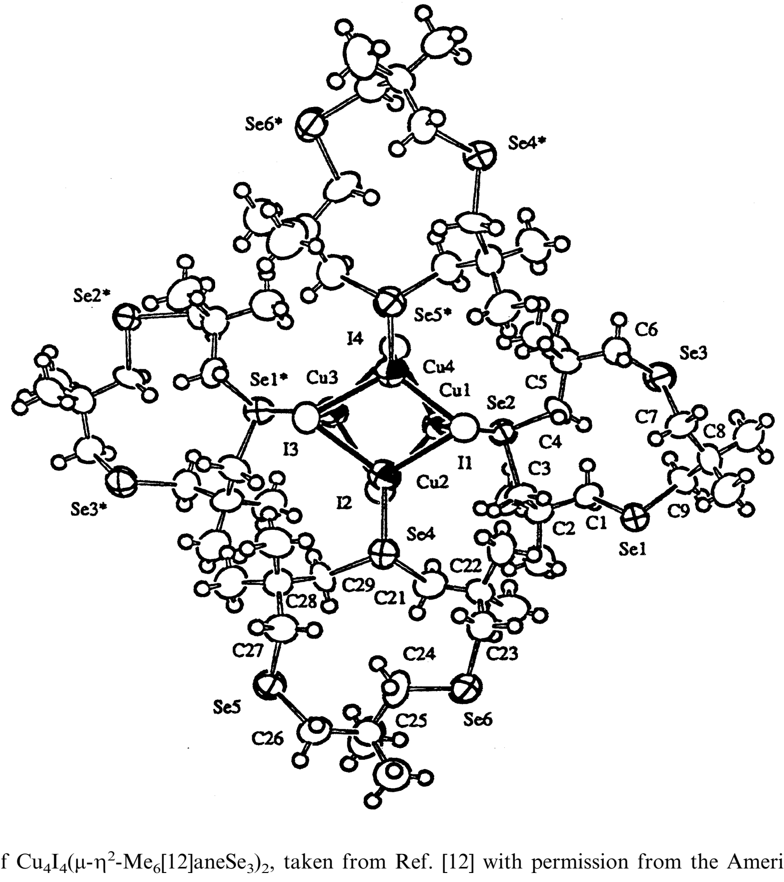


Fig. 35. Crystal structure of $Cu_4I_4(\mu\text{-}\eta^2\text{-}Me_6[12]aneSe_3)_2$, taken from Ref. [12] with permission from the American Chemical Society.

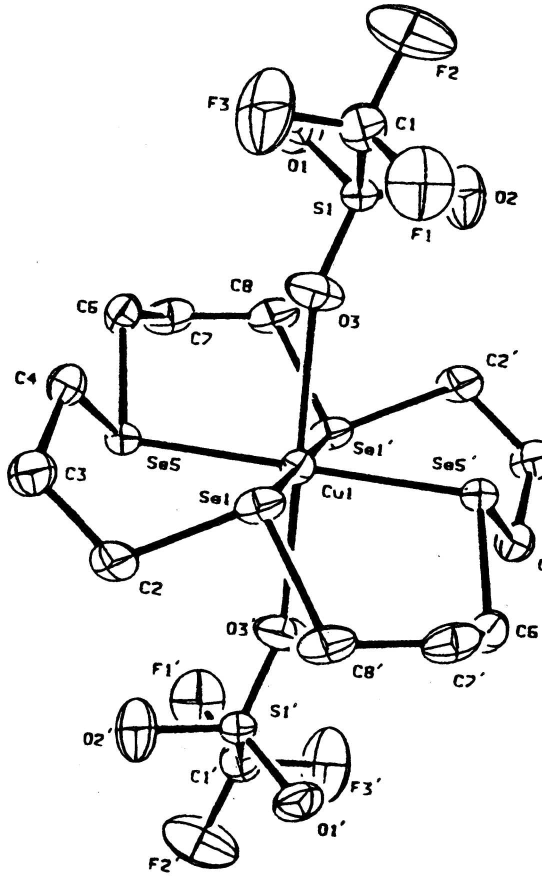


Fig. 36. Crystal structure of $[Cu([16]aneSe_4)](CF_3SO_3)_2$, taken from Ref. [154] with permission from the Canadian Journal of Chemistry.

bidentate coordination from one tripod ligand and monodentate coordination from another, giving a distorted trigonal planar geometry at Ag(I). The remaining Se atoms of these ligands bridge to adjacent Ag(I) ions [81].

Very poorly soluble silver(I) derivatives of the new mixed S/Te-donor macrocycles, $[9]aneS_2Te$, $[11]aneS_2Te$, $[12]aneS_2Te$ and $[14]aneS_3Te$ are prepared by reaction of the macrocyclic ligand with one molar equivalent of $Ag(CF_3SO_3)$ in CH_2Cl_2. The crystal structure of $[Ag([11]aneS_2Te)](CF_3SO_3)$ shows that the cation is a 1-dimensional polymer incorporating both distorted tetrahedral and distorted trigonal planar geometries at Ag(I) (Fig. 44). The trigonal planar geometry is obtained from bidentate coordination of one macrocyclic ligand through the thioether functions, with the remaining coordination site occupied by a Te-donor from a neighbouring macrocycle. The tetrahedral Ag(I) is similar, with the fourth coordination site occupied by a bridging thioether which assembles the $\{[Ag([11]aneS_2Te)]^+\}_2$ dimers to generate the polymer [162].

The corresponding tetrafluoroborate derivative, $[Ag([11]aneS_2Te)]BF_4$, was obtained similarly using $AgBF_4$. The crystal structure of this compound reveals different structural features from the triflate salt described above. In the tetrafluoroborate salt the cation assumes a 1-dimensional polymeric structure (Fig. 45), in which Ag ions are bridged by $[11]aneS_2Te$ ligands with a different Ag ion bonded to each door atom. The stereochemistry at Ag(I) is distorted trigonal planar, with $d(Ag–Te) = 2.674(1)$, $d(Ag–S) = 2.521(3)$, $2.634(3)$ Å [21].

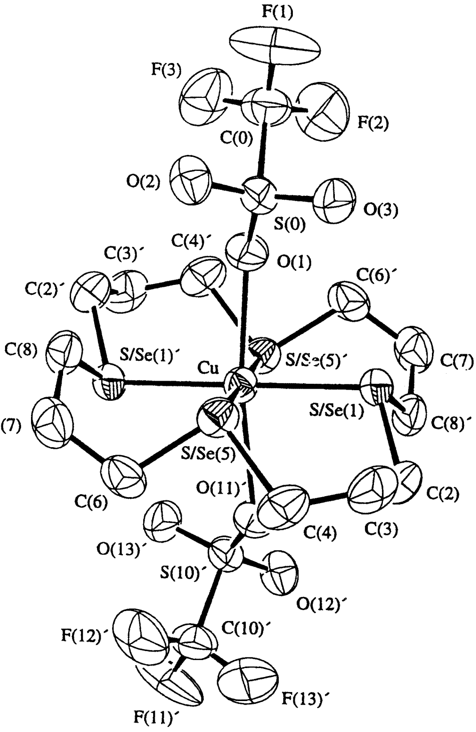


Fig. 37. Crystal structure of $[Cu([16]aneS_2Se_2)]^+$, taken from Ref. [10] with permission from the American Chemical Society.

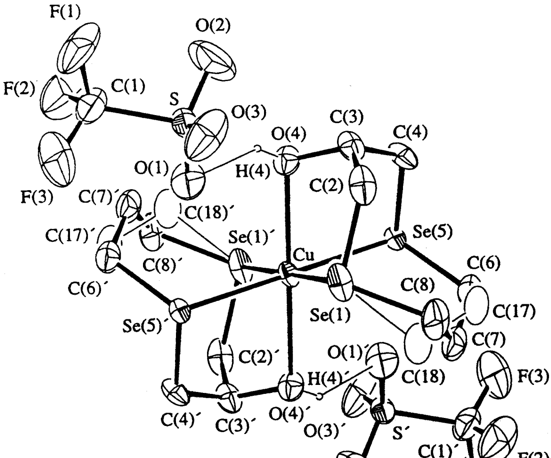


Fig. 38. Crystal structure of $[Cu\{[8]aneSe_2(OH)\}_2](CF_3SO_3)_2$, taken from Ref. [10] with permission from the American Chemical Society.

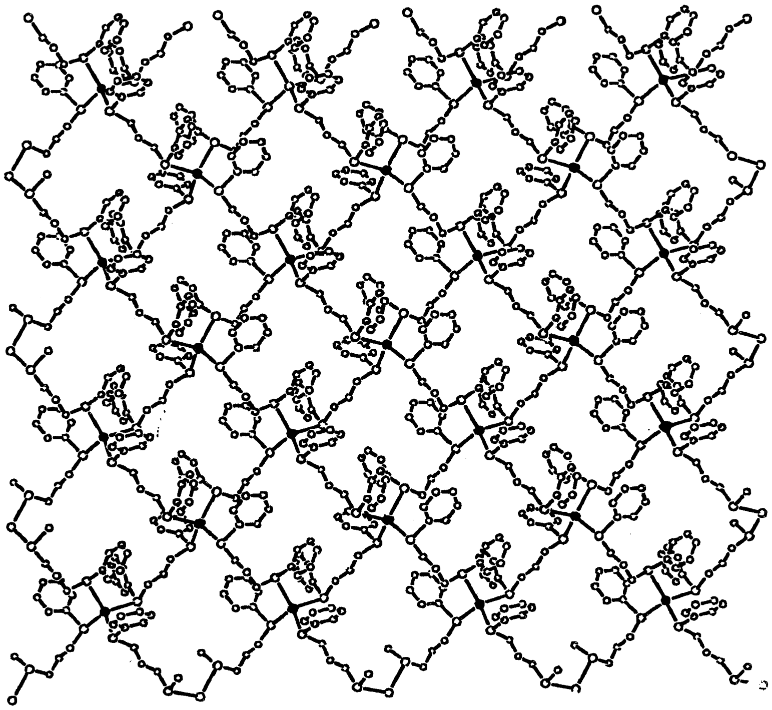


Fig. 39. Crystal structure of $[Ag\{PhSe(CH_2)_3SePh\}_2]^+$, taken from Ref. [158] with permission from the Royal Society of Chemistry.

4.9.3. Gold

The crystal structure of the tetrahydroselenophene complex $[Au(C_4H_8Se)I]$ has been determined. The structure comprises linear $[Au(C_4H_8Se)_2]^+$ cations and linear $[AuI_2]^-$ anions, which alternate to give zigzag chains, with $d(Au\cdots Au) = 2.987(2)$ and $3.001(2)$ Å, and $d(Au–Se) = 2.430(3)–2.436(3)$ Å [163]. The tripodal $MeC(CH_2SeMe)_3$ reacts with $[AuCl(SMe_2)]$ or $[AuCl(tht)]$ (tht = tetrahydrothiophene) to afford the trimetallic species $[\{MeC(CH_2SeMe)_3\}(AuCl)_3]$, involving linear Au(I) [119]. The cyclic diselenoethers $[8]aneSe_2$ and sebc react similarly with [AuCl(tht)] to afford the dinuclear species $[(AuCl)_2([8]aneSe_2)]$ and $[(AuCl)_2(sebc)]$, respectively, as white solids [8].

4.10. Group 12

4.10.1. Zinc

There are no new reports of zinc halide complexes with seleno- or telluroether ligands, although alkylzinc(II) adducts $R_2Zn–SeR_2$ (R = alkyl) have been shown to provide a good source for the manufacture of thin film ZnSe for laser, semiconductor and diode applications, through MOCVD processes [164,165]. The 1:1 and 1:2 adducts, $Me_2Zn–SeMe_2$ and $Me_2Zn–2SeMe_2$ are formed by merged jet codeposition of the reagents using matrix isolation and cryogenic thin film techniques and have been examined spectroscopically [166].

4.10.2. Cadmium

The 1:1 and 1:2 $Me_2Cd:SeR_2$ (R = alkyl) adducts formed in Ar matrices and cryogenic thin films have been prepared and characterised spectroscopically [167]. A short report on organotellurium precursors for MOCVD of mercury cadmium telluride has appeared [168].

Reaction of 2,6-diacetylpyridine with aminoalkyl phenyl selenides gives N_3Se_2-donor Schiff base ligands, L. Reaction with $CdCl_2$ gives $[CdCl_2(L)]$ which has been structurally characterised, showing bidentate ligation of L [169]. The mixed S_2Te-donor ligand $MeS(CH_2)_2Te(CH_2)_2SMe$ reacts with Cd(II) in the presence of PPh_3 to afford $[Cd(PPh_3)_2\{MeS(CH_2)_2Te(CH_2)_2SMe)](ClO_4)_2$, which has been characterised spectroscopically and assigned a four-coordinate geometry with bidentate ligation of the S_2Te ligand [170].

4.10.3. Mercury

The mixed Se/O macrocycles I–III (see Section 2) react with HgI_2 in thf solution to afford the dinuclear species $[(HgI_2)_2(L)]$, through coordination via the Se atoms. The crystal structure of $[(HgI_2)_2(III)]$ confirms bidentate ligation of III to each Hg(II) ion via two Se-donor atoms, affording distorted tetrahedral coordination, $d(Hg–Se) = 2.717(2), 2.796(2)$ Å [15].

The Te-containing macrocyclic Schiff base reacts with two molar equivalents of $HgCl_2$ to give $[(HgCl_2)_2(L)]$ as a yellow solid. A tetrahedral $NTeCl_2$ donor set is postulated at Hg(II) on the basis of spec-

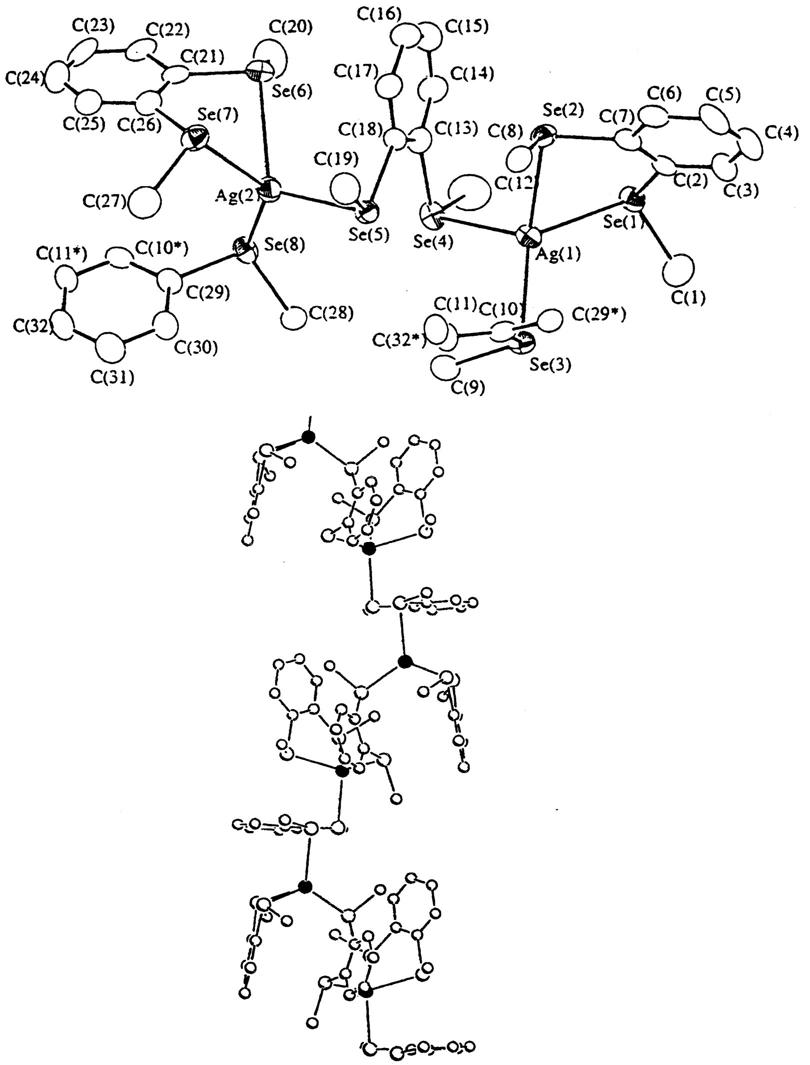


Fig. 40. Crystal structure of $[Ag\{o\text{-}C_6H_4(SeMe)_2\}_2]^+$, taken from Ref. [152] with permission from the American Chemical Society.

troscopic data, with the macrocyclic ligand functioning as a bidentate chelate to each Hg(II) ion [22].

The $HgCl_2$ adducts of the ditelluroether $ArTeCH_2CH(OH)CH_2TeAr$ and monotelluroether $ArTeCH_2CH(CH)CH_2OH$ ($Ar = 4\text{-Me-}o\text{-}C_6H_4$) have been described although no structural data are presented [128,129].

4.11. Group 13

There are no reports of selenoether or telluroether complexes of aluminium. The 1/1 molar adducts of $GaMe_3$ with $SeMe_2$ have been isolated in an argon matrix and characterised spectroscopically [171]. The $^{69,71}Ga$- and ^{115}In-NQR spectra of a series of complexes of gallium and indium alkyls have been studied, including $[R_3GaL]$ ($R = Me$, Et; $L = SeMe_2$, $TeMe_2$). The behaviour of the quadrupole coupling constants is de-

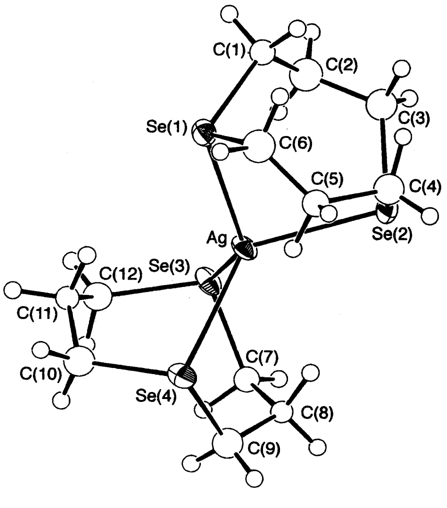
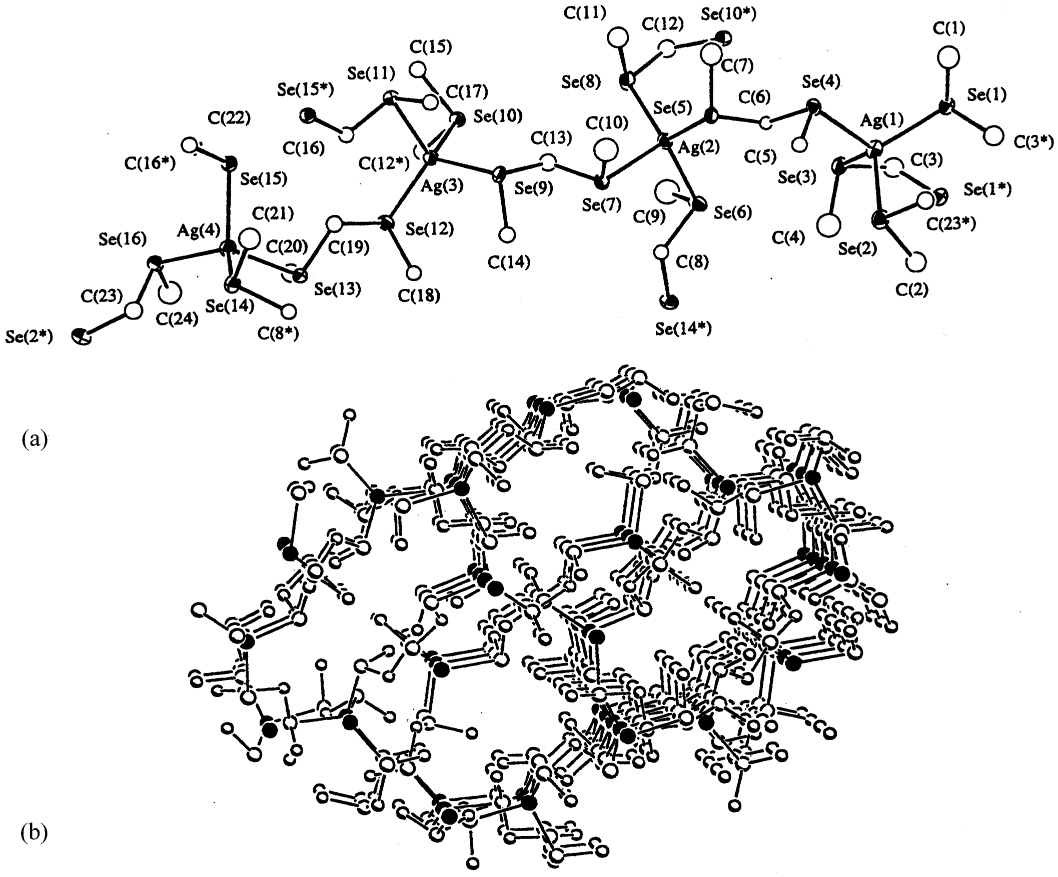


Fig. 41. Crystal structure of $[Ag([8]aneSe_2)_2]^+$, taken from Ref. [8] with permission from the Royal Society of Chemistry.



(a)

(b)

Fig. 42. Crystal structure of $[Ag\{MeSeCH_2SeMe\}_2]^+$ (Ag atoms shaded), taken from Ref. [153] with permission from the American Chemical Society.

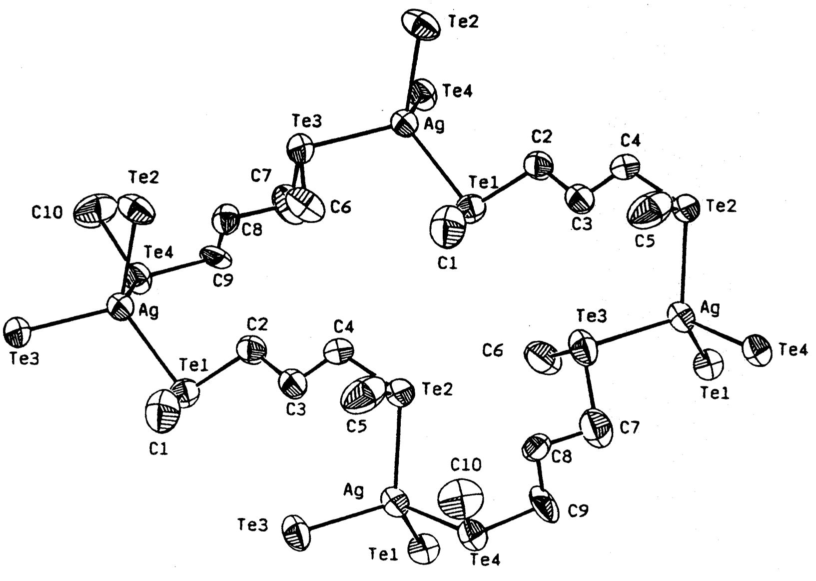


Fig. 43. Crystal structure of $[Ag\{MeTe(CH_2)_3TeMe\}_2]^+$, taken from Ref. [161] with permission from the American Chemical Society.

termined by the geometry of the complexes [172]. Triisopropylindium diisopropyltelluride, $[In(CHMe_2)_3\{Te(CHMe_2)_2\}]$ has been synthesised and used as a universal n-type dopant for both II/VI and III/V semiconductor materials [173,174]. Selenoether and telluroether complexes of thallium are unknown.

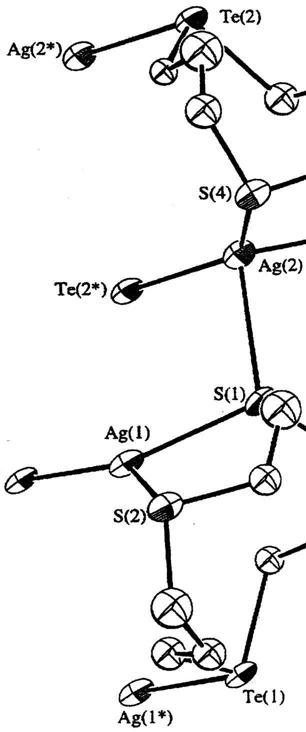


Fig. 44. Crystal structure of $[Ag([11]aneS_2Te)]^+$ ($CF_3SO_3^-$ salt), taken from Ref. [162].

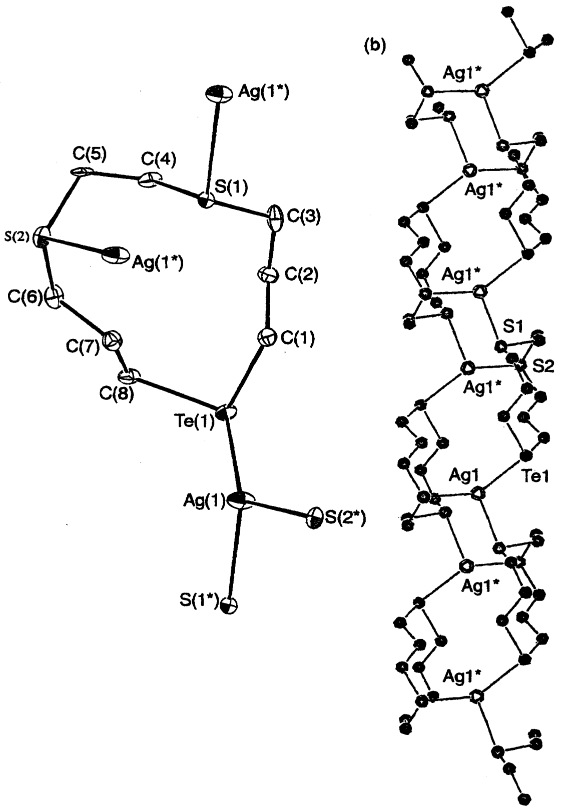
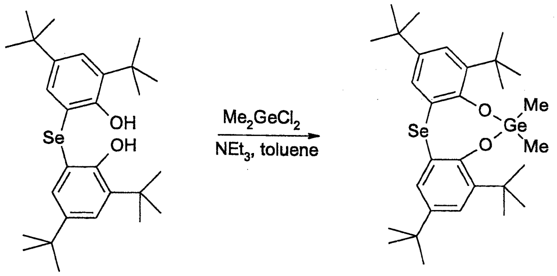


Fig. 45. Crystal structure of $[Ag([11]aneS_2Te)]^+$ (BF_4^- salt), taken from Ref. [21] with permission from the Royal Society of Chemistry.



Scheme 8.

4.12. Group 14

Variable temperature in situ multinuclear (^1H, ^{29}Si, ^{73}Ge, ^{77}Se) NMR studies on mixtures of $SiCl_4$ or $GeCl_4$ with $SeMe_2$ (or SMe_2 or $MeS(CH_2)_2SMe$) in anhydrous CH_2Cl_2 reveal no adduct formation even at 180 K [175].

A sterically hindered dioxaselenagermocin has been obtained by treatment of the selenabisphenol with Me_2GeCl_2 as in Scheme 8 in the presence of triethylamine. Its crystal structure shows (Fig. 46) that the eight-membered ring adopts a boat–boat conformation with transannular bonding of Se to Ge giving a Ge–Se bond length of 3.10 Å, significantly shorter than the sum of the van der Waals radii (3.85 Å) [176].

Reaction of the same selenabisphenol with $GeCl_4$ and NEt_3 affords the spiracyclic derivative, the crystal structure of which reveals (Fig. 47) a distorted octahedral geometry at Ge, now coordinated to the four phenolic O donor atoms and to the two Se atoms, d(Ge–Se) = 2.5959(6) Å, the ligands functioning as *fac* tridentates [176]. The Se atoms occupy mutually *cis* coordination sites and the $Ge–O_{trans\text{-}O}$ bond distances are longer than $Ge–O_{trans\text{-}Se}$.

There are no new examples of lead complexes with these ligands.

4.12.1. Tin

Multinuclear (^1H, ^{77}Se, ^{119}Sn, ^{125}Te) VTNMR studies have been conducted on the known species $[SnX_4(EMe_2)_2]$ (X = Cl or Br; E = Se or Te) [177]. The results show that for the $SeMe_2$ complexes both *cis* and *trans* isomers are present (Fig. 48), with fast exchange occurring at room temperature. As expected, the rate of exchange is faster for the telluroether complexes compared to the selenoether systems.

In situ NMR studies on mixtures of SnI_4 with excess $SeMe_2$ reveal broad resonances at low temperature, consistent with adduct formation, although these species could not be isolated [177]. Crystal structures show that in the solid state both $[SnCl_4(SeMe_2)_2]$ and $[SnBr_4(SeMe_2)_2]$ (Fig. 49) are centrosymmetric with mutually *trans* selenoethers, d(Sn–Se) = 2.7001(9), 2.731(2) Å. Detailed spectroscopic studies have been undertaken on a series of diseleno- and ditelluroether complexes of tin tetrahalides and the properties have been compared with those of the analogous thioether species [175,177].

Reaction of SnX_4 (X = Cl or Br) with $MeSe(CH_2)_2SeMe$, $MeE(CH_2)_3EMe$, $PhE(CH_2)_3EPh$ or *o*-$C_6H_4(EMe)_2$ (E = Se or Te) (L–L) in rigorously anhydrous CH_2Cl_2 affords the complexes $[SnX_4(L–L)]$ as yellow to brown, very hydrolytically unstable powdered solids [175,177,178]. Variable temperature multinuclear NMR studies (^1H, ^{77}Se, ^{119}Sn, ^{125}Te) have been used to investigate their solution behaviour. In all cases pyramidal inversion and reversible chelate ring opening are rapid at room temperature, although for the chloro derivatives both of these processes are slow at low temperatures, the spectra revealing the presence of both *meso* and *DL* isomers. The ^{77}Se- and ^{125}Te-NMR spectra reveal that large positive chelate ring shifts occur for 5-membered chelate rings and small negative shifts for 6-membered chelate rings. The crystal structures of $[SnCl_4\{meso\text{-}o\text{-}C_6H_4(SeMe)_2\}]$, $[SnBr_4\{meso\text{-}o\text{-}C_6H_4(SeMe)_2\}]$, $[SnCl_4\{DL\text{-}MeSe(CH_2)_3SeMe\}]$, $[SnCl_4\{meso\text{-}o\text{-}C_6H_4(TeMe)_2\}]$ and $[SnBr_4\{meso\text{-}o\text{-}C_6H_4(TeMe)_2\}]$ (Fig. 50) have been obtained. All of these exhibit distorted octahedral geometries at Sn(IV), with the diselenoether or ditelluroether chelating and therefore the Group 16 atoms occupying mutually *cis* coor-

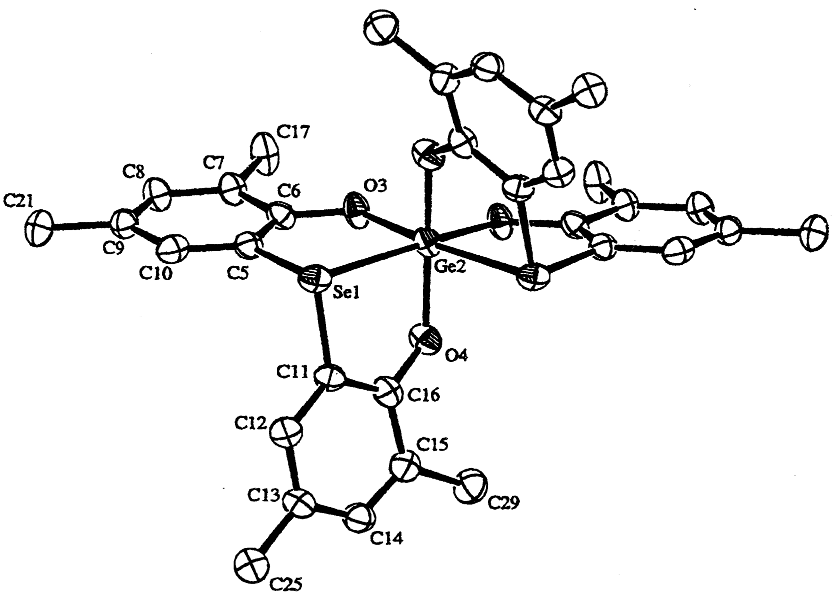


Fig. 46. Crystal structure of the diselenagermocin, taken from Ref. [176] with permission from the American Chemical Society.

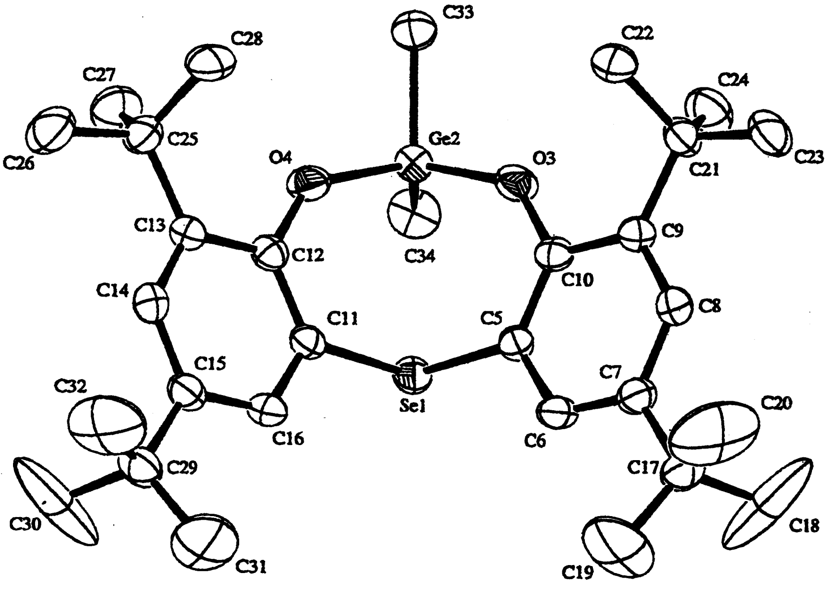


Fig. 47. Crystal structure of the product from reaction with $GeCl_4$, taken from Ref. [176] with permission from the American Society.

Fig. 48. ^{77}Se-NMR spectrum of [$SnCl_4(SeMe_2)_2$] showing the presence of both the *cis* and *trans* isomers, taken from Ref. [177] with permission from the Royal Society of Chemistry.

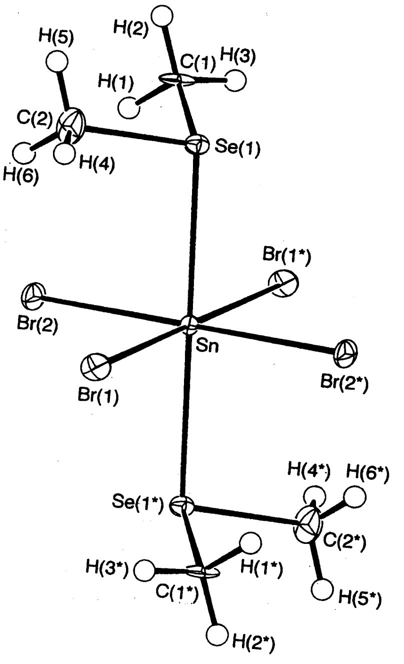


Fig. 49. Crystal structure of [$SnBr_4(SeMe_2)_2$], taken from Ref. [177] with permission from the Royal Society of Chemistry.

dination sites. In all of these compounds (and in the thioether analogues) the axial X groups tilt towards the neutral Group 16 ligand with X–Sn–X typically ca. 170°.

Interestingly, for a given L–L, *d*(Sn–Se) for the bromo derivatives are longer than in the chloro species, consistent with the former being a better acceptor than the latter. Further, *d*(Sn–X) *trans* X are consistently longer than *d*(Sn–X) *trans* E (E = Se or Te), suggesting that the X ligands exert a greater *trans* influence than the Se or Te atoms in these compounds [175,177,178]. The hydrolytically unstable compound [$SnCl_4$\{MeSeCH$_2$SeMe\}] has also been prepared and its crystal structure reported [179]. The structure confirms (Fig. 51) that the diselenoether is chelating and adopts the *meso* form, forming a strained four-membered chelate ring, with $<$ Se–Sn–Se = 69.11(5)°. This is the first example of 2,4-diselenapentane functioning as a chelating ligand. VTNMR studies on this compound reveal no ^{77}Se signal, suggesting that this compound is more labile than the other diselenoether complexes of Sn(IV) [179].

From the spectroscopic and structural data on this series of compounds it is clear that the affinity of Group 14 Lewis acids for Group 16 ligands falls in the orders $SR_2 > SeR_2 > TeR_2$, $SnCl_4 \gg GeCl_4$, $SiCl_4$ and $SnCl_4 > SnBr_4 > SnI_4$.

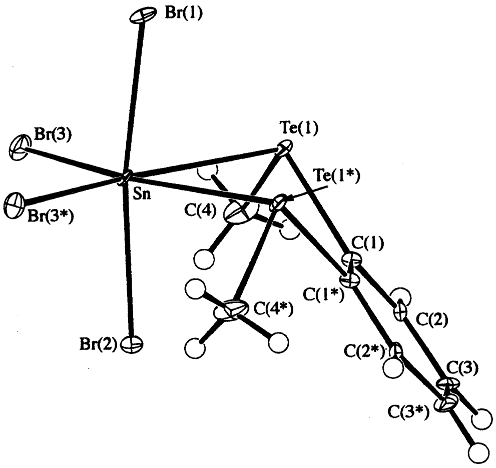


Fig. 50. Crystal structure of [$SnBr_4$\{*meso-o*-$C_6H_4(TeMe)_2$\}], taken from Ref. [175] with permission from the Royal Society of Chemistry.

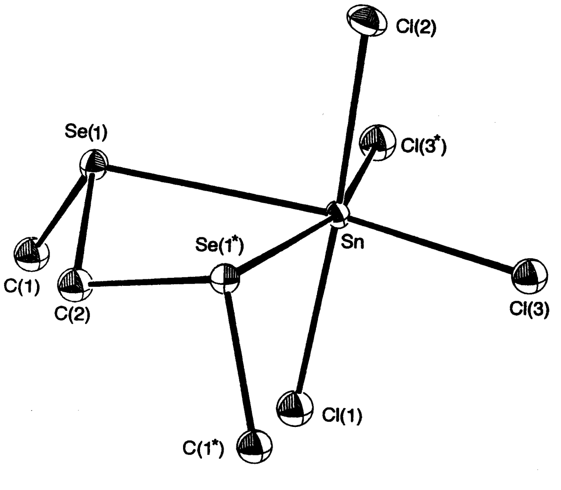


Fig. 51. Crystal structure of [$SnCl_4$\{*meso*-MeSeCH$_2$SeMe\}], taken from Ref. [179] with permission from the Royal Society of Chemistry.

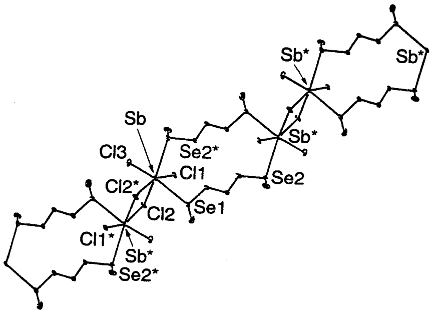


Fig. 52. Crystal structure of [$SbCl_3\{DL\text{-}MeSe(CH_2)_3SeMe\}$], taken from Ref. [180] with permission from the Royal Society of Chemistry.

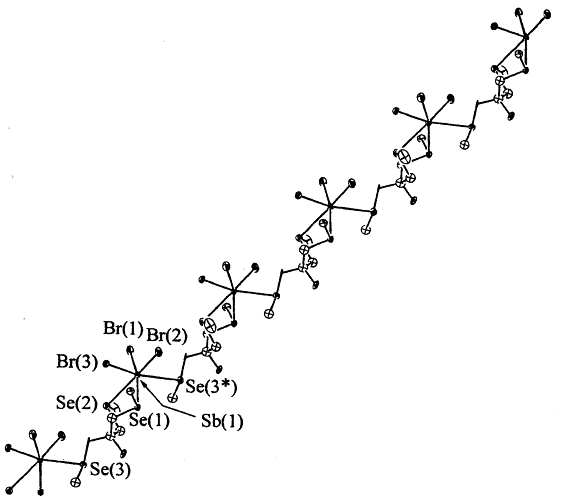


Fig. 53. Crystal structure of [$SbBr_3\{MeC(CH_2SeMe)_3\}$], taken from Ref. [181] with permission from the Royal Society of Chemistry.

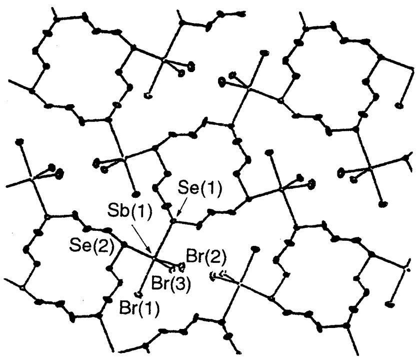


Fig. 54. Crystal structure of [$(SbBr_3)_2([16]aneSe_4)$], taken from Ref. [180] with permission from the Royal Society of Chemistry.

4.13. Group 15

There are no reports of any compounds formed with either PX_3 or AsX_3 behaving as Lewis acids (however, see Addendum).

4.13.1. Antimony

The first series of compounds involving coordination of SbX_3 ($X = Cl$, Br or I) with the bidentate selenoethers $MeSe(CH_2)_nSeMe$ ($n = 2$ or 3) has been reported and compared with their thioether analogues [180,181]. The compounds are obtained by treatment of SbX_3 with the Group 16 ligand in anhydrous MeCN (or thf) solution. These compounds exhibit unusual infinite 1- or 2-dimensional structures derived from primary Sb–X bonding with weak, secondary Sb–Se (or S) interactions to bridging selenoethers (or thioethers), with $d(Sb\cdots Se)$ ca. 3.2 Å. Thus, [$SbCl_3\{MeSe(CH_2)_3SeMe\}$] adopts a chain structure derived from dinuclear Sb_2Cl_6 linked by bridging selenoether ligands to give a distorted octahedral geometry at Sb(III), with two Se atoms occupying mutually *cis* coordination sites (Fig. 52). In all of the structures the pyramidal SbX_3 unit present in the parent antimony halide is retained and dominates the bonding [180].

The compounds [$SbX_3\{MeC(CH_2SeMe)_3\}$] are also obtained by reaction of SbX_3 with the tripodal $MeC(CH_2SeMe)_3$. The thioether derivatives have been obtained similarly. The compound [$SbBr_3\{MeC(CH_2SeMe)_3\}$] (Fig. 53) adopts an infinite chain structure assembled by coordination of the pyramidal $SbBr_3$ to bridging tripodal selenoether units. The latter function as bidentate ligands to one Sb centre with the third Se atom bridging to an adjacent Sb centre.

The thioether derivatives [$SbCl_3\{MeC(CH_2SMe)_3\}$] and [$SbI_3\{MeC(CH_2SMe)_3\}$] are also chain polymers, with subtle differences in the structures dependent upon the halide and the Group 16 element [181].

The macrocyclic selenoethers [8]aneSe_2, [16]aneSe_4 and [24]aneSe_6 form 1:1 compounds (usually) or 2:1 (occasionally) macrocycle:SbX_3 complexes. The crystal structure of [$(SbBr_3)_2([16]aneSe_4)$] (Fig. 54) shows a 2-dimensional sheet structure with pyramidal $SbBr_3$ units coordinated weakly to two Se atoms from different selenoethers, giving distorted trigonal bipyramidal Sb(III). The crowns therefore function as exocyclic ligands, with μ_4-bridging [16]aneSe_4 ligands [180,181].

Reaction of $MeTe(CH_2)_3TeMe$ or $MeC(CH_2TeMe)_3$ (L) with one molar equivalent of SbX_3 in rigorously anhydrous MeCN yields orange/brown powdered solids of stoichiometry [SbX_3L], although no structural data have been obtained to date [182].

4.13.2. Bismuth

The reactions of BiX_3 ($X = Cl$, Br or I) with $MeSe(CH_2)_nSeMe$ ($n = 2$ or 3) and $MeC(CH_2SeMe)_3$ in dry MeCN have been reported, yielding compounds with a 1:1 Bi:selenoether ligand ratio [183]. The structure of [$BiCl_3\{MeSe(CH_2)_3SeMe\}$] (Fig. 55) adopts a 2-dimensional network with coplanar Bi_2Cl_6 units bridged by selenoether ligands. The two Se atoms at each Bi(III) centre occupy mutually *trans* coordination

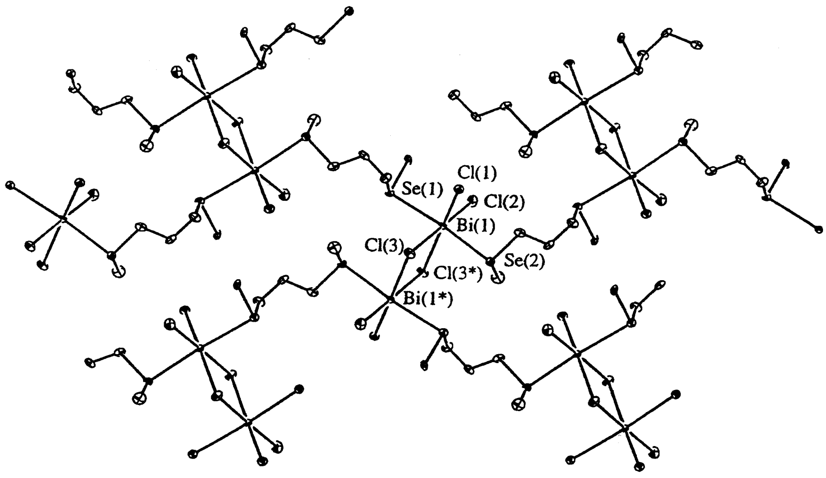


Fig. 55. Crystal structure of [BiCl$_3${MeSe(CH$_2$)$_3$SeMe}], taken from Ref. [183] with permission from the Royal Society of Chemistry.

sites, contrasting with the *cis* arrangement seen for most other ligands such as phosphines. The Bi–Cl distances of 2.55–2.88 Å are indicative of primary interactions, while the Bi–Se distances of 2.988(2) and 3.036(2) Å should be regarded as weak, secondary bonds. [BiBr$_3${MeSe(CH$_2$)$_3$SeMe}] is isostructural with the chloro species.

The structure of [BiCl$_3${MeC(CH$_2$SeMe)$_3$}] is also a 2-dimensional sheet (Fig. 56), in this case incorporating 7-coordinate Bi(III) ions coordinated to two bridging Cl atoms, two terminal Cl atoms, two Se atoms from a bidentate selenoether and one Se from a monodentate selenoether. The triselenoethers therefore cross-link these Bi units to give the infinite network. Similar Bi–Cl and Bi–Se bond length distributions are observed.

Surprisingly, the iodo analogue, [Bi$_2$I$_6${MeC(CH$_2$SeMe)$_3$}$_2$] is quite different from the chloro species above. The iodo complex comprises discrete dinuclear units derived from a twisted Bi$_2$I$_6$ rhomboidal core, with one bidentate triselenoether coordinated to each Bi centre, giving a distorted octahedral geometry [183].

The macrocyclic complexes [BiX$_3$(L)] (L = [8]aneSe$_2$, [16]aneSe$_4$ and [24]aneSe$_6$) are obtained as intensely coloured yellow to red solids in moderate yield by treatment of the parent BiX$_3$ with L in anhydrous MeCN [184]. The crystal structures of [BiCl$_3$([8]aneSe$_2$)] and [BiBr$_3$([16]aneSe$_4$)] (Fig. 57) each reveal infinite 1-dimensional ladder structures assembled from nearly coplanar Bi$_2$X$_6$ ‘rungs’ linked by bridging L ‘uprights’, the Se atoms occupying mutually *trans* coordination sites. The selenoether macrocycles adopt exocyclic arrangements and in [BiBr$_3$([16]aneSe$_4$)] it is alternate Se atoms which coordinate to the Bi centres, leaving the other two Se atoms non-coordinating [184]. These species contrast with structures reported for BiCl$_3$ complexes with a variety of thioether macrocycles, all of which are discrete molecules involving pyramidal BiCl$_3$ units coordinated through weak, secondary interactions to the face-capping thioether crown. Comparisons with the Sb(III) complex of [16]aneSe$_4$ (Section 4.13.1) also reveals surprising differences, the latter comprising a 2-dimensional sheet with all four Se atoms coordinating to distinct Sb(III) centres.

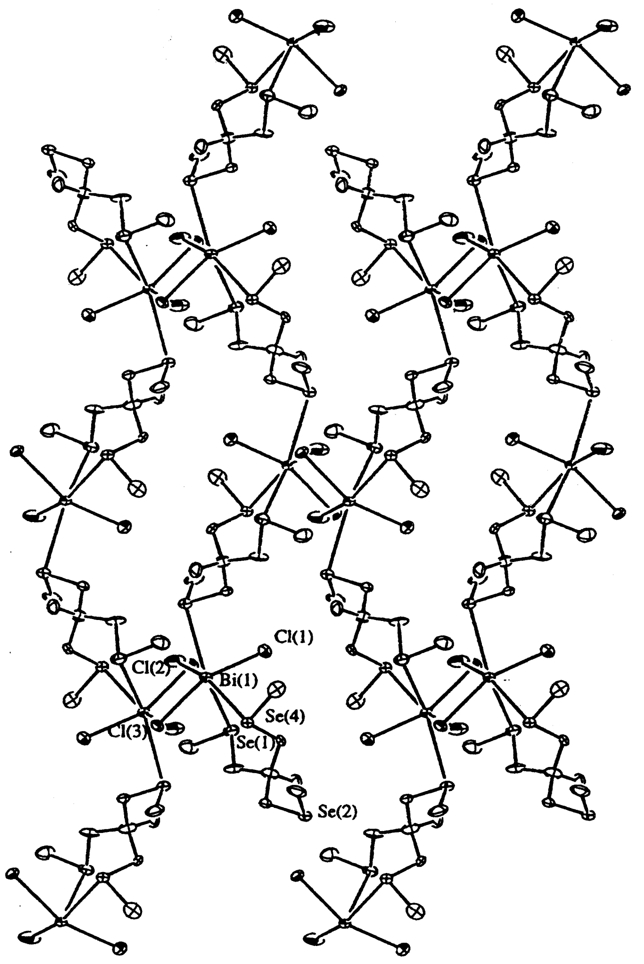


Fig. 56. Crystal structure of [BiCl$_3${MeC(CH$_2$SeMe)$_3$}], taken from Ref. [183] with permission from the Royal Society of Chemistry.

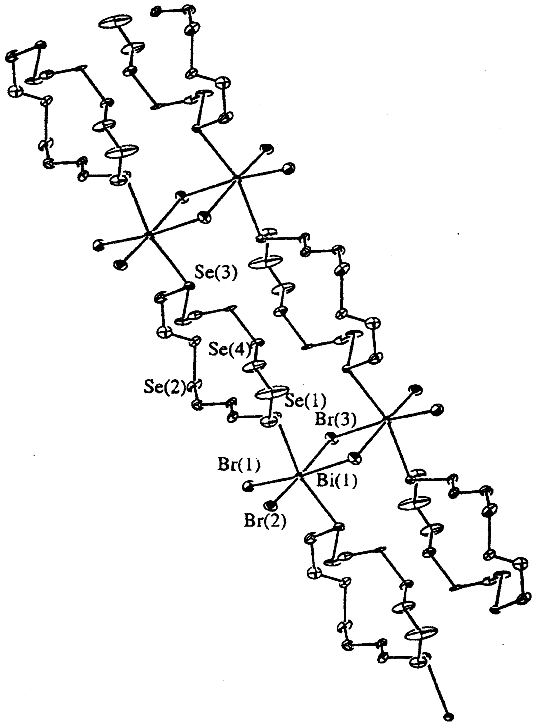


Fig. 57. Crystal structure of [$BiBr_3$([16]aneSe_4)], taken from Ref. [184] with permission from the Royal Society of Chemistry.

5. ^{77}Se- and ^{125}Te-NMR spectroscopy

Both nuclei have $I = 1/2$ and sensitivities somewhat better than ^{13}C, making them valuable probes for the study of selenoether and telluroether complexes, and contrasting with the case of thioethers where only the insensitive, quadrupolar ^{33}S is available. At the time of the last review [1], the applications of these two nuclei were relatively recent, and data correspondingly limited. During the 1990s, much more data were acquired, and this section collects together an overview of these developments.

5.1. Pyramidal inversion

The combination of multinuclear (^{1}H, ^{13}C{^{1}H}, ^{77}Se or ^{125}Te) NMR spectroscopies is the method of choice to study pyramidal inversion at the coordinated Group 16 atom. The field was comprehensively reviewed some time ago [185], and although there is only one quantitative study of inversion barriers in ditelluroethers [186], the trends are not in doubt. For corresponding systems inversion barriers are $S < Se < Te$, whilst for a fixed Group 16 donor, the barriers decrease with unsaturated substituents and with backbone (in bidentates) $-(CH_2)_2- > o\text{-}C_6H_4 > -(CH_2)_3-$. The barriers also vary with the metal ion, its oxidation state, and co-ligands (especially the *trans* ligands). Recent qualitative studies conform to the pattern described. Few studies have addressed pyramidal inversion in macrocycles, although the invertomers have been identified in the planar [M([16]aneSe_4)]$^{2+}$ (M = Pd or Pt) [117,122].

5.2. Chemical shifts

It was noted earlier [1] that coordination of a selenoether or telluroether to a metal centre usually resulted in a substantial high frequency coordination shift. Whilst this is mostly true for positive oxidation states of the platinum metals, and probably also for medium or high oxidation of the earlier metals (although data are presently limited in the latter area), there are now many examples where this observation does not hold. For complexes of the electron-rich d^{10} Cu(I) or Ag(I) the usual trend is that the coordination shifts are to low frequency [151,158], although the [Cu{o-$C_6H_4(EMe)_2$}$_2$]$^+$ (E = Se or Te) exhibit small high frequency coordination shifts [152]. In low valent metal carbonyl systems the coordination shifts are often relatively small and may be to high or low frequency [34,36,64,187].

It was also established relatively early that the coordination shift was sensitive to chelate ring size and that ^{77}Se- and ^{125}Te-NMR shifts could be interpreted [188–190] in terms of a 'chelate ring contribution' as popularised in ^{31}P-NMR studies of diphosphines by Garrou [191]. In summary the coordination shifts in 5-membered rings are very large, those in 6-membered much smaller, and if data on closely related complexes of monodentate analogues are available the effect may be semi-quantified in terms of a 'chelate ring parameter' [1]. Interestingly the pattern with ring size appears to hold whether the coordination shift is to high or low frequency. More recent work has added data on 4- and 7-membered rings. In the strained 4-membered ring in [$PdCl_2${(4-$MeOC_6H_4Te)_2CH_2$}] the coordination shift is − 62 ppm [115] and taking [$PdCl_2(TeMePh)_2$] as the equivalent monodentate [190] yields the chelate ring parameter = 219. The latter number should be viewed with caution since substituents as remote as the γ-C affect the ^{125}Te chemical shifts and thus TeMePh is not an exact match as the 'equivalent monodentate', although the trend is almost certainly reliable. For complexes of the 7-membered ring ditelluroether o-$C_6H_4(CH_2TeMe)_2$ the coordination shifts seem similar to those in 6-membered rings, but a more quantitive comparison is prevented by the absence of data on an exactly equivalent monodentate [54].

Studies of the NMR spectra of organoselenium and -tellurium compounds established that for comparable compounds $\delta(^{125}Te) = \delta(^{77}Se) \times 1.8$ [192], and perhaps more surprisingly it was observed that this ratio held for corresponding selenoether and telluroether complexes of Pd(II) and Pt(II) [193]. An approximately similar ratio has been observed in several series of complexes of transition metal halides. However in the series of complexes $[(\eta^5\text{-}C_5H_5)Fe(CO)(EMe_2)L]^+$ (E = Se or Te), it was observed that the ^{125}Te-NMR chemical shifts were much greater than expected of this basis [187]. Subsequently, studies of a range of other carbonyl or carbonyl halide complexes including those of Mn [24,34,37], Cr, Mo and W [36] showed similar effects with the $\delta(^{125}Te)/\delta(^{77}Se)$ ratio ca. 2.5. Detailed studies of the metal nuclei NMR (^{55}Mn and ^{95}Mo) and the force constants resulting from analysis of the IR active carbonyl stretches, concluded that the results were attributable to very good σ-donation from the tellurium resulting in a large build up of electron density on the metal centre and in the π* orbitals of the carbonyl groups. It has recently been shown [37] that the effect is also seen in low valent non-carbonyl complexes, since $\delta(^{125}Te)/\delta(^{77}Se)$ is ca. 2.4 in $[M^I(COD)\{MeC(CH_2EMe)_3\}]PF_6$ (M = Rh or Ir) compared with a more 'normal' value ca. 2.1 in the $[M^{III}(\eta^5\text{-}C_5Me_5)\{MeC(CH_2EMe)_3\}]^{2+}$.

5.3. Coupling constants

The trends in one bond coupling constants, especially $^1J(^{77}Se-^{195}Pt)$ or $^1J(^{125}Te-^{195}Pt)$ have been discussed elsewhere [1], and these show similar dependence on oxidation state, *trans* ligands etc., as do the familiar $^1J(^{31}P-^{195}Pt)$. Coupling constants of both Group 16 atoms to Rh(III) are also known e.g. Refs. [37,78], as are $^1J(^{77}Se-^{119}Sn)$ [177]. In other cases where 1-bond couplings to dipolar metal nuclei might have been expected they have not been observed, even in low temperature studies, probably due to the lability of the ligands. Included in this group are silver(I) complexes of both seleno- and telluroethers [152,158] and tin(IV)-ditelluroethers [175]. Although the last few years have seen several NMR studies of systems containing quadrupolar nuclei, including ^{63}Cu, ^{95}Mo, and ^{55}Mn, in these complexes the metal nucleus is in a low symmetry environment and the corresponding substantial electric field gradients promote fast quadrupolar relaxation, resulting in broad resonances and the absence of resolved spin–spin couplings.

6. Uses

Detailed studies of selenoether and telluroether coordination chemistry are relatively recent, and hence applications of these complexes are correspondingly at an early stage. Examples have been noted in the descriptive sections of this review. Here we gather together some illustrative examples for convenient reference.

In contrast to the importance of Group 15 ligand complexes in homogeneous catalysis, the catalytic applications of metal thioether complexes have developed relatively recently, and there is little work utilising heavier Group 16 ligands. A number of palladium or platinum complexes of selenoether crowns [149,150] and ferrocenyl selenoethers [112] have been assessed as hydrosilylation catalysts. There are also continuing indications in the patent literature [194] that some palladium telluroether complexes have sensitising properties for silver film emulsions.

However, the major area of interest concerns CVD or MOCVD applications, where the complexes provide precursors to MSe_n or MTe_n films. In many such studies mixtures of R_2E and the metal alkyl or halide are used, and it is unclear whether pre-formation of a complex is involved. In other cases, although pre-isolated complexes may be used, there is the possibility that dissociation in the vapour phase precedes thermal decomposition. Attempts to deposit $TiSe_2$ films using $[TiCl_4(SeMe_2)_2]$ suffered from poor reproducibility, but $[TiCl_4(SeEt_2)_2]$ is more promising, in that decomposition at 500–600 °C produced $TiSe_2$ films, although these degraded on exposure to moist air [41].

Pyrolysis of $[RCOMn(CO)_4(TeR'_2)]$ in hydrogen produced films containing both Te and Mn, although pre-dissociation of the complexes was problematic [62]. In the case of $[Co(CO)_2(NO)(TeMe_2)]$, the thermal decomposition of the vapour in hydrogen gave a cobalt film and $TeMe_2$, although the complex decomposes at too low a temperature to form $CoTe_x$ films [87]. The use of TeR_2 complexes as precursors for MOCVD manufacture of mercury cadmium telluride films has been reviewed [168]. Other studies include $R'_2Zn{\cdot}SeMe_2$ and $R_2Zn{\cdot}TeEt_2$ complexes for similar applications [195–198]. Although there are few studies of the coordination chemistry of p-block metals with SeR_2 or TeR_2 (q.v.), we note reports of such complexes for MOCVD applications, e.g. $^iPr_3In.Te^iPr_2$ used to dope II/VI semiconductors with indium [173,174].

7. Addendum—new results to June 2001

A number of new selenoether and telluroether compounds are added here, the organisation following that in the main body of the review.

Several new Se- and Te-containing Schiff base macrocycles have been reported [199].

A range of six- and eight-coordinate Zr(IV) and Hf(IV) chloride complexes involving $MeSe(CH_2)_nSeMe$ ($n = 2$, 3) and $MeC(CH_2SeMe)_3$ and their thioether analogues have been prepared from $[MCl_4(SMe_2)_2]$ and ligand in rigorously anhydrous CH_2Cl_2. The structures of several have been determined, including the six-coordinate $[HfCl_4\{MeSe(CH_2)_2SeMe\}]$ [200].

Ruthenium(II) and platinum(II) complexes of *N*-{2-(4-MeOC$_6$H$_4$Te)CH$_2$CH$_2$}morpholine, which bonds through the Te atom, have been reported [201].

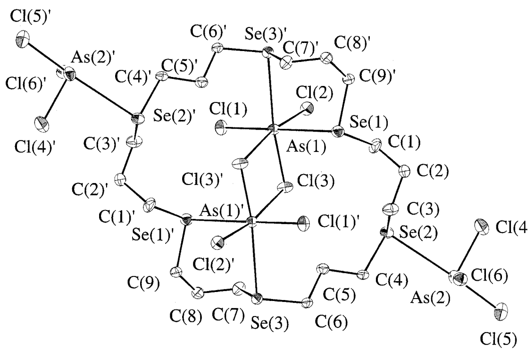


Fig. 58. Crystal structure of [$(AsCl_3)_4$([24]aneSe$_6$)], taken from Ref. [203].

A series of Mn(I), Rh(III) and Pt(II) complexes of the mixed S_2Te-donor ligand, $MeS(CH_2)_3Te(CH_2)_3SMe$ have been synthesised. The first two involve *fac*-coordination of the ligand, while a crystal structure of [PtCl(S_2Te)](PF_6) reveals the expected square planar coordination through all three ligand donor atoms [202].

The first examples of As(III) halide complexes with thio- and seleno-ethers have been prepared by reaction of AsX_3 with the ligands in anhydrous MeCN. The crystal structure of [$(AsCl_3)_4$([24]aneSe$_6$)] shows both *endo* and *exo* coordination of the As(III) centres. A very unusual feature is the occurrence of an asymmetric As_2Cl_6 μ^2-chloro bridged dinuclear unit coordinated within the macrocyclic ring. The *exo* As centres adopt a different coordination number and geometry from the *endo* As atoms, with those *exo* to the ring forming 4-coordinate distorted sawhorse units through coordination to three terminal Cl atoms and a single Se atom (Fig. 58). [$(AsBr_3)_2$([16]aneSe$_4$)] is polymeric with 5-coordinate As(III), through three terminal Cl atoms and two Se donor atoms from *exo* coordination to two different macrocyclic rings—similar to [$(SbBr_3)_2$-([16]aneSe$_4$)] [203].

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