Coordination Chemistry Reviews, 122 (1993) 109–170

Recent developments in the coordination chemistry of selenoether and telluroether ligands

Eric G. Hope
Department of Chemistry, University of Leicester, Leicester LE1 7RH (UK)

William Levason
Department of Chemistry, University of Southampton, Southampton SO9 5NH (UK)

CONTENTS

Correspondence to: W. Levason, Department of Chemistry, University of Southampton, Southampton SO9 5NH, UK.

0010-8545/93/$24.00

ABBREVIATIONS

acacH	acetylacetone
3-ClacacH	3-chloroacetylacetone
3-MeacacH	3-methylacetylacetone
bpy	2,2′-bipyridyl
CD	circular dichroism
COD	cyclooctadiene
Cp	η^5-cyclopentadienyl
MeCp	η^5-methylcyclopentadienyl
nbd	norbornadiene
THF	tetrahydrofuran
tby	2,2′,6′,2″-terpyridyl
tren	tris(2-aminoethyl)amine
E	S, Se, or Te
R	alkyl or aryl group

A INTRODUCTION

Although the first examples of metal complexes of seleno- (R_2Se) and telluroether (R_2Te) ligands were reported near the beginning of the 20th century, detailed studies of their coordination chemistry date from the 1970s. This neglect stemmed from a variety of causes, including the widely held view that they were weak donors with poor coordinating ability except to soft (class B) metals and, even in these cases, little different from the more familiar thioether analogues. Combined with their reputation as toxic and extremely malodorous compounds, commercial unavailability, and the apparent lack of any applications, this accounts for the very limited interest and late development. Recent interest in this area can be traced to a number of factors, including the fact that both selenium and tellurium have isotopes of half-integral nuclear spin with reasonable natural abundance [1] and, coupled with modern multinuclear FT NMR instrumentation, these provide a sensitive spectroscopic probe. In contrast, sulphur has only an insensitive quadrupolar nucleus in ^{33}S ($I = 3/2$, 0.76%, $Rp = 1.71 \times 10^{-5}$). Practical applications of metal selenoether and telluroether complexes (or of mixtures of metal halides or alkyls and R_2Se or R_2Te) include various types of chemical vapour deposition processes for the thin-film fabrication of new electronic materials such as II–VI semiconductors.

Previous review articles describing the coordination chemistry of seleno- and telluroethers include those by Murray and Hartley (thio-, seleno-, and telluroether transition metal complexes) [2], and Gysling (Te ligand complexes) [3], and (ligand properties of organic selenium and tellurium compounds) [4]. Pyramidal inversion in coordinated thio-, seleno-, and telluroethers has been reviewed twice [5,6].

The present review describes recent results in the coordination chemistry of selenoether and telluroether ligands. It also discusses developments in ligand synthesis and the spectroscopic and structural properties of the complexes, with particular emphasis on ^{77}Se and ^{125}Te NMR results. Literature coverage in the last detailed review [4] extended through 1983, and the present article focusses on work published in the last ten years (1981–1991), although some mention of earlier work is necessary for comparison purposes. Pyramidal inversion was reviewed as recently as 1989 [6] and is thus not treated here.

B. LIGAND SYNTHESIS

The routes used to synthesise monodentate ligands R_2Se, RR′Se, R_2Te, and RR′Te, have been discussed in standard texts [7,8] and few fundamentally new routes have been described. However, the recent commercial availability and convenience of powerful reductants such as BEt_3H^- or RLi, which are soluble in organic media, have encouraged their use in place of traditional reagents such as Na/liquid NH_3 or Rongalite (NaO_2SCH_2OH) in the production of the ligands. A few of the simplest ligands (including Me_2Se, Me_2Te, Et_2Se, Ph_2Se, $^iPr_2Te$, Ph_2Te) and related precursors RSeSeR and RTeTeR have become available commercially in the last few years.

Although various diselenoethers and a few polydentates have been known for some years [7], the syntheses of ditelluroethers and selenoether macrocycles have been achieved only recently, and very few polytelluroethers are known. Some of the routes to bi- and polydentate ligands, including hybrids (i.e. ligands containing other donor groups such as $-NR_2$, $-PR_2$, or $-OR$, in addition to $-SeR$ or $-TeR$) are discussed in the following section, the coverage being illustrative rather than comprehensive.

(i) Diselenoethers

Diselena-alkanes $MeSe(CH_2)_nSeMe$ ($n = 1$–3, 6, 12, etc.) are pale yellow oils made cleanly and in high yield from the reaction of MeSeLi (or Na) with the appropriate α,ω-dihaloalkane in liquid ammonia, alcohols, or most conveniently tetrahydrofuran [9,10]. Phenyl-substituted analogues are viscous oils or low-melting solids made similarly from PhSeNa [10,11]. *Cis*-1,2-dichloroethylene does not react with RSeLi in tetrahydrofuran, but in ethanol in the presence of NaOEt stereospecific substitution occurs to produce *cis*-RSeCH = CHSeR (R = Ph or Me) [10]. Acetylenic backbones can be introduced by reaction of NaC≡CH, Se and RI, or by addition of RSeSeR to acetylene in the presence of base [12,13].

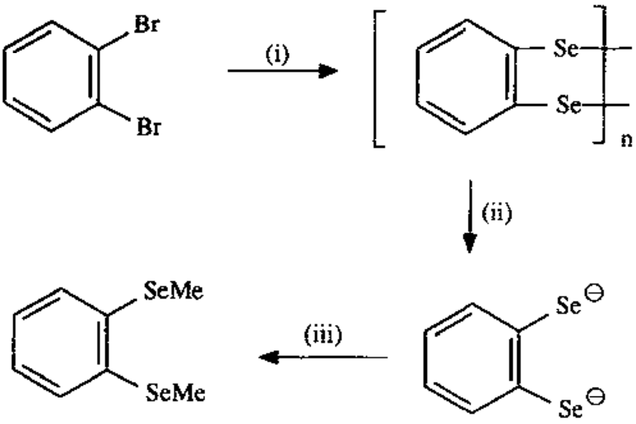
o-Phenylenebis(selenoether) ligands are rather more difficult to obtain, since *o*-dihalobenzenes do not react with RSeLi in ether or alcohol solutions. The addition of the diselenide RSeSeR (R = Me or Ph) to benzyne affords *o*-$C_6H_4(SeR)_2$, although the yield for R = Ph is very poor [10]. A better route to *o*-$C_6H_4(SeMe)_2$ is via the poly-*o*-phenylenediselenide (Scheme 1) [14]. Ferrocenyl analogues $(\eta^5\text{-}C_5H_4SeR)_2Fe$ are known [15].

The alkyl-substituted diselenoethers are air-stable and have repulsive, persistant odours, but the aryl-substituted analogues have only mild odours when pure*.

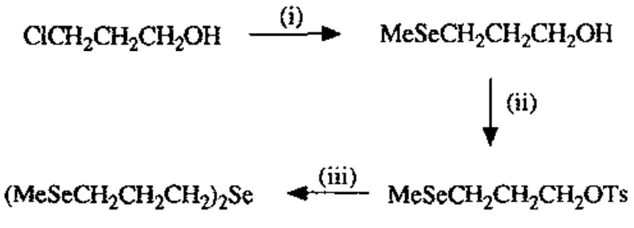
(ii) Polyselenoethers

The $CH_3C(CH_2SeR)_3$ (R = Me or Ph) and $C(CH_2SeMe)_4$ are formed straightforwardly from RSeLi and the appropriate organohalide [10]. The open-chain ligands $(MeSeCH_2CH_2CH_2)_2Se$ [10], $(MeSeCH_2CH_2)_2Se$ [16], and $(MeSeCH_2CH_2SeCH_2)_2CH_2$ [17] require stepwise introduction of the selenium as, for example, in Scheme 2.

In contrast to the intensive studies of the thioether analogues, surprisingly little



Scheme 1. Reagents: (i) Na_2Se_2–DMF; (ii) Rongalite; (iii) MeI.

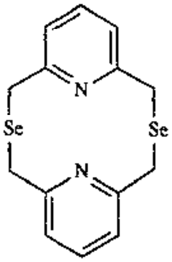


Scheme 2. Reagents: (i) MeSeLi–THF; (ii) *p*-$MeC_6H_4SO_2Cl$; (iii) Na_2Se.

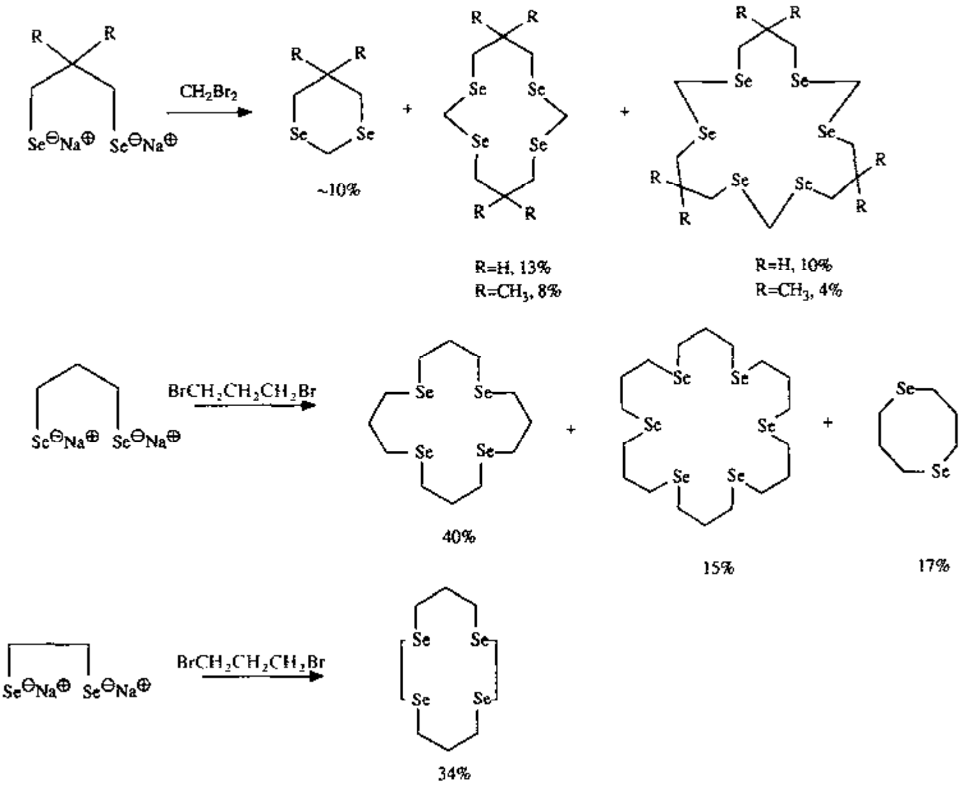
---

* The infamous reputation of selenoether ligands is probably mostly derived from impure samples containing the corresponding selenols.

effort has been devoted to selenoether macrocycles. Pinto and co-workers [18] found that Na/liquid NH_3 reduction of α,ω-alkanebis(selenocyanate) to the bis(selenide) followed by addition of dihaloalkanes gave mixtures of macrocycles which were separated by chromatography (Scheme 3). The conformations of several examples were established by single-crystal X-ray studies. Other workers have described different macrocycles [19], and selenium-containing cyclophanes, e.g. 2,11-diselena[3.3](2,6)pyridinophane (1) [20].



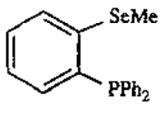
(1)



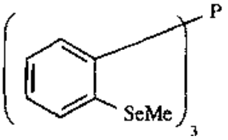
Scheme 3.

(iii) Hybrid selenoethers

Many organic compounds containing an RSe– group in combination with another functional group are known, including selenium-containing amino acids [7], but relatively few have been used as ligands. Early examples made for coordination purposes were **2** and **3**, made by reaction of *o*-$C_6H_4(SeMe)Br$ with ^nBuLi and Ph_2PCl or PCl_3, respectively [21].



(2)

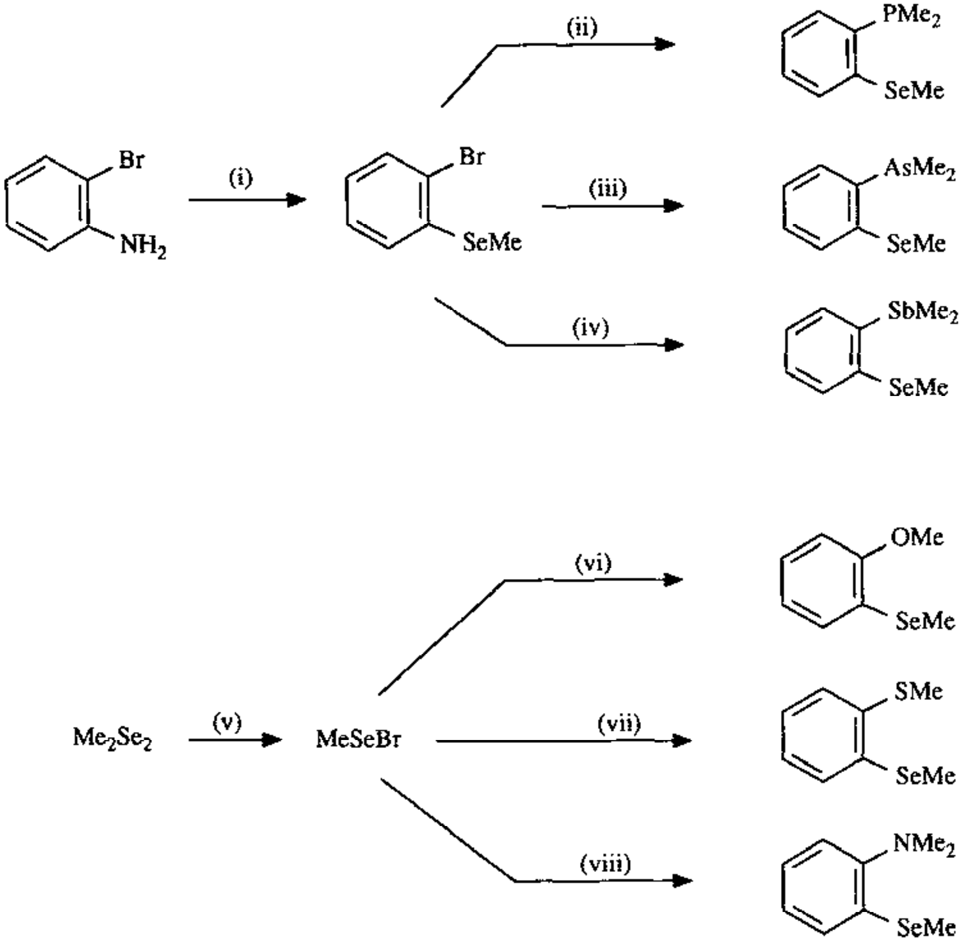


(3)

Other examples of hybrids containing group 15 or 16 donors combined with –SeMe are shown in Scheme 4 [14]. The key intermediate in many of these preparations, *o*-$C_6H_4Br(SeMe)$, is usually made from *o*-bromoaniline [21], but *o*-$C_6H_4Cl(SeMe)$, which is easily made in high yield from *o*-$C_6H_4Cl_2$ and MeSeLi in *N*, *N*-dimethylformamide [22,23], may be a convenient substitute. Fewer hybrids with alkane backbones have been described; examples include $MeSCH_2SeMe$ [24], $MeSeCH_2CH_2SMe$ [25], and $(MeSCH_2CH_2)_2Se$ [16].

(iv) Ditelluroethers

In marked contrast to the selenium analogues, ditelluroalkanes, $RTe(CH_2)_nTeR$, have proved difficult to obtain, and are known only for certain values of *n*. For $n=1$, a range of complexes (R = Me, Et, ^nPr, ^iPr, ^nBu, etc.) were made by reaction of the appropriate RTeTeR with diazomethane [26]. More conventional syntheses from RTe^- and CH_2X_2 yield $RTeCH_2TeR$ (R = Me, Ph, 4-$EtOC_6H_4$) [27,28], but with 1,2-dihaloalkanes, only $CH_2{=}CH_2$ and R_2Te_2 are produced under all reaction conditions [27–29]. The course of similar reactions with other dihaloalkanes are very dependent upon the conditions. Thus $X(CH_2)_nX$ (X = Br or I, $n=3,4$) with (4-$EtOC_6H_4$)TeNa in aqueous ethanol produced telluronium salts, whilst corresponding reactions for $n=6$–10 gave $RTe(CH_2)_nTeR$. For the single case of $n=5$, both products can be formed [27,29]. When RTeLi (R = Me or Ph) in tetrahydrofuran was used to introduce the tellurium, very different products were formed. These reactions are summarised in Scheme 5 [28,30]. Particularly notable are the reactions with $Cl(CH_2)_3Cl$, which gave R_2Te_2 and olefin at room temperature, but high yields of $RTe(CH_2)_3TeR$ at low temperatures. Once isolated, the latter are thermally stable well above room temperature. The tendency of telluride nucleophiles to promote elimination rather than substitution is also observed with *cis*-CHCl=CHCl, when R_2Te_2 are the only Te-containing reaction products, and ditelluroalkene ligands are



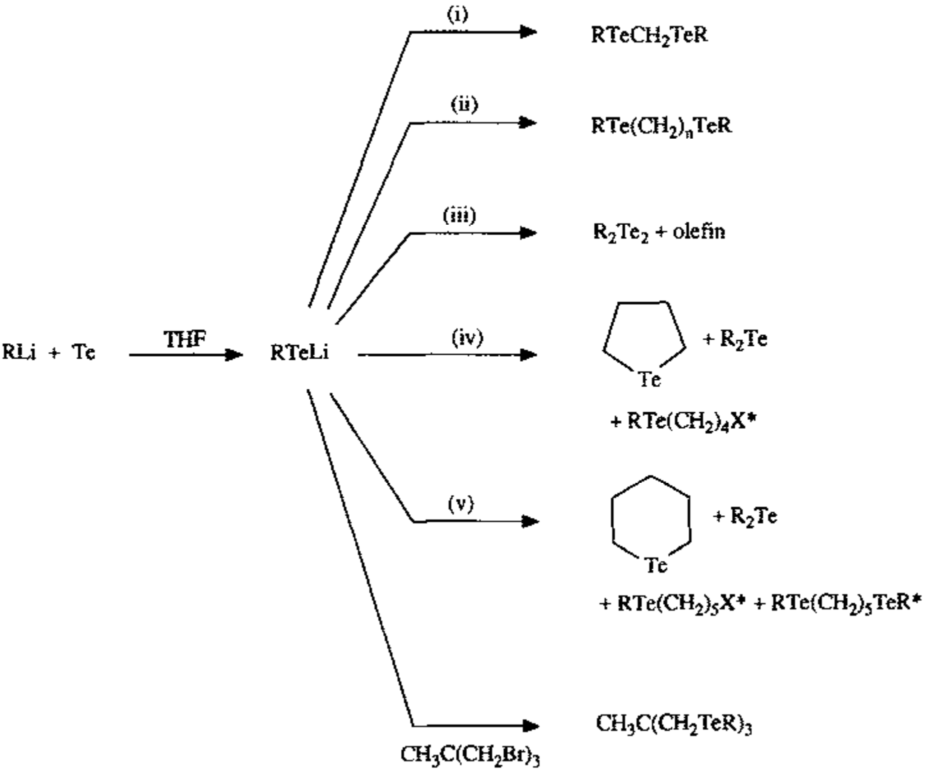
Scheme 4. Reagents: (i) KSeCN–MeI; (ii) LiPMe$_2$·THF; (iii) NaAsMe$_2$–THF; (iv) NaSbMe$_2$–liquid NH$_3$; (v) Br$_2$; (vi) o-$C_6H_4(MgBr)OMe$; (vii) o-$C_6H_4(SMe)Li$; (viii) o-$C_6H_4(NMe_2)MgBr$.

presently unknown [28]*. The ditellura-alkanes are pale yellow oils with persistent highly repulsive odours, which, in marked contrast to their sulphur or selenium analogues, slowly oxidise in air to intractable white materials.

o-Phenylenebis(telluroether) ligands, *o*-$C_6H_4(TeR)_2$ ($R = Ph$, *p*-tolyl, *p*-$MeOC_6H_4$), were first reported to be formed by addition of the appropriate R_2Te_2 to benzyne, although the claim for the successful reaction with $R = Ph$ was subsequently withdrawn [31,32]. In contrast to the cases with MeS^- or $MeSe^-$, $MeTe^-$ in tetrahydrofuran reacts with *o*-$C_6H_4Br_2$ to give a good yield of *o*-$C_6H_4(TeMe)_2$, and *o*-$C_6H_4(TePh)_2$ can be made from PhTeLi and *o*-C_6H_4BrI [23]. Indeed, the ditelluroether is formed even with excess *o*-dichlorobenzene, and *o*-$C_6H_4(TeMe)Cl$ was only

---

* See Note added in proof, p. 163.



Scheme 5. Reagents, $X(CH_2)_nX$: (i) $n = 1$; (ii) $n = 3, 6, 10$; (iii) $n = 2$; (iv) $n = 4$; (v) $n = 5$. X = halide; R = Me, Ph; * indicates minor products.

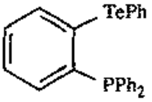
obtained from the monoGrignard o-$C_6H_4Cl(MgBr)$, Te, and MeI [23]. Phenyl-substituted ditelluroethers are yellow oils or low-melting solids, which appear to be air-stable when pure.

(v) Polytelluroethers

Few examples have been prepared, and neither open-chain multidentates such as $Te(CH_2CH_2CH_2TeR)_2$ nor Te-containing macrocycles have been reported. The $CH_3C(CH_2TeR)_3$ (R = Me, Ph) [28], and $C(CH_2TeR)_4$ (R = Ph, 4-$EtOC_6H_4$) [28,33] are made straightforwardly, but, curiously, $C(CH_2Br)_4$ and MeTeLi in tetrahydrofuran gave the cyclopropane derivative $\overline{CH_2CH_2C}(CH_2TeMe)_2$ [28].

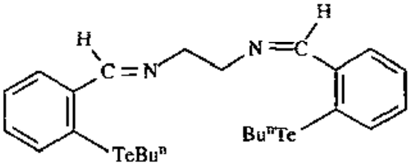
(vi) Hybrid telluroethers

These are currently attracting considerable interest. The first example was the phosphine-telluroether (**4**), prepared from o-$LiC_6H_4PPh_2$ and PhTeBr [34].



(4)

A range of mixed donors containing TeMe and group 15 or 16 donors with *o*-phenylene linkages were subsequently prepared (Scheme 6) [23]. Other examples include 1-NMe_2-2-TeR-4-MeC_6H_3 [35], $RTeCH_2CH_2NH_2$ [36], $RTeCH_2CH_2SMe$ [37], $RTeCH_2CO_2H$ [38], $(RTeCH_2CH_2)_2NR'$ (R′ = Me or H) [39], and $(RTeCH_2CH_2)_3N$ [40] (R = 4-$MeOC_6H_4$ or 4-$EtOC_6H_4$). The existence of the hybrids with dimethylene backbones is notable in view of the failures to prepare $RTeCH_2CH_2TeR$ (above), but has parallels with antimony chemistry where $R_2SbCH_2CH_2SbR_2$ are unknown but $(R_2SbCH_2CH_2)_2NMe$ have been described [41]. One open-chain tetradentate (5) has been described [42].



(5)

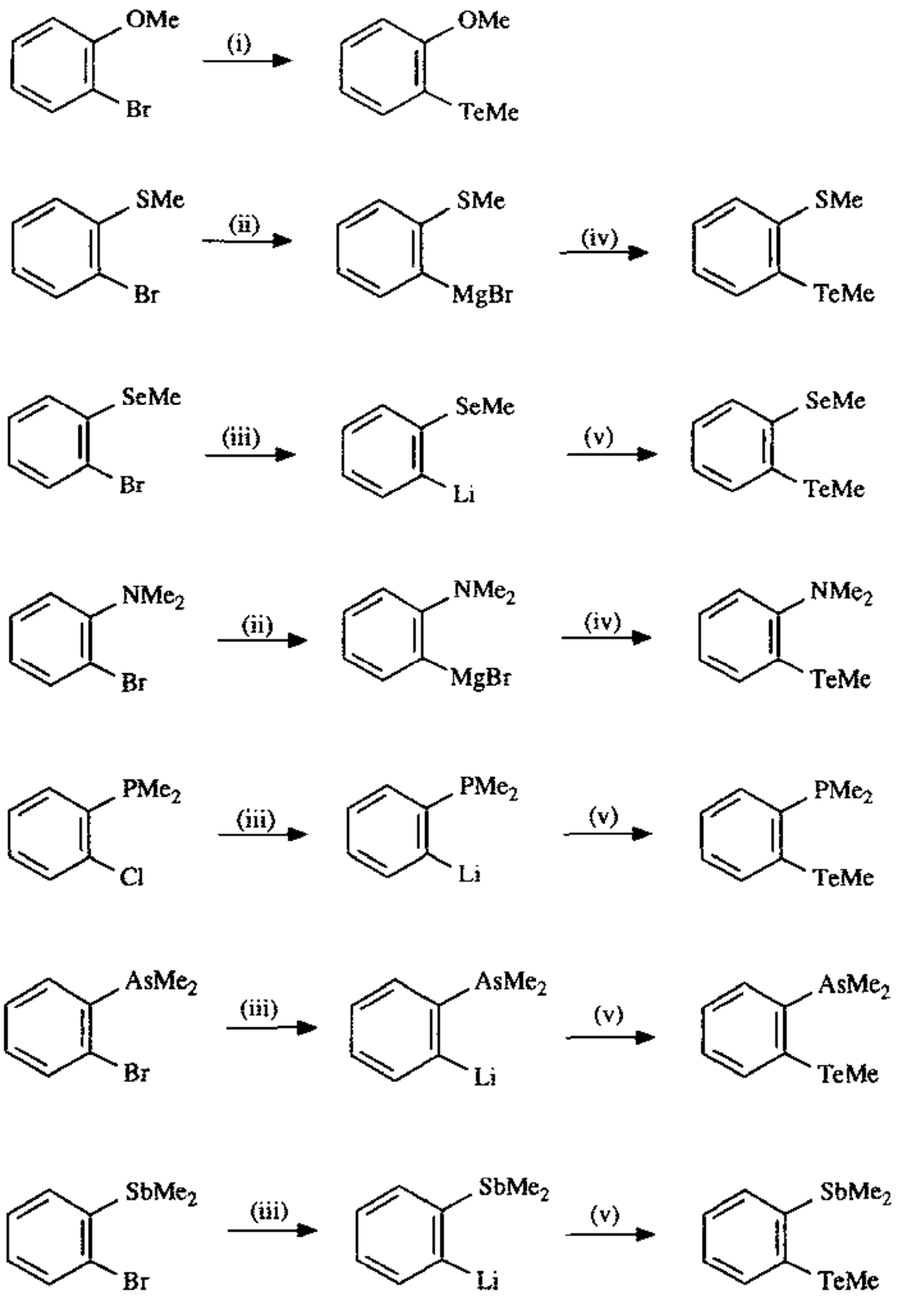
C. SELENOETHER COMPLEXES

As has been noted in previous reviews in this area [2,4], the coordination chemistry of selenoethers continues to be, with a few notable exceptions, unsystematic. Frequently, reports consist of a single complex, often with dimethylselenide as ligand, mentioned in papers dealing with a range of group 15 and 16 donor ligand complexes. However, these isolated accounts, when drawn together, appear to give a fairly comprehensive picture of the occurrence and stability of transition-metal selenoether complexes.

(i) Monodentate selenoether complexes

(a) Dimethylselenide complexes

The most extensively studied type of dimethylselenide complex is the cyclopentadienyl iron carbonyl cations, studied as part of a range of group 16 ligand complexes. The three parent complexes, $[CpFe(CO)_{3-n}(Me_2Se)_n]^+$ ($n = 1,2,3$), have been prepared by a variety of routes. Substitution of THF by Me_2Se readily affords $[CpFe(CO)_2(Me_2Se)][BF_4]$ [43], for which a single crystal X-ray study [44] confirms the expected pseudo-pianostool structure. Nucleophilic anions (e.g. CN^-, I^-) replace



Scheme 6. Reagents: (i) LiTeMe; (ii) Mg; (iii) ^{n}BuLi; (iv)Te–MeI; (v) Me_2Te_2.

dimethylselenide selectively, whilst CO substitution occurs under UV irradiation in the presence of neutral group 15 or 16 donor ligands, affording [CpFe(CO)(Me$_2$Se)L][BF$_4$] (L = PMe$_3$, P(NMe$_2$)$_3$, PPh$_3$, AsPh$_3$, SbPh$_3$, SMe$_2$, SeMe$_2$, TeMe$_2$) [43,45]. Pyramidal inversion at the coordinated chalcogen has been studied for these, and the related dimethylsulphide and dimethyltelluride, complexes by variable-temperature ^{1}H NMR spectroscopy, which shows the usual barriers to inversion (Te > Se > S) [46]. Hückel molecular orbital calculations on [CpFe(CO)$_2$(Me$_2$E)][BF$_4$] (E = O, S, Se, Te) confirm the stability of the Fe—E bond as Te ≫ Se > S > O, on the basis of electronegativity, orbital diffuseness, and size considerations. The [CpFe(Me$_2$Se)$_3$][BF$_4$] cannot be prepared by CO substitution. It has been prepared, but not isolated, by the reaction of [CpFe(C$_6$H$_8$)][BF$_4$] with excess Me$_2$Se; it decomposes at > −50C [47]. The [CpFe(CO)$_2$(Me$_2$Se)][BF$_4$] has also been prepared, as have the other dimethylselenide complexes, *trans*-[Co(CO)$_3$(Me$_2$Se)$_2$][BF$_4$], *cis*- and *trans*-[CpMo(CO)$_2$(Me$_2$Se)$_2$] [BF$_4$], using [Cp$_2$Fe] [BF$_4$], in the presence of a neutral donor ligand, as a one-electron oxidising agent to cleave the metal–metal bonds in [CpFe(CO)$_2$]$_2$, [Co$_2$(CO)$_8$] and [CpMo(CO)$_3$]$_2$ [48].

Related cyclopentadienyl cationic complexes may also be prepared by substitution reactions. Dimethylselenide replaces the diene in [CpNi(C$_5$H$_6$)][BF$_4$] to give [CpNi(Me$_2$Se)$_2$] [BF$_4$] [49], and completely replaces dimethylsulphide in [CpCo(Me$_2$S)$_3$] [BF$_4$]$_2$ to give [CpCo(Me$_2$Se)$_3$] [BF$_4$]$_2$ [50]. The related [CpMo(CO)$_3$(Me$_2$Se)][BF$_4$] is prepared by the reaction of [CpMo(CO)$_3$I] with AgBF$_4$ with added neutral ligand [51]. Neutral [CpV(CO)$_3$(Me$_2$Se)] is made by the reaction of [CpV(CO)$_4$] with dimethylselenide in solution under UV irradiation, but cannot be isolated [52]. By comparison of solution IR data of this complex with the corresponding thioether complex, for which there has been a single crystal X-ray study, the complex is assigned a pseudo-pianostool structure. Competitive equilibrium and kinetic measurements in solution show an increase in stability and kinetic inertness in this type of dimethylchalcogenide complex Me$_2$S < Me$_2$Se < Me$_2$Te. The unusual dimeric complex [(MeCp)Mn(CO)$_2$]$_2$SeMe$_2$ has been isolated from the reaction of [(MeCp)Mn(CO)$_3$] with dimethylselenide under UV irradiation in *n*-hexane [53], while the reaction of [CpMn(CO)$_2$THF] with Me$_2$Se affords the analogous [CpMn(CO)$_2$]$_2$SeMe$_2$ [54]. A single-crystal X-ray study confirmed the ability of the Me$_2$Se ligand to act as an unsupported 4-electron donor bridge (Fig. 1). A comparable ligand-bridged structure is believed to exist for [Cr(CO)$_5$]$_2$SeMe$_2$, prepared from [Cr(CO)$_5$THF] and dimethylselenide [54].

Two groups report dimethylselenide complexes of rhenium(I). Abel et al. [55] cleaved the dimeric [Re$_2$X$_2$(CO)$_8$] in the preparation of *fac*-[ReX(CO)$_3$(Me$_2$Se)$_2$] (X = Cl, Br) and *mer*- and *fac*-[ReI(CO)$_3$(Me$_2$Se)$_2$], which have been investigated for pyramidal inversion by dynamic NMR techniques. Belforte et al. [53] cleaved [Re$_2$Br$_2$(CO)$_6$(THF)$_2$] to give a mixture of *mer*- and *fac*-[ReBr(CO)$_3$(Me$_2$Se)$_2$]. Carbonylation of this mixture at atmospheric pressure over three days gave *cis*- and *trans*-[ReBr(CO)$_4$(Me$_2$Se)]. Kinetic experiments suggest that the mer isomer carbonyl-

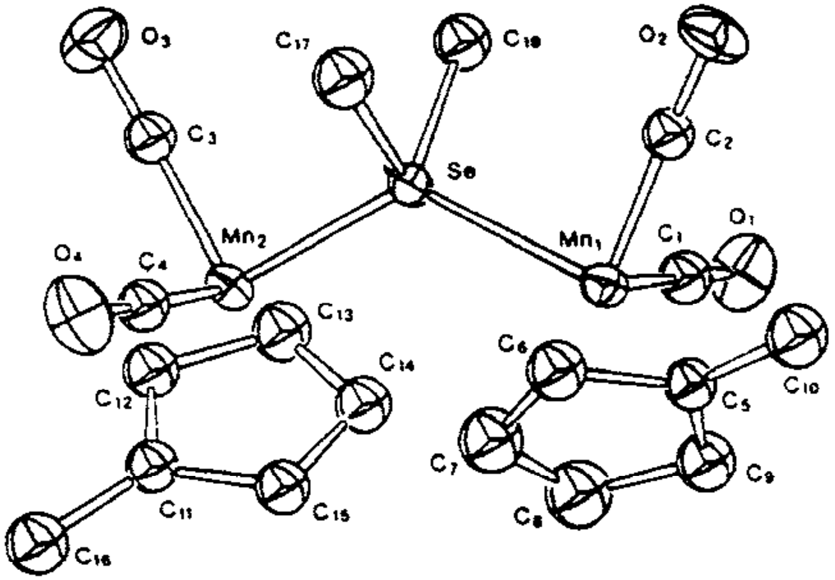


Fig. 1. Molecular structure of $[\{(MeCp)Mn(CO)_2\}_2(SeMe_2)]$. (From ref. 53 by permission of *Gazzetta Chimica Italiana*.)

ates faster than the fac isomer, and, by comparison with the analogous Me_2S and Me_2Te complexes, reaction rates decrease S > Se > Te [53]. The reaction of $[Mn_2Br_2(CO)_8]$ with two equivalents of Me_2Se gave only *cis*-$[MnBr(CO)_4(Me_2Se)]$ [53]. Dimethylselenide displaces CO from the hydrido clusters $[HRuCo_3(CO)_{12}]$ and $[HRuRh_3(CO)_{12}]$ to give $[HRuCo_3(CO)_{11}(Me_2Se)]$, $[HRuCo_3(CO)_{10}(Me_2Se)_2]$ and $[HRuRh_3(CO)_9]_2(SeMe_2)_3$ [56]. Single-crystal X-ray studies indicate that, in the cobalt clusters, dimethylselenide acts as a monodentate ligand coordinating preferentially to cobalt (Fig. 2). Structural isomerism was observed in solution for the disubstituted complex. The ^1H NMR spectrum, recorded immediately after the reaction of the cluster with two equivalents of dimethylselenide, showed two cluster hydride resonances. One resonance was assigned to the isomer characterised by the single-crystal study (Fig. 2), the other resonance to a cluster with one Me_2Se ligand coordinated to cobalt and one Me_2Se to the ruthenium. In solution, this second isomer slowly converts to the first, indicating preferential coordination of the selenoether to cobalt. In the rhodium complex, the Me_2Se ligands are bridging bidentate occupying all the axial positions on the two Rh_3 faces (Fig. 2).

There are few reports of non-carbonyl low oxidation-state metal dimethylselenide complexes. Addition of Me_2Se to a solution of $[\{Rh(SC_6F_5)(COD)\}_2]$ caused substantial changes in the electronic spectra, accounted for by the formation of $[Rh(SC_6F_5)(Me_2Se)(COD)]$ which could not be isolated [57]. The $[Ru(bpy)(tby)(Me_2Se)][PF_6]$ has been reinvestigated, particularly by cyclic voltammetry [58]; E^0 for the oxidation Ru(II) to Ru(III) occurs at 1.3 eV, which, in comparison with

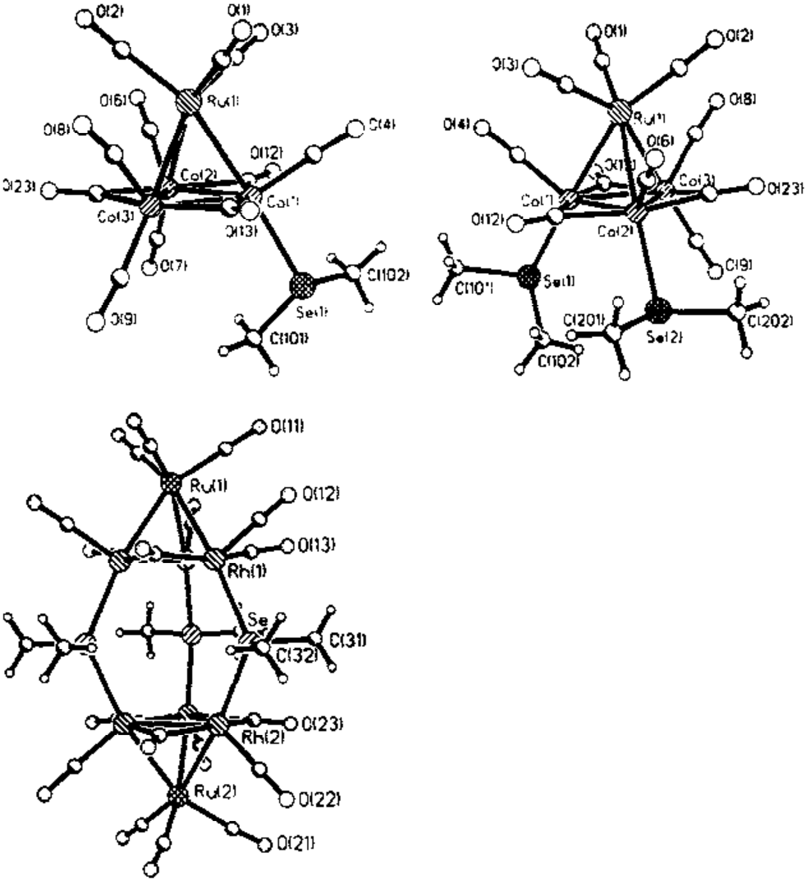


Fig. 2. Molecular structures of $[HRuCo_3(CO)_{11}(SeMe_2)]$, $[HRuCo_3(CO)_{10}(SeMe_2)_2]$ and $[\{HRuRh_3(CO)_9\}_2(SeMe_2)_3]$. (From ref. 56 by permission of Elsevier Sequioa SA.)

analogous complexes of other group 15 and 16 donor ligands, confirms the synthetic observations that softer ligands stabilize Ru(II) better than harder ones. Although much effort is being devoted to the study of mixtures or adducts of groups 12 and 16 alkyls as precursors to II–VI electronic materials, investigations of the underlying coordination chemistry are limited to a single paper on the $[Me_2Zn \cdot SeMe_2]$ adduct [59].

The ability of dimethylselenide to stabilize higher oxidation-state transition metals has been more systematically studied, particularly for the metals in groups 8–10. The *cis*-$[TiX_4(Me_2Se)_2]$ (X = Cl, Br) have recently been reinvestigated [60] as part of an extensive investigation of the chemistry of titanium(IV). Low-temperature ^{1}H NMR spectroscopy, used to investigate the stabilities of a range of $[TiX_4L_2]$ complexes (L = group 16 donor ligand), suggested that the "TiX_4" group may be regarded as a soft acid. ^{1}H NMR spectroscopy at room temperature indicates a dissociative pathway for the exchange between free and coordinated ligands in solution, and gives a qualitative correlation between thermodynamic stability and kinetic lability. The palladium(IV) complexes $[R_4N][Pd(Me_2Se)X_5]$ (X = Cl, Br), prepared by the cautious oxidation of their palladium(II) analogues by X_2/CCl_4, have been characterised by analysis, conductivity measurements, IR and electronic spectroscopies [61]. Comparison with platinum(IV) analogues and with the oxidation of the palladium(II) complexes of dimethylsulphide and dimethyltelluride indicate that palladium(IV) is significantly harder than platinum(IV). Attempts to oxidise neutral palladium(II) complexes, e.g. $[PdCl_2(Me_2Se)_2]$, with a variety of oxidising agents failed. However, $[PtCl_4(Me_2Se)_2]$ is readily prepared by Cl_2/CCl_4 oxidation of $[PtCl_2(Me_2Se)_2]$; the mixture of cis and trans isomers is confirmed by ^{77}Se and ^{195}Pt NMR spectroscopies [62]. The thermally unstable platinum(IV) $[PtMe_3X(Me_2Se)_2]$ (X = Cl, Br) have also been prepared for pyramidal inversion studies in solution [63].

Attempts to prepare anionic iridium(IV) complexes were initially unsuccessful. However, $[NEt_4][IrCl_5(Me_2Se)]$ was prepared [64] by an unusual ligand exchange from the pyridine analogue $[NEt_4][IrCl_5(py)]$ by initial reduction with ascorbic acid, treatment with dimethylselenide followed by oxidation with Cl_2/HCl. Comparison of the electrochemistry of a range of $[IrCl_5L]^-$ anions (L = group 15 or 16 donor ligand) indicated that the Ir(III)–Ir(IV) couple was insensitive to L. The neutral *trans*-$[IrCl_4(Me_2Se)_2]$ was prepared more straightforwardly by the Cl_2/CCl_4 oxidation of the iridium(III) anion, $[NMe_4][IrCl_4(Me_2Se)_2]$ [65]. The electrochemistry of these complexes (Fig. 3) and their thioether analogues suggested that selenium was marginally better at stabilizing iridium(IV) than sulphur. Cyclic voltametry on the analogous bromo complex, *trans*-$[IrBr_4(Me_2Se)_2]$, and the rhodium(III) anion, *trans*-$[RhCl_4(Me_2Se)_2]^-$, indicated that the iridium(IV) bromo-selenoether complex has a half-life of only a few seconds and hence cannot be isolated chemically, while the irreversible oxidation of the rhodium complex occurred at a much higher potential, indicating that the rhodium(IV) complexes are also unstable.

Neutral *trans*-$[OsX_4(Me_2Se)_2]$ (X = Cl, Br) are readily prepared from dimethylselenide and $[OsX_6]^{2-}$ in *n*-butanol as air-stable green-purple and brown-purple solids, respectively, soluble in a wide range of organic solvents [66]. The Os(III)–Os(IV) couple has been studied electrochemically for these complexes and compared with a range of osmium group 15 or 16 donor ligand complexes. Dimethylselenide also stabilizes the unusually high oxidation state osmium(VI) species $[OsO_2X_2(Me_2Se)_2]$ (X = Cl, Br), which are prepared from osmium tetraoxide and dimethylselenide in ethanol/HX [67]. ^1H NMR spectroscopy suggests that only one species is present in solution, which is assigned on the basis of IR data to the all-trans isomer.

(b) Other dialkylselenide complexes

Reports on the coordination chemistry of other dialkylselenides are fragmentary. During studies on carbonyl hydrogen-chalcogenide complexes of group 6 metals

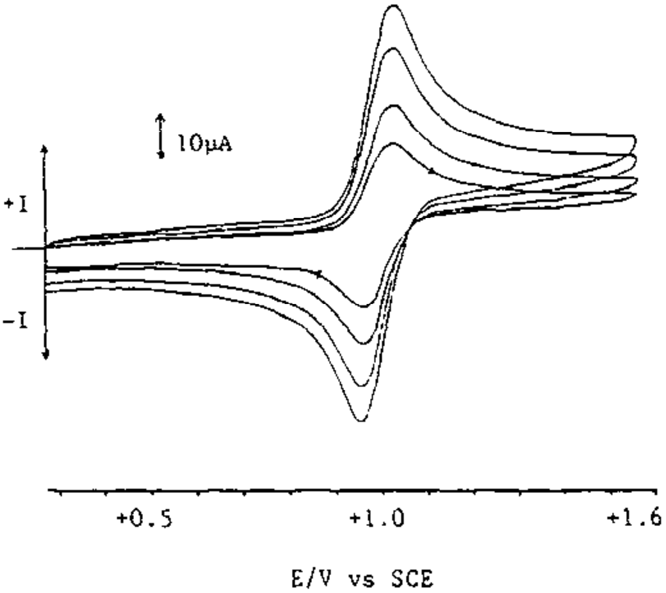


Fig. 3. Cyclic voltammogram of $[Me_4N][IrCl_4(Me_2Se)_2]$ at potential scan rates of 0.05, 0.1, 0.2 and 0.3 $V s^{-1}$. (From ref. 65 by permission of the Royal Society of Chemistry).

[68], $[Cr(CO)_5(Et_2Se)]$ was prepared by the alkylation of either $Na[Cr(CO)_5(SeH)]$ or $[N(PPh_3)_2][\{Cr(CO)_5\}_2SeH]$ with $[Et_3O][BF_4]$. Irradiation of $[Cr(CO)_5(Et_2Se)]$ in solution gave $[Cr(CO)_4(Et_2Se)_2]$ [69]. $[PtPh_2(Et_2Se)_2]$ was prepared for comparison with a range of phenyl platinum(II) thioether complexes [70]. Pyramidal inversion at coordinated selenium in the $[Ru(NO)X_3L_2]$ ($L = Et_2Se$, PhEtSe; X = Cl, Br) has been investigated [71] by variable-temperature ^1H NMR techniques in the range 200–375 K as a follow-up to a previous preparative paper [72] in this area. As expected, inversion is faster in the thioether complexes than selenoether complexes.

The bulky pseudo-alkyl ligands $[Me_3M'CH_2SeR]$ (M′ = Si, Ge; R = Me, Ph) act as monodentate ligands to transition metals, and their complexes appear to afford crystals readily. Complexes isolated are the monomeric *trans*-$[MCl_2(Me_3M'CH_2SeR)_2]$ (M = Pd, Pt) where the trans stereochemistry has been confirmed by single-crystal X-ray studies for two complexes, M = Pd, M′ = Si, R = Me (Fig. 4) and M = Pt, M′ = Ge, R = Me [73], and the dinuclear halide-bridged $[HgX_2(Me_3M'CH_2SeR)]_2$ (X = Cl, Br, I) where single-crystal X-ray studies for the complexes in which M′ = Si, X = Cl (Fig. 4), Br and I confirm the pseudo-tetrahedral geometry about mercury in these centrosymmetric complexes [74]. Three complexes have been prepared using $(Me_3SiCH_2)_2Se$ as a bulky monodentate ligand, $[W(CO)_5L]$, $[CpMCl_2L]$ (M = Rh, Ir) [75,76], and pyramidal inversion in solution investigated. The iridium(III) complex is isolable, but the rhodium(III) complex is not.

Selenaphanes readily act as monodentate ligands to transition metals, or trans-

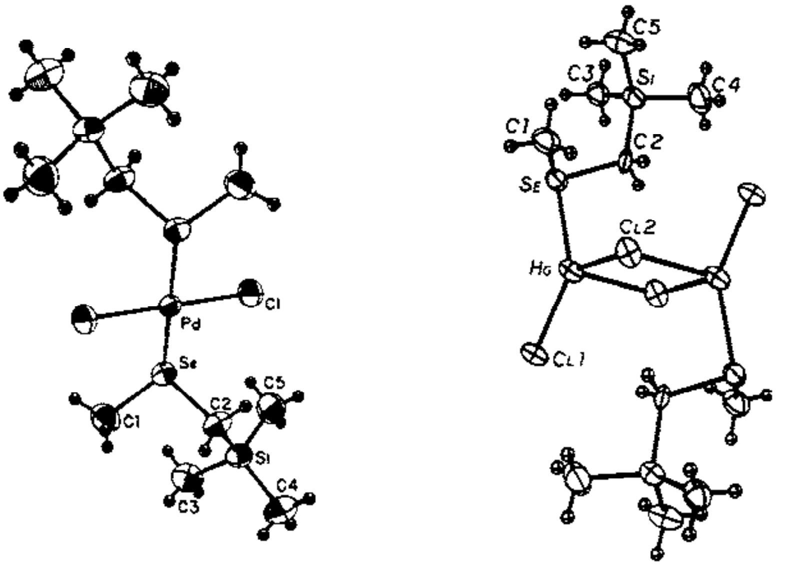


Fig. 4. Representative examples of the monodentate coordination of bulky selenoether ligands. Single-crystal X-ray structures of $[PdCl_2(Me_3SiCH_2SeMe)_2]$ (from ref. 73 by permission of the American Chemical Society), and $[\{HgCl_2(Me_3SiCH_2SeMe)\}_2]$ (from ref. 74 by permission of the Canadian Chemical Society).

ition metal selenaphane complexes may be generated in situ. Tetrahydraselenaphane (C_4H_8Se) displaces CO from $[CpNb(CO)_4]$ under UV irradiation to give $[CpNb(CO)_3(C_4H_8Se)]$ [77]. The kinetics of the displacement of the selenoether with phosphines has been compared with the other C_4H_8E ($E=O$, S, Te), suggesting that the heavier chalogenides form more stable complexes. A range of *trans*-$[PdX_2L_2]$ ($X=Cl$, Br, I; $L=\overline{Se(CH_2)}_n$ ($n=4$, 5, 6), $\overline{SeCHCMe_2CH_2}$) have been prepared for investigation by variable-temperature ^1H NMR spectroscopy [78]. Single-crystal X-ray studies on the tetrahydroselenophane complexes of mercury(II) indicate that $[HgCl_2(C_4H_8Se)]$ is isomorphous with the tetrahydrothiophene analogue containing an infinite double chain structure with distorted trigonal-bipyramidal coordination about mercury [79], while $[HgX_2(C_4H_8Se)_2]$ ($X=Br$, I) are monomeric with distorted tetrahedral coordination about mercury [80]. [4+2]-Cycloaddition of 2,3-dimethyl-1,3-butadiene to the transition metal-coordinated selenoketone {Se=CRPh} ($R=H$, Ph) gives $[W(CO)_5(\overline{SeCRPhCH_2CMe{=}CMeCH_2})]$ [81]. The monodentate coordination of the selenoether was confirmed by a single-crystal X-ray study on the complex when $R=Ph$ (Fig. 5).

(c) Diarylselenide complexes

Vanadium and manganese complexes of diphenylselenide have been prepared as part of a range of complexes of group 15 or 16 donor ligands to investigate the effects of ligand donor strength on ^{51}V and ^{55}Mn NMR parameters. Displacement

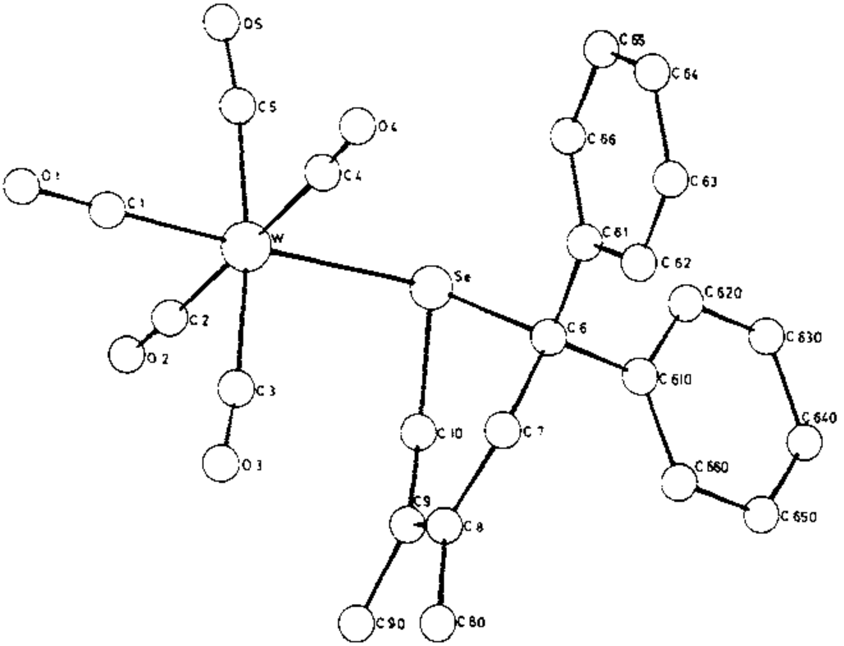
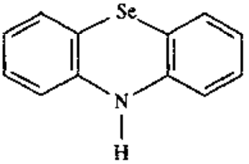


Fig. 5. Molecular structure of $[W(CO)_5(\overline{SeCPh_2CH_2CMe{=}CMeCH_2})]$. (From ref. 81 by permission of Elsevier Sequioa SA.)

of THF from low oxidation state vanadium and manganese THF adducts yields the $[CpV(CO)_3(Ph_2Se)]$ [82], $[Et_4N][V(CO)_5(Ph_2Se)]$ [83,84] and $[Mn(NO)_3(Ph_2Se)_2]$. None of these products has been isolated as a solid material. Green $[AuCl(Ph_2Se)]$ and brown $[AuCl_3(Ph_2Se)]$ are prepared by the direct reaction of diphenylselenide with [AuCl] or $[Au_2Cl_6]$, respectively [85]. Single-crystal X-ray studies confirm the expected monomeric linear {Au(I)} or square-planar {Au(III)} structures. The Au(I)–Se bond length is 7 pm shorter than the Au(III)–Se bond length, indicating that the softer Au(I) coordinates more strongly to the diphenylselenide than the harder Au(III).

In a study into the factors involved in oxygen transfer to metal carbonyls, $[Cr(CO)_5\{(p\text{-}MeOC_6H_5)_2Se\}]$ was isolated from the reaction of $[Cr(CO)_6]$ with $(p\text{-}MeOC_6H_5)_2Se{=}O$ [86]. Bis-2,4-dinitrophenylselenide (L) is reported to give the complexes [AgLX], $[CdLX_2]$ and $[HgL_2X_2]$ (X = Cl, OCl, ClO_4, SCN, OAc, $OCOCF_3$) [87]. The phenoselenazine (**6**) complexes $[MCl_2(\mathbf{6})_2]$ (M = Pd, Pt) were prepared by the reactions of $[(PhCN)_2PdCl_2]$ and $K[PtCl_3(C_2H_4)]$ with the ligand [88].



Phenoselenazine

(6)

The palladium complex is assigned as the cis isomer on the basis of vibrational data, while the platinum complex can be separated into cis and trans isomers. Treatment of the platinum complexes with iodine partially oxidises the ligand to give *trans*-$[PtCl_2(6)_2I_{3.5}]$ and *cis*-$[PtCl_2(6)_2I_{3.9}]$. Raman spectroscopy shows the presence of I_3^- and I_5^- ions, suggesting oxidation of the ligand and the coordination of the resulting cation radical to platinum(II), giving conducting materials.

(ii) Diselenoether complexes

(a) Complexes with diselena-alkanes, -alkenes and o-phenylene ligands

Of the 17 papers published in this area since 1980, 10 have been published by Abel et al., particularly on the dynamic processes of rhenium carbonyl selenoether and trimethylplatinum(IV) selenoether complexes, and seven by Levason et al. on diselenoether complexes of the platinum group metal halides. Generally, the diselenoether complexes appear to be more stable than their dithioether analogues. When a bidentate selenoether coordinates to a metal, geometric isomers are possible (Fig. 6), the meso- and the DL-, which may be distinguished by NMR spectroscopy. Pyramidal inversion at coordinated selenium which interconverts these isomers, has been reviewed recently [5,6] and will not be discussed extensively here.

The reaction of the free ligand with $[Re(CO)_5X]$ (X = Cl, Br, I) under reflux in chloroform gave the *fac*-$[Re(CO)_3X(L{-}L)]$ (L−L = $MeSe(CH_2)_2SeMe$, $MeSe(CH_2)_3SeMe$, MeSeCH=CHSeMe), which were characterised by elemental analysis, IR spectroscopy and variable-temperature ^1H NMR spectroscopy [89]. Four diastereoisomers (two *meso* and a degenerate DL pair) (Fig. 7) are present, but the relative invertomer populations are dependent on a number of factors, including halogen. A single-crystal X-ray study on *fac*-$[Re(CO)_3I(MeSe(CH_2)_2SeMe)]$ (Fig. 8), revealed the presence of the meso-2 invertomer, which correlates with the solution NMR data where the meso-2 form was the most abundant.

For the platinum(II) complexes *cis*-$[PtXMe(MeSe(CH_2)_2SeMe)]$ (X = Cl, Br, I), prepared by diselenoether-olefin exchange with $[PtXMe(COD)]$, variable-temperature NMR experiments indicate that the selenium *trans*-methyl inverts faster than the selenium *trans*-halogen [90]. The platinum(IV) complexes *fac*-$[PtXMe_3(L{-}L)]$ (X = Cl, Br, I; L−L = $MeSe(CH_2)_2SeMe$, $MeSe(CH_2)_3SeMe$,

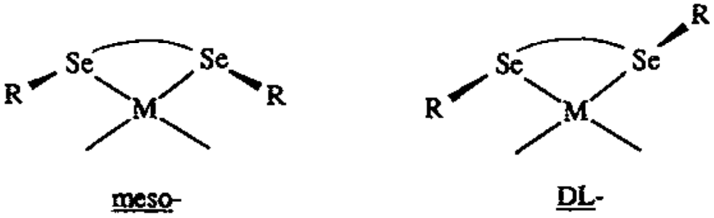


Fig. 6. Meso and DL invertomers of a metal complex of a chelating diselenoether.

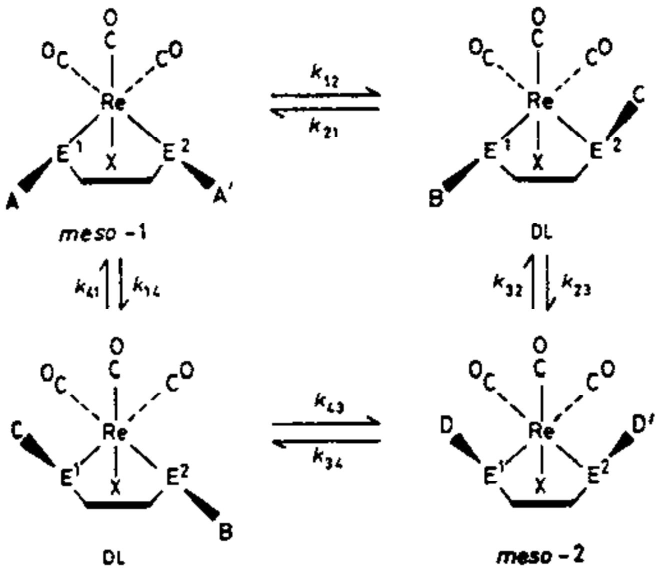


Fig. 7. Four invertomers of *fac*-octahedral transition-metal complexes of chelating diselenoethers. (From ref. 89 by permission of the Royal Society of Chemistry.)

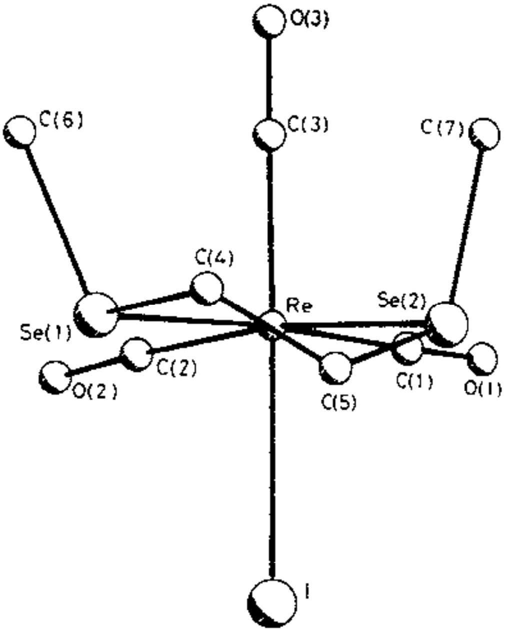


Fig. 8. Molecular structure of *fac*-[ReI(CO)$_3$(*meso*-2-MeSe(CH$_2$)$_2$SeMe)]. (From ref. 89 by permission of the Royal Society of Chemistry.)

MeSeCH=CHSeMe) were prepared by the reaction of $[PtXMe_3]_4$ with the ligand in $CHCl_3$ [91–93]. Multinuclear (^1H, ^{13}C, ^{77}Se, ^{195}Pt) and variable-temperature NMR studies show the anticipated four diastereoisomers (Fig. 7), and show that inversion at coordinated selenium is a higher-energy process than at coordinated sulphur, is a higher-energy process for five-membered than six-membered chelate rings, and is a higher-energy process for ligands with aliphatic than olefinic backbones. Invertomer populations are halogen- and temperature-dependent, but the predominant invertomer in solution has the same configuration as that observed in two single-crystal X-ray structure investigations, *fac*-$[PtClMe_3($*meso*-1-MeSeCH=CHSeMe)] and *fac*-$[PtIMe_3($*meso*-2-MeSeCH=CHSeMe)].

Three related papers [94–96] describe the preparation (from $[M(CO)_5THF]$) of, and variable-temperature ^1H NMR studies on $[M(CO)_5L]$ (M = Cr, Mo, W; L = $MeSeCH_2SeMe$, $MeSeCH_2SMe$). The bite-angle in these ligands is too small for chelation to transition metal centres, and they act as monodentate ligands. The NMR studies indicate a 2,4-intramolecular metal shift, possibly via a seven-coordinate intermediate. Analysis of the data from the mixed donor ligand ($MeSeCH_2SMe$) complexes gave the first quantitative evidence that the Se—M bond is stronger than the S—M bond. Monodentate coordination of 2,4-diselenapentane has also been observed in the platinum(II) complexes, *cis*- and *trans*-$[PtCl_2(MeSeCH_2SeMe)_2]$ [97], while bridging bidentate coordination is seen in the $[\{PdCl_2(MeSeCH_2SeMe)\}_n]$ [97] and $[(PtXMe_3)_2(MeSeCH_2SeMe)]$ (X = Cl, Br, I) [98]. Variable-temperature ^1H NMR spectroscopy on the platinum(IV) complexes indicates that there are four dynamic processes: six-membered ring reversal, pyramidal inversion, selenium-atom switching between platinum pairs and halogen-bridge cleavage.

The reaction of NiX_2 (X = Cl, Br, I) with $MeSe(CH_2)_2SeMe$ in ethanol affords green, paramagnetic, octahedral $[NiX_2(L\text{—}L)_2]$ [99]. Treatment of the chloro and bromo complexes with a variety of oxidising agents resulted in the decomposition of the nickel(II) complex, while treatment of $[NiI_2(MeSe(CH_2)_2SeMe)_2]$ with iodine gave the polyiodide $[Ni(I_3)_2(L\text{—}L)_2]$. An extensive range of *cis*-$[MX_2(L\text{—}L)]$ (M = Pd, Pt; X = Cl, Br, I; L—L = $MeSe(CH_2)_2SeMe$, $MeSe(CH_2)_3SeMe$, MeSeCH=CHSeMe, $o\text{-}C_6H_4(SeMe)_2$, $PhSe(CH_2)_2SePh$, $PhSe(CH_2)_3SePh$) have been isolated from the reactions of free ligand with $[MX_2(MeCN)_2]$ in dichloromethane [100]. ^1H, ^{77}Se and ^{195}Pt NMR spectroscopies confirm the presence of the two invertomers in solution, but the poor solubility and poor thermal stability of these compounds precluded investigations of any dynamic processes. The palladium(II) complexes could not be oxidised, but the *cis*-$[PtX_4(L\text{—}L)]$ were readily prepared by X_2/CCl_4 oxidation of the platinum(II) species [62]. A single-crystal X-ray study of *meso*-$[PtCl_4(o\text{-}C_6H_4(SeMe)_2)]$ (Fig. 9) correlated with the NMR studies, which showed that the predominant invertomer in solution was the meso isomer.

The reaction of CoX_2 (X = Cl, Br, I) with 2,5-diselenahexane and $NaBPh_4$ in the presence of dry air gave the dry-air-stable cobalt(III) complexes $[CoX_2(MeSe(CH_2)_2SeMe)_2][BPh_4]$ [101] as a mixture of cis and trans isomers (X = Cl, Br) and

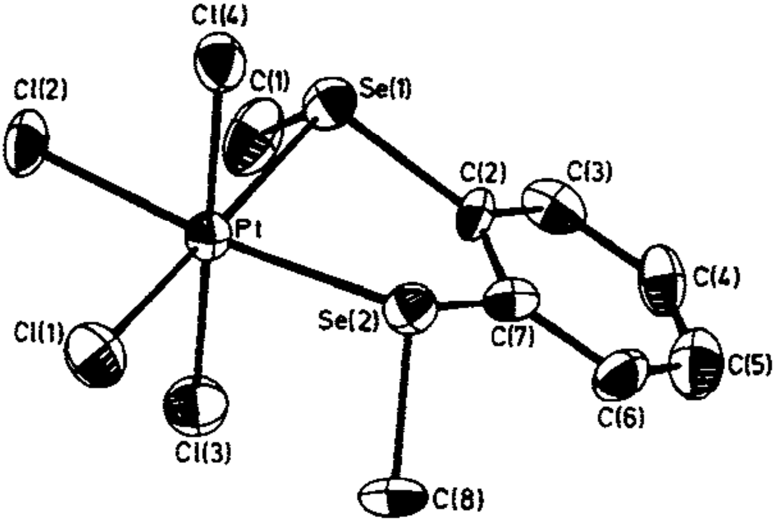


Fig. 9. Molecular structure of [$PtCl_4$(*meso-o*-$C_6H_4(SeMe)_2$)]. (From ref. 62 by permission of the Royal Society of Chemistry.)

only the trans isomer (X = I) assigned on the basis of UV-visible data. The ^{59}Co NMR chemical shifts are in agreement with the data found for other cobalt(III) complexes of group 16 donor ligands, but the presence of the quadrupolar cobalt nucleus broadened the ^{1}H and ^{77}Se NMR signals such that information on invertomer populations was lost. The additional stability conferred by methyl substituents on selenium and the five-membered chelate rings are essential to stabilize cobalt(III)–selenoether complexes since the comparable reactions with $MeSe(CH_2)_3SeMe$ and $PhSe(CH_2)_2SePh$ gave no isolable products.

Four types of rhodium(III)–diselenoether complex have been prepared. The insoluble chloride-bridged polymeric [{$RhCl_3(MeSe(CH_2)_2SeMe)$}$_n$] is precipitated when the ligand is added to a solution of rhodium trichloride in ethanol [97]. Concentration of the filtrate from the reaction yields *cis*-[$RhCl_2(MeSe(CH_2)_2SeMe)_2$][Cl] assigned on the basis of IR, ^{1}H and ^{77}Se NMR spectroscopies, the latter showing a large number of ^{77}Se NMR signals arising from the plethora of diastereoisomers with ^{77}Se chemical shifts characteristic of both $Se_{trans\text{-}Se}$ and $Se_{trans\text{-}Cl}$. Surprisingly, with 1,2-bis(phenylseleno)ethane, only the cationic complex *trans*-[$RhCl_2(PhSe(CH_2)_2SePh)_2$][Cl] could be isolated by a comparable reaction sequence. The corresponding 2,5-diselenahexane complex, *trans*-[$RhCl_2(MeSe(CH_2)_2SeMe)_2$][$ClO_4$] may be prepared from rhodium carbonyl chloride, the free ligand and perchloric acid. The ^{77}Se NMR spectra of these complexes only show six ^{77}Se signals, all with chemical shifts characteristic of $Se_{trans\text{-}Se}$. The anionic rhodium(III) complex [PPh_4] [$RhCl_4(MeSe(CH_2)_2SeMe)$] is readily prepared from the reaction of ligand with rhodium trichloride and tetraphenylphosphonium chloride in refluxing ethanol [100]. None of these rhodium(III) complexes could be oxidised chemically to Rh(IV). Electrochemically, the rhodium(III) anion shows an irreversible one-electron oxidation at a very positive potential, confirming that the rhodium(IV) complex is unstable [102]. Analogous halide-bridged iridium polymers $[\{IrX_3(L{-}L)\}_n]$ (X = Cl, Br, L–L = $MeSe(CH_2)_2SeMe$, $PhSe(CH_2)_2SePh$; X = Cl, L–L = $MeSe(CH_2)_3SeMe$) are prepared by refluxing iridium trihalides with the ligands in ethanol for 16 h. Refluxing these polymers in 2-methoxyethanol in the presence of tetraalkylammonium halides gave the anionic $[NR_4][IrX_4(L{-}L)]$. The chloro complexes may be oxidised chemically [62] or electrochemically [102] to the neutral red-brown $[IrCl_4(L{-}L)]$.

The reaction of 2,5-diselenahexane with ruthenium trichloride in ethanol at room temperature gave a mixture of paramagnetic chloride-bridged polymeric ruthenium(III) selenoether complexes [62], while the reaction under reflux in 2-methoxyethanol gave the diamagnetic *trans*-$[RuCl_2(MeSe(CH_2)_2SeMe)_2]$ [97]. Ruthenium trichloride and 2,5-diselenahexane in the presence of a very bulky counterion, such as $[Ph_4As]Cl$, gave the anionic ruthenium(III) complex $[Ph_4As][RuCl_4(MeSe(CH_2)_2SeMe)]$ for which a single crystal X-ray study gave the first solid-state example of the DL invertomer of a diselenoether coordinated to a transition metal [103] (Fig. 10).

Paramagnetic osmium(IV) complexes $[OsX_4(L{-}L)]$ (X = Cl, L–L = $MeSe(CH_2)_2SeMe$, $MeSe(CH_2)_3SeMe$, $MeSeCH{=}CHSeMe$, $PhSe(CH_2)_2SePh$; X = Br, L–L = $MeSe(CH_2)_3SeMe$) may be prepared from Na_2OsX_6 and the free ligands

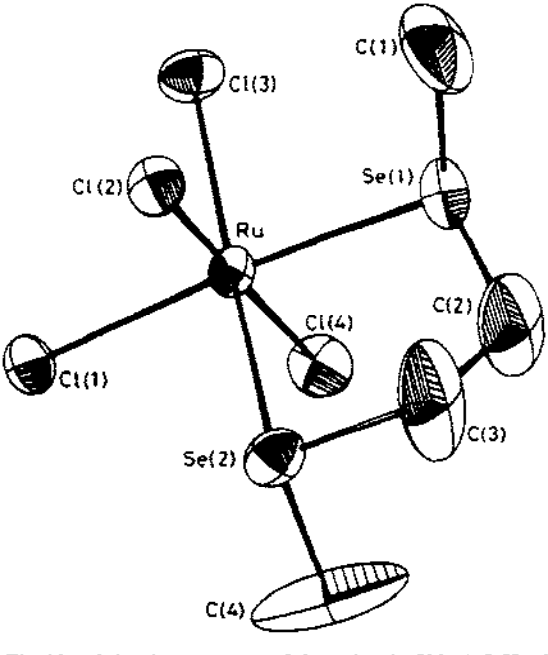
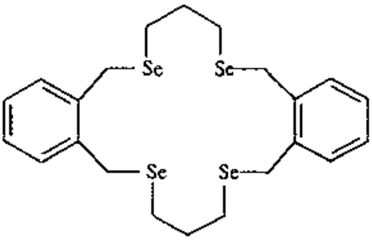
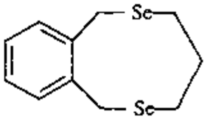


Fig. 10. Molecular structure of the anion in $[Ph_4As]$ $[RuCl_4$ (DL-$MeSe(CH_2)_2SeMe)]$. (From ref. 103 by permission of the Royal Society of Chemistry.)

under cautious reflux in 2-methoxyethanol [62], while the diamagnetic osmium(VI) $[OsO_2X_2(MeSe(CH_2)_2SeMe)]$ (X = Cl, Br) may be isolated from the reaction of 2,5-diselenahexane with osmium tetraoxide in ethanol/HX [67]. IR spectroscopy confirms the expected *trans*-osmyl unit and NMR spectroscopy showed the presence of meso and DL invertomers. 2,6-Diselenaheptane displaces THF from $[MoOCl_3(THF)]$ to give the molybdenum(V), *fac*-$[MoOCl_3(MeSe(CH_2)_2SeMe)]$, assigned on the basis of IR data [104].



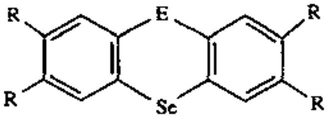
(7)

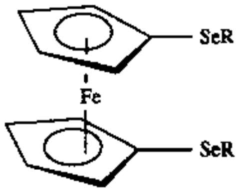


(8)

The selenacrowns **7** and **8** act as bidentate ligands when coordinated to metals in the complexes $[\{HgCl_2\}_2(\mathbf{7})]$, $[HgCl_2(\mathbf{8})_2]$, $[\{Hg(SCN)_2\}_2(\mathbf{7})]$, $[\{Hg(SCN)_2\}_2(\mathbf{8})]$, $[PdCl_2(\mathbf{8})]$ and $[Ag_2(\mathbf{7})](CF_3SO_3)_2$ [19].

Selenanthrenes **9** and **10** may coordinate as monodentate ligands as in $[PdCl_2L_2]$, bidentate ligands as in $[PtX_2(L{-}L)]$ (X = Cl, Br), $[HgCl_2(L{-}L)]$ and $[Ag(L{-}L)][NO_3]$ [105] or four-electron donor bridging bidentate ligands as in $[Re_2Br_2(CO)_6(L{-}L)]$ and $[Pt_2X_2Me_6(L{-}L)]$ (X = Cl, Br) [106].





E = Se, R = OMe (**9**) E = S, R = OMe (**19**) R = Me (**11**)

E = Se, RR = OCH_2O (**10**) E = S, RR = OCH_2O (**20**) R = Ph (**12**)

Spectroscopy and a single-crystal X-ray study on $[PtCl_2(\mathbf{10})]$ confirm the expected cis-square planar geometry about platinum, while comparable studies on $[HgCl_2(\mathbf{9})]$ suggest a very weak chelate complex (Hg–Se = 3.056Å) with distorted tetrahedral symmetry. In $[Pt_2Cl_2Me_6(\mathbf{9})]$ (Fig. 11), both "$PtMe_3$" groups are facial, and undergo an exchange process at room temperature which may be frozen out at 233 K.

(b) Bidentate ferrocenyl selenoether complexes

A third area of bidentate selenoether coordination chemistry which has attracted considerable attention is the complexes with 1,1′-bis-methylseleno- and 1,1′-bis-phenylseleno-ferrocene (**11** and **12**).

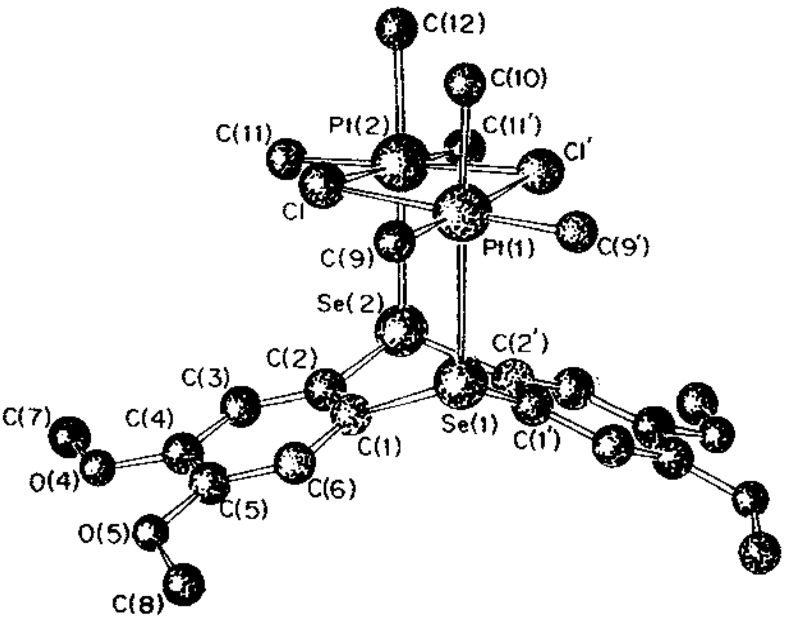


Fig. 11. Molecular structure of [{PtClMe$_3$}$_2$(9)]. (From ref. 106 by permission of Chapman and Hall.)

Displacement of norbornadiene from [M(CO)$_4$(nbd)] (M = Cr, Mo, W) gives *cis*-[M(CO)$_4$(11)] [107]. A single-crystal X-ray study on the tungsten complex (Fig. 12) is the second solid-state example of a DL invertomer which correlates with the predominant species in solution as assigned from ^{77}Se NMR spectroscopy. Pyramidal inversion at the coordinated selenium in these complexes has also been investigated [107]. Preparative routes to the *fac*-[ReX(CO)$_3$(**11**)] (X = Cl, Br, I) [108] and *fac*-[PtXMe$_3$(**11**)] (X = Cl, Br, I) [109] mirror those used to prepare the analogous diselena-alkane complexes (Sect. C. (ii) (a)). NMR spectroscopy confirms the presence of *meso* and DL invertomers in solution, the ^{195}Pt NMR spectra of the platinum complexes, in particular, showing two sets of ^{77}Se satellites arising from the inequivalent selenium atoms (Fig. 13). Variable-temperature NMR studies indicate that the barriers to selenium inversion are considerably lower than in five- and six-membered chelate ring diselena-alkane analogues as a result of the high flexibility of the ferrocenyl-selenide ring. The palladium(II) and platinum(II) complexes [PdCl$_2$(**12**)] [15], [PtCl$_2$(**11**)] [110], [Pd(PPh$_3$)(**11**)][BF$_4$]$_2$ and [Pd(PPh$_3$)(**12**)][BF$_4$]$_2$ [111] have also been prepared, the latter two complexes appearing to have some Fe···Pd interaction.

(iii) Multidentate selenoether complexes

Research in this area has been limited to a few papers describing the coordination of linear and cyclo tri- and tetra-selena-alkanes. Cyclo-1,3,5-triselenahexane

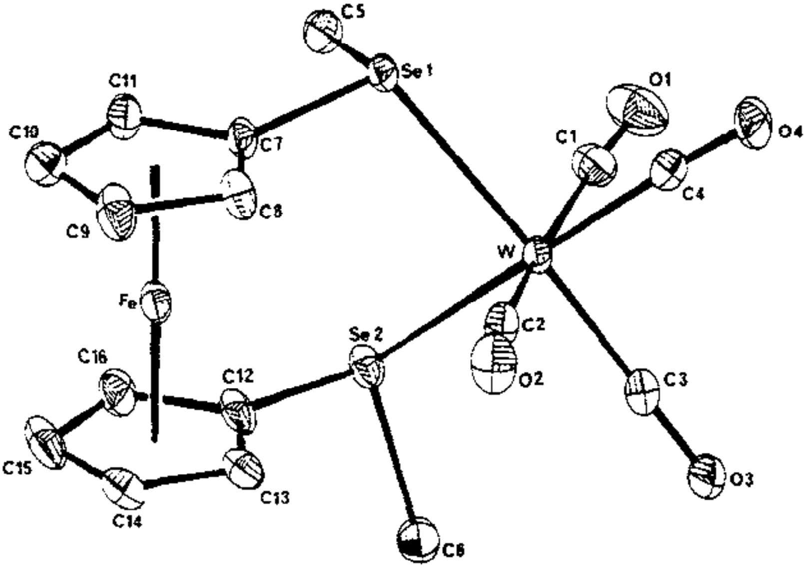


Fig. 12. Molecular structure of a ferrocenyl selenoether complex of tungsten(0). (From ref. 107 by permission of Elsevier Sequoia SA.)

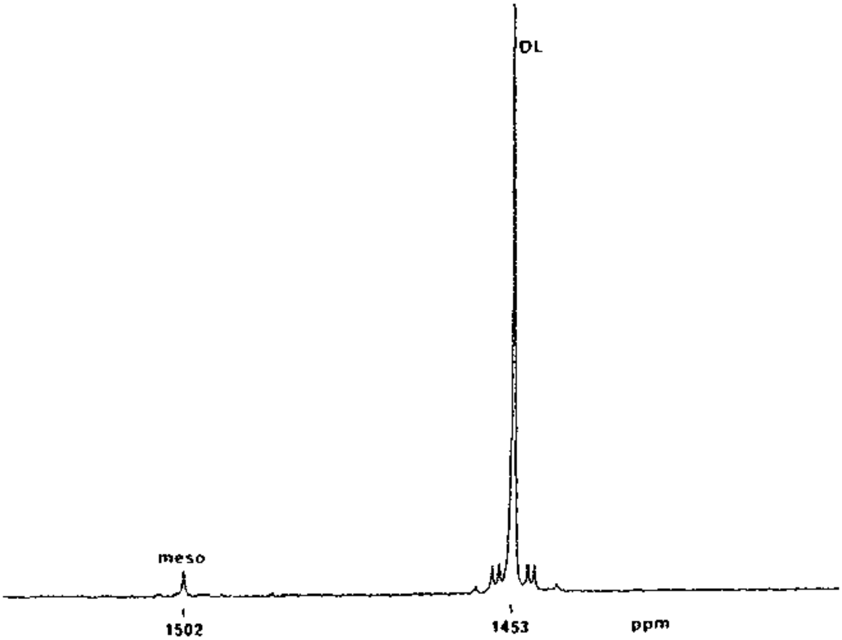


Fig. 13. ^{195}Pt NMR spectrum of [PtClMe$_3$(11)]. (From ref. 109 by permission of Elsevier Sequoia SA.)

reacts with $AgAsF_6$ in SO_2 to give $[\{CH_2Se\}_3-Ag-\{CH_2Se\}_3][AsF_6]\cdot 2SO_2$ [112]. A single- crystal X-ray study (Fig. 14) reveals isolated cations in which all six selenium atoms coordinate irregularly to the silver(I) metal centre. The linear 2,5,8-triselenanonane, $NaBF_4$ and $[PtIMe_3]_4$ afford *fac*-$[PtMe_3(MeSeCH_2CH_2SeCH_2CH_2SeMe)][BF_4]$ [113, 114]. Molecular models indicate that only four diastereoisomers (two meso and a degenerate DL pair) are possible since inversion at the central coordinated selenium forms highly strained conformers. Low-temperature dynamic NMR studies indicate that the terminal seleniums undergo the expected pyramidal inversion.

The isomeric tris-selenoethers $[MeC(CH_2SeMe)_3]$ (**13**) and $[(MeSeCH_2CH_2CH_2)_2Se]$ (**14**) form a number of platinum metal halide complexes dependent on the steric constraints of the ligands [115]. The tripodal ligand (**13**) acts as a bidentate ligand to palladium, platinum and osmium(IV) in *cis*-$[MCl_2(\mathbf{13})]$ (M = Pd, Pt) and *cis*-$[OsCl_4(\mathbf{13})]$, and as a tridentate ligand in *fac*-$[MCl_3(\mathbf{13})]$ (M = Ru, Os, Rh, Ir). All complexes may be prepared by routes analogous to those used to prepare the corresponding diselena-alkane complexes (Sect. C. (ii) (a)). The diamagnetic complexes have been characterised by, in particular, ^{77}Se NMR spectroscopy. For palladium(II) at room temperature, rapid pyramidal inversion of the six-membered chelate ring, affords a deceptively simple ^{77}Se NMR spectrum with two resonances due to coordinated and un-coordinated selenium atoms. At 223 K, inversion is frozen out, and four resonances assignable to coordinated selenium and one resonance due to uncoordinated selenium are observed. For the platinum(II) complex, pyramidal inversion at room temperature is slow and the ^{77}Se NMR spectrum is comparable with the low-temperature spectrum for the palladium(II) complex with platinum-195 satellites, and is explained in terms of four invertomers (two meso and a degenerate DL pair). The ^{195}Pt NMR spectrum confirms this assignment. For the rhodium(III)

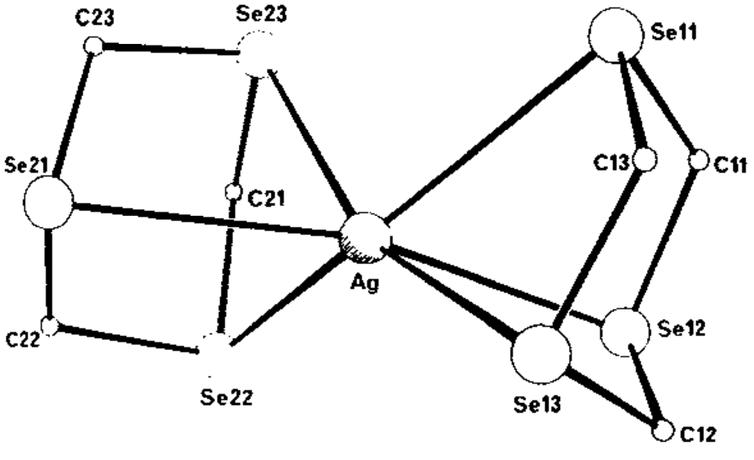


Fig. 14. Molecular structure of the cation, $[\{(CH_2Se)_3\}_2Ag]^+$. (From ref. 112 by permission of Elsevier Sequoia SA.)

and iridium(III) complexes, three doublets (coupling to ^{103}Rh) and three singlets, respectively, are reported in the ^{77}Se NMR spectra, assigned to the three selenium environments of the two possible invertomers (Fig. 15).

The linear ligand (**14**) acts as a bidentate ligand in *cis*-[PdCl$_2$(**14**)] and *cis*-[OsCl$_4$(**14**)], and as a tridentate ligand in [PtCl(**14**)][PF$_6$] and *fac*-[MCl$_3$(**14**)] (M = Ru, Os, Rh, Ir) [115]. Physical data confirm the "Se$_3$Cl" donor set of the four invertomers possible for the platinum(II) complex (the ^{77}Se NMR spectrum is shown in Fig. 16), and the *fac*-octahedral symmetry for the [MCl$_3$(**14**)]. Eight invertomers

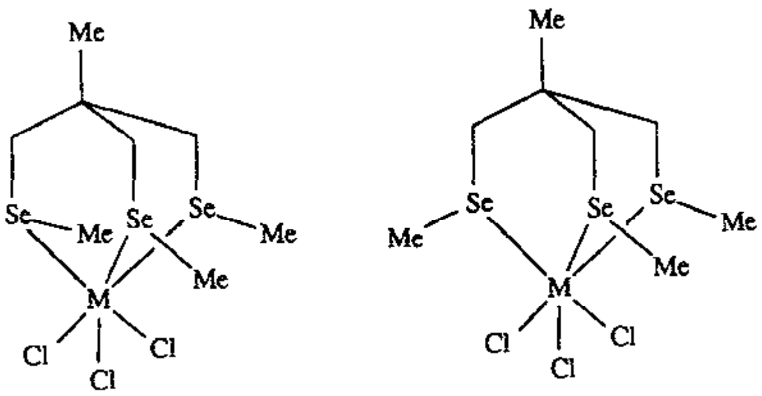


Fig. 15. Syn and anti isomers of [MCl$_3$(**13**)] complexes.

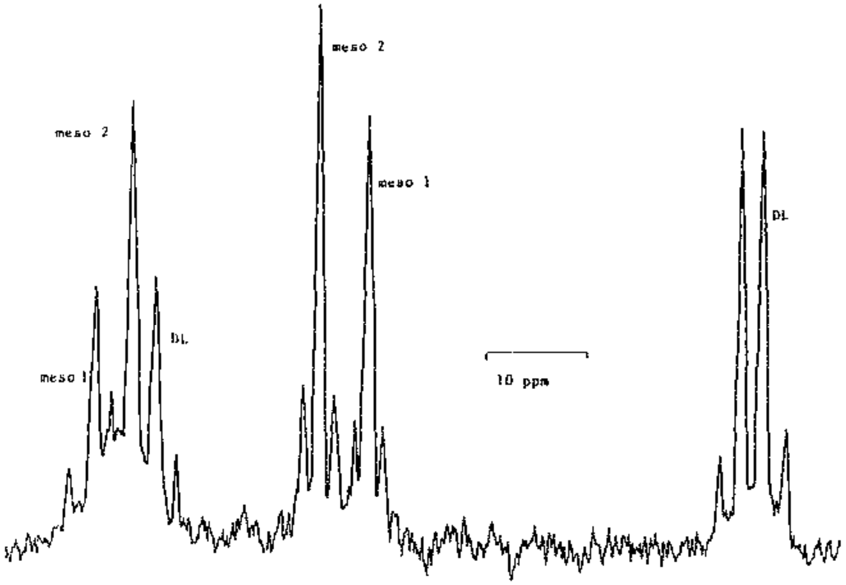


Fig. 16. ^{77}Se NMR spectrum of [PtCl$_2$(**14**)]. (From ref. 115 by permission of the Royal Society of Chemistry.)

are possible for this stereochemistry, but four may be excluded on steric grounds using similar arguments to those put forward for the *fac*-[$PtMe_3(MeSeCH_2CH_2SeCH_2CH_2SeMe)$][$BF_4$] [113], leaving seven different coordinated selenium environments. In the ^{77}Se NMR spectra of the rhodium and iridium(III) complexes, seven doublets (coupling to ^{103}Rh) and five singlets are seen, respectively.

The macrocyclic ligand 1,5,9,13-tetraselenacyclohexadecane ($16Se_4$) forms a complex with copper(II), [$Cu(16Se_4)$][SO_3CF_3]$_2$, which is unstable in organic solvents [116]. A single-crystal X-ray study indicates square-planar Se_4 coordination with the anions weakly coordinating via oxygen on the tetragonal axis (Fig. 17). This complex readily decomposes by a one-electron transfer, presumed to be via the radical cation $(16Se_4)^{\cdot +}$ to give the three-dimensional polymeric [$Cu(16Se_4)$][SO_3CF_3] and [$(16Se_4)$][SO_3CF_3]$_2$. The single-crystal X-ray study of the copper(I) complex (Fig. 18) shows four selenium atoms, from different ligands, coordinating Cu(I) in a pseudo-tetrahedral arrangement [117]. Each selenium in the ($16Se_4$) coordinates to different, though symmetry-related, Cu(I) ions as a bridging tetradentate ligand. Comparable coordination is observed for [$Hg(CN)_2(16Se_4)$] which contains linear "$Hg(CN)_2$" units which interact very weakly (Hg–Se ≈ 3.4 Å) with

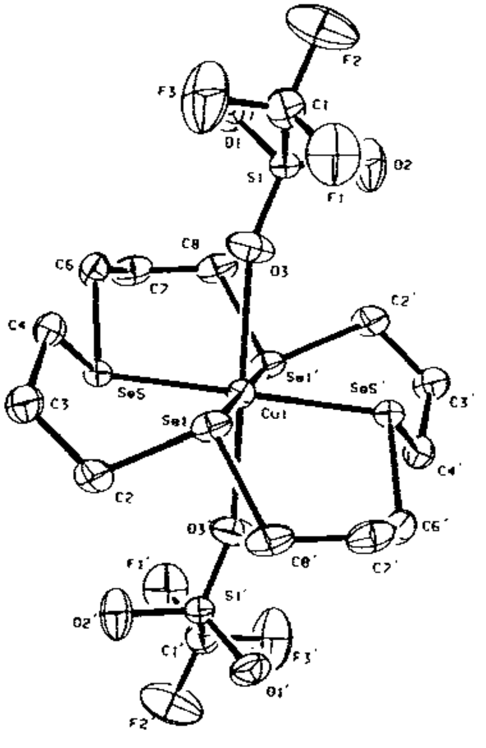


Fig. 17. Molecular structure of a copper(II) tetraselenoether macrocycle complex. (From ref. 116 by permission of the American Chemical Society.)

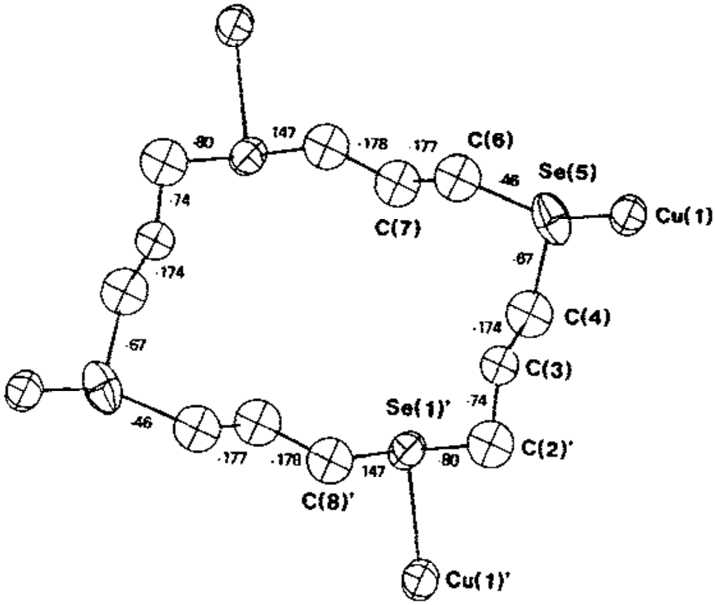


Fig. 18. Bridging tetradentate coordination of the selenoether in the $[Cu(16Se_4)][BF_4]$. (From ref. 117 by permission of Elsevier Sequioa SA.)

selenium atoms from different ligands [117]. The spirocyclic $[C(CH_2SeMe)_4]$ also acts as a bridging tetradentate ligand in the dimeric palladium(II) complex $[Cl_2Pd\{C(CH_2SeMe)_4\}PdCl_2]$ [97].

(iv) Hybrid selenoether complexes

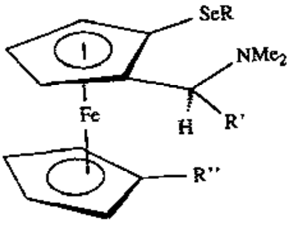
(a) Complexes of mixed nitrogen–selenium donor ligands

A range of cobalt(III) complexes of the $RSeCH_2CH_2NH_2$ (R = alkyl) ligands, readily prepared by the alkylation of selenolato precursors, include $[Co(en)_2(RSeCH_2CH_2NH_2)][ClO_4]_3$ (R = Me,Et,$C_6H_5CH_2$,$CH_3COCH_2CH_2$) [118–121], $[Co(tren)(MeSeCH_2CH_2NH_2)][ClO_4]_3$ [122], t-$[Co\{NCH_2CH_2NH_2)_3\}(RSeCH_2CH_2NH_2)]Cl_3$ (R = Me, Et, $C_6H_5CH_2$ t- = Se *trans*-tertiary amine) [123,124], p-$[Co\{N(CH_2CH_2NH_2)_3\}(MeSeCH_2CH_2NH_2)]Br_3$ (p- = Se *cis*-tertiary amine) [123] and $[Co(\beta\text{-diketonate})_2(MeSeCH_2CH_2NH_2)][PF_6]$ (β-diketonate = acac, 3-chloroacac, 3-methylacac,1,3-diphenyl-1,3-propanedionato) [125–127]. All these complexes are chiral, may be found as a mixture of diastereoisomers, and have been characterised by a combination of electronic spectroscopy (spectra are typical of N_5Se or O_4NSe donor sets to Co(III)), CD, ^1H and ^{13}C NMR spectroscopies. For the ethylenediamine complexes, the selenato-cobalt(III) reagents were rationalised before alkylation, such that they exist as a single (R) diastereoisomer. This was confirmed by a single-crystal X-ray study on $[Co(en)_2(MeSeCH_2CH_2NH_2)][ClO_4]_3$

[120]. Kinetic studies on the alkaline hydrolysis of these ethylenediamine complexes suggests a dissociative mechanism with cleavage of the Co–Se bond to give [Co(en)$_2$(OH)(RSeCH$_2$CH$_2$NH$_2$)]$^{2+}$. The rates of reaction are comparable with the analogous thioether complexes, implying that the Co—E bond strengths are similar, but the selenoethers rechelate in acid 100–1000 times faster than the thioethers as a result of the higher nucleophilicity of selenium.

Optically pure tris(aminoethyl)amine and β-diketonato cobalt(III) complexes may be resolved by SP-sephadex column chromatography and SE-toyopearl HPLC, respectively, suggesting high barriers to inversion at coordinated selenium. First-order kinetics for selenium inversion are indicated by variable-temperature CD, and the highest ΔH (Se inversion) of 113 kJ mol^{-1} is reported for [Co(acac)$_2$(MeSeCH$_2$CH$_2$NH$_2$)][PF$_6$] [125]. An analogous rhodium(III) complex p-[Rh{N(CH$_2$CH$_2$NH$_2$)$_3$}(MeSeCH$_2$CH$_2$NH$_2$)]Br$_3$ has also been prepared, characterised and resolved [124]. This rhodium(III) complex racemises more slowly than its cobalt(III) analogue.

Ferrocenylamine selenide ligands (**15**) act as SeN bidentate ligands to nickel(II), palladium(II) and platinum(II), although the studies have not been systematic [15,128–131].



(**15**)

Complexes isolated include cis-[PdCl$_2$(**15**)] (R = 4-ClC$_6$H$_4$, R' = Me, R'' = SeC$_6$H$_4$Cl; R = C$_6$H$_5$CH$_2$, 4-MeC$_6$H$_4$, R' = H, R'' = SeC$_6$H$_5$, SeC$_6$H$_4$Me; R = Ph, R' = Me, R'' = H; R = Me, R' = Me, R'' = H) and cis-[PtCl$_2$(**15**)] (R = Ph, R' = Me, H, R'' = SePh; R = Me, R' = Me, R'' = H). The ferrocenylamine selenide ligands with two selenoether groups act only as SeN bidentate ligands forming six-membered chelate rings on coordination. Although the ferrocenylamine sulphide complexes catalyse the hydrogenation of alkenes, the ferrocenylamine selenide complexes are inactive. The nickel(II) complex [NiCl$_2$(**15**)] (R = 4-ClC$_6$H$_4$, R' = Me, R'' = SeC$_6$H$_4$Cl) prepared in situ homogeneously catalyses Grignard cross-coupling reactions of 1-chloro-1-phenylethane with allylmagnesiumchloride with higher stereoselectivity than the isolable palladium(II) complexes [131].

The cyclophane (**1**) acts as an Se$_2$N$_2$ tetradentate ligand in [Ni(H$_2$O)$_2$(**1**)][ClO$_4$]$_2$, [Cu(H$_2$O)$_2$(**1**)][ClO$_4$] and [CuCl$_2$(**1**)], which have been characterised by electronic and EPR spectroscopies [20]. Stability constants indicate that both metals fit equally well into the ligand cavity and a single-crystal X-ray study on the nickel(II) complex indicates that the ligand adopts a syn conformation (Fig. 19). All three complexes are semiconductors at room temperature.

(b) Complexes of other mixed group 15–selenium donor ligands

The only complexes in this category contain cis chelates with the *o*-phenylene-backboned *o*-$C_6H_4(SeMe)(ER_2)$ ligands. The phenyl-substituted phosphine, *o*-$C_6H_4(SeMe)(PPh_2)$ (**16**) gives stable monomeric *trans*-$[CoX_2(16)_2][BF_4]$ (X = Cl, Br) characterised by, in particular, ^{1}H, ^{31}P, ^{77}Se and ^{59}Co NMR spectroscopies [132], $[NiBr_3(\mathbf{16})]$ characterised by EPR [133], and *cis*-$[PdX_2(\mathbf{16})]$ (X = SCN, Cl, Br) [133,134]. The methyl-substituted phosphine *o*-$C_6H_4(SeMe)(PMe_2)$ (**17**) reacts with nickel(II) halides to give $[NiX_2(\mathbf{17})_2]$ (X = Cl, Br); the bromocomplex may be cautiously oxidised in the presence of a non-coordinating anion to $[NiBr_2(\mathbf{17})_2][BF_4]$ [133]. The analogous diarsine *o*-$C_6H_4(SeMe)(AsMe_2)$ (**18**) yields comparable nickel(II) and nickel(III) complexes and also affords *cis*-$[MX_2(\mathbf{18})]$ (M = Pd, Pt, X = Cl, Br) by the reaction of the free ligand with the $[MX_2(MeCN)_2]$ in dichloromethane. Oxidation by X_2/CCl_4 yields all the corresponding *cis*-$[MX_4(\mathbf{18})]$, including the first isolable neutral palladium(IV) selenoether complex [133].

(c) Complexes of mixed group 16–selenoether ligands

Most of the research in this category involves mixed thioseleno ligands complexed to metals for comparison with the dithio- and diselenoether analogues. The

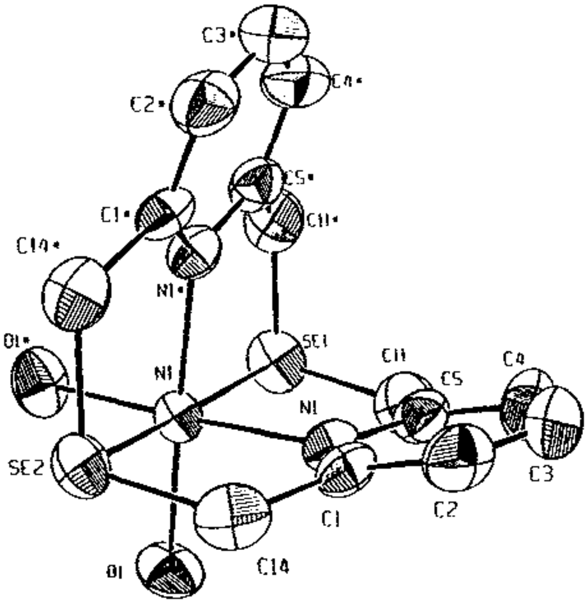


Fig. 19. Molecular structure of the cationic $[Ni(H_2O)_2(1)]^{2+}$, showing the ligand in the syn-conformation. (From ref. 20 by permission of the American Chemical Society.)

2-thia-4-selenapentane acts as a bridging bidentate ligand in $[\{PtMe_3X\}_2MeSCH_2SeMe]$ (X = Cl, Br, I) [135]; the complex undergoes the same fluxional processes as $[\{PtMe_3X\}_2MeSeCH_2SeMe]$ (q.v.) [98]. The mixed chalcogenanthrene (**19**) also acts as a bridging bidentate ligand in $[Pt_2Cl_2Me_6(19)]$ [106]. The monomeric complexes, *cis*-$[PtXMe(MeS(CH_2)_2SeMe)]$ (X = Cl, Br, I) contain two geometrical pairs of diastereoisomers [94], while *fac*-$[PtMe_3X(MeS(CH_2)_2SeMe)]$, *fac*-$[PtMe_3X(o\text{-}C_6H_4(SeMe)(SMe)]$ [136], *fac*-$[Re(CO)_3X(MeS(CH_2)_2SeMe)]$ and *fac*-$[Re(CO)_3X\{o\text{-}C_6H_4(SMe)(SeMe)\}]$ [137] (for all, X = Cl, Br, I) have four distinct diastereoisomers (meso-1, meso-2, DL-1, DL-2). Platinum(IV) methyl complexes *fac*-$[PtMe_3\{(MeSeCH_2CH_2)_2E\}][BF_4]$ (E = O, S) and *fac*-$[PtMe_3\{(MeSCH_2CH_2)_2Se\}]I$ are readily prepared from $[PtMe_3I]_4$ with free ligand; the presence of BF_4 is essential for oxygen coordination to platinum(IV) [113]. Dynamic NMR studies indicate that pyramidal inversion only occurs at the terminal chalcogens and for *fac*-$[PtMe_3\{(MeSCH_2CH_2)_2Se\}]I$, a further high-temperature fluxional process involves dissociation of a terminal MeS group to give the neutral *fac*-$[PtMe_3I(MeSCH_2CH_2SeCH_2CH_2SMe)]$ containing a five-membered-S, Se-chelate ring [114].

(d) Other hybrid selenoether complexes

The selena-alkenes, 2-selenahex-5-ene and 5-selenanona-2,8-diene, chelate in the *cis*-$[PtX_2(MeSeCH_2CH_2CH{=}CH_2)]$ and *cis*-$[PtX_2(CH_2{=}CHCH_2CH_2SeCH_2CH_2CH{=}CH_2)]$ (X = Cl, Br, I) complexes which have, very recently, been characterised by elemental analysis, IR and ^1H NMR spectroscopies [138,139]. Dynamic NMR studies suggest that alkene exchange occurs in the nonadiene ligand complex, but that selenium inversion does not occur in the available temperature range. The related 2,8-dimethyl-5-selenanona-2,8-diene acts as a tridentate ligand in the unstable $[PtX(CH_2{=}CMeCH_2CH_2SeCH_2CH_2CMe{=}CH_2)]^+$ (X = Cl, Br, I) which undergo facile selenium dealkylation to give dimeric alkenyl selenato complexes [140].

D. TELLUROETHER COMPLEXES

(i) Monodentate telluroether complexes

Although many complexes of R_2Te ligands are reported in the older literature [3], characterisation was often limited to an analysis and a melting point. Only in the last 20 years has a reasonable body of spectroscopic data been collected, and the available data are still much more limited and fragmented than that upon other group 15 or 16 donor ligands. Structural data are sparse, with less than 15 single crystal X-ray studies reported. In view of the fragmentary nature of the recent reports, the work has been divided into three sections dealing with low, medium, and high oxidation state metal centres.

(a) Low oxidation state complexes

These are mostly substituted carbonyl complexes, and often reports consist of a single complex mentioned in papers dealing with sulphur or selenium ligands.

Photolysis of $Et_4N[V(CO)_6]$ and $TePh_2$ in THF yields brown $Et_4N[V(CO)_5(TePh_2)]$ [83,84], and the $[CpV(CO)_3L]$ ($L = TeMe_2, TePh_2$) are made similarly from $[CpV(CO)_4]$ [52,82]. The ^{51}V NMR resonances of $[CpV(CO)_3L']$ shift to low frequency in the order $L' = SPh_2 > SeMe_2 > TeMe_2$ [82]. Photolysis of $[CpNb(CO)_4]$ and telluracyclopentane ($\overline{Te(CH_2)_3CH_2}$, L) in THF, gave red $[CpNb(CO)_3L]$ [77]. A comparison of the kinetics of substitution of the group 16 ligand by phosphines in the series $[CpNb(CO)_3L]$ ($L = THF$, $\overline{S(CH_2)_3CH_2}$, $\overline{Se(CH_2)_3CH_2}$, $\overline{Te(CH_2)_3CH_2}$) showed that reactivity decreased down group 16 consistent with stronger σ-donation by the heavier donor atoms [77]. Substituted chromium carbonyl complexes include $[\{Cr(CO)_5\}_2\text{-}\mu\text{-}Me_2Te]$ [54], and $[Cr(CO)_5\{(p\text{-}MeOC_6H_4)_2Te\}]$ [86], the latter made by an unusual route involving oxygen atom transfer between $(p\text{-}MeOC_6H_4)_2TeO$ and $Cr(CO)_6$ (CO_2 is the other product). The crystal structure of the complex (Fig. 20) reveals a slightly distorted octahedron, with $Cr{-}Te = 2.684(1)$ Å. A novel route to $[Cr(CO)_5(TeEt_2)]$ is alkylation of $[Cr(CO)_5(TeH)]^-$ with Et_3O^+ [68]. The reaction of $[CpMo(CO)_3I]$ with $AgBF_4$ and $TeMe_2$ gave $[CpMo(CO)_3(TeMe_2)]^+$, whilst oxidation of $[\{CpMo(CO)_2\}_2]$ with $[Cp_2Fe]^+$ in the presence of $TeMe_2$ gave cis and trans isomers of $[CpMo(CO)_2(TeMe_2)_2]^{2+}$ [51]. [4+2] Cycloaddition of cyclopenta-

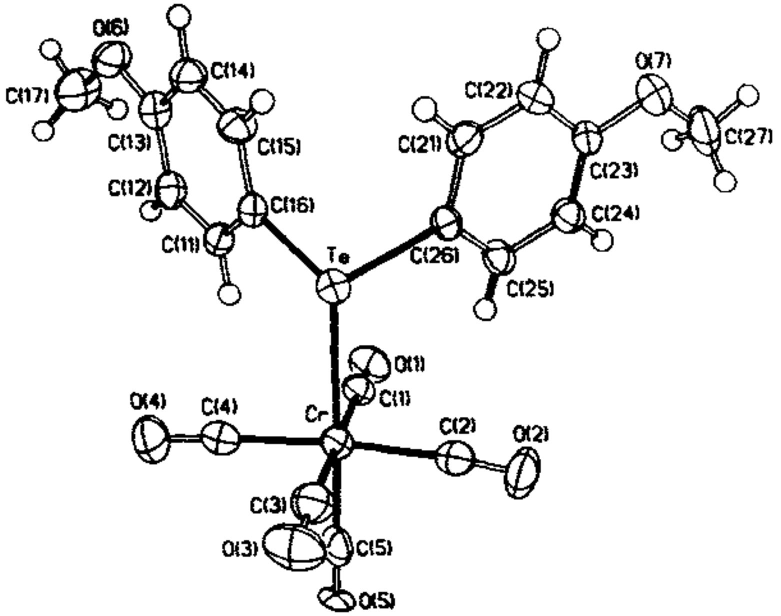


Fig. 20. Molecular structure of $[Cr(CO)_5\{(p\text{-}MeOC_6H_4)_2Te\}]$. (From ref. 90 by permission of the American Chemical Society.)

diene or 2,3-dimethyl-1,3-butadiene to [$W(CO_5(Ph_2C{=}Te)$] gives cyclic telluroether complexes [141].

Manganese and rhenium carbonyls react with α-Me_2TeI_2 to produce *cis*-[$M(CO)_4(TeMe_2)I$] (M = Mn or Re) [141a]. Other complexes are the group 16 bridged dimers [$\{Mn(CO)_5\}_2(\mu$-$TeMe_2)$] [141a] and [$\{CpMn(CO)_2\}_2(\mu$-$Me_2Te)$] [54], and [$Mn(NO)_3(TePh_2)$] [83].

The tetrahydrofuran in [$CpFe(CO)_2(THF)]^+$ is substituted by ER_2 ligands ($ER_2 = TeMe_2$, $SeMe_2$, various thioethers) to give [$CpFe(CO)_2(ER_2)]^+$, which substitute further photochemically to give [$CpFe(CO)(ER_2)_2]^+$ [43]. Nucleophiles X^- (X = NCS, I), or other neutral ligands, L (L = PPh_3, $AsPh_3$, $SbPh_3$), substitute one ER_2 group to give the chiral complexes [$CpFe(CO)(ER_2)X$] and [$CpFe(CO)(ER_2)L]^+$, and $TeMe_2$, also displaces $SeMe_2$ or SMe_2 [43,45]. Carbonyl-free cations [$CpFe(TeMe_2)L_2]^+$ are also known where $L_2 = 2PMe_3$, $2P(OMe)_3$, or $Ph_2P(CH_2)_nPPh_2$ [45]. The X-ray structure of [$CpFe(CO)_2(TeR_2)]BF_4$ has been determined, revealing the familiar "piano-stool" geometry, Fe–Te = 2.533(1) Å [44]. Detailed comparisons between the various group 16 ligand complexes have yielded information about the bonding of group 16 ligands, and these studies are discussed in Sect. F. Stepwise displacement of the BF_4 group and cyclohexadiene from [$CpFe(C_6H_8)FBF_3$] by $TeMe_2$ yields [$CpFe(C_6H_8)TeMe_2]^+$, [$CpFe(C_6H_8)(TeMe_2)_2]^+$, and [$CpFe(TeMe_2)_3]^+$ [47]. A most unusual alkane activation occurs when [$Os_3(CO)_{11}(MeCN)$] is treated with $Te(CF_3)_2$ in cyclohexane. In the dark the product is [$Os_3(CO)_{11}\{TeCF_3(c$-$C_6H_{11})\}$] but in light, both CF_3 groups are replaced to give [$Os_3(CO)_{11}\{Te(c$-$C_6H_{11})_2\}$], the X-ray structure of which reveals the telluroether occupying an equatorial site on one osmium [142]. A similar activation occurs with *n*-pentane.

Cobalt carbonyl derivatives include [$\{Co(CO)_3(TeMe_2)\}_n$] and [$\{Co(CO)_4\}_2(TeMe_2)$] [141a]. The mixed-metal cluster carbonyls [$HRuCo_3(CO)_{12}$] and [$HRuRh_3(CO)_{12}$] undergo selective substitution of carbonyls on treatment with $TeMe_2$ or $TePh_2$ [143]. The isolated products include the three structurally characterised examples in Fig. 21, and the dinuclear [$\{HRuRh_3(CO)_9\}_2(TeMe_2)_3$], in which the $TeMe_2$ groups behave as 4e bridging donor ligands occupying all the axial positions on the two Rh_3 triangles and linking them together.

(b) Medium oxidation state complexes

There are no recent reports of such complexes with the metals of groups 4–7. Cobalt(III) complexes include the violet [$CpCo(TeMe_2)_3]^{2+}$ and the green [$CpCo(TeMe_2)_2I]BF_4$ [47,50], and for nickel(II) there are the red-brown [$CpNi(TeMe_2)_2]^+$ and [$CpNi(TeMe_2)I$] [49].

Diethyltelluride reacts with CuCl in EtOH/HCl to give [$\{CuCl(TeEt_2)\}_n$], also obtainable from $CuCl_2$ and excess $TeEt_2$. The structure consists of infinite sheets with Et_2Te ligands bridging $Cu(\mu^2$-$Cl)_2Cu$ units, the geometry about both Cu and Te being distorted tetrahedral (Fig. 22) [144].

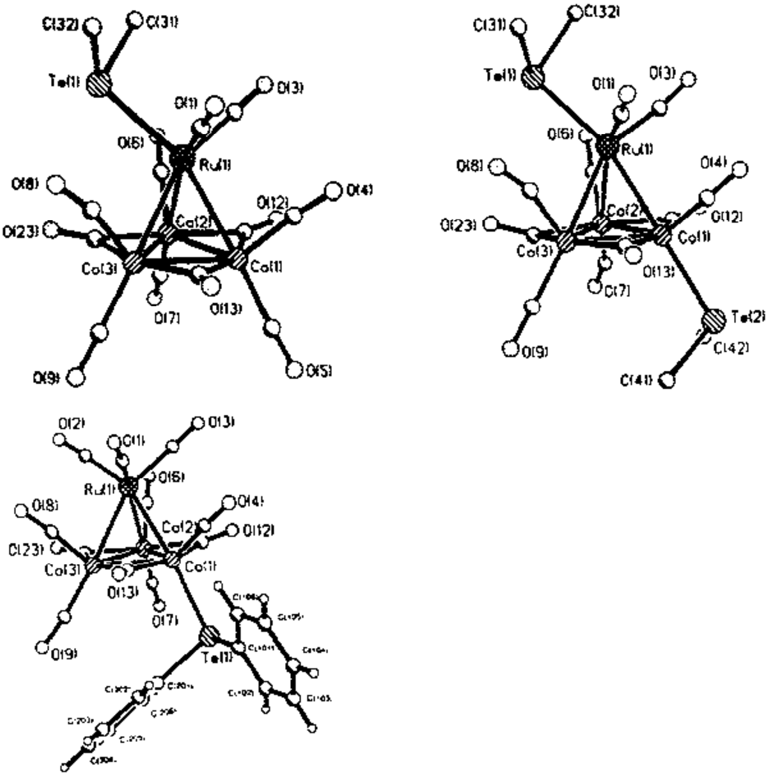


Fig. 21. Molecular structures of three telluride-substituted tetranuclear cluster carbonyls. (From ref. 143 by permission of Elsevier Sequoia SA.)

One new Ru(II) complex has been described, [Ru(2,2′-bipyridyl)(terpyridyl)(TeMe$_2$)]$^+$, obtained from the corresponding chlorocomplex, Ag$^+$, and TeMe$_2$ in acetone [145]. Mer-[RhL$_3$Cl$_3$] complexes have been prepared with a number of heterocyclic telluroethers, including $\overline{\text{Te(CH}_2)_3\text{C}}\text{H}_2$, and $\overline{\text{Te(CH}_2)_2\text{O(C}}\text{H}_2)_2$, from which CO displaces one telluroether to give [RhL$_2$(CO)Cl$_3$] [146–148]. Very poor yields of [NMe$_4$] *trans*-[Ir(TeMe$_2$)$_2$Cl$_4$] are obtained from IrCl$_3$·nH$_2$O, NMe$_4$Cl, and TeMe$_2$ in EtOH/HCl [65].

Palladium(II) and platinum(II) telluroether complexes were among the earliest examples reported. A recent re-examination of the [ML$_2$X$_2$] (M = Pd or Pt; L = TeMe$_2$, TePh$_2$, TeMePh; X = Cl, Br, I) by ^{125}Te and ^{195}Pt NMR spectroscopy showed that in CH$_2$Cl$_2$ solution both cis and trans isomers were present for all complexes, except for the [Pd(Ph$_2$Te)$_2$X$_2$] and the six iodides for which only one isomer was detected. Since the cis/trans ratio decreases Pt > Pd and Cl > Br, it is likely that, where only a single isomer is found, it will have trans geometry. The differences in ^{125}Te chemical shifts between the two isomers of each complex are small ($\leqslant$20 ppm) and the $^1J(^{125}\text{Te}-^{195}\text{Pt})$ coupling constants cis > trans are a better indicator of

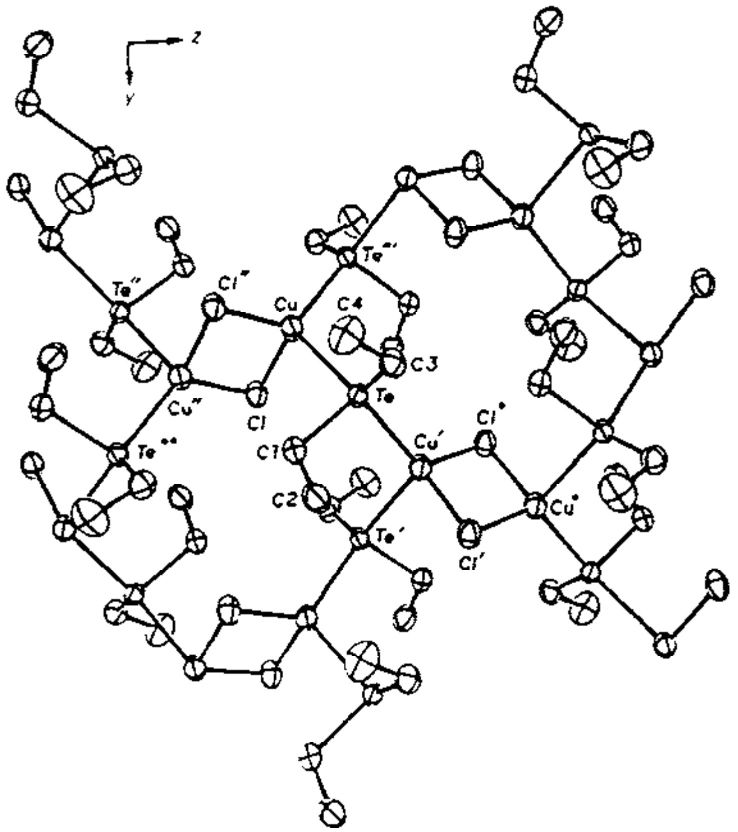


Fig. 22. Structural units in $[\{\mathrm{CuCl(TeEt_2)}\}_n]$. (From ref. 144 by permission of Elsevier Sequoia SA.)

structure where both forms are present [149]. The structure of *trans*-$[\mathrm{Pt(TeMePh)_2I_2}]$ has been determined (Fig. 23) [150]. Complexes of this unsymmetrical telluroether can exist in RR/SS or RS/SR enantiomeric forms, which will interconvert by pyramidal inversion at tellurium, and in the crystal studied the RR/SS form was present.

Palladium(II) halide complexes $[\mathrm{PdL_2X_2}]$ have been reported for telluracyclopentane, benzotelluracyclopentane, and telluracyclohexane; all except the chlorocomplex of the last ligand appear to be trans isomers [151]. The corresponding platinum(II) complexes of telluracyclopentane have been prepared [148]. In $\mathrm{CH_2Cl_2}$ solution, ^{125}Te NMR studies showed that the $\mathrm{PtL_2Cl_2}$ (L = telluracyclopentane) complex exists as both cis and trans isomers, but the other halocomplexes and the palladium complexes contain only a single form, probably the trans isomer [148]. The structure of $[\mathrm{Pd}\{\overline{\mathrm{Te(CH_2)_3CH_2}}\}_2\mathrm{Cl_2}]$ has been confirmed as trans by an X-ray study [148]. The *trans*-$[\mathrm{Pd(TePh_2)_2Cl_2}]$ and *trans*-$[\mathrm{Pd_2(TePh_2)_2(\mu\text{-}Cl)_2Cl_2}]$ have been re-examined [152]. The brown $[\mathrm{N^nBu_4}][\mathrm{Pd(TeMe_2)X_3}]$ (X = Cl or Br) are prepared from $[\mathrm{N^nBu_4}]_2[\mathrm{Pd_2X_6}]$ and the appropriate quantity of $\mathrm{TeMe_2}$ in acetone [61].

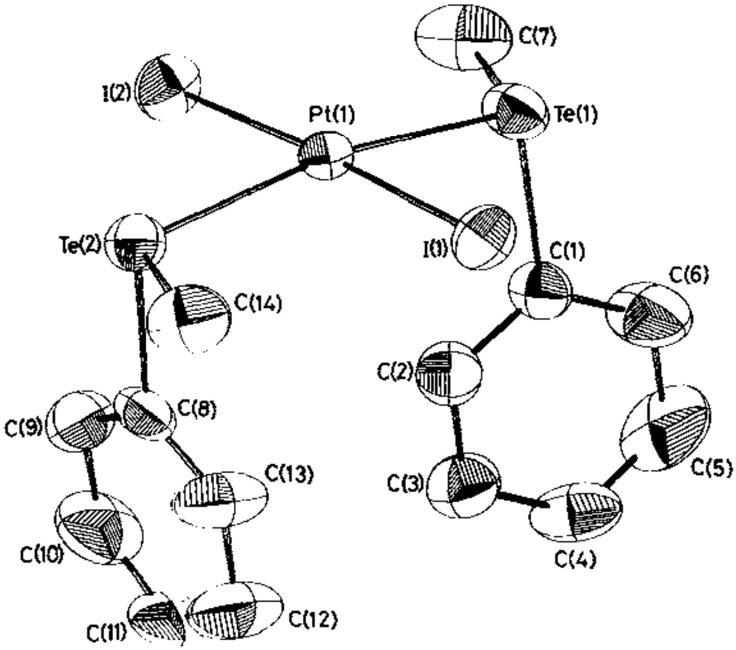


Fig. 23. Molecular structure of RR/SS-*trans*-[Pt(PhMeTe)$_2$I$_2$]. (From ref. 150 by permission of *Acta Crystallographica*.)

Silver acetate and perchlorate complexes with (p-MeOC$_6$H$_4$)$_2$Te, Ph$_2$Te and related ligands with a 1 : 1 stoichiometry have been described [153]; the structures are unclear.

Much effort is being devoted to the study of mixtures or adducts of group 12 halides or alkyls with group 16 alkyls, as precursors to II–VI electronic materials in chemical vapour deposition processes. Although many of the reports concentrate on the technology rather than the underlying coordination chemistry, some studies of the latter have been reported (see, for example, refs. 59, 154, and 155). Whilst the cadmium halide–R$_2$Te adducts have been described [2,3], there is little evidence for the existence of adducts between cadmium alkyls and R$_2$Te at room temperature or above, although weak adducts have been trapped out in argon matrices at 14 K [155]. Many mercury halide complexes of telluroethers were made early in the 20th century [3], but only the stoichiometries were established. Comparisons with the rich structural chemistry of mercury with other group 15 and 16 donor ligands suggests a variety of structures may be expected, but the only single-crystal X-ray study of a simple telluroether complex is [HgI$_2$(TePh$_2$)], which proves to be tetrameric (Fig. 24) with two different Hg environments [156]. Vibrational spectra for [HgX$_2$(TePh$_2$)], (X = Cl or Br) suggest a different structure to the iodide, but the detailed geometries are unclear. A 1 : 1 complex is formed between HgCl$_2$ and 2(2-pyridyl)phenyl(p-EtOC$_6$H$_4$)Te, but on heating this rearranges to [RHgCl·EtOC$_6$H$_4$TeCl] [157].

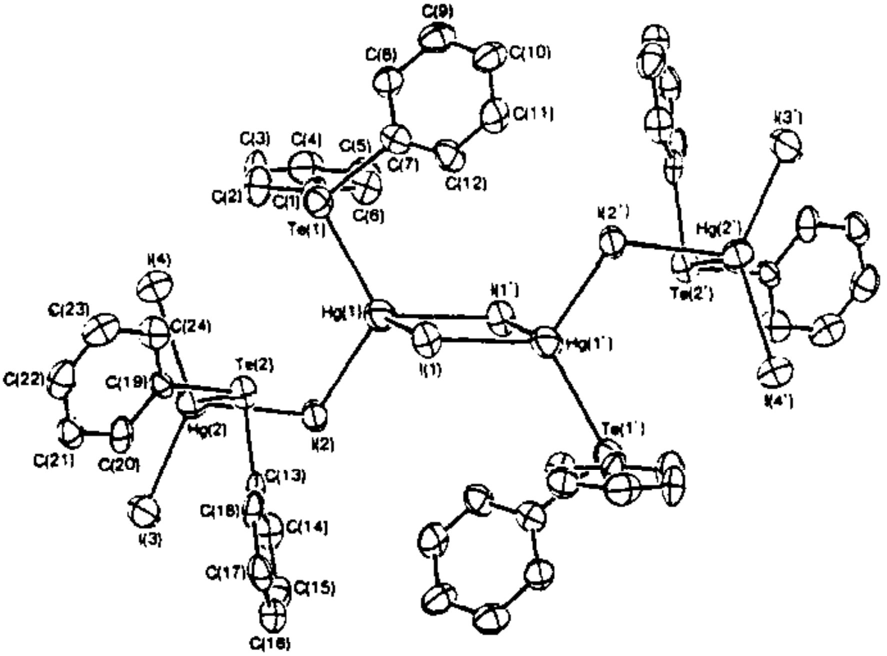


Fig. 24. The structure of the tetrameric [{$HgI_2(TePh_2)$}$_4$]. (From ref. 156 by permission of the American Chemical Society.)

(c) *High oxidation state complexes*

The differences between telluroethers and the lighter homologues are expected to be particularly noticeable as the metal centre becomes smaller and harder. Selenoether complexes have been prepared for Os(VI), Os(IV), Ir(IV), and Pt(IV) (q.v., above) but so far all attempts to prepare the telluroether analogues have failed [61,64–67].

(ii) *Ditelluroether complexes*

Ditelluroethers have been prepared only recently, and a very limited amount of their chemistry has been explored. It is convenient to deal with the chemistry of those ligands which produce five- or six-membered rings separately from the longer backboned ligands. Although $RTeCH_2TeR$ ligands can be prepared, no complexes have been reported, and as all attempts to obtain $RTeCH_2CH_2TeR$ have failed (q.v., Sect. B.), the shortest-chain ditellura-alkane complexes known are those of $RTe(CH_2)_3TeR$ (R = Me or Ph). Examples of complexes with five-membered chelate rings contain o-$C_6H_4(TeR)_2$ ligands.

Attempts to prepare complexes of $MeTe(CH_2)_3TeMe$ with nickel(II) or cobalt(II) halides were unsuccessful [158], but red-brown cobalt(III) complexes [Co{o-$C_6H_4(TeMe)_2$}$_2X_2$]BPh_4 (X = Br or I) were produced by air-oxidation of mixtures of the ligand, CoX_2, and $NaBPh_4$ in nitromethane [101]. ^{59}Co NMR and UV–visible spectroscopy showed that the iodocomplex was the trans isomer, but that the bromide was a mixture of cis and trans forms. The complexes decompose rapidly in moist air, and the ditelluroether is displaced by strong donor solvents. The reaction of *o*-$C_6H_4(TeMe)_2$ and $RTe(CH_2)_3TeR$ (R = Me or Ph) with iridium trichloride in ethanol gave insoluble fawn complexes $[Ir(L{-}L)Cl_3]$, probably halide-bridged polymers, which are converted into $[N^nBu_4][Ir(L{-}L)Cl_4]$ by boiling with N^nBu_4Cl in 2-methoxyethanol [102,149]. The $[N^nBu_4][Ir\{o\text{-}C_6H_4(TeMe)_2\}Br_4]$ is also known [149]. The ^{125}Te NMR spectra all contain two resonances consistent with the presence of meso and DL invertomers. Attempts to oxidise these Ir(III) anions chemically to Ir(IV) have failed, and cyclic voltammetric studies show that the oxidations are completely irreversible even with fast scans, indicating that the Ir(IV) species are not stable [102]. These results contrast with the isolation of Ir(IV) complexes with dithioether and diselenoether ligands [102,159]. Brown, paramagnetic osmium(IV) complexes $[Os(MeTe(CH_2)_3TeMe)X_4]$ (X = Cl, Br) are made by heating the ligand with Na_2OsX_6 in ethanol [160].

The largest number of complexes of these ligands are, as might be expected, with Pd(II) and Pt(II). The first examples were the yellow or orange $[M(RTe(CH_2)_3TeR)X_2]$ (R = Me, Ph; X = Cl, Br, I) obtained from $[M(MeCN)_2X_2]$ or $[MX_4]^{2}$ and the ligands; 2:1 complexes are not formed even with excess ligand [161]. Multinuclear (^1H, ^{195}Pt, and ^{125}Te) NMR studies revealed the presence of meso and DL invertomers, with the former the most abundant. Further details of the trends in the NMR data are in Sect. E. The structure of $[Pd\{meso\text{-}PhTe(CH_2)_3TeMe\}Br_2]$ is shown in Fig. 25 [161].

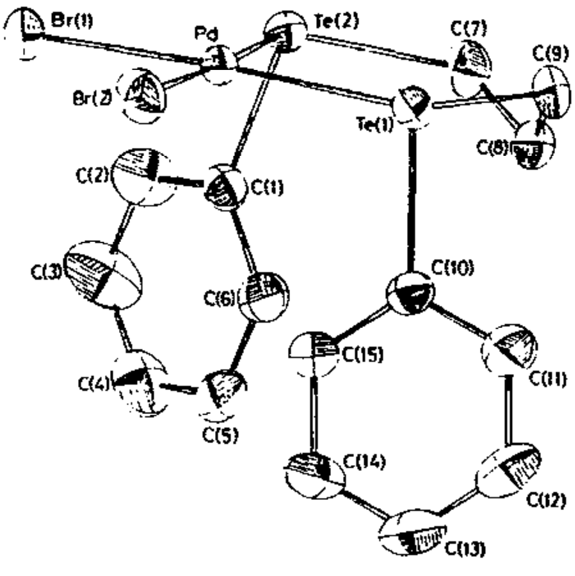
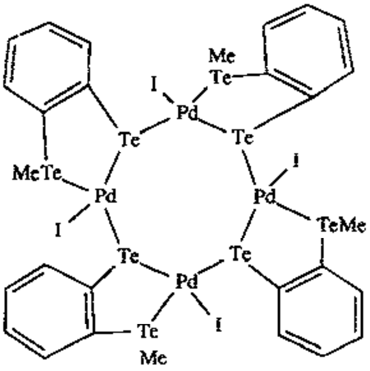


Fig. 25. The molecular structure of $[Pd\{meso\text{-}PhTe(CH_2)_3TePh\}Br_2]$. (From ref. 161 by permission of the American Chemical Society.)

Subsequently, the complexes of o-$C_4H_4(TeMe)_2$ [149] and o-$C_6H_4(TePh)_2$ [158] were obtained, although the complexes of the latter ligand proved too poorly soluble for NMR studies. Comparison of the ^{125}Te NMR coordination chemical shifts ($\delta_{complex}-\delta_{free\ ligand}$) in the complexes of the five- and six-membered chelate ring complexes, reveal large high-frequency shifts in the former which are characteristic of this ring size (Sect. E.). In contrast to the corresponding diselenoether complexes (q.v.), the Pt(II) ditelluroether complexes are not oxidised to Pt(IV) by halogens [161].

When solutions of [Pd{o-$C_6H_4(TeMe)_2$}I_2] in dimethylsulphoxide are heated for short periods or allowed to stand at room temperature for several days, monodemethylation of the ditelluroether occurred [162].



(20)

An X-ray study of the resulting complex showed it to be the novel tetramer **20**, and the environment about one of the four equivalent palladiums is shown in Fig. 26. There are three different Pd—Te distances: Pd(1)—Te(1) = 2.55, Pd(1)—Te(2) = 2.52, and Pd(1)—Te(8) = 2.60 Å. Re-alkylation does not occur on treatment with MeI.

Although attempts to prepare Pt(IV) halide complexes failed, three Pt(IV) complexes of the type [$PtMe_3I(L-L)$] (L—L = $RTe(CH_2)_3TeR$, and o-$C_6H_4(TeMe)_2$) were prepared from [{$PtMe_3I$}$_4$] and the ligand in $CHCl_3$ [163]. For these complexes, four isomers are expected (Fig. 7) meso-1, meso-2, and an NMR-indistinguishable DL pair. A combination of variable temperature NMR and 2D NMR experiments on these complexes provided the first quantitative data on the energy barriers for pyramidal inversion in coordinated telluroethers. These confirmed the results of earlier qualitative studies that the pyramidal inversion barriers decrease Te > Se > S for analogous complexes, the barrier energies in the series [$PtMe_3I${MeE $(CH_2)_3$EMe}] fall by ca. 12 kJ mol^{-1} from Te to Se, and by a further ca. 10 kJ mol^{-1} to S [163].

The ligand o-C_6H_4{$CH_2Te(p$-$C_6H_4OEt)$}$_2$, which would give seven-membered rings if it chelated to a metal, is reported to form intractable Pd(I) and Pt(I) complexes

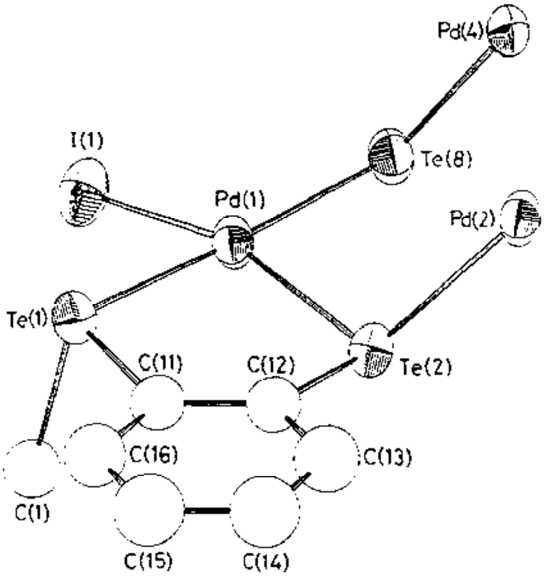


Fig. 26. The environment about one palladium atom in the structure of the tetramer $[\{Pd\{o\text{-}C_6H_4(TeMe)Te\}I\}_4]$. (From ref. 162 by permission of the American Chemical Society.)

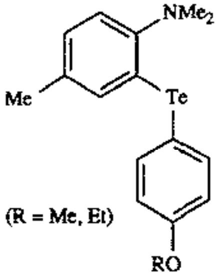
on reaction with $[MCl_4]^{2-}$ [33]. The formulations as M(I) complexes rest on C,H analytical data, and from the very limited spectroscopic data it seems more likely that the complexes contain M(II).

Palladium(II) and platinum(II) complexes $[M(L-L)X_2]$ ($X = Cl$, Br) have been prepared with long-chain ditelluroethers $(p\text{-}EtOC_6H_4)Te(CH_2)_nTe(p\text{-}EtOC_6H_4)$ ($n = 6$–10). The complexes with $n = 6$ are insoluble in common solvents and are probably ligand-bridged polymers. The other complexes appear to be a mixture of isomers, although the systems are not understood in detail [164]. The ^{125}Te NMR spectra show small high-frequency coordination shifts with two broad resonances in each complex, in the platinum cases without resolvable Pt–Te couplings at room temperature. Detailed studies of $[Pt(p\text{-}EtOC_6H_4Te(CH_2)_{10}Te\,p\text{-}EtOC_6H_4)Cl_2]$ show that the ^{125}Te NMR spectra exhibit significant variations in line-width with temperature, and at ca. 70°C $^1J(^{125}Te-^{195}Pt)$ couplings characteristic of cis and trans Te–Pt–Te arrangements are resolved, although whether these changes are reversible on cooling was not stated. The reported ^{195}Pt chemical shifts [164] are ca. 2000 ppm to high frequency of those of other platinum–telluroether complexes [149,161] and since platinum chemical shifts are mainly influenced by the donor atoms and the stereochemistry, and are insensitive to substituents on the ligand, this anomaly is difficult to explain. Some mercury(II) chloride complexes of these long-chain ligands were also described [164].

(iii) Hybrid telluroether complexes

A considerable number of complexes of hybrid telluroether ligands have been reported, mostly with Pd(II), Pt(II) and Hg(II). In view of the often-complicated coordination chemistry of hybrid ligands, it is unfortunate that, with three exceptions, the structures are based upon spectroscopic rather than crystallographic data.

The reactions of the sodium salts of 2-R-telluroethanols (R = 4-$MeOC_6H_4$ or 4-$EtOC_6H_4$) with Pd(II), Pt(II) or Hg(II) gave complexes $[\{M(RTeCH_2CH_2O)Cl\}_2]$ which are formulated as halide-bridged dimers on the basis of IR, ^1H and ^{13}C NMR data [165]. Halide-bridged dimeric complexes also appear to be formed by the (2-hydroxy-5-methylphenyl)aryltellurides (aryl = 4-$MeOC_6H_4$, 4-$EtOC_6H_4$ or Ph) with palladium(II), platinum(II) or mercury(II) chlorides, with the ligands binding as chelating monoanions, via the deprotonated phenol function and Te [166]. The bis(2-hydroxy-5-methylphenyl)telluride gives a 1:1 complex with $HgCl_2$ of unknown structure [166]. Complexes of telluroacetic $RTeCH_2CO_2H$ (R = Ph, 4-$MeOC_6H_4$, 4-$EtOC_6H_4$) [38] and tellurobenzoic acids *o*-(4-$EtOC_6H_4Te)C_6H_4CO_2H$ [167] have been described. The complexes of $RTeCH_2CH_2SMe$ (R = 4-$MeOC_6H_4$, 4-$EtOC_6H_4$) of type $[M(L{-}L)Cl_2]$ (M = Pd, Pt) are square planar with $TeSCl_2$ donor sets [37]. A variety of hybrid tellurium–nitrogen donor ligands have been studied. Mercury(II) halides from 1:1 complexes with the telluroamines $RTeCH_2CH_2NH_2$ and **22** (R = 4-$MeOC_6H_4$, 4-$EtOC_6H_4$) [36,168].



(**21**)

Spectroscopic data suggested that the latter bond as monodentates via the Te, and this was confirmed by an X-ray study of $[\{HgBr_2L\}_2]$ (L = **21**), which revealed the bromide-bridged dimer (Fig. 27) [168]. The structures of the telluroethylamine complexes were suggested to involve coordination via both N and Te [36]. Towards Pd(II) and Pt(II) the ligands **21** behave as N,Te chelates giving planar $[M(\mathbf{21})Cl_2]$ complexes [35], demonstrated most clearly by the presence of two ^1H NMR resonances (with satellites due to coupling to ^{195}Pt in the platinum case) for the coordinated NMe_2 groups. The inequivalence is due to the slow pyramidal inversion at tellurium, which results in two N–Me environments, syn or anti to the R–Te group.

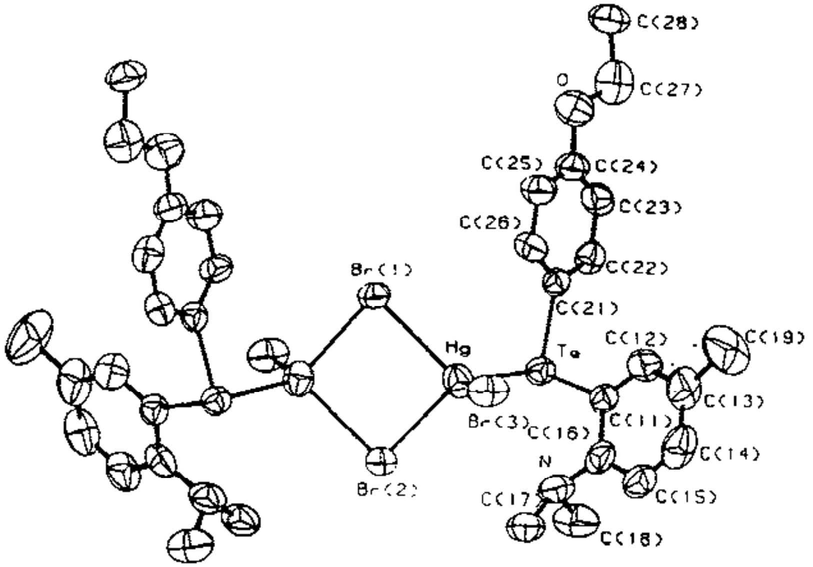
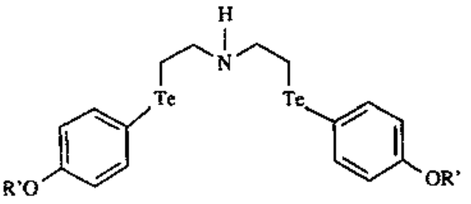


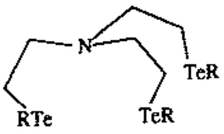
Fig. 27. Molecular structure of [{$HgBr_2$(p-$EtOC_4H_4$)(o-$Me_2NC_6H_3Me$)Te}$_2$]. (From ref. 168 by permission of Pergamon Press.)



(R' = Me, Et)

(22)

The potentially tridentate **22** give 1 : 1 complexes with $HgCl_2$, which are monomeric non-electrolytes, and probably contain a Te_2Cl_2 donor set around the tetrahedrally coordinated mercury [39]. The palladium(II) and platinum(II) complexes [M(**22**)Cl_2] are monomeric and non-electrolytes in chloroform, but exhibit varying conductances in more polar solvents [39]. The structures were suggested [39] to be five-coordinate with Te_2NCl_2 donor sets, but since neither Te nor N are known to favour five-coordination for these two metal centres, an alternative possibility is that they are planar ($TeNCl_2$) with fast exchange between free and bound tellurium groups in solution, coupled with some ionisation (and partial formation of a Te_2NCl donor set) in polar solvents. An X-ray study coupled with ^{125}Te and ^{195}Pt NMR studies in solution would be interesting.



(23)

The tetradentate $N(CH_2CH_2TeR)_3$ ($R = 4MeOC_6H_4$, $4\text{-}EtOC_6H_4$) (**23**) coordinate to HgX_2 ($X = Cl$, Br) via two telluriums, and in solution fast exchange involving all three tellurium centres is likely [40]. The linear tetradentate TeNNTe ligand (**5**) forms a 1 : 1 complex with $HgCl_2$ [42], the structure of which revealed coordination via the terminal telluriums, Hg–Te = 2.819(1), 2.769(1) Å, in a highly unusual 13-membered ring (Fig. 28). The ligand **5** also behaves as a Te_2 donor towards Pd(II), Pt(II) and Rh(III), although the detailed structures are unclear, and the platinum complex is reported to de-alkylate in solution [169].

The phosphine-telluroether (**4**) reacts with $K_2[Pt(SCN)_4]$ in aqueous acetone to give $[Pt(4)(SCN)_2]$, which, on recrystallisation form *N*,*N*-dimethylformamide, rearranged into the Magnus salt $[Pt(4)_2][Pt(SCN)_4]$ [34]. The X-ray structure of the latter reveals a trans planar structure (Fig. 29).

E. ^{77}Se AND ^{125}Te NMR STUDIES

Selenium-77 and tellurium-125 are both attractive nuclei for NMR studies, and although early studies relied upon indirect double resonance methods, with the

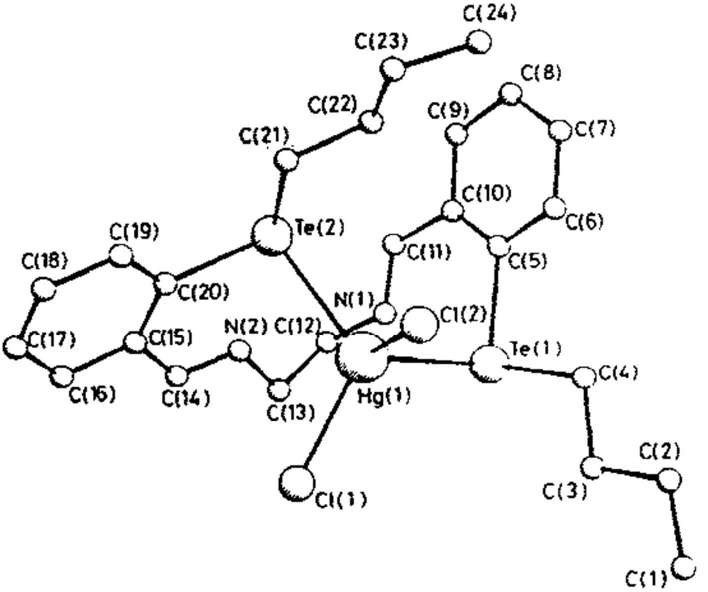


Fig. 28. Molecular structure of $[HgCl_2(5)]$. (From ref. 42 by permission of the Royal Society of Chemistry.)

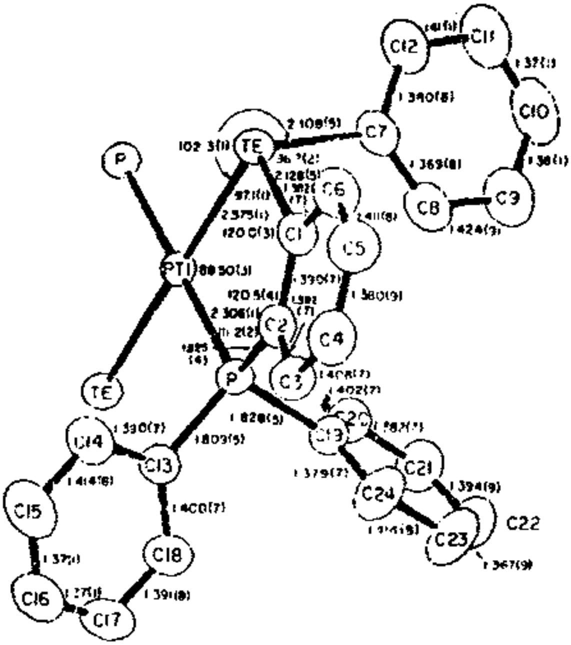


Fig. 29. The molecular structure of the cation in $[Pt(4)_2][Pt(CNS)_4]$. (From ref. 34 by permission of the American Chemical Society.)

advent of modern multinuclear FT instrumentation direct observation is straightforward. The essential properties of these two nuclei are summarised in Table 1. A recent review provides a good overview of NMR studies with both nuclei [170], and there is a relatively recent detailed review of NMR studies of organoselenium and organotellurium compounds [171]. This latter article provides detailed coverage of the relaxation times and chemical shift ranges for particular types of compound, and discusses the effects of concentration, temperature, and solvent upon the observed chemical shifts. Two useful observations are that for isostructural compounds the

TABLE 1

NMR properties [1]

	Spin	Natural abundance (%)	Receptivity[a]	Resonance frequency[b]	Reference[c]
^{77}Se	1/2	7.58	2.98	19.07	Neat Me_2Se
^{125}Te	1/2	6.99	12.5	31.55	Neat Me_2Te

[a] Relative to ^{13}C.

[b] Approximate resonance frequency when ^{1}H resonance frequency is 100 MHz.

[c] Due to the appreciable solvent dependence of their chemical shifts, care should be taken to refer data to neat Me_2Se or Me_2Te. See ref. 171.

ratio of the ^{125}Te : ^{77}Se chemical shifts are usually ca. 1.7–1.8, and that the coupling constants to ^{125}Te are ca. 2–3 times the corresponding coupling to ^{77}Se [171], although, of course, exceptions to both generalisations are known. Although a few complexes of selenium and tellurium ligands were studied in the early 1970s [172,173], a reasonable body of data has only become available in the last few years, and here we summarise these recent results and attempt to extract the key trends. It is reasonable at this point to enter the caveat that the available data are both limited and fragmented, and more extensive data when they become available may require some modifications to the conclusions below. It is convenient to discuss the data on monodentate and bidentate ligands separately.

(i) Complexes of monodentate selenoethers and telluroethers

The ^{77}Se and ^{125}Te NMR chemical shifts of the complexes are usually found to high frequency of those of the free ligands, and vary with the metal, its oxidation state, the trans ligand, and the other (cis) ligands in the coordination sphere. Small shifts are also observed on changing the solvent, although these appear to be considerably smaller than in the case of the free ligands.

Many of the [ML_2X_2] (M = Pd, Pt; X = halide, L = R_2Se, R_2Te) exist in both cis and trans forms in solution, readily detected by the presence of two δ(Se) or δ(Te) resonances [149,173,174] (Fig. 30). The differences in chemical shift are usually $\leqslant$ 30 ppm, and thus the chemical shift alone is an uncertain guide to isomer identification (for platinum complexes, the ^{195}Pt chemical shifts and the coupling constants

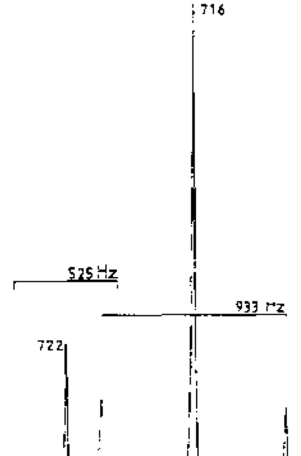


Fig. 30. The ^{125}Te NMR of [$Pt(Ph_2Te)_2Br_2$] in CH_2Cl_2 showing the presence of cis and trans isomers. (From ref. 175).

are much better indicators). The coordination shifts $(\delta_{\text{complex}} - \delta_{\text{ligand}})$ are usually greater for complexes of alkyl rather than aryl substituted ligands [149], and irrespective of the geometric isomer the δ(Se) and δ(Te) resonances shift to lower frequency $Cl > Br > I$, and to high frequency with metal $Pd > Pt$ [149]. The effect of changing oxidation state is also clear-cut: oxidative addition of halogen to $[Pt(Me_2Se)_2X_2]$ or $[Pt(Me_2Se)X_3]^-$ results in a large high-frequency shift in δ(Se) [62]. A much smaller high frequency shift was observed on oxidation of $[Pd(Me_2Se)X_3]^-$ to $[Pd(Me_2Se)X_5]^-$, which was ascribed to the weaker interaction of the ligand with the hard Pd(IV) centre. Note that a consequence of this is that, for the M(IV) complexes, the coordination shifts are $Pt > Pd$, the reverse of that observed for the M(II). For complexes $[ML_2X_2]$ of unsymmetrical ligands such as $RSeCH_2R'$ ($R =$ Ph, Me; $R' = SiMe_3$, $GeMe_3$) or MeTePh, extra complexity results from the presence of RR/SS and RS/SR enantiomers, which interconvert by pyramidal inversion. Providing inversion is slow, the enantiomers will be reflected by the presence of two closely spaced resonances (separated by $\leqslant$ ca. 3ppm) in the ^{77}Se or ^{125}Te NMR spectra [73,149] (an example is shown in Fig. 31).

In the complexes $[CpFe(CO)(EMe_2)L]^+$ ($E = Se$, Te, $L = PR_3$, AsR_3, SbR_3, SMe_2, etc.) the δ(Se) or δ(Te) vary with L in a systematic way, but curiously the δ(Te) are much greater than the "expected" $\delta(Se) \times 1.8$, indicating a much stronger interaction with the tellurium [45]. For other metal complexes, the data are too scattered to extract useful trends.

The one-bond coupling constant data for monodentate ligand complexes are mostly limited to couplings to ^{195}Pt. For $[PtL_2X_2]$, $[PtLX_3]^-$, and $[PtLX_5]^-$ complexes the $^1J(^{195}Pt-^{77}Se)$ and $^1J(^{195}Pt-^{125}Te)$ couplings decrease with X, $Cl > Br > I$ [62,73,149,173,174]. In the $[PtL_2X_2]$ for fixed X, the cis complexes have larger coupling constants than the trans, e.g. $^1J(^{195}Pt-^{125}Te)$ is 824 Hz in *cis*-$[Pt(Me_2Te)_2Cl_2]$ and 489 Hz in the trans isomer, and this is a reliable way of distinguishing the isomers when both are present [149,174]. When only one isomer is known, the evidence is less unequivocal. For example, the ca. 240 Hz coupling in the single geometric isomer observed for $[Pt(MePhTe)_2I_2]$, compared with ca. 825 Hz and ca. 490 Hz in *cis*- and *trans*-$[Pt(MePhTe)_2Br_2]$, repectively, does not for certain identify the geometry of the iodocomplex [149]. Oxidation to Pt(IV) results in a marked decrease in $^1J(^{195}Pt-^{77}Se)$, for example 670 Hz in $[Pt(Me_2Se)Cl_3]^-$ and 250 Hz in $[Pt(Me_2Se)Cl_5]^-$ [62,173]. An interesting observation, although based only upon two complexes, is that coordination of the second chalcogen lone pair, as in the dimeric $[X_3Pt(\mu\text{-}TeMe_2)PtX_3]^{2-}$, results in a large increase in the one-bond couplings, e.g. 5923 Hz in the dimer with $X = Cl$, and 1553 Hz in $[Pt(Me_2Te)Cl_3]^-$ [173].

(ii) Complexes of di- and poly-selenoethers and telluroethers

Many of the observations above are relevant to the spectra of the corresponding complexes of bidentate ligands. The added complication is that a chelated bidentate

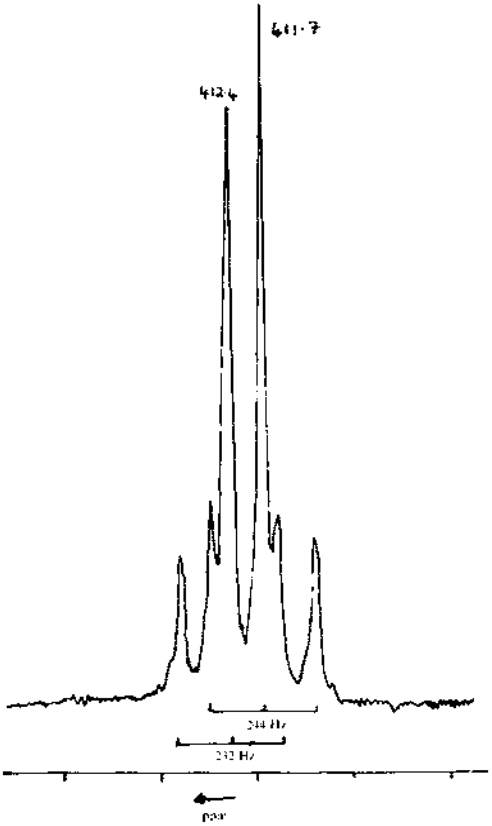


Fig. 31. The ^{125}Te NMR spectrum of *trans*-[Pt(MeTePh)$_2$I$_2$] showing the two resonances (with ^{195}Pt satellites) due to RS/SR and RR/SS enantiomers [174a].

RSe—SeR or RTe—TeR exists in meso and DL forms (Fig. 6) and, provided pyramidal inversion is slow on the NMR timescale [5], both forms will be seen in the NMR spectra (Fig. 32 is a typical example). The ^{77}Se, ^{125}Te (and, where appropriate, a metal nucleus such as ^{195}Pt) spectra are much easier ways of identifying the invertomers than the corresponding ^{1}H spectra due to the much greater chemical shift ranges. In cases where pyramidal inversion is fast at ambient temperatures, e.g. [Pd{MeSe(CH$_2$)$_3$SeMe}X$_2$] [100], only a single ^{77}Se resonance is observed for each complex, although on cooling the solution, the inversion rate is slowed, and two resonances appear. The meso:DL ratio depends upon the metal, the co-ligands, and the particular diselenoether or ditelluroether present. It appears [100,161] that, for RSeCH$_2$CH$_2$SeR five-membered ring complexes of planar coordinated Pt(II) or Pd(II), the DL form has the higher frequency ^{77}Se NMR resonance and is the more abundant form ($\leqslant$4:1), whilst in six-membered rings produced by RSe(CH$_2$)$_3$SeR or RTe(CH$_2$)$_3$TeR, the meso has the higher frequency resonance and predominates, the meso:DL ratio increasing Se<Te. This presumably reflects subtle ring strain and

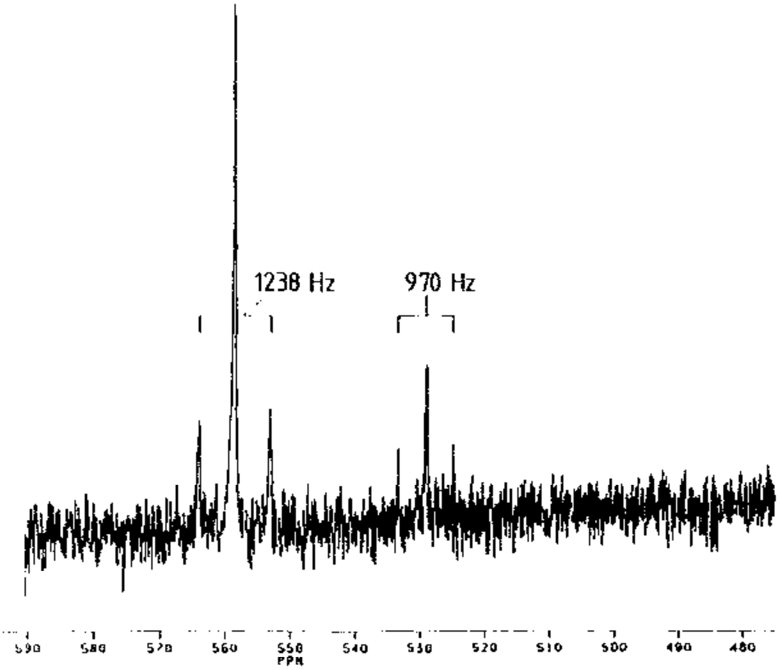


Fig. 32. A typical ^{125}Te NMR spectrum of a chelating ditelluroether complex showing the resonances of the meso and DL enantiomers. ([Pt(PhTe(CH$_2$)$_3$TePh)Br$_2$] from ref. 175.)

orientational effects of the free lone pairs. The effect of the trans halide co-ligands is also different in five- and six-membered rings, the shifts moving to higher frequency with heavier halogen in the five-membered ring complexes, but to lower frequency with heavier halogen in the six-membered ring species. The data are less complete and isomer identification harder in complexes of ligands with o-C_6H_4 backbones [100,149], but it appears that, along the donor series S→Se→Te, the relative abundance of the meso form increases, and in the telluroethers it is the major enantiomer.

For platinum complexes, the $^1J(^{195}Pt-^{77}Se)$ or $^1J(^{195}Pt-^{125}Te)$ coupling constants differ between the meso and DL enantiomers, usually (but not exclusively) being greater in the meso isomer, but since the coupling constants will reflect, among other factors, the orientations of the free lone pairs, a direct correlation with bond strength is over-simplistic.

In six-coordinate complexes $[M(L-L)X_4]^{n-}$, the data are limited to Pt(IV) ($n=0$), Ir(III) or Rh(III) ($n=1$) [62,100,149,161] but similar trends are discernible. It is notable that, in the Pt(IV) complexes, the low-frequency shift of δ^{77}Se with trans halogen Cl→Br is now seen in *both* five- and six-membered chelate ring complexes. For bis(ligand) complexes such as *trans*-$[Rh(MeSeCH_2CH_2SeMe)_2Cl_2]^+$ the number of possible isomers when inversion is slow is five, with eight selenium environments, and, in practice, six doublets (due to $^1J(^{103}Rh-^{77}Se)$) were observed [100]. The spectrum of the cis isomer is even more complex with eight major resonances observed lying in two groups probably due to $Se_{trans\text{-}Cl}$ and $Se_{trans\text{-}Se}$, although more examples are needed on these complicated systems before reliable trends can be identified.

Extensive studies by Abel and Orrell and their co-workers have been concerned with complexes of type $[PtMe_3X(L-L)]$, and here three invertomers (meso-1, meso-2, and an NMR-indistinguishable DL pair in which the two RSe(Te) groups *are* distinguishable) are possible (Figs. 7 and 33). The ^{77}Se and ^{125}Te NMR studies are concentrated in three papers [92,93,163]. Generally, the $^1J(^{195}Pt-^{77}Se)$ coupling constants increase with the heavier halogen in the cis position, and the $\delta(^{77}Se)$ resonances move to low frequency with heavier halogen. The coupling constants vary with the invertomer and generally decrease with increasing chelate ring size.

One particularly notable observation is that the magnitude of the coordination shift in the ^{77}Se or ^{125}Te NMR spectra depends upon ring size [92,100,149]. Garrou [176] systematised the effect of chelate ring size in diphosphine complexes upon the ^{31}P NMR chemical shifts in terms of a *chelate ring parameter*. Essentially, the coordination shift Δ is defined as

$$\Delta = \delta_{\text{complex}} - \delta_{\text{free ligand}}$$

and the chelate ring parameter ΔR as

$$\Delta R = \Delta_{\text{chelate complex}} - \Delta_{\text{equivalent monodentate ligand complex}}$$

The "equivalent monodentate ligand complex" is that of the nearest structurally

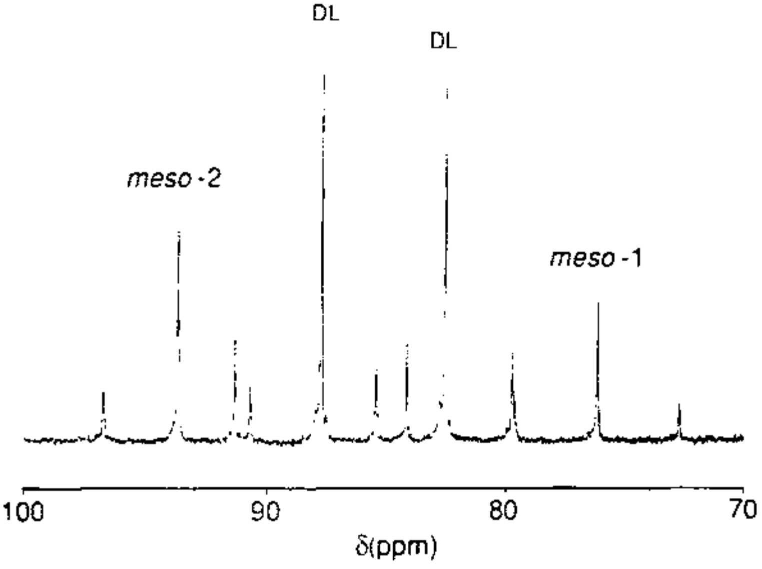


Fig. 33. The ^{125}Te NMR spectrum of $[Pt\{MeTe(CH_2)_3TeMe\}Me_3I]$ showing the three enantiomers meso-1, meso-2, and DL. Note that the two MeTe groups are inequivalent in the DL form, hence the two resonances. (From ref. 163 by permission of the Royal Society of Chemistry.)

related ligand, e.g. for $Ph_2PCH_2CH_2PPh_2$ the "equivalent monodenate" would be Ph_2EtP, and thus one would compare the ^{31}P NMR data from $[Pt(Ph_2PCH_2CH_2PPh_2)Cl_2]$ with that in *cis*-$[Pt(Ph_2EtP)_2Cl_2]$ using the above relationships. Garrou observed that, in five-membered chelate rings, ΔR was large and positive, whilst in four- or six-membered rings (and also in larger rings), ΔR is small and may be positive or negative. The theoretical explanation of the "chelate ring effect" is unclear [177], but its practical value in establishing chelation (compared with bridging or monodenate behaviour) for five-membered rings is clear. Similar relationships have been found in ^{77}Se and ^{125}Te NMR data [92,100,149], where the five-membered rings have very large and positive ΔR values, whereas in six-membered rings, the ΔR values are small. It appears that the magnitude of the effect is sufficiently great, that even when the data on the "equivalent monodenate" are unavailable, the very large coordination shifts, Δ, may themselves be a good guide to the presence of a five-membered chelate ring [149]. Data on four-membered chelate rings have not been reported.

The ^{77}Se chemical shifts are also useful in assigning stereochemistry and identifying invertomers in complexes of polydenate ligands (no examples of tellurium polydentates have been reported); see refs. 113 and 115 for examples.

Observation of ^{125}Te NMR spectra from solid telluroether complexes does not seem to have been reported, and the relatively low sensitivity and wide chemical shift range constitute considerable experimental challenges, even with current developments in CP-MAS techniques. However, for ^{77}Se, CP-MAS spectra have been reported for the several selenoether macrocycles [18] and correlated with the X-ray structures of the free ligands. Similar data have also been obtained for the Cu(I) and $Hg(CN)_2$ complexes of $16Se_4$ [117].

F. SOME COMPARISONS

Intensive research efforts have been devoted to studying the bonding of tertiary phosphines to transition metals, and the subtle interplay of steric and electronic factors have been reviewed on a number of occasions (see ref. 182 and refs. cited therein). Corresponding factors in neutral group 16 donor ligands have attracted surprisingly little effort, and most of the limited work is restricted to thioethers. In their review published in 1981, Murray and Hartley [2] summarised the relevant data on the structures and bonding in metal thio-, seleno- and telluroether complexes, although the data dealing with the heavier donor ligands were very limited (e.g. only four X-ray structures had been reported). The past ten years have seen a considerable improvement, and there are now some 50 X-ray studies reported (see Table 2). Nonetheless, it is true that our understanding of the $M-SeR_2$ or $M-TeR_2$ bonding is still limited, not least by the scattered nature of much of the data, which at present precludes the required detailed comparisons. In this section we summarise the

TABLE 2

X-Ray structural data

Complex	d(M–Se/Te) (Å)	Fig.[a]	Ref.
$[W(CO)_5(\overline{SeCPh_2CH_2CMeCMeCH_2})]$	2.674(1)	5	81
$[W(CO)_4\{1,1'\text{-}(MeSeC_5H_4)_2Fe\}]$	2.674(4), 2.692(4)	12	107
$[\{Mn(MeCp)(CO)_2\}_2SeMe_2]$	2.375(1), 2.378(1)	1	53
$[Re(CO)_3I(MeSeCH_2CH_2SeMe)]$	2.593(1), 2.597(1)	8	89
$[Ph_4As][Ru(MeSeCH_2CH_2SeMe)Cl_4]$	2.446(1), 2.457(1)	10	103
$[HRuCo_3(CO)_{11}(SeMe_2)]$	Co–Se 2.390 (1)	2	56
$[HRuCo_3(CO)_{10}(SeMe_2)_2]$	Co–Se 2.392(2), 2.392(2)	2	56
$[Co(en)_2(H_2NCH_2CH_2SeMe)][ClO_4]_3$	2.386(1)		120
$[\{HRuRh_3(CO)_9\}_2(SeMe_2)_3]$	Rh–Se 2.551(6), 2.567(6)	2	56
$[Ni(H_2O)_2(1)][ClO_4]_2$	2.479(2), 2.477(2)	19	20
$[Pd(Et_2Se)_2Cl_2]$	2.424(7)		178
$[Pd(Me_3SiCH_2SeMe)_2Cl_2]$	2.429(1)	2	73
$[Pd(^iPrSeCH_2CH_2Se^iPr)Cl_2]$	2.40(1), 2.36(1)		179
$[Pt(\overline{SeCH_2CH_2OCH_2CH_2})_2Br_2]$	2.430(2)		180
$[Pt(Me_3GeCH_2SeMe)_2Cl_2]$	2.418(2)		73
$[Pt(\overline{C_6H_4SeC_6H_4N}H)_2Cl_2]$	2.376(2), 2.400(2)	-	88
$[Pt\{SeC_6H_2(OMe)_2\}_2Cl_2]$	2.374(5), 2.384(2)	-	105
$[PtMe_3Cl(MeSeCHCHSeMe)]$	2.532(4), 2.525(4)		93
$[PtMe_3I(MeSeCHCHSeMe)]$	2.531(2), 2.535(3)		93
$[PtCl_4(o\text{-}C_6H_4(SeMe)_2)]$	2.432(2), 2.441(1)	9	62
$[\{PtMe_3Cl\}_2\{(SeC_6H_2(OMe)_2\}_2]$	2.569(1), 2.620(1)	11	106
$[Cu(16Se_4)][SO_3CF_3]$	2.42–2.52	18	117
$[Cu(16Se_4)][SO_3CF_3]_2$	2.4593(6), 2.4554(6)	17	116
$[Ag\{(CH_2Se)_3\}_2][AsF_6]$	2.78(1)–3.05(1)	14	112
$[AuCl(Ph_2Se)]$	2.378(1)		85
$[AuCl_3(Ph_2Se)]$	2.445(1)		85
$[\{HgCl_2(Me_3SiCH_2SeMe)\}_2]$	2.528(2)	4	74
$[\{HgBr_2(Me_3SiCH_2SeMe)\}_2]$	2.558(4)		74
$[\{HgI_2(Me_3SiCH_2SeMe)\}_2]$	2.687(2)		74
$[HgCl_2(\overline{SeCH_2CH_2CH_2CH_2})]$	2.535(1)		79
$[HgBr_2(\overline{SeCH_2CH_2CH_2CH_2})]$	2.648(1)	-	80
$[HgI_2(\overline{SeCH_2CH_2CH_2CH_2})]$	2.688(1), 2.718(1)		80
$[Hg(CN)_2(16Se_4)]$	3.437(1), 3.379(1)		117
$[HgCl_2\{SeC_6H_2(OMe)_2\}_2]$	3.053(4), 3.058(4)		105
$[Cr(CO)_5\{(p\text{-}MeOC_6H_4)_2Te\}]$	2.684(1)	20	90
$[Fe(Cp)(CO)_2TeMe_2]BF_4$	2.533(1)	-	44
$[HRuCo_3(CO)_{11}TeMe_2]$	Ru–Te 2.666(2)	21	143
$[HRuCo_3(CO)_{10}(TeMe_2)_2]$	Ru–Te 2.68(1)		
	Co–Te 2.52(1)	21	143
$[HRuCo_3(CO)_{11}(TePh_2)]$	Co–Te 2.539(1)	21	143
$[Os_3(CO)_{11}\{Te(c\text{-}C_6H_{11})_2\}]$	2.6704(11)		142
$[Pd\{Te(CH_2CH_2CH_2SiMe_3)_2\}_2(SCN)_2]$	2.606(1)		181
$[PdCl_2(\overline{TeCH_2CH_2CH_2CH_2})_2]$	2.593(3)	-	148
$[PdBr_2(MeTeCH_2CH_2CH_2TeMe)]$	2.528(1), 2.525(1)	25	161

TABLE 2 (*continued*)

Complex	d(M Se/Te) (Å)	Fig.[a]	Ref.
$[\{Pd(o\text{-}C_6H_4(TeMe)Te)I\}_4]$	2.540(2)–2.554(2)	26	162
$[Pt(MePhTe)_2I_2]$	2.578(1), 2.586(1)	23	150
$[Pt(o\text{-}C_6H_4(TePh)(PPh_2))_2][Pt(SCN)_4]$	2.575(1)	29	34
$[CuCl(TeEt_2)]$	2.535(1), 2.625(1)	22	144
$[HgI_2(Ph_2Te)]$	2.753(1)	24	156
$[\{HgBr_2(22)\}_2]$	2.728(1)	27	167
$[HgCl_2(5)]$	2.819(10), 2.769(1)	28	42

[a] Figure number in text.

thermodynamic, kinetic, structural, and spectroscopic data which bear on the nature of the bonding in heavy group 16 donor ligand–transition metal complexes.

Compared with group 15 ligands, steric effects are less important here, since the group 16 donor carries only two R groups. Although seleno- and telluroethers with very bulky R groups have been prepared, their coordination chemistry is unexplored and for the complexes of the small ligands described in previous sections, steric effects would not be expected to be particularly significant. Conversely, the presence of a second lone pair is a complication in that it may potentially take part in π-donation to the metal, or may be a source of π-repulsion. The problems about establishing π-acceptor behaviour, so familiar in tertiary phosphine complexes [182], are present in group 16 analogues. The acceptor orbital is usually assumed to be S(Se/Te)nd, but this proposal is open to the same criticism levelled against it in group 15, i.e that the nd orbital energy is too high to contribute significantly to the bonding. Analogous to recent proposals for metal phosphines [182], the acceptor orbitals could be mainly (or exclusively) S(Se/Te)–C σ^* combinations.

Thermodynamic data for a variety of Pd(II) and Pt(II) complexes have been compiled by Mortimer and co-workers [183,184]. Standard enthalpies of formation (ΔH_f/kJ mol^{-1}) for *trans*-$[PdL_2Cl_2]$ are $L = SEt_2$ -564; $SeEt_2$ -529; $TeEt_2$ -764; PEt_3 -644; with mean bond dissociation energies D(Pd–E) ca. 200 ± 10 kJ mol^{-1} for Pd–S, Pd–Se, and Pd–Te bonds. A number of studies of the displacement of carbon monoxide by ER_2, or of ER_2 by $E'R_2$ or other ligands, in low valent metal carbonyl complexes have been reported [43–46, 53, 77]. Based upon the kinetics and products of the displacements, the effects of various ER_2 upon the ν(CO) frequencies, and the ^{13}C NMR spectroscopic data, the relative stability of the chalcogenoether complexes was established to be $TeR_2 > SeR_2 > SR_2$ ($> OR_2$), which may be compared with the usual order in group 15 of $PR_3 > AsR_3 > SbR_3 > NR_3 > BiR_3$. The results were also interpreted in terms of the M–ER_2 bond being predominantly σ in character, with little or no π component. Schumann et al. [44] have stressed the importance of separating the thermodynamic and kinetic factors in such studies (i.e.

bond stability vs. lability) and have reported structural data for $[CpFe(CO)_2L]^+$ ($L = SMe_2$, $SeMe_2$, $TeMe_2$) and carried out extended Hückel MO calculations on this series of complexes. These confirmed the inertness and stability of the Fe—E bonds lay in the order $Te \gg Se > S > O$. Comparable calculations on group 15 analogues, and upon the model $Fe-EH_3$ systems where the second lone pair was protonated, were consistent with negligible π bonding in the group 16 complexes. The electronegativity of the group 16 donor atoms (Pauling scale S (2.58), Se (2.55), Te (2.10), cf. P (2.19)) are consistent with increased σ donor power as group 16 is descended, and at least in low oxidation state metal complexes where the spatial extension of the metal d orbitals is greatest, overlap with the larger Te σ orbital will be adequate.

In medium to high oxidation states, the limited electrochemical data [64-66,102] suggest that selenoethers form stronger bonds than the corresponding thioethers, but that the telluroether analogues are much less stable and often cannot be isolated by chemical syntheses. The most obvious rationalisation here is in terms of poor orbital match both in size and energy between the large, soft tellurium σ orbital and the contracted metal d orbitals. The stability $Se > S$ is consistent with the reduced electronegativity and hence better donation by the selenium.

The available X-ray studies of selenoether and telluroether complexes (Table 2), show that the coordinated chalcogenoethers have pyramidal geometries, and the majority have ER_2 groups coordinated to a single metal centre. A small number of cases have been reported [53,144] where the chalcogenoether behaves as a four-electron bridging group (μ^2-), utilising both lone-pairs. The bond length data (Table 2) in principle should also provide evidence about the nature of the $M-ER_2$ bond. In practice, the wide range of complexes makes detailed comparisons difficult, and we arrive at the cautious conclusion that the bond lengths are similar to, or slightly shorter than, those expected for single bonds on the basis of the appropriate covalent radii. This is consistent with the ligands behaving as σ donors, with small or negligible π components. Even when X-ray data are available on a series of complexes, the interpretation of the results in terms of the bonding may be far from straightforward. For example in the Hg(II) complexes, $[HgX_2(Me_3SiCH_2SeMe)_2]$ or $[HgX_2(\overline{SeCH_2CH_2CH_2CH_2})_2]$ where $X = Br$ or I (see Table 2), the Hg—Se bond lengths are significantly longer in the iodides than the bromides. This probably reflects poorer Lewis acid behaviour of the HgI_2 compared with $HgBr_2$ (weaker σ acceptance). Certainly π backbonding is unlikely in the d^{10} mercury(II). The relative trans influence of SeR_2 or TeR_2 ligands is evident in the X-ray data, and are less than PR_3, but greater than Cl^-. The bond length data on the $[\{Pd(o\text{-}C_6H_4(TeMe)Te)I\}_4]$ complex are consistent with a trans influence $RTe > R_2Te$, as would be expected [162].

Finally, we note that surprisingly few new examples of metal complex mediated Se(Te)—C bond fission (dealkylation) have been reported, although there is increasing interest in RSe^- and RTe^- as ligands made by other routes.

G. USES

Current interest in new electronic materials and their fabrication by various chemical vapour deposition processes has stimulated research into the synthesis of ultra-pure R_2Se and R_2Te and into the chemistry of their group 12 halide or alkyl adducts, which are potential precursors for II–VI semi-conductors. Relatively little of this research has been published, and most of that which has is in the patent literature and contains very limited chemical information. It is far from clear that adducts $R_2Se(Te)/Zn(Cd)R'_2$ rather than mixtures of the constituents are present in the vapour phase in most of these systems. Certainly a detailed spectroscopic study of CdR_2–$TeMe_2$ systems [155], found no evidence for adduct formation in the gas phase. Typical examples of reports from the patent literature are of ZnSe [185–188] and of $ZnS_{1-x}Se_x$ [189–193] film manufacture. A different potential application is in photography, where some Pd and Cu telluroether complexes have been reported to have imaging properties [194].

ACKNOWLEDGEMENTS

We thank the Royal Society of Chemistry, the American Chemical Society, the Canadian Chemical Society, *Acta Crystallographica*, *Gazzetta Chimica Italiana*, Pergamon Press, Chapman and Hall, and Elsevier Sequoia SA for permission to reproduce the figures.

NOTE ADDED IN PROOF

We list below relevant papers which appeared after submission of the main text.

(a) The X-ray structure of $[CpFe\{P(OPh)_3\}_2TeMe_2]BF_4$ (Fe–Te = 2.5394(11) Å) [195].

(b) The X-ray structure of *cis*-$[PtCl_2(p\text{-}EtOC_6H_4TeCH_2CH_2SMe)]$ (Pt–Te = 2.514(1) Å [196].

(c) The synthesis of 1,2-bis(R-telluro)ethenes [197].

(d) Fragmentation of 2-(2′-pyridyl)phenyl(p-$EtOC_6H_4$)Te on reaction with Pd(II) and Pt(II) salts [198].

(e) The addition of vinyl ethers to selenocarbonyl complexes of tungsten to form selenetanes [199].

(f) The reaction of tungsten selenetanes with $SeCN^-$ and $TeCN^-$ [200].

(g) The reaction of palladium(II) acetate with Se^iPr_2 and arenes to form polynuclear palladium complexes [201].

(h) The reaction of $Se(CH_2CH_2CH{=}CH_2)_2$ (L) with Rh(I) to yield a trimer $[\{RhLCl\}_3]$ in which TBP Rh centres are linked by asymmetric selenium bridges [202].

(i) The reaction of $Se(CH_2CH_2CH{=}CH_2)_2(L)$ with $[Pt(Me_2S)_2Me_2]$ to give $[PtLMe_2]$, and the formation of $[Pt_2Me_4(\mu\text{-}L)]$ in which the bridging selenium centre is tetrahedrally coordinated (Pt_2C_2) [203].

(j) The synthesis of *trans*-$[Ru(PhSeCH_2CH_2SePh)_2X_2]BF_4$ (X=Cl, Br) and *trans*-$[Ru(MeSeCH_2CH_2SeMe)_2Br_2]BF_4$ [204].

(k) Solid state ^{13}C NMR spectroscopic studies of the structure and dynamics of $[CpFe(CO)_2(EMe_2)]BF_4$ (E=S, Se, Te) [205].

(l) Rhodium(I) and rhodium(III) complexes of the hybrid ligands $HN(C_2H_4TeAr)_2$ and 1-(NMe_2)-2-(TeAr)-4-MeC_6H_3 (Ar = 4-$MeOC_6H_4$ or 4-$EtOC_6H_4$) [206].

REFERENCES

1 J. Mason (Ed.), Multinuclear NMR Plenum Press, New York, 1987.
2 S.G. Murray and F.R. Hartley, Chem. Rev., 81 (1981) 365.
3 H.J. Gysling, Coord. Chem. Rev., 42 (1982) 133.
4 H.J. Gysling, in S. Patai and Z. Rappoport (Eds.), The Chemistry of Organic Selenium and Tellurium Compounds, Vol 1, Wiley, New York, 1986. p. 679.
5 E.W. Abel, S.K. Bhargava and K.G. Orrell, Prog. Inorg. Chem., 32 (1984) 1.
6 K.G. Orrell, Coord. Chem. Rev., 96 (1989) 1.
7 D.L. Klayman and W.H.H. Gunther (Eds.), Organic Selenium Compounds, Wiley, New York, 1973.
8 K.J. Irgolic, The Organic Chemistry of Tellurium, Gordon and Breach, New York, 1974.
9 E.E. Aynsley, N.N. Greenwood and J.B. Leach, Chem. Ind., (1966) 379.
10 D.J. Gulliver, E.G. Hope, W. Levason, S.G. Murray, D.M. Potter and G.L. Marshall, J. Chem. Soc. Perkin Trans. 2, (1984) 429.
11 A.D. Westland and L. Westland, Can. J. Chem., 43 (1965) 426.
12 L.M. Kataeva, E.G. Kataeva and D.Y. Idiyatullina, Zh. Strukt. Khim., 7 (1966) 380.
13 L. Brandsma, Recl. Trav. Chim. Pays Bas, 83 (1964) 307.
14 E.G. Hope, T. Kemmitt and W. Levason, J.Chem.Soc. Perkin Trans. 2, (1987) 487.
15 R.V. Honeychuck, M.O. Okoroafor, L-H. Shen and C.H. Brubaker. Jr., Organometallics, 5 (1986) 482.
16 E.W. Abel, K. Kite and P.S. Perkins, Polyhedron, 5 (1986) 1459.
17 W. Levason, C.A. McAuliffe and S.G. Murray, J. Chem. Soc. Dalton Trans., (1976) 269.
18 R.J. Batchelor, F.W.B. Einstein, I.D. Gray, J.-H. Gu, B.D. Johnson, and B.M. Pinto, J. Am. Chem. Soc., 111 (1989) 6582.
19 T. Kumagai and S. Akabori, Chem. Lett., (1989) 1667.
20 S. Muralidharan, M. Hojjatie, M. Firestone and H. Freiser, J. Org. Chem., 54 (1989) 393.
21 G. Dyer and D.W. Meek, Inorg. Chem., 6 (1967) 149; J. Am. Chem. Soc., 89 (1967) 3983.
22 M. Tiecco, L. Testaferri, M. Tingoli, D. Chianelli and M. Montanucci, J. Org. Chem., 48 (1983) 4289.
23 T. Kemmitt and W. Levason, Organometallics, 8 (1989) 1303.
24 E.W. Abel, K. Kite, K.G. Orrell, V. Sik and B.L. Williams, J. Chem. Soc. Dalton Trans., (1981) 2439.
25 E.W. Abel, S.K. Bhargava, K. Kite, K.G. Orrell, V. Sik and B.L. Williams, J. Chem. Soc. Dalton Trans., (1982) 583.
26 C.H.W. Jones and R.D. Sharma, Organometallics., 5 (1986) 805.

27 K.G.K. De Silva, Z. Monsef-Mirzai and W.R. McWhinnie, J. Chem.Soc. Dalton Trans., (1983) 2143.

28 E.G. Hope, T. Kemmitt and W. Levason, Organometallics, 7 (1988) 78.

29 H.M.K.K. Pathirana and W.R. McWhinnie, J. Chem. Soc. Dalton Trans., (1986) 2003.

30 E.G. Hope, T. Kemmitt and W. Levason, Organometallics, 6 (1987) 206.

31 N. Petragnani and V.G. Toscano, Chem. Ber., 103 (1970) 1652.

32 J.B.S. Bonilha, N. Petragnani and V.G. Toscano, Chem. Ber., 111 (1978) 2510.

33 H.M.K.K. Pathirana, W.R. McWhinnie and F.J. Berry, J. Organometal. Chem., 312 (1986) 323.

34 H.J. Gysling and H.R. Luss, Organometallics., 3 (1984) 596.

35 A.K. Singh, V. Srivastava and B.L. Khandelwal, Polyhedron, 9 (1990) 495.

36 A.K. Singh and V. Srivastava, Phosphorus, Sulfur, Silicon. Relat. Elem., 47 (1990) 471.

37 A.K. Singh and V. Srivastava, J. Coord. Chem., 21 (1990) 269.

38 A.K. Singh, S. Thomas and B.L. Khandelwal, J. Coord. Chem., 21 (1990) 71.

39 A.K. Singh, V. Srivastava and B.L. Khandelwal, Polyhedron., 9 (1990) 851.

40 A.K. Singh and V. Srivastava, J. Coord. Chem., 21 (1990) 39.

41 W. Levason and B. Sheikh, J. Organometal. Chem., 209 (1981) 161.

42 N. Al-Salim, T.A. Hamor and W.R. McWhinnie, J. Chem. Soc. Chem. Commun., (1986) 453.

43 N. Kuhn and H. Schumann, J. Organomet. Chem., 276 (1984) 55.

44 H. Schumann, A.A. Arif, A.L. Rheingold, C. Janiak, R. Hoffmann and N. Kuhn, Inorg. Chem., 30 (1991) 1618.

45 N. Kuhn, H. Schumann and E. Zauder, J. Organomet. Chem., 327 (1987) 17.

46 N. Kuhn and H. Schumann, Inorg. Chim. Acta, 116 (1986) L11.

47 N. Kuhn, H. Schumann, M. Winter and E. Zauder, Chem. Ber., 121 (1988) 111.

48 H. Schumann, J. Organomet. Chem., 304 (1986) 341.

49 N. Kuhn and M. Winter, J. Organomet. Chem., 249 (1983) C28.

50 N. Kuhn, H. Brueggemann, M. Winter and V.M. DeBellis, J. Organomet. Chem., 320 (1987) 391.

51 N. Kuhn, H. Schumann and E. Zauder, J. Organomet. Chem., 354 (1988) 161.

52 A. Belforte, F. Calderazzo and P.F. Zanazzi, Gazzetta, Chin. Ital., 115 (1985) 71.

53 A. Belforte, F. Calderazzo, D. Vitali and P.F. Zanazzi, Gazzetta, 115 (1985) 125.

54 G. Bremer, R. Boesse, M. Keddo and T. Kruck, Z. Naturforsch. Teil B, 41 (1986) 981.

55 E.W. Abel, M.M. Bhatti, K.G. Orrell and V. Sik, J. Organomet. Chem., 208 (1981) 195.

56 S. Rossi, J. Pursiainen, M. Ahlgren and T.A. Pakkanen, J. Organomet. Chem., 391 (1990) 403.

57 D. Cruz-Garritz, B. Rodriguez, H. Torrens and J. Leal, Transition Metal Chem., 9 (1984) 403.

58 M.J. Root and E. Deutsch, Inorg. Chem., 24 (1985) 1464.

59 B.V. Lebedev and T.G. Kulagina, J. Chem. Thermodyn., 22 (1990) 21.

60 E. Turin, R.M. Nielson and A.E. Merbach, Inorg. Chim. Acta., 134 (1987) 67, 79.

61 D.J. Gulliver and W. Levason, J. Chem. Soc. Dalton Trans., (1982) 1895.

62 E.G. Hope, W. Levason, M. Webster and S.G. Murray, J. Chem. Soc. Dalton Trans., (1986) 1003.

63 E.W. Abel, A.R. Khan, K. Kite, K.G. Orrell and V. Sik, J. Organomet. Chem., 225 (1982) 357.

64 R.A. Cipriano, W. Levason, R.A.S. Mould, D. Pletcher and N.A. Powell, J. Chem. Soc. Dalton Trans., (1988) 2677.

65 R.A. Cipriano, W. Levason, D. Pletcher, N.A. Powell and M. Webster, J. Chem. Soc. Dalton Trans., (1987) 1901.

66 R.A. Cipriano, W. Levason, R.A.S. Mould, D. Pletcher and M. Webster, J. Chem. Soc. Dalton Trans., (1990) 339.
67 S.K. Harbron and W. Levason, J. Chem. Soc. Dalton Trans., (1985) 205.
68 H. Hausmann, M. Hoefler, T. Kruck and H.W. Zimmermann, Chem. Ber., 114 (1981) 975.
69 G. Bremer, P. Kluefers and T. Kruck, Chem. Ber., 118 (1985) 4224.
70 G. Alibrandi, D. Minniti, L.M. Scolaro and R. Romeo, Inorg. Chem., 28 (1989) 1939.
71 C.T. Page and J.E. Fergusson, Aust. J. Chem., 36 (1983) 855.
72 J.E. Fergusson and C.T. Page, Aust. J. Chem., 29 (1976) 2159.
73 R.K. Chadha, J.M. Chehayber and J.E. Drake, Inorg. Chem., 25 (1986) 611.
74 R.K. Chadha, J.E. Drake, N.T. McManus and A. Mislankar, Can. J. Chem., 65 (1987) 2305.
75 E.W. Abel, S.K. Bhargava, P.K. Mittal, K.G. Orrell and V. Sik, J. Chem. Soc. Dalton Trans., (1985) 1561.
76 E.W. Abel, M.A. Beckett, D. Ellis, K.G. Orrell, V. Sik and D. Stephenson, J. Chem. Res., (1988) 232.
77 J.W. Freeman and F. Basolo, Organometallics, 10 (1991) 256.
78 E.W. Abel, T.E. Mackenzie, K.G. Orrell and V. Sik, J. Chem. Soc. Dalton Trans., (1986) 205.
79 C. Staalhandske and F. Zintl, Acta Crystallogr. Sect. C, 42 (1986) 1449.
80 C. Staalhandske and F. Zintl, Acta Crystallogr. Sect. C, 44 (1988) 253.
81 H. Fischer, U. Gerbing and J. Riede, J. Organomet. Chem., 364 (1989) 155.
82 M. Hoch and D. Rehder, J. Organomet. Chem., 288 (1985) C25.
83 K. Ihmels and D. Rehder, Organometallics, 4 (1985) 1340.
84 D. Redher, K. Ihmels, D. Wenke and P. Oltmanns, Inorg. Chim. Acta, 100 (1985) L13.
85 P.G. Jones and C. Thoene, Z. Naturforsch. Teil B, 46 (1991) 50.
86 J.K. Shen, Y.-C. Gao, Q-Z. Schi, A.L. Rheingold and F. Basolo, Inorg. Chem., 30 (1991) 1868.
87 T.N. Srivastava, J.D. Singh and S. Srivastava, Indian J. Chem. Sect. A, 28 (1989) 422.
88 A.R. Siedle, M.C. Retter, M.E. Jones, G. Filipovich, H.E. Mishmash and W. Bahmet, Inorg. Chem., 21 (1982) 2624.
89 E.W. Abel, S.K. Bhargava, M. Bhatti, K. Kite, M.A. Mazid, K.G. Orrell, V. Sik, B.L. Williams, M.B. Hursthouse and K.M. Malik, J. Chem. Soc. Dalton Trans., (1982) 2065.
90 E.W. Abel, S.K. Bhargava, K. Kite, K.G. Orrell, V. Sik and B.L. Williams, Polyhedron, 1 (1982) 289.
91 E.W. Abel, A.R. Khan, K. Kite, K.G. Orrell and V. Sik, J. Chem. Soc. Dalton Trans., (1980) 1169, 1175.
92 E.W. Abel, K.G. Orrell and A.W.G. Platt, J. Chem. Soc. Dalton Trans., (1983) 2345.
93 E.W. Abel, S.K. Bhargava, K.G. Orrell, A.W.G. Platt, V. Sik and T.S. Cameron, J. Chem. Soc. Dalton Trans., (1985) 345.
94 E.W. Abel, S.K. Bhargava, T.E. Mackenzie, P.K. Mittal, K.G. Orrell and V. Sik, J. Chem. Soc. Chem. Commun., (1982) 983.
95 E.W. Abel, T.E. Mackenzie, K.G. Orrell and V. Sik, Polyhedron, 6 (1987) 1785.
96 E.W. Abel, S.K. Bhargava, T.E. Mackenzie, P.K. Mittal, K.G. Orrell and V. Sik, J. Chem. Soc. Dalton Trans., (1987) 757.
97 E.G. Hope, Ph.D. Thesis, University of Southampton, 1985.
98 E.W. Abel, A.R. Khan, K. Kite, K.G. Orrell and V. Sik, J. Chem. Soc. Dalton Trans., (1980) 2208.
99 L.R. Gray, S.J. Higgins, W. Levason and M. Webster, J. Chem. Soc. Dalton Trans., (1984) 1433.

100 D.J. Gulliver, E.G. Hope, W. Levason, S.G. Murray and G.L. Marshall, J. Chem. Soc. Dalton Trans., (1985) 1265.

101 J.L. Brown, T. Kemmitt and W. Levason, J. Chem. Soc. Dalton Trans., (1990) 1513.

102 R.A. Cipriano, L.R. Hanton, W. Levason, D. Pletcher, N.A. Powell and M. Webster, J. Chem. Soc. Dalton Trans., (1988) 2483.

103 E.G. Hope, H. Jewiss, W. Levason and M. Webster, J. Chem. Soc. Dalton Trans., (1986) 1479.

104 C.A. McAuliffe and A. Werfalli, Inorg. Chim. Acta, 64 (1982) L19.

105 U. Behrens, P. Berges, R. Bieganowski, W. Hinrichs, C. Schiffling and G. Klar, J. Chem. Res., (1986) 326.

106 H. Kacholdt, P. Berges, G. Klar and W. Hinrichs, Transition Met. Chem., 12 (1985) 515.

107 E.W. Abel, N.J. Long, K.G. Orrell, A.G. Osbourne, V. Sik, P.A. Bates and M.B. Hursthouse, J. Organomet. Chem., 367 (1989) 275.

108 E.W. Abel, N.J. Long, K.G. Orrell, A.G. Osbourne, V. Sik, P.A. Bates and M.B. Hursthouse, J. Organomet. Chem., 383 (1990) 253.

109 E.W. Abel, N.J. Long, K.G. Orrell, A.G. Osbourne and V. Sik, J. Organomet. Chem., 378 (1989) 473.

110 E.W. Abel, N.J. Long, K.G. Orrell, A.G. Osbourne and V. Sik, J. Organomet. Chem., 405 (1991) 375.

111 M. Sato, M. Sekino, M. Katada and S. Akabori, J. Organomet. Chem., 377 (1989) 327.

112 H. Hofmann, P.G. Jones, M. Noltemeyer, E. Peymann, W. Pinkert, H.W. Roesky and G.M. Sheldrick, J. Organomet. Chem., 249 (1983) 97.

113 E.W. Abel, K. Kite and P.S. Perkins, Polyhedron, 5 (1986) 1459.

114 E.W. Abel, K. Kite and P.S. Perkins, Polyhedron, 6 (1987) 549.

115 E.G. Hope, W. Levason, S.G. Murray and G.L. Marshall, J. Chem. Soc. Dalton Trans., (1985) 2185.

116 R.J. Batchelor, F.W.B. Einstein, I.D. Gay, J.H. Gu, B.M. Pinto and X.M. Zhou, J. Am. Chem. Soc., 112 (1990) 3706.

117 R.J. Batchelor, F.W.B. Einstein, I.D. Gay, J.H. Gu and B.M. Pinto, J. Organomet. Chem., 411 (1991) 3706.

118 T. Konno, K. Okamoto and J. Hidake, Chem. Lett., (1982) 535.

119 L. Roeker, M.H. Dickman, D.L. Nosco, R.J. Doedens and E. Deutsch, Inorg. Chem., 22 (1983) 2022.

120 T. Konno, K. Okamoto and J. Hidaka, Bull. Chem. Soc. Jpn., 57 (1984) 3104.

121 L. Roeker and E. Deutsch, Inorg. Chem., 24 (1985) 16.

122 T. Konno, K. Okamata, H. Einaga and J. Hidaka, Bull. Chem. Soc. Jpn., 58 (1985) 1119.

123 K. Nakajima, M. Kojima and J. Fujita, Chem. Lett., (1982) 925.

124 K. Nakajima, K. Tozaki, M. Kojima and J. Fujita, Bull Chem. Soc. Jpn., 58 (1985) 1130.

125 K. Nakajima, M. Kojima, M. Fujita and J. Fujita, J. Chromatogr., 301 (1984) 241.

126 K. Nakajima, M. Kojima and J. Fujita, J. Chromatogr., 362 (1986) 281.

127 K. Nakajima, M. Kojima and J. Fujita, Bull. Chem. Soc. Jpn., 59 (1986) 3505.

128 M.O. Okorafor, L.H. Shen, R.V. Honeychuck and C.H. Brubaker, Jr., Organometallics, 7 (1988) 1297.

129 C.K. Lai, A.A. Naiini and C.H. Brubaker, Jr., Inorg. Chim. Acta, 164 (1989) 205.

130 A.A. Naiini, C.K. Lai, D.L. Ward and C.H. Brubaker, Jr., J. Organomet. Chem., 390 (1990) 73.

131 H.M. Ali and C.H. Brubaker, Jr., J. Mol. Catal., 60 (1990) 331.

132 H.C. Jewiss, W. Levason, M.D. Spicer and M. Webster, Inorg. Chem., 26 (1987) 2102.

133 S.K. Harbron, S.J. Higgins, E.G. Hope, T. Kemmitt and W. Levason, Inorg. Chim. Acta, 130 (1987) 43.

134 D.M. Roundhill, S.G.N. Roundhill, W.B. Beaulieu and U. Bagchi, Inorg. Chem., 19 (1980) 3365.

135 E.W. Abel, K. Kite, K.G. Orrell, V. Sik and B.L. Williams, J. Chem. Soc. Dalton Trans., (1981) 2439.

136 E.W. Abel, S.K. Bhargava, K. Kite, K.G. Orrell, V. Sik and B.L. Williams, J. Chem. Soc. Dalton Trans., (1982) 583.

137 E.W. Abel, S.K. Bhargava, K. Kite, K.G. Orrell, V. Sik and B.L. Williams, J. Chem. Soc. Dalton Trans., (1984) 365.

138 E.W. Abel, D.G. Evans, J.R. Koe, V. Sik, P.A. Bates and M.B. Hursthouse, J. Chem. Soc. Dalton Trans., (1989) 985.

139 E.W. Abel, D.G. Evans, J.R. Koe, V. Sik, P.A. Bates and M.B. Hursthouse, J. Chem. Soc. Dalton Trans., (1989) 2315.

140 E.W. Abel, D.G. Evans, J.R. Koe, M.B. Hursthouse, M. Mazid, M.F. Mahon and K.C. Molloy, J. Chem. Soc. Dalton Trans., (1990) 1697.

141 H. Fischer and U. Gerbing, J. Organometal. Chem., 299 (1986) C7.

141a P. Jaitner and W. Winder, Inorg. Chim. Acta, 134 (1987) 201.

142 G. Suss-Fink, M. Langenbahn. H. Stoeckli-Evans, and D. Naumann, J. Chem. Soc. Chem. Commun., (1991) 447.

143 S. Rossi, J. Pursiainen, and T.A. Pakkanen, J. Organomet. Chem., 397 (1990) 81.

144 R.K. Chadha and J.E. Drake, J. Organomet. Chem., 286 (1985) 121.

145 M.J. Root and E. Deutsch, Inorg. Chem., 24 (1985) 1464.

146 A.Z. Al-Rubaie, Y.N. Al-Obaidi, and L.Z. Yousif, Polyhedron, 9 (1990) 1141.

147 A.Z. Al-Rubaie, Y.N. Al-Obaidi, and L.Z. Yousif, Thermochim. Acta, 162 (1990) 409.

148 T. Kemmitt, W. Levason, R. Oldroyd and M. Webster, Polyhedron, in press.

149 T. Kemmitt and W. Levason, Inorg. Chem., 29 (1990) 731.

150 W. Levason, M. Webster and C.J. Mitchell, Acta Crystallogr. Sect. C, in press.

151 P.K. Khanna and H.B. Singh, Transition Met. Chem., 16 (1991) 311.

152 K. Ohe, H. Takahashi, S. Uemura, and N. Sugita, J. Organomet. Chem., 326 (1987) 35.

153 T.N. Srivastava, V.K. Srivastava and S. Srivastava, Indian J. Chem. Sect. A, 26 (1987) 265.

154 J.B. Mullin, D.J. Cole-Hamilton, D.V. Shenai-Khatkhate and P. Webb, UK Patent. WO 8905293: Chem. Abstr., 112 (1990) 35288h.

155 M.J. Almond, C.E. Jenkins, D.A. Rice and C.A. Yates, J. Mol. Struct., 222 (1990) 219.

156 F.W.B. Einstein, C.H.W. Jones, T. Jones and R.D. Sharma, Inorg. Chem., 22 (1983) 3924.

157 S.A. Mbogo, W.R. McWhinnie and T.S. Lobana, J. Organomet. Chem., 384 (1990) 115.

158 T. Kemmitt and W. Levason, unpublished work 1987–1988.

159 D.J. Gulliver, W. Levason, K.G. Smith, M.J. Selwood and S.G. Murray, J. Chem. Soc. Dalton Trans., (1980) 1718.

160 W. Levason and R.A.S. Mould, unpublished work, 1989.

161 T. Kemmitt, W. Levason and M. Webster, Inorg. Chem., 28 (1989) 692.

162 T. Kemmitt, W. Levason, M.D. Spicer and M. Webster, Organometallics, 9 (1990) 1181.

163 E.W. Abel, K.G. Orrell, S.P. Scanlan, D. Stevenson, T. Kemmitt and W. Levason, J. Chem. Soc. Dalton Trans., (1991) 591.

164 H.M.K.K. Pathirana, A.W. Downs, W.R. McWhinnie and P. Granger, Inorg. Chim. Acta, 143 (1988) 161.

165 A.K. Singh and S. Thomas, Polyhedron, 10 (1991) 2065.

166 A.K. Singh, S. Thomas and B.L. Khandelwal, Polyhedron, 10 (1991) 2693.

167 S. Al-Salim and W.R. McWhinnie, Inorg. Chim. Acta, 135 (1989) 213.

168 B.L. Khandelwal, A.K. Singh, V. Srivastava, D.C. Povey and G.W. Smith, Polyhedron, 9 (1990) 204.
169 N.I. Al-Salim and W.R. McWhinnie, Polyhedron, 8 (1989) 2769.
170 W. McFarlane and H.C.E. McFarlane, in J. Mason (Ed.), Multinuclear NMR, Plenum Press, New York, 1987, Chap. 14.
171 N.P. Luthra and J.D. Odom, in S. Patai and Z. Rappoport (Eds.), The Chemistry of Organic Selenium and Tellurium Compounds, Vol. 1, Wiley, New York, 1986, Chap. 6.
172 W. McFarlane and R. Wood, J. Chem. Soc. Dalton Trans., (1972) 1397.
173 P.L. Goggin, R.J. Goodfellow and S.R. Haddock, J. Chem. Soc. Chem. Commun., (1975) 176.
174 H.J. Gysling, N. Zumbulyadis and J.A. Robertson, J. Organomet. Chem., 209 (1981) C41.
174a T. Kemmitt, unpublished work, 1988.
175 T. Kemmitt, Ph.D. Thesis, University of Southampton, 1988.
176 P.E. Garrou, Chem. Rev., 81 (1981) 229.
177 J.G. Verkade and L.D. Quin (Eds.), Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis, VCH, Deerfield Beach, FL, 1987.
178 P.E. Skakke and S.E. Rasmussen, Acta Chem Scand., 24 (1970) 2634.
179 H.J. Whitfield, J. Chem. Soc. A, (1970) 113.
180 J.C. Barnes, G. Hunter and M.W. Lown, J. Chem. Soc. Dalton Trans., (1977) 458.
181 H.J. Gysling, H.R. Luss and D.L. Smith, Inorg. Chem., 18 (1979) 2696.
182 W. Levason, in F.R. Hartley (Ed.), The Chemistry of Organophosphorus Compounds, Vol. 1, Wiley, New York, 1990, Chap. 15.
183 A. Evans and C.T. Mortimer, Thermochim. Acta, 131, (1988) 103.
184 C.T. Mortimer, Rev. Inorg. Chem., 6 (1984) 233.
185 N. Ito, T. Shimobayashi, T. Mizumoto, N. Okomoto, Jpn. Patent JP 61166969; Chem. Abstr., 106 (1986) 225063e.
186 N. Okamoto, N. Ito, T. Shimobayashi, T. Mizumoto, M. Fujisawa and A. Ichikawa, Jpn. Patent JP 61225188; Chem. Abstr., 106 (1986) 225065g.
187 N. Ito, T. Mizumoto, T. Shimobayashi and N. Okamoto, Jpn. Patent JP 61166972; Chem. Abstr., 106 (1986) 225064f.
188 N. Ito, T. Shimobayashi, T. Mizumoto and N. Okamoto, Jpn. Patent JP 61232627; Chem. Abstr., 106 (1986) 130201j.
189 N. Ito, Jpn. Patent JP 62122134; Chem. Abstr., 107 (1987) 208536q.
190 N. Ito, T. Shimobayashi, T. Mizumoto and N. Okamoto, Jpn. Patent JP 62047174; Chem. Abstr., 107 (1987) 30964n.
191 N. Ito, T. Shimobayashi, T. Mizumoto and N. Okamoto, Jpn. Patent JP 62047175; Chem. Abstr., 107 (1987) 30965p.
192 N. Ito, T. Shimobayashi, T. Mizumoto and N. Okamoto, Jpn. Patent JP 62047176; Chem. Abstr., 107 (1987) 30966q.
193 N. Ito and T. Shimobayashi, Jpn. Patent JP 63060536; Chem. Abstr., 109 (1988) 121027s.
194 H.J. Gysling, Eur., Patent EP 11754; Chem. Abstr., 93 (1980) 177337m.
195 H. Schumann, E.J.W. Lam, J.M.M. Smits and P.T. Beurskens, J. Cryst. Mol. Struct., 21 (1991) 667.
196 A.K. Singh, V. Srivastava, S.K. Dhingra, J.E. Drake and J.E. Bailey, Acta Crystallogr. Sect. C, 48 (1992) 655.
197 A. Ogawa, K. Yokoyama, H. Yokoyama, R. Obayashi, N. Kombe and N. Sunoda, J. Chem. Soc. Chem. Commun., (1991) 1748.
198 S.A. Mbongo, W.R. McWhinnie and T.S. Lobana, Inorg. Chim. Acta, 193 (1992) 5.
199 H. Fischer, C. Kalbas and U. Gerbing, J. Chem. Soc. Chem. Commun., (1992) 563.

200 H. Fischer, C. Kalbas and J. Hofmann, J. Chem. Soc. Chem. Commun., (1992) 1050.
201 Y. Fuchida, H. Oka and Y. Okamura, Inorg. Chim. Acta, 194 (1992) 213.
202 E.W. Abel, D.G. Evans, J.R. Koe, V. Sik, M.B. Hursthouse and M. Mazid, Polyhedron, 11 (1992) 401.
203 E.W. Abel, D.G. Evans, J.R. Koe, M.B. Hursthouse and M. Mazid, J. Chem. Soc. Dalton Trans., (1992) 663.
204 N.R. Champness, W. Levason, D. Pletcher and M. Webster, J. Chem. Soc. Dalton Trans., in press.
205 A.P.M. Kentgens, H. Karrenbeled, E. De Boer and H. Schumann, J. Organomet. Chem., 429 (1992) 99.
206 V. Srivastava, A.K. Singh and B.L. Khandelwal, Transition Met. Chem., 17 (1992) 177.