*Coordination Chemistry Reviews, 135/136* (1994) 469–515

# Intramolecular coordination in tellurium chemistry

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(Received 28 May 1993; accepted 3 February 1994)

CONTENTS

## ABSTRACT

Intramolecular coordination in organotellurium derivatives is reviewed. The various types of complexes are discussed according to the types of donor atoms involved. Structural and spectroscopic evidence in support of intramolecular coordination, where Te(II) and Te(IV) behave as Lewis acids, is emphasized.

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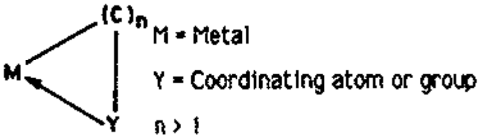
*Dedicated to my teacher Professor W.R. McWhinnie, pioneer of organotellurium chemistry, with sincere thanks for his encouraging interest over the years and fine personal example as teacher and researcher.

0010-8545/94/$26.00
*SSDI* 0010-8545(94)01110-W

## 1. INTRODUCTION

The last 15–20 years have witnessed the extremely rapid development of organotellurium chemistry. Outlets for the considerable current interest include (a) application of organotellurium compounds in organic synthesis [1–3], (b) nuclear medicine [4,5], (c) non-silver imaging [6,7], (d) new conducting materials [8,9], (e) ligand chemistry [10–12] and (f) precursors for metal organic chemical vapour deposition (MOCVD) of $Hg_{1-x}Cd_xTe$ [13,14]. The basic chemistry of organotellurium compounds and bonding is well covered in books and reviews [15–18], whereas only scattered information is available on the coordination behaviour of tellurium [19]. The main object of this review will be the presentation of work on intramolecularly coordinated organotellurium compounds with a view to promoting interest in this area. The compounds have been classified on the basis of the ligating atom.

Organometallic intramolecular coordination compounds **1** are, in a general sense, those which have at least one M–C bond and one group forming an intramolecular coordination bond.



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Omae, in a series of reviews [20], has classified organometallic intramolecular coordination compounds based on the type of coordination of Y to the metal. The compounds have mainly N, P, As, O or S as the ligating atom and tend to form five-membered rings.

## 2. INTRAMOLECULAR COORDINATION COMPOUNDS OF TELLURIUM

Intramolecular coordination compounds of tellurium(II) and tellurium(IV) have attracted attention since the built-in functional groups not only stabilize the synthetically important but otherwise unstable organyltellurenyl derivatives but also afford novel bi-, tri- and tetradentate ligands containing both "hard" and "soft" bases. Furthermore, these complexes are interesting in their own right owing to their structural variety. Intramolecular coordination compounds of tellurium also find potential applications in the synthesis of stoichiomeric monomeric precursors of the type RHgTeR′ for MOCVD. Encouragement for the detailed investigation of these systems was provided by the application of analogous organosulphur and organoselenium compounds in organic synthesis [21–24]. The simpler members of aryltellurenyl halides are thermally unstable and polymeric in nature [25] and the only exception for many years has been 2-naphthyltellurenyl iodide [26]. However, aryltellurenyl halides prepared *in situ* have found application in important transformations [27–29]:

$$\underset{\mathbf{2}}{\mathrm{ArTeTeAr}} \xrightarrow[\mathrm{THF}]{\mathrm{Br_2}} \underset{\mathbf{3}}{[2\mathrm{ArTeBr}]} \xrightarrow{\mathrm{RMgX}} \underset{\mathbf{4}}{2\mathrm{ArTeR}} \qquad (1)$$

(Ar = $C_6H_5$, $p$-$CH_3OC_6H_4$, 3,4-$(CH_3O)_2C_6H_3$, $p$-$C_6H_5$-$C_6H_4$; X = Br, I)

Stable aryltellurenyl halides can be obtained by (a) complexation with external ligands [30], (b) formation of anionic complexes [31], and (c) chelation with donor groups already incorporated in the molecule.

### 2.1. *Lewis acidity*

Tellurium exhibits an exceptionally wide variety of formal oxidation states. The two most common oxidation states are II and IV. Tellurium compounds (in oxidation states II and IV), because of the presence of a lone pair of electrons and also vacant 5d orbitals, can function as both electron donors and electron acceptors depending on the partner. Compounds of the type RTeX and $R_nTeX_{4-n}$ (where X is a halide) act as good acceptors. The Lewis acidity of tellurium becomes less important as the more electronegative halogen atoms in $TeCl_4$ are replaced by less electronegative organic groups. Thus the order of Lewis acidity is as follows:

$TeX_4 > RTeX_3 > R_2TeX_2 > R_3TeX > R_4Te$

In the case of tellurium(II) compounds,

$RTeX > R_2Te$

### 2.2. *Structural considerations [32]*

In recent years, several crystal structures of tellurium compounds have become available. In this review complexes of tellurium(II) and tellurium(IV) with at least one built-in ligand coordinating through oxygen, nitrogen, phosphorus and chlorine are considered. The term "complex" in this presentation is used in the traditional sense, it is defined as an arrangement of electron donating ligands bonded to a central atom, Te(II) or Te(IV), which functions as electron donors.

Other than *ortho*-tellurated compounds, all organyltellurenyl compounds whose structures have been determined are stabilized by complex formation. Complex formation either may occur via reaction with anions or may be intermolecular. Around 1960, Foss and co-workers published a series of papers [33–35] on the synthesis and structure of Te(II) intermolecular complexes with thioureas, halogens, pseudohalogens and phenyl groups as ligands. The complexes prefer a square planar geometry. From the stereochemistry, bond lengths and trans effects in these complexes it has been proposed that the bonding is of the three-centre–four-electron type [33–35]. For instance in thiourea complexes of tellurium, with a $TeS_4$ core, two S–Te–S bonds 3c–4e systems are supposed to be formed. Here suitable s orbitals on two sulphur atoms overlap with the same 5p orbitals on tellurium in each system. Since only two bonding electrons are available for two bonds, the bonds should be weak. The strong trans bond lengthening effects observed in many complexes can be easily explained when one assumes that one p orbital on a central tellurium atom participates in two bonds trans to each other. Thus a ligand with a strong trans effect overlaps more efficiently with the p orbital, weakening the ligand trans to itself when this has a smaller trans effect.

In Te(II) complexes the two lone pairs of electrons are stereochemically active, being located above and beneath the coordination plane while in Te(IV) complexes the lone pair is stereochemically active for coordination numbers less than 6 [36,37]. For Te(IV) complexes the structures, although more complex, seem to obey the VSEPR theory of Gillespie and Nyholm [38] up to coordination number 5.

### *2.2.1. Three-coordinate tellurium(II) complexes*

Although tellurium(II) strongly prefers square planar coordination, tellurium in some organyltellurium(II) complexes is three coordinate. All the complexes have a typical "T-shape" structure (Fig. 1).

A pseudo-trigonal bipyramidal geometry can be defined for these type of compounds with five electron pairs (two of which are non-bonding) distributing themselves around the metal atom. When the tellurium atom is not part of a ring system, the observed bond angles are close to 90° and 180°. A fourth (secondary) bond may form along an axis bisecting the angle between the lone pairs.

### *2.2.2. Four-coordinate tellurium(II) complexes*

Among intermolecular complexes, four-coordinate tellurium(II) complexes with monodentate ligands have a square planar structure while those with bidentate ligands form a trapezoidal planar structure.

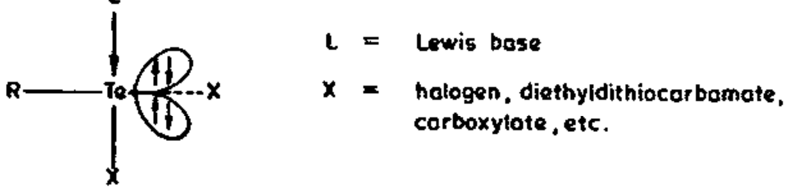


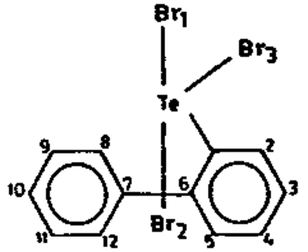
Fig. 1. Typical structure of three-coordinate tellurium compounds.

### 2.2.3. *Four- and five-coordinate tellurium(IV) complexes*

The structures of four-coordinate intermolecular tellurium(IV) complexes may be described as pseudo-trigonal bipyramidal with one lone pair of electrons in an equatorial position. The structures of five-coordinate tellurium(IV) complexes can be considered pseudo-octahedral with a lone pair of electrons in the sixth coordination position. This is then a square pyramidal structure.

## 2.3. *Intramolecular coordination compounds of tellurium having a Te---C bond*

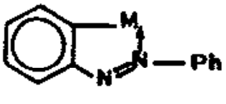
An interesting example where an intramolecular Te---C ineraction exists is 2-biphenyltellurium tribromide **5**. The molecular structure of this compound is influenced to a lesser degree by the effects of intermolecular bonding than is the triiodide [39]. A surprisingly short Te---C(12) separation of 2.945(9) Å is observed which is even shorter than the Te · · · C(12) separation of 3.317 Å observed in the triiodide. A possible chemical significance of this short Te · · · C(12) separation involves the conversion of the trihalide to the dibenzotellurophene dihalide. This may be visualized as the formation of a bond between Te and C(12) as the Te–Br(3) and C(12)–H(12) bonds are broken.



**5**

## 2.4. *Intramolecular coordination compounds of tellurium having a Te---N bond*

In recent years interest has grown in compounds in which intramolecular coordination (secondary) N---Te and O---Te bonds are present with the participating Te atom in various degrees of oxidation. Analogues of these bonds are well documented in the organic chemistry of sulphur and selenium [40,41]. The presence of such bonds considerably strengthens the thermal and hydrolytic stability of organic derivatives of tellurium and permits access to some novel type of organotellurium compounds. The major nitrogen compounds are conveniently divided into four groups depending on the nature of the ligand: azobenzenes **6**, heteroatomic compounds **7**, benzylamines **8** and imines **9**.



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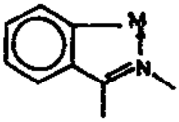

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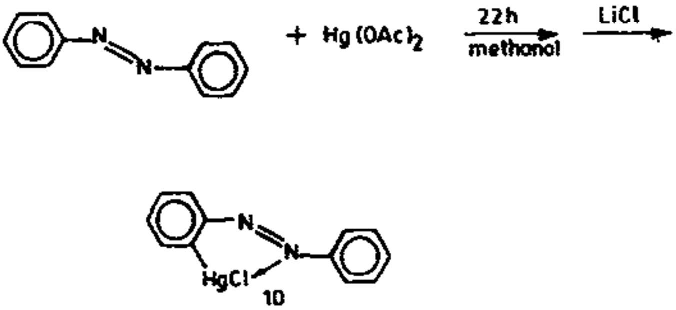
M = Te(II) or Te(IV)

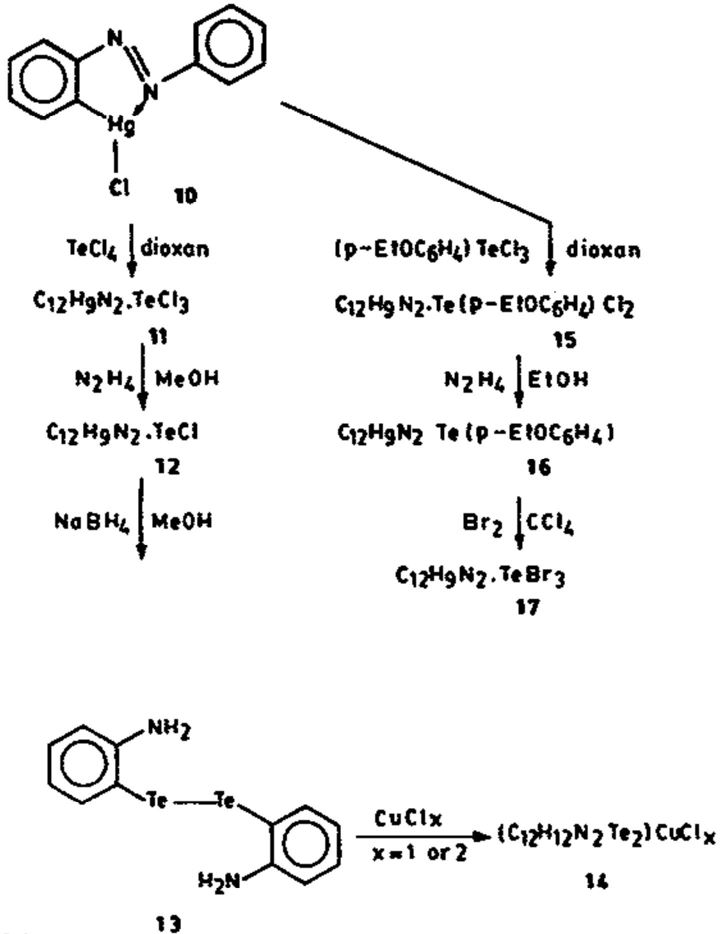
### 2.4.1. *Ortho-tellurated azobenzene compounds*

An extensive series of azobenzene derivatives of tellurium(II) and tellurium(IV) are known [42]. The general procedure for linking tellurium to azobenzene involves the generation of the mercurated azobenzene derivative and its subsequent reaction with tellurium tetrachloride or organotellurium(IV) trihalides. In the preparation of synthetically valuable *ortho*-mercurated azobenzene **10** [43] (Scheme 1), the regiospecificity of the reaction suggests that the mercury is directed into an *ortho* position by coordination of mercury to an azo nitrogen.

Precursor **10** has been recently prepared by the use of a domestic microwave oven [44]. The mercuration reaction is much faster under the conditions used; however, the overall yield was the same as when the reaction was carried out conventionally [43]. The synthetic route linking the tellurated derivatives of azobenzene is illustrated in Scheme 2 and (2-phenylazophenyl-*C*,*N*′)tellurium(II) chloride



Scheme 1.



Scheme 2.

**12** is considered as one of the first compounds containing an intramolecular Te---N bond to be crystallographically characterized. If stereochemical activity is ascribed to the two tellurium lone pairs, the geometry around the tellurium atom can be considered to be distorted trigonal–bipyramidal (Fig. 2) [45]. The phenylazophenyl

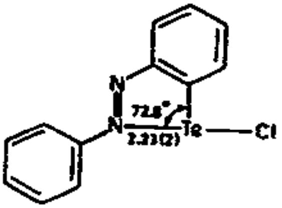


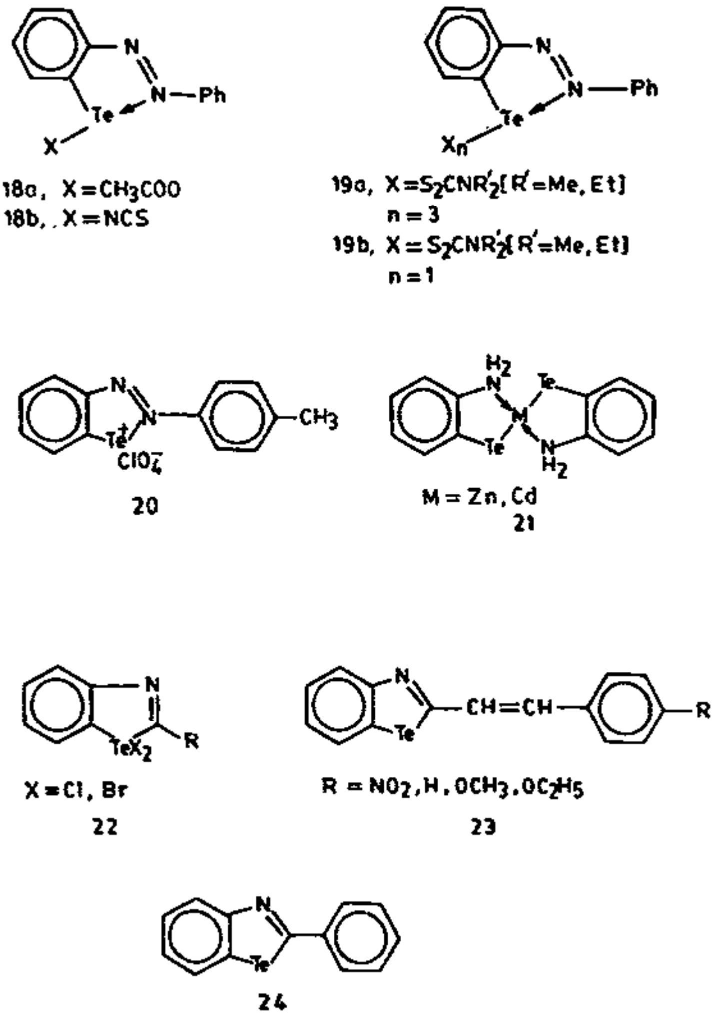
Fig. 2. Schematic representation of RTeCl (R = azobenzene).

group acts as a bidentate ligand resulting in a five-membered chelate ring. The carbon atoms and the lone pairs are in the equatorial plane and the more electronegative nitrogen and chlorine atoms occupy the axial positions. This stereochemistry is in agreement with that predicted by valence shell electron pair repulsion theory [46]. The asymmetric unit consists of two discrete molecules A and B with similar stereochemistry and (Fig. 2) shows molecule A with atom numbering. The Te---N distances of 2.23(2) and 2.19(2) Å in the two molecules are equivalent within the limits of experimental error. The N=N distances of 1.25(2) and 1.28(2) Å are similar to values observed in other *ortho*-metallated azo compounds [47] and only slightly longer than the value of 1.24(3) Å found in free azobenzene [48].

Several direct tellurations of aromatic substrates activated by *ortho*- and *para*-directing groups with $TeCl_4$ are known. However, it is only with great difficulty that direct telluration of azobenzene is achieved and that also in moderate yield [49]. Synthesis of the ditelluride by reduction of trichloride **11** with excess hydrazine hydrate completes the series of tellurated azobenzenes. The structure of the monomeric trichloride **11** indicates no significant Te ··· Cl and Cl ··· Cl intermolecular interactions and the coordination is essentially octahedral. In view of the novel structures found in organotellurium compounds there have been further studies on the tellurated derivatives of azobenzene. While the crystal structure of tellurium(II) acetate complex of azobenzene **18a** (Fig. 3) consists of discrete molecules in which weak intramolecular Te---O (2.9534 Å) interaction occurs, the structure of the tellurium(II) thiocyanate complex of azobenzene **18b** reveals a weak intermolecular Te ··· N interaction which links the molecules into dimers [50]. The bonding between tellurium and the 2-phenylazophenyl group is quite similar in the two compounds. Weak interactions clustered around the tellurium lone pairs of electrons in the equatorial plane roughly trans to the carbon atom of an organic ligand appear to be common in organotellurium(II) derivatives [32,36].

The lack of thermal stability of the solutions of $Te(C_6H_4N_2C_6H_5)(S_2CNR'_2)_3$ (where R′ = Me, Et or $CH_2C_6H_5$) **19a** made it impossible to obtain crystals [51]. However, the $^{125}Te$ nuclear magnetic resonance (NMR) data indicate that the tris compounds dissociate to tellurium(II) compounds in solution and $^{125}Te$ Mössbauer data suggest that the tris compounds are better formulated as loose charge-transfer compounds $Te^{II}(C_6H_4N_2C_6H_5)(S_2CNR'_2) \cdots R'_2NC(S)S{-}S(S)CNR'_2$. The structure of tellurium(II) dithiocarbamate derivative **19b** consists of one discrete repeating molecule. Although the coordination about tellurium can be considered as distorted square planar, the description "trapezoid planar" is preferred since it has been reported for many four-coordinate tellurium(II) complexes with bidentate ligands [36].

2-Chlorotellurenyl azobenzene **12** has been used in the preparation of *N*-arylbenzotelluradiazolium perchlorates of the type **20** [52]. Di(*o*-aminophenyl)ditelluride **13**, which is obtained by the reduction of **12** with $NaBH_4$ in methanol, acts as a bidentate ligand with both Cu(I) and Cu(II)



18a, X=$CH_3COO$
18b, X=NCS

19a, X=$S_2CNR'_2$[R'=Me, Et]
n=3
19b, X=$S_2CNR'_2$[R'=Me, Et]
n=1

20

M=Zn, Cd
21

X=Cl, Br
22

R=$NO_2$, H, $OCH_3$, $OC_2H_5$
23

24

Fig. 3. *Ortho*-tellurated azobenzenes and other related compounds.

(Scheme 2). *o*-Aminophenyltellurolates of Zn(II) and Cd(II) **21** are the first examples of metal chelates with coordination skeleton $MN_2Te_2$ [53]. The ditelluride **13** has also been used in the synthesis of five-membered tellurium containing heterocycles such as **22–24** [54–56]. In the structure of 2-phenylbenzotellurazole **24**, the heterocyclic fragment is planar. Somewhat shortened Te···N intermolecular contacts are seen in the crystal; however, these do not substantially affect the physical properties of the compound [57]. Complex compounds of **13** with Pearson's acids exhibit di- or oligomeric structures. Conformation of diaryl ditellurides in solution offers a possibility of oligomer formation on account of participation of nitrogen atoms of the amino groups of neighbouring molecules of the ligand in intermolecular coordination with the metal [58]. Complexes of **13** with $CuCl_2$ **10** and complexes of $NiCl_2$ and $NiBr_2$ with the sulphur analogue of **13** [59] have identical compositions and properties.

### 2.4.2. Heteroatomic compounds

Nitrogen-containing heteroatomic compounds such as pyridine, *N*-tosylpyrrole and *N*-tosylindole undergo facile lithiation at the position *ortho* to the hetero nitrogen and the resulting heterocyclic lithiumtellurolates are worked up to give the corresponding ditellurides **25** [60] (Fig. 4).

A new type of organotellurium(IV) compound **26** where the organic moiety functions as a unique tridentate C, N, O ligand has been obtained by the condensation reaction of $TeCl_4$ with 2,6-diacetylpyridine [61]. The coordination geometry can be considered as distorted pentagonal bipyramid. Both the Te---N (2.402 Å) and Te---O (2.876 Å) distances are much longer than the sum of covalent radii (2.07 Å and 2.03 Å respectively). The steric requirements of the five-membered rings prevent a close approach of all three coordinating atoms in the tridentate ligand. The reaction of $TeCl_4$ with 2-acetylpyridine gives a product having a polymeric formulation with intermolecular coordination of the pyridine nitrogen.

Trans-metallation reactions involving arylmercury(II) chlorides of the type RHgCl (R = 2-(2′-pyridyl)phenyl and 2-(quinoline-2′-yl)phenyl) with tellurium tetrahalides have resulted in a wide range of *ortho*-tellurated derivatives [62]. The structures of $RTeBr_3$ and RTe(dmdtc) (R = 2-(2′-pyridyl)phenyl) show that strong Te---N bonding holds the corresponding organic ligand in a near-planar geometry, whereas in RTeR′ (R′ = $p$-$EtO_6H_4$) the Te---N distance of 2.695(4) Å is much longer than the sum of the covalent radii and much greater than the comparable distances in $RTeBr_3$ and RTe(dmdtc). The occurrence of a Te–C covalent bond trans to the Te---N vector significantly weakens the Te---N interaction. Of particular interest is the existence of a short Te---N non-bonded interaction (2.554(7) Å) which appears to hold the novel tritelluride **27** in a planar geometry. However, pyridyl and phenyl rings are bent slightly relative to one another to form a shallow V shape with internal angle 177.2(4)° [63]. The structure of the compounds dimethyldithiocarbamato-2-(2′-quinolinyl)phenyltellurium(II) **28** shows that the compounds can be regarded as "T shape" with the position trans to the bonded phenyl carbon unoccupied [64]. This is consistent with the results described for three-coordinate tellurium(II) complexes where the trans effect of the phenyl group is pronounced [33,35]. In this compound the sulphur atoms are coplanar with both the tellurium atom and coordinating C and N atoms of the organic ligand. However, a weak Te···S(2) (3.222(1) Å) interaction is noted as in $Te(C_6H_4N_2C_6H_5)(S_2CNMe_2)$ (Te···S(2) 3.225 Å) [51].

The structure of the novel telluronium salt $RR'TeCl^+HgCl_3^-$ (R = 2-(2′-pyridyl)phenyl, R′ = $p$-ethoxyphenyl) [65] consists of discrete cations and chlo-

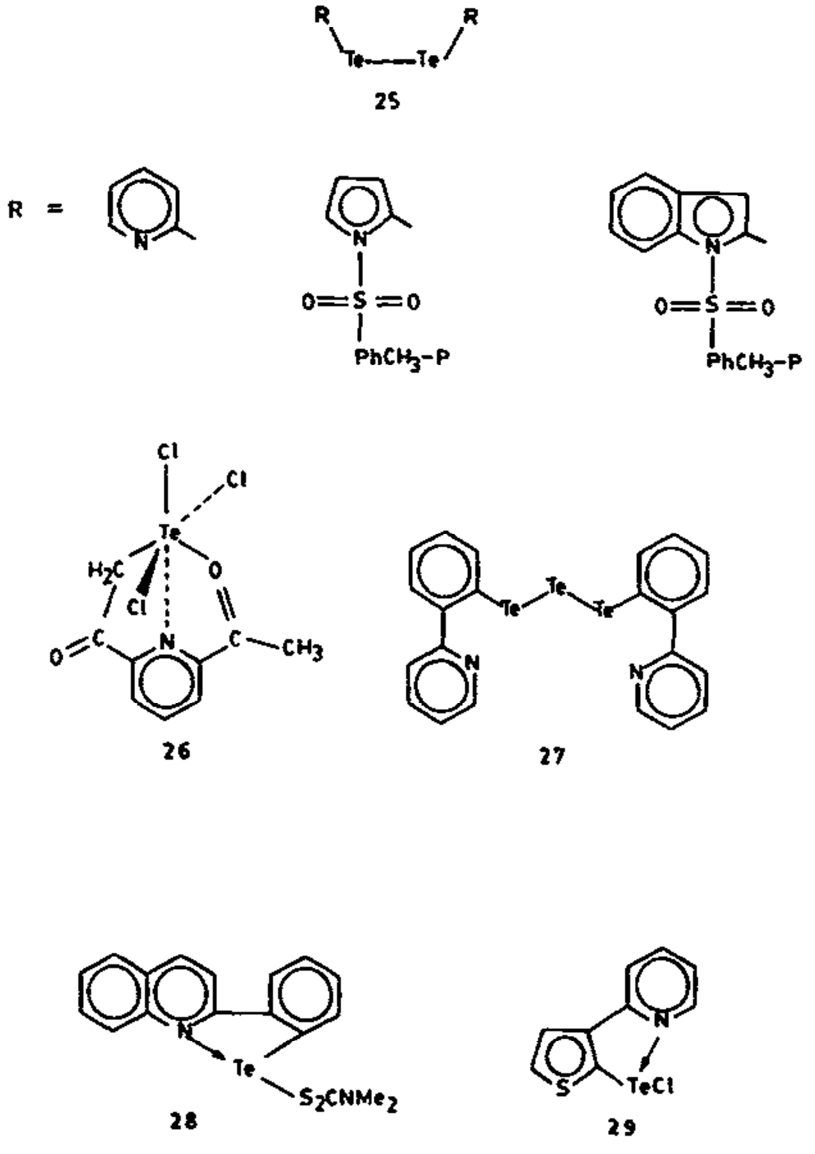


Fig. 4. *Ortho*-tellurated derivatives of pyridines and substituted pyridines.

romercurate anions. Interest centres on the structure of the cation. The geometry around tellurium is pseudo-trigonal bipyramidal. A significant amount of data are now available for Te---N interactions in 2-(2′-pyridyl)phenyltellurium compounds. If the length of the Te---N coordinate bond can be taken as a measure of the Lewis acidity of the central tellurium atom, then the following order of Lewis acidity has been reported by McWhinnie and co-workers [65] (Te---N distances in parentheses):

$\mathrm{RTeBr_3}$ (2.244 Å) > R(R′)TeCl$^+$ (2.31 Å) > RTe(dmdtc) (2.35 Å)

> $\mathrm{R_2Te_3}$ (2.554 Å) > R(R′)Te (2.695 Å)

R = 2-(2′-pyridyl)phenyl; R′ = *p*-ethoxyphenyl; dmdtc = dimethyldithiocarbamate

Organomercury reagents are known to be effective trans metallation reagents in the presence of inorganic tellurium compounds [66]. Recently an unusual case of reverse trans metallation has been observed in the reaction of 2-(2′-pyridyl)phenyl(*p*-ethoxyphenyl)tellurium(II) (RR′Te) with $\mathrm{HgCl_2}$. Initially an adduct is obtained. On setting aside or on warming, transfer of a *p*-ethoxyphenyl group between the metal centres gives [R′HgCl·$\mathrm{(RTeCl)_2}$] [67]. In order to explore the generality of this reaction the behaviour of RR′Te with other metal centres such as Cu(I) and Cu(II) has been investigated [68]. Although a novel synthesis of organocopper(I) complexes is indicated in terms of labilization of organic groups from tellurium to copper(I) centres and from comparison with other results [69], further evidence is required.

The structures of both RTeBr and [R′HgCl·$\mathrm{(RTeCl)_2}$], where R = 2-(2′-pyridylphenyl) and R′ = *p*-ethoxyphenyl, have six molecules in the unit cell with no obvious intermolecular interactions between them [70]. They are essentially pseudo-trigonal bipyramidal. The latter may be regarded as an "inclusion compound" derived by replacement of two RTeX (R = Cl or Br) molecules by two R′HgCl entities. For Te(II) complexes of the type RTeX where R = 2-(2′-pyridylphenyl) and X = Cl, Br, dimethyldithiocarbamate and *p*-ethoxyphenyl, the following trans influence series has been suggested:

Br = Cl < S < C

Among the substituted pyridine substrates, 2-(3-thienyl)pyridine is known to give five-membered ring compounds. The substrate has been *ortho* tellurated for the first time [71]. The aryltellurenylhalide **29** owes its stability to a stable Te---N interaction.

### 2.4.3. *Ortho-tellurated benzylamine compounds*

Gysling and co-workers [61] attempted the telluration of *o*-lithiodimethylbenzylamine by reaction with $\mathrm{TeCl_4}$ in THF at −78°C. Their work up led to decomposition to elemental tellurium. *o*-Lithiodimethylbenzylamine has been shown to react with organochalcogens to afford tellurides of the type **30** [72] (Fig. 5). An extensive series of *ortho*-tellurated benzylamine compounds **31** have been prepared from *o*-lithiodimethylbenzylamine and elemental tellurium [73]. Interestingly the telluride $\mathrm{RTeC_4H_9}$ (R = 2-$\mathrm{Me_2NCH_2C_6H_4}$) gives the hydrochloride salt **33** rather than the expected dichloride. If the Te---N interaction is considered to be significant, the geometry around tellurium in $\mathrm{RTeBr_3}$ (R = 2-$\mathrm{Me_2NCH_2C_6H_4}$) can be considered

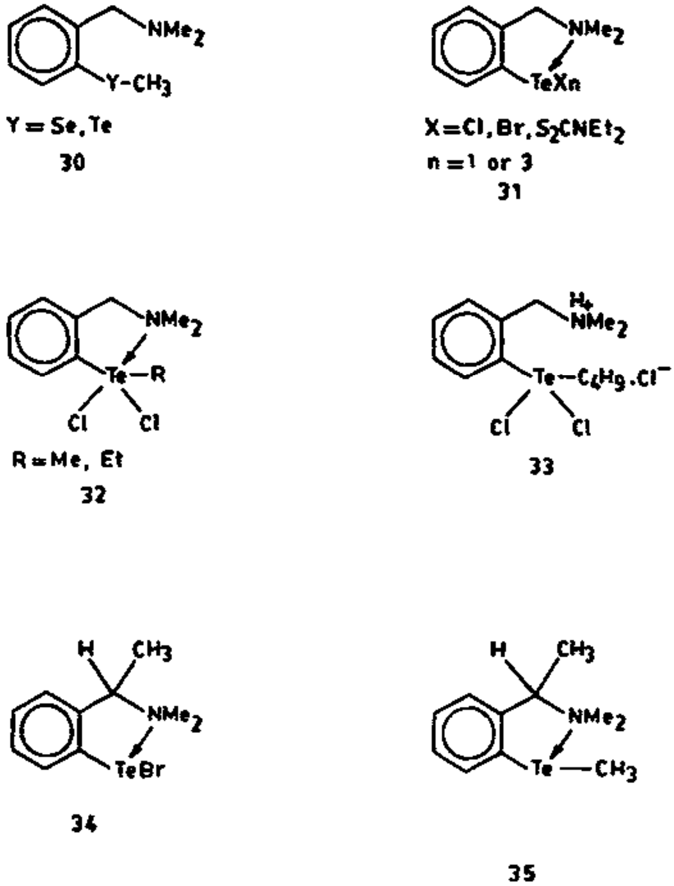


Fig. 5. *Ortho*-tellurated benzylamine compounds.

as octahedral. In structure **33** there is no interaction between the protonated nitrogen and tellurium, as the nitrogen atom is twisted away from the central tellurium atom (Te ··· N 4.380(4) Å). The geometry around tellurium is octahedral and the chloride ion forms a hydrogen bond with the dimethylbenzylammonium group (H ··· $Cl^-$ 2.327 Å).

The first examples of novel optically pure chiral tellurenyl halide **34** and bidentate ligand **35** show that the intramolecular Te---N interaction not only results in five-membered chelate rings [74] but also gives nitrogen a stable tetrahedral coordination. Anisochronous $NMe_2$ resonances are observed at temperatures as high as 140°C indicating a strong Te ··· N bond. The most interesting feature in the structure of [(*S*)-2-$Me_2NCH(Me)C_6H_4$]$TeCl_3$ (Fig. 6) is the occurrence of H ··· Cl intermolecular interaction between Cl(2) and H(7) which is not seen in any of the intramolecularly coordinated tellurium complexes.

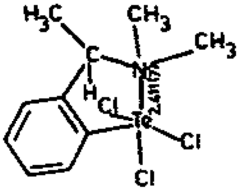
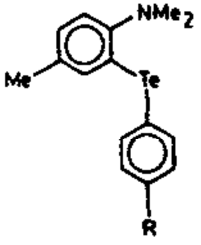


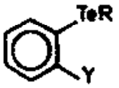
Fig. 6. Schematic representation of $RTeCl_3$ ($R = C_6H_4CH(CH_3)NMe_2$).

Other than five-membered tellurated benzylamine compounds, four-membered amine compounds are also known. Potentially bidentate **36** and **37** [75,76] containing both Te and N donor atoms are of current interest for two reasons. First, these donor atoms may strongly ligate with the "hard" metals of the first and second transition series and consequently generate a system in which the forced interaction (if any) of Te with such metals can be investigated. Second, they can favourably influence catalytic activity of Pt group metallic centres (e.g. for hydrogenation) if incorporated into their coordination sphere. When compared with the starting dichlorides, in the NMR spectra of the tellurides **36** shielding of the $NMe_2$ protons by about 0.2 ppm is observed. This may be due to a decrease in electronegativity of Te and strength of Te···N interaction which otherwise seems to be very weak in nature. The $ipso_{Te}$ resonances of the telluroethers **37** exhibit significant variation in chemical shift with variation in the *ortho* Y group and are in the range 104–126 ppm where they could be identified. Also, the tellurium chemical shifts of **37** are sensitive to the nature of the Y group and $\delta(^{125}Te)$ increases as the Y group descends group 15 or 16.



R = H, OMe, OEt

36



R = Me

Y = $NMe_2$, $PMe_2$, $AsMe_2$, $SbMe_2$,
OMe, SMe, SeMe, TeMe.

37

### 2.4.4. *Ortho-tellurated imine compounds*

Owing to stabilization by Te···N coordination in the aromatic tellurenyl compounds containing an azomethine function in the *ortho* position of the aryl ring, the synthesis of novel organic tellurium compounds bearing this functional group becomes possible.

*ortho*-tellurated Schiff bases and phenylhydrazones **38** and **39** (Fig. 7), serve as examples of aryltelluriium compounds carrying potentially chelating *ortho* substituents [77]. The formation of a Te---N bond is inferred from the IR data. A 10–30 $cm^{-1}$ shift of the $\nu$(C=N) bond towards the longer wavelength region is the same as the shift in $\nu$(N=N) bond seen for tellurated azobenzenes where crystallographic support is available for Te---N coordination.

In the 2-halogenotellurium(II) and 2-halogenotellurium(IV) derivatives of azomethine **40**, the crystal and molecular structure of **40a** exhibits a pseudo-tetragonally

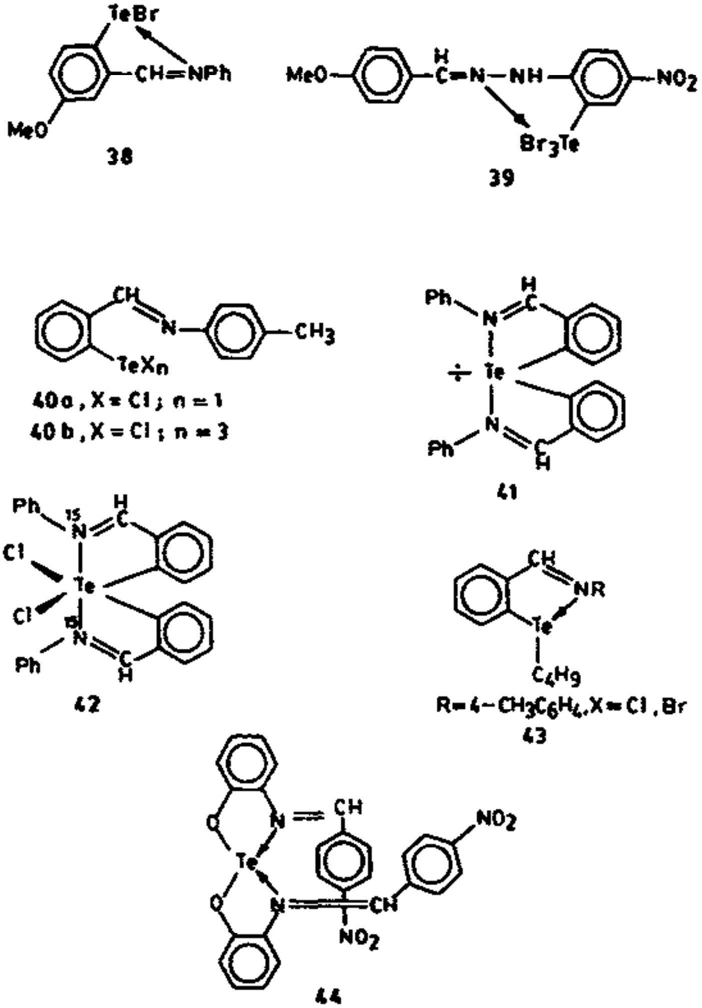


Fig. 7. *Ortho*-tellurated azomethines.

shaped configuration with planar geometry but with slightly hindered *p*-tolyl ring [78]. In the crystal, two crystallographically independent molecules exist with identical geometries, where the Te---N distance in molecule A is 2.218 Å and in molecule B is 2.239 Å.

In the $^{125}$Te NMR spectra of azomethine **41** which contains a Te(II) atom and azomethine **42** which contains a Te(IV) atom, the signals of the $^{125}$Te nuclei are observed in the form of $^{125}$Te—$^{15}$N triplets with spin–spin coupling constants equal to 61 Hz and 122 Hz respectively. This attests to the participation of both nitrogen atoms in **41** and **42** in coordination with tellurium [79]. The $^{125}$Te chemical shifts (600 ppm for **41** and 636 ppm for **42**) correspond to the ranges of chemical shift for tetra- and hexa-coordinate tellurium atoms respectively. Thus according to the N–X–L nomenclature of chalcogenuranes and perchalcogenuranes [80], the compounds are 12–Te–4 **41** and 14–Te–6 pertellurane **42**. The $^{125}$Te chemical shift corresponds to 12–Te–4 and 14–Te–6 pertellurane structure.

The unexpected rupture of $C_{aliph}$—Te bonds during halogenolysis of **43** is due to the strong stabilization of the 10–Te–3 structure **40a** resulting from intramolecular coordination of the azomethine nitrogen atom with the tellurium atom [81]. In the diorganyldiaryloxytelluranes of type **44**, the central tellurium atom would possess two intramolecular Te---N coordination bonds and thus belong to the 14–Te–6 type [82]. A capacity for such coordination has been rendered by the structure of two bidentate ligands linked with Te(IV) which bring the azomethine groups into positions sterically accessible for coordination. Intramolecular Te---N coordination causes the high stability of *ortho*-tellurated derivatives of azomethine **45–47** [83] (Fig. 8).

Minkin and co-workers have studied the molecular and crystal structures of a range of *ortho*-tellurated azomethines [84,85]. In the crystalline form, **47** is exactly similar to **40a** (X = Cl) and of tellurenyl azobenzenes. The telluride **49** has a T-shaped 10–Te–3 structure shown by resonance forms **48** and **50** with one intramolecular Te---N (2.702 Å) bond occupying an axial position [86]. With the help of $^{125}$Te NMR studies it has been shown that in solution a faster (on the NMR time scale) exchange reaction proceeds which is attributed to the concomitant formation and rupture of the Te---N bonds **48–50**. To elucidate the effect of the basicity of the imine N atom on the length of the N---Te bond, the structure of bis[(2-isopropyliminomethinyl)phenyl]telluride has been studied [84]. Despite the large basicity of the imine nitrogen in this compound, in comparison with its aryl analogue **49**, the structures of both compounds are similar and only one nitrogen serves as the donor centre coordinated to Te; the N---Te bond length is the same as that of **49**. Although there is a positive charge on the Te atom in cation **51**, the N---Te bond is long (2.75 Å). In the crystal, weak intermolecular contacts between Te and O atoms of perchlorate anions link the molecules to centrosymmetric dimers, forming a distorted pentagonal bipyramid around the tellurium atom.

Interestingly, Lewis acid and base character is exhibited by the novel bis-

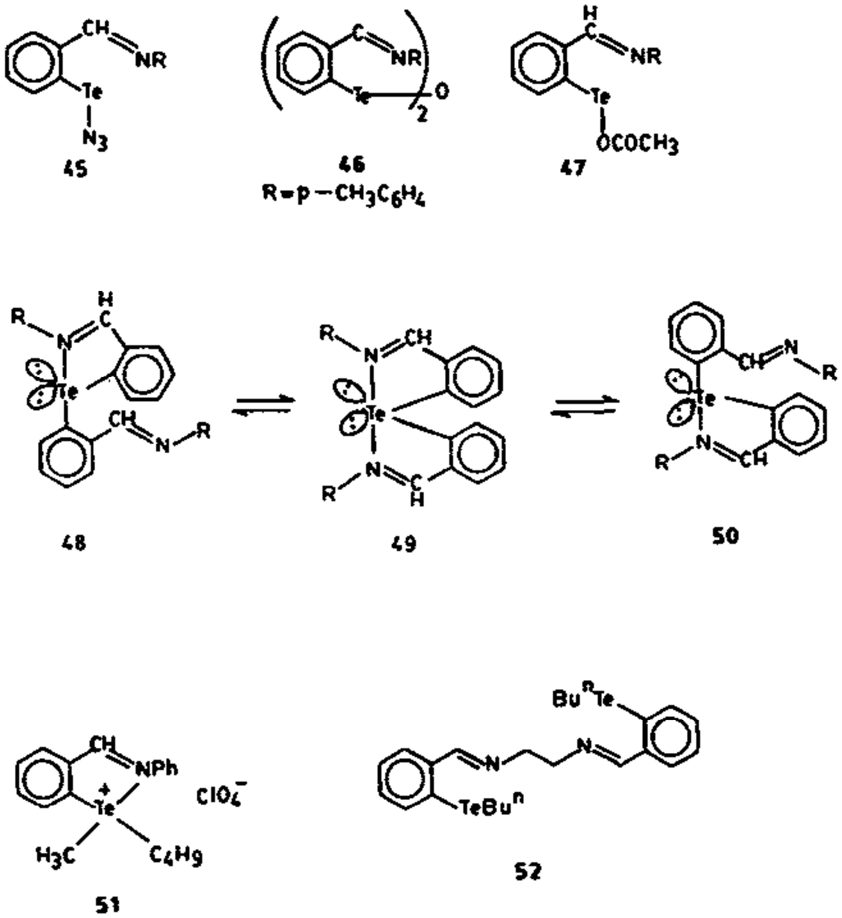
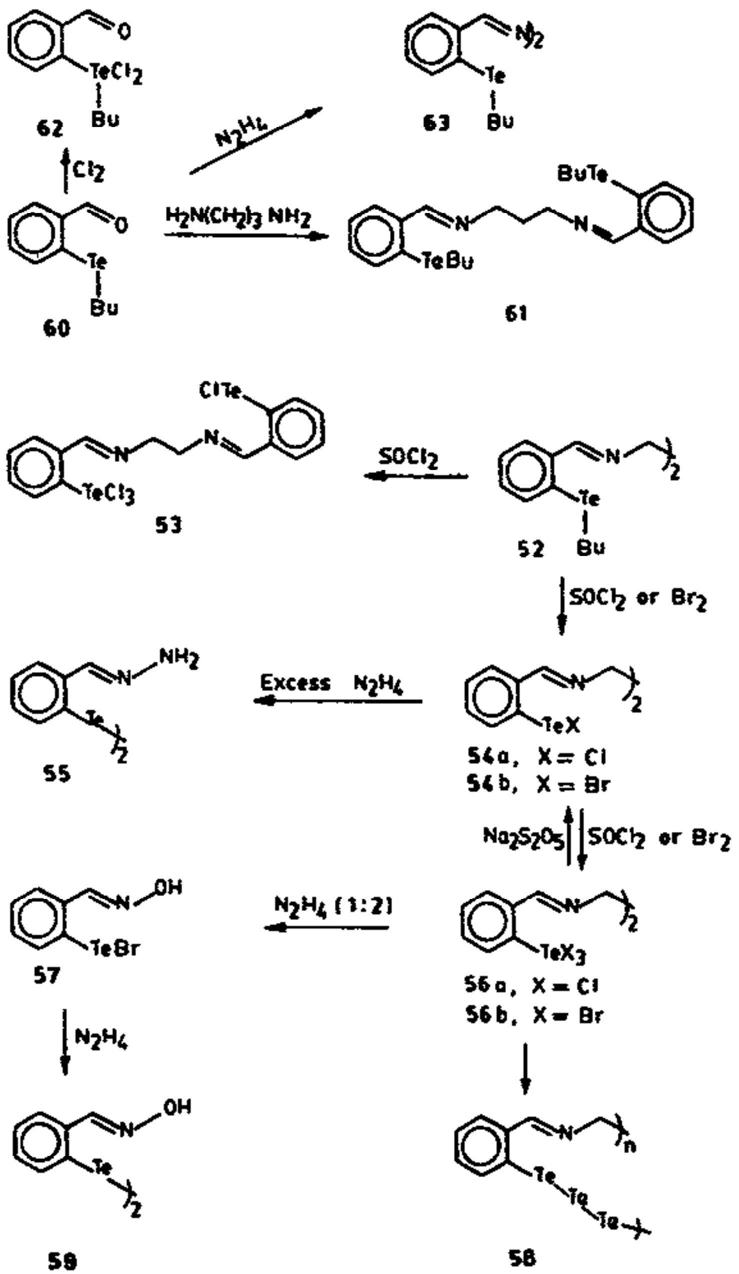


Fig. 8. *Ortho*-tellurated azomethines.

telluride ligand **52** which is believed to be the first example of three-coordinate $R_2Te \cdots X$ involving nitrogen [87]. The Te···N distance (2.773 Å) is well within the van der Waals distance (3.61 Å) and the Te–C–C–C–N moiety is planar. The ligand forms a complex with $HgCl_2$ resulting in a 13-membered macrocyclic chelate ring.

The loss of butyl group on treatment of compound **52** with halogen led to the discovery of a range of new compounds (Scheme 3) [88].

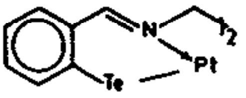
The poly-tritelluride **58** (Scheme 3) is stabilized by coordination of tellurium with the imino nitrogen atom. The Te–Bu linkage survives intact in the tellurium(IV) compound **62** even after halogenolysis. The structure of **62** reveals a weak Te···O interaction (2.839(4) Å) with a distorted pseudo-octahedral coordination. The Te···N distances in the ditelluride **59**, 2.822(5) and 2.876(5) Å, are within the van der Waals distance, 3.61 Å, and represent a weak interaction. Formation of aryltellurolate


62
63
N2H4
Cl2
H2N(CH2)3 NH2
60
61
53
SOCl2
52
SOCl2 or Br2
55
Excess N2H4
54a, X = Cl
54b, X = Br
Na2S2O5
SOCl2 or Br2
57
N2H4 (1:2)
56a, X = Cl
56b, X = Br
N2H4
59
58

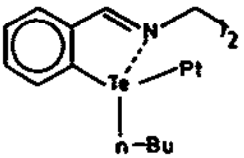
Scheme 3.

complexes of Pt(IV) **64** and alkyl aryl telluride complex of Pt(II) **65** shows the potential application of tetradentate ligands in coordination chemistry [89]. An interesting example where the bis-telluride **52** may function as a terdentate ligand is **66**.

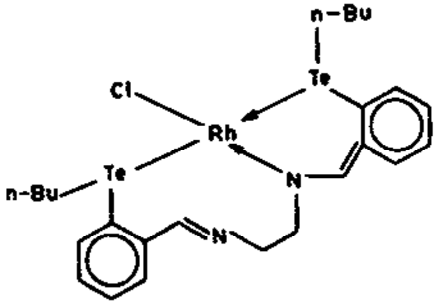
Solution of $Na_2Te_2$ in *N,N*-dimethylformamide reacts with the solvent to give small yields of an unusual ditelluride **67** (Te(1)---O(1) 2.984 Å, Te(2)---O(2) 2.986 Å, Te(1)---N(1) 3.019 Å, Te(2)---N(2) 3.039 Å) [90]. Photochemical decomposition of **67** occurs at low temperatures on exposure to UV radiation but Te atoms do not migrate from the unit cells unless the temperature is sufficiently high.



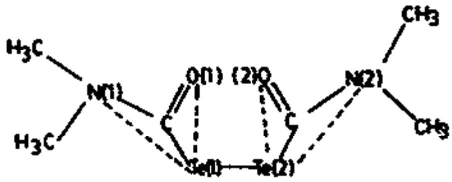
**64**



**65**



**66**

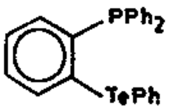


**67**

## *2.5. Intramolecular coordination compounds of tellurium having a Te---P bond*

Unlike intramolecular coordination compounds of tellurium having a Te---N bond, little has been reported on compounds having a Te---P bond. Gysling and Luss have reported the first hybrid bidentate ligand **68** incorporating tellurium and phosphorus donor atoms [91]. It forms a monomeric complex with $K_2Pt(SCN)_4$.

A functionally substituted telluroether of the type **37** (Y = $PMe_2$) offers the prospect of coordination of the ligand to hard metal ions such as Co(III), Ni(III), Pt(IV) [76].



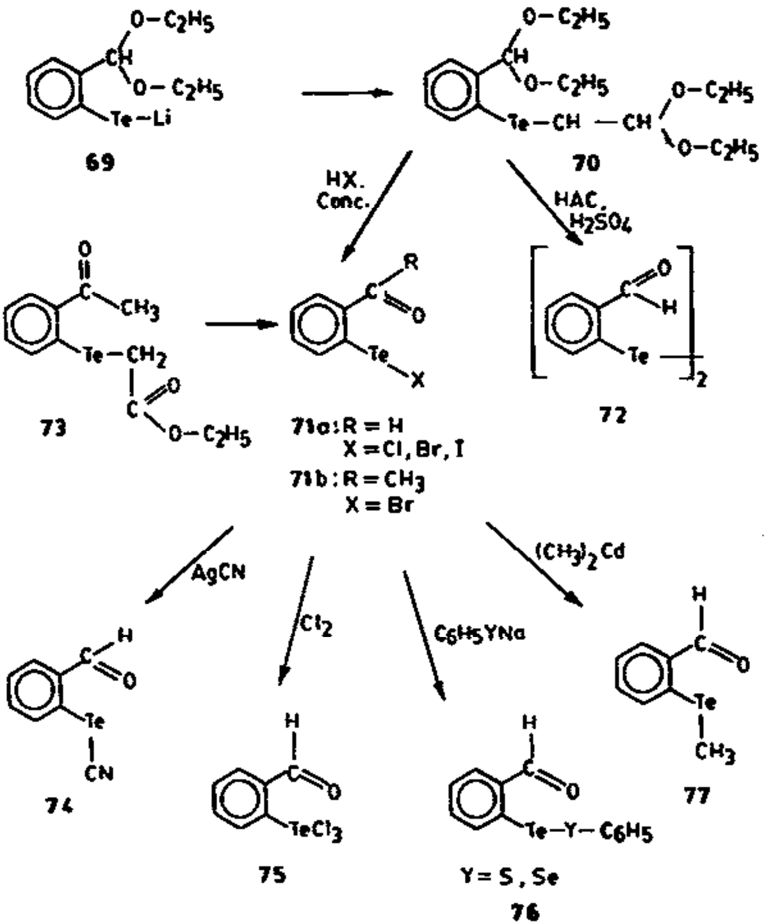
**68**

*2.6. Intramolecular coordination compounds of tellurium having a Te---O bond*

Studies on the oxygen donor atom facilitated *ortho* tellurations started in 1970 [92]. Intramolecular coordination compounds containing an oxygen donor atom have been studied extensively since then. Among the carbonyl oxygen ligands, the tellurated compounds which have attracted attention are the *ortho*-tellurated aldehydes, ketones and amides. Renson and co-workers were the first to report aryltellurenyl compounds stabilized by *ortho*-carbonyl function [93–95] (Scheme 4). In a carbonyl orientation relative to the *ortho* substituent there are two possible planar conformations, as proposed for the *ortho*-substituted benzaldehydes [96]. The conformation can be deduced from NMR experiments. The existence of long-range $^{13}J$ coupling in 2-halotellurenyl benzaldehydes and 2-methyltelluro benzaldehyde detected by double-resonance experiments shows that they all have a "cis" conformation. A simple electronic model proposes that the halogen atom X bonded to the Te atom polarises the Te–X bond to give $Te^{\delta+}$–$X^{\delta-}$ and a spatial electrostatic effect polarizes the carbonyl yielding $C^{\delta'+}$–$O^{\delta'-}$. In the case of formylphenyltellurenyl halides this agrees with IR measurements. Preliminary results of structural investigations also confirm the conformation [97]. The crystal and molecular structures of aryltellurenyl compounds **71** [98] and **78** [99] (Fig. 9) indicate that these compounds owe their stability to an intramolecular Te---O interaction. Heterocyclic compounds **79** and **80** exhibit partial bonding between oxygen and neighbouring hetero atoms [100,101]. An estimate of O---X distances in **80** reveals that the O---X interaction is weak when X = S and increases with the covalent radius of X. In the course of electrophilic cyclization attempts, it has been found that *o*-phenyltellurobenzylchloride undergoes intramolecular carbodetelluration to 2-chlorotellurobenzophenone **81** [102].

The reaction between diaryl ditellurides and $SeO_2$ results in the insertion of selenium between the tellurium atoms [103]. The products are identified as benzenetellurenyl benzenetellurinyl selenides, Ar–Te–Se–Te(O)–Ar. When a carbonyl group is present *ortho* to the tellurium atom **72** a bis(benzenetellurenyl)selenide **82** is formed. The stability of the latter is attributed to Te---O=C interaction.

Compared with the corresponding ditelluride, the tellurium atom of the bis(ben-



Scheme 4.

zenetellurenyl)selenide **83** is appreciably deshielded. The $^{125}$Te chemical shift is downfield to the ditelluride by 493 ppm. In the crystal structure of **83** the Te···O distance (2.658 Å) is of some interest. Although it is larger than the calculated covalent single bond distance (2.04 Å), it is less than the sum of the van der Waals radii (3.60 Å). This explains the stability of *o*-carbonyl derivatives and their failure to produce mixed derivatives of the type Ar–Te–Se–Te(O)–Ar.

The use of regiospecific *ortho* lithiation reactions leading to the elaboration of *ortho*-substituted alkyl chalcogenobenzenes has been investigated by Christiaens *et al.* [72]. In the process of preparation of benzo[*d*]-3-aza-tellurophenes, introduction of a tellurium containing group into an aromatic ring, in an *ortho* position to an amino group has been achieved **84** [104]. *ortho*-carbonyl alkyltellurothiophenes are synthesized from organolithium compounds **85–87** [105] (Fig. 10).

Bis[diaryl(2-formylaryloxy)tellurium] oxides of the type **88** [106],

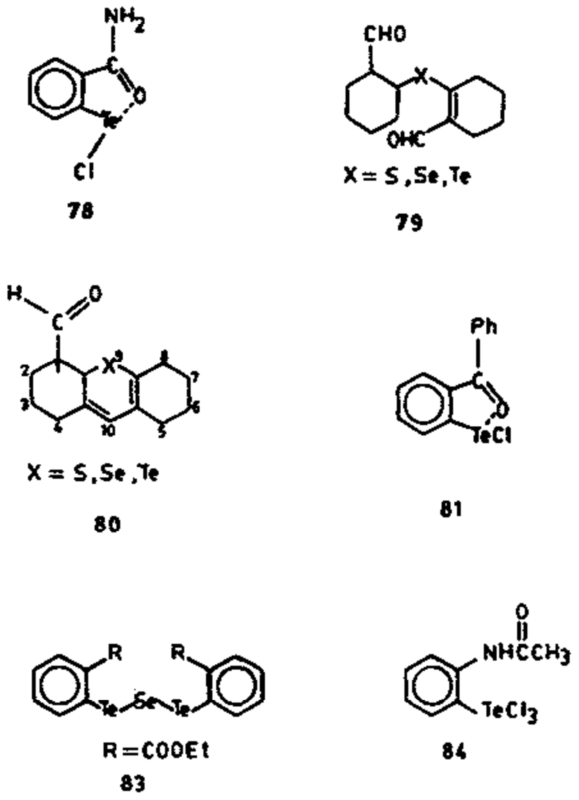
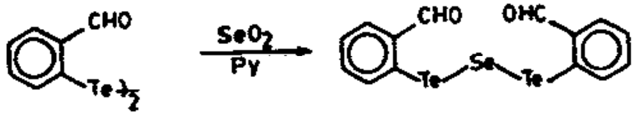


Fig. 9. *Ortho*-tellurated derivatives stabilized by oxygen donor atom.



72

82

(2-formylaryl)oxytellurium trichlorides of the type **89** [107] and dimethyldiaryloxy derivatives of Te(IV) **90** [108] have also been shown to be stabilized by intramolecular Te---O interactions. The ready accessibility of (*o*-nitrophenyl)tellurenyl bromide **91**, as well as its stability, makes it an ideal substance for study as a potential analogue of arylselenyl halide reagents [109].

*ortho*-tellurated derivatives bearing an alkoxy group constitute further examples of stable isolable entities. The addition of $TeCl_4$ or $C_6H_5TeBr_3$ to cyclic alkenes gives compounds in which carbon halogen bonds are readily solvolysed to ethoxy derivatives **92–95** [110–112] (Fig. 11). The ethoxo group is well situated to coordinate to give monomeric five-coordinate complexes. Bergman and Engman [113]

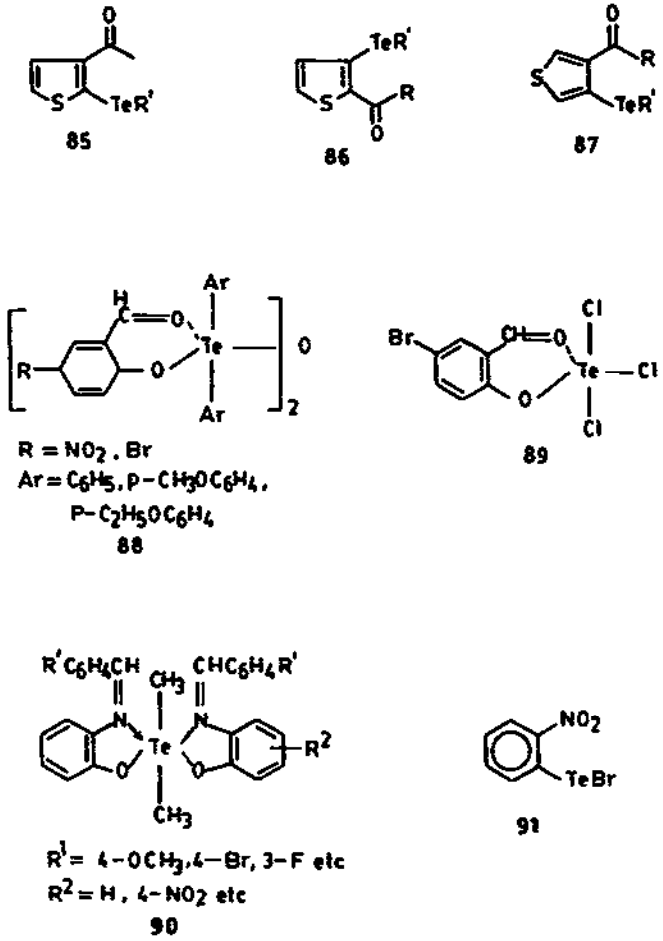


Fig. 10. *Ortho*-tellurated derivatives stabilized by an oxygen donor atom.

have shown that an electron-deficient atom, at least in the solid state, can coordinate to an electron-rich ligand such as the oxygen of an ethoxy group **95**.

1,3-Addition compounds **96** and **97** of $TeCl_4$ and allylic esters contain an acyloxy group in the $\beta$ position [114]. The carbonyl frequencies of different adducts exhibit a dramatic lowering (100–130 $cm^{-1}$) of the frequency, as compared with a normal ester carbonyl. This effect is undoubtedly caused by coordination of the carbonyl oxygen to tellurium. This effect has also been observed for several other organotellurium compounds containing an electron-deficient tellurium atom [102,115]. Bis($\beta$-alkoxyalkyl)ditellurides **98** and their corresponding trichlorides have been recently prepared by Engman [116]. Non-terminal olefins do not give isolable yields of ditellurides, cyclohexene being the only exception giving 11% of **99**. If a suitably positioned nucleophile is present in the olefin, cyclic ethers are

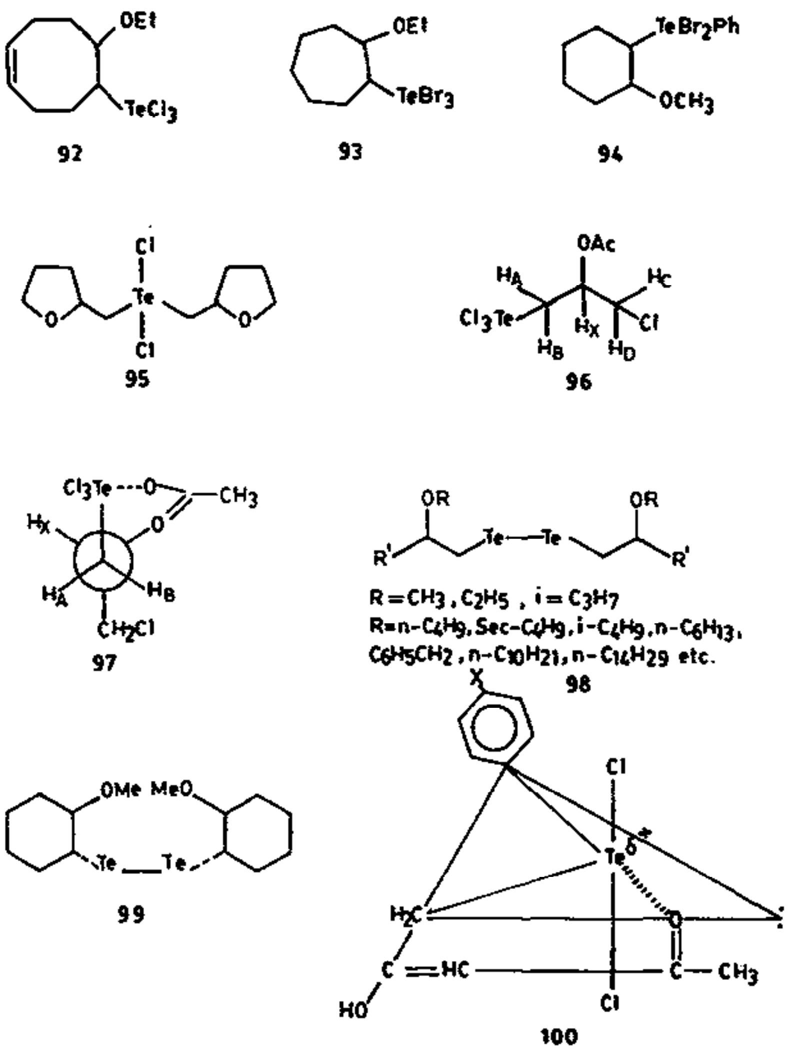


Fig. 11. *Ortho*-tellurated derivatives stabilized by an oxygen donor atom.

obtained. Similar results have been observed in the acetoxyalkyl ditellurides and their corresponding trihalides [117].

In comparison with pure acetylacetone, the $CH_3$ ($\delta = 1.92, 2.11$ ppm) and $CH–CH_2$ resonances ($\delta = 5.5, 3.5$ ppm) are observed to be shielded in the spectrum of $C_1$-bonded acetylacetonates of tellurium(IV) **100** [118]. This indicates that oxygen has significant secondary interaction with tellurium made positive by two electronegative chlorine atoms, which in turn brings the $CH_3$ protons under the influence of the tellurium lone pair and shields them. The shielding of $CH–CH_2$ seems also to result from the delocalization of electron density arising out of this interaction. The crystal structure of the trichloride **101** (Fig. 12) shows that tellurium is bonded to the alkenyl methyl rather than the carbonyl methyl [119]. A significant feature of this structure is the short distance between the carbonyl oxygen and the tellurium (2.44 Å). The tellurium is coordinated to oxygen in an almost planar six-membered ring. Alkyltellurenyl halides are expected to be more unstable than their aryl analogues owing to the lack of Te–π conjugation offered by the aromatic nucleus. The first aliphatic tellurenyl halide **102** has been synthesized as an unstable but isolable compound by the halogenolysis of a tellurophthalide [115].

Engman [120] has shown that the stability of a C–Te bond next to a carbonyl is decreased with increasing substitution on carbon. Reactions of cycloalkanones with $TeCl_4$ have been carried out in order to obtain 2:1 condensation products of the type **103**. Cyclohexanone and cycloheptanone afford

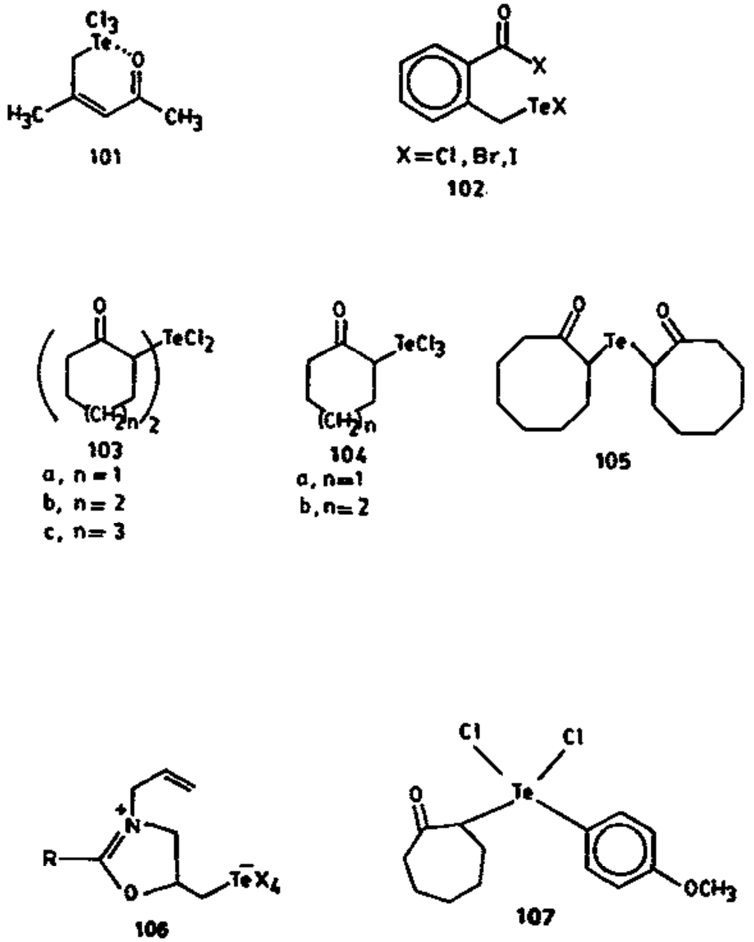


Fig. 12. *Ortho*-tellurated derivatives stabilized by an oxygen donor atom.

2-(trichlorotelluro)cyclohexanone **104a** and 2-(trichlorotelluro)cycloheptanone **104b** respectively. However, $Na_2S_2O_5$ reduction of **103c** gives an unstable new compound presumably bis(1-oxo-2-cyclooctyl)telluride **105** as indicated by a quick NMR. Because of its lability this compound could not be further characterized. The IR spectrum of diphenacyl telluride $C_6H_5COCH_2TeCH_2COC_6H_5$ exhibits remarkably low carbonyl absorption (1640 $cm^{-1}$) as compared with diphenacyl selenide (1660 and 1670 $cm^{-1}$) and diphenacyl sulphide (1690 $cm^{-1}$). The weak carbon–tellurium bonds present in these compounds might be of value in carbon–carbon bond forming reactions.

Interaction of $TeCl_4$ with *N*-methyldiallyamine in $CH_3CN$ gives a zwitterionic 2-oxazoline **106** [121].

The reaction of equimolar amounts of ketones or ketone trimethylsilylenonl ethers with organyltellurium trichlorides in boiling benzene produces α-(dichloroorganyltelluro)ketones [122]. The introduction of an $RTeCl_2$ group in the α position of a ketone reduces the ν(C=O) frequency. The structure of 2-[dichloro(*p*-methoxyphenyl)telluro]cyclohexanone **107** shows that the intramolecular distance between the tellurium atom and the carbonyl oxygen (2.93, 2.94 Å) is shorter than the sum of the van der Waals radii of the Te and O of 3.60 Å and is much shorter than the upper range of 3.3–3.4 Å found for weak bonds. Similar results obtained for tellurium compounds containing tellurium–halogen bonds in the neighbourhood of carbonyl oxygen bonds have been interpreted in terms of three-centre bonds between X, Te and O. Such an interaction in **107** should be possible in view of the conformation of cyclohexane ring shown in the Newman projection in Fig. 13 [123].

Interest in the tellurium analogues of various heterocyclic systems has been increasing. Arylellurenyl halides stabilized by *ortho*-carbonyl function have been used in the synthesis of such heterocyclic systems as telluroindoxyl [124], telluroindigo [124,125], tellurochromones [126,127] and telluroxanthones [128,129]. Novel heterocyclic systems of the type **108** [94], **109** [130], **110** [131] and **111** [132] (Fig. 14) have also been obtained from aryltellurenyl halides bearing an *ortho*-carbonyl function.

The rearrangement of tellurochroman-4-one-1,1-dihalides has been facilitated by intramolecular Te···O coordination to give the compounds **112** [133]. The

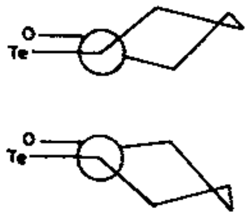


Fig. 13. Newman projections of cyclohexane rings.

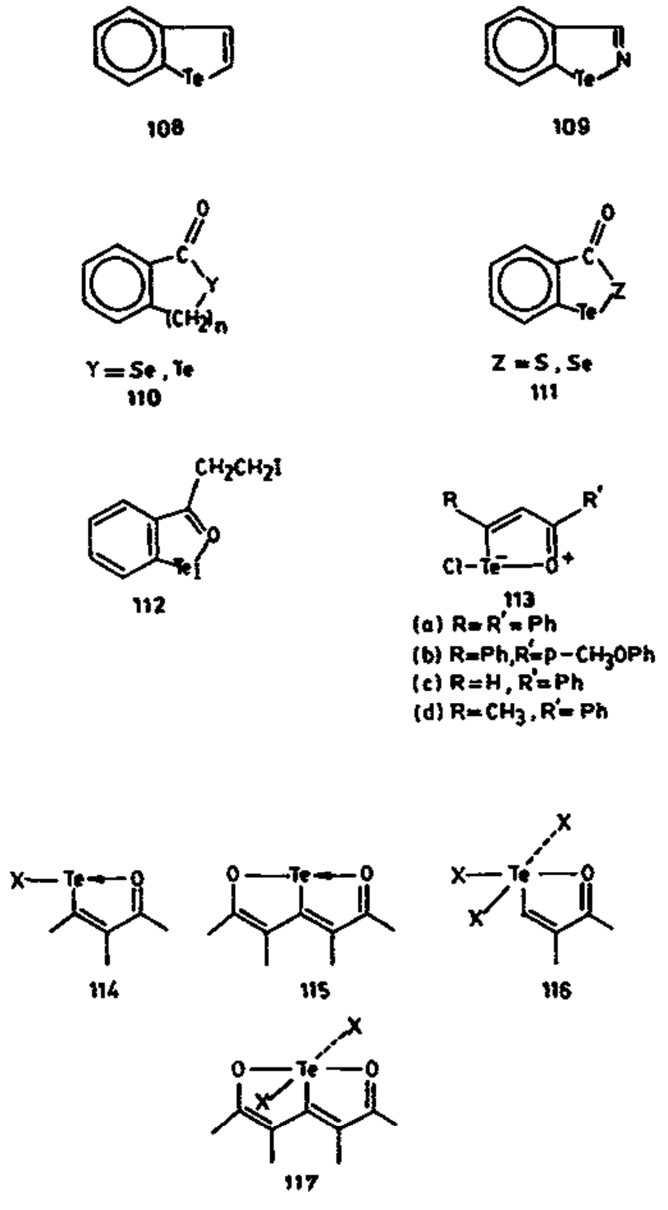


Fig. 14. Aryltellurenyl compounds in the synthesis of tellurium-containing heterocycles.

compound has a T-form configuration, the structure typical of 10–Te–3 telluranes, with a strong non-valent Te···O (2.368 Å) interaction at the apical position.

The first telluroflavone derivatives have been described by Detty and co-workers [134,135]. 1,2-Oxatellurol-1-ium chlorides of the type **113a–113d** are easily prepared by Lewis acid or thermally catalysed rearrangement of $\beta$-(aryltelluro)acryloyl or -cinnamoyl chlorides [134]. All the compounds display very low carbonyl stretching frequencies (1520–1530 cm$^{-1}$) indicating a strong tellurium–oxygen interaction. An X-ray crystal structure of **113b** shows strong, nearly equal fractional bonds from tellurium to both chlorine and oxygen. The observed bond lengths and bond orders are best explained by a three-centre, four-electron bond among chlorine, tellurium and oxygen. Spectroscopically both $^{13}$C and $^{1}$H NMR show that the ring carbons appear to delocalize a considerable amount of positive charge, which would be consistent with negative charge being localized at chlorine and oxygen. The $^{125}$Te NMR spectra of some of the oxatellurolium halides suggest that Te(IV) may be the approximate oxidation state in these compounds.

In the organotellurium species, oxatellurolium halides **114**, dioxatellurapentalenes **115**, oxatellurolium trihalides **116** and dioxatellurapentalene dihalides **117**, three-centre, four-electron bonding with tellurium oxygen and a halide should involve electron donation from oxygen to tellurium [136]. X-ray photoelectron spectroscopic studies show that O(1s) binding energies of these compounds are higher than those of model Te(II) and Te(IV) compounds, indicating that oxygen is electron deficient when involved in a three-centre, four-electron bonding.

### *2.7. Intramolecular coordination compounds of tellurium having a Te---S bond*

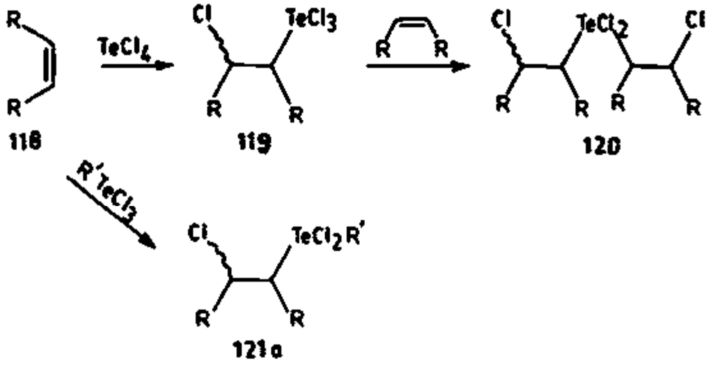
No well-substantiated *ortho*-tellurated compound stabilized by an intramolecular Te---S bond has been reported so far. Reaction of 2-thienyl mercuric chloride with $TeCl_4$ in refluxing dioxane gives a mercuric(II) chloride dioxane complex which can be reduced to furnish di-2-thienyl ditelluride [13]. Similarly, the condensation reaction of $TeCl_4$ with 2-acetylthiophene gives only the $R_2TeCl_2$ product with no evidence for interaction of the ring sulphur with tellurium [61].

Heterocyclic lithiumtellurolates derived from benzo[*b*]thiophene and dibenzothiophene react with methyl iodide to yield the corresponding methyl telluro compounds [60]. Organosulphenyl-containing tellurium(II) species of the type $Te[S(CH_2)_nCOOH]_2$ owe their stability to an intramolecular interaction between the tellurium and the acid carbonyl group [138].

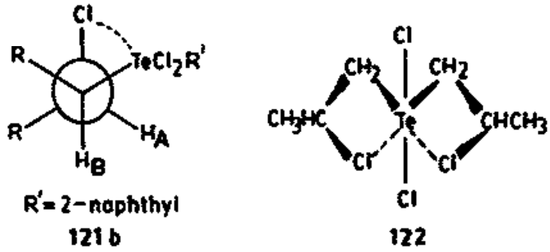
### *2.8. Intramolecular coordination compounds of tellurium having a Te---Cl bond*

The metal–halogen coordinate bond is compared with those in compounds containing ligating atoms such as N, P, O, S [20]. $TeCl_4$ and alkyl- or aryltellurium trichlorides, $RTeCl_3$ undergo addition reactions with olefins to give the corresponding $\beta$-chloroalkyltellurium species [139–141] (Scheme 5 in Fig. 15).

When $TeCl_4$ is used as the reagent, 2 mol of olefin may add to give the 2:1 adduct **120**. The tellurium atom is electron deficient in these compounds. Engman and co-workers have proposed a weak interaction in solution between tellurium and



Scheme 5.



Scheme 6.

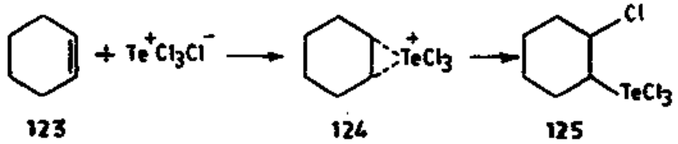
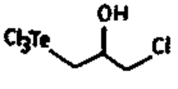


Fig. 15. Tellurated derivatives bearing a halogen donor atom.

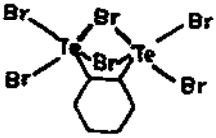
the electron-rich β-chlorine atom [142] **121b**. This phenomenon is observed in the solid state for the 2:1 adduct of propene and $TeCl_4$ **122** [143]. The formation of dichlorides, i.e. the addition of intermediate trichloride to a second molecule of the olefin, is promoted by increasing the dielectric constant of the solvent. An *anti* addition involving a transient telluronium ion has been postulated (Scheme 6 in Fig. 15).

The stereochemistry and mechanism of chlorotelluration of olefins by $TeCl_4$ and 2-naphthyltellurium trichloride have been determined using $^1H$ NMR spectroscopy [142]. Additions of the latter to all olefins are consistent with a cyclic tellurium ion intermediate. However, the mechanism of $TeCl_4$ addition to olefins is more complex and involves a possible radical chain reaction.

The reaction of $TeCl_4$ with allyl alcohol gives an isolable 1:1 adduct with proposed structure **126** [114]. The crystal structure of $Te_2Br_6C_6H_{10}$ **127** shows that each tellurium atom is surrounded by four in a plane and one carbon atom at the apex of the pyramid. The two tellurium atoms are linked by two bromine atoms and the cyclohexane group [143].



**126**



**127**

Pathirana and McWhinnie [144] have shown that the reaction of bis(aryltelluro)alkenes of the type $[\{(p\text{-}EtOC_6H_4)Te\}_2(CH_2)_n]$, ($n = 6$ or 10) with bromine led to rupture of the Te–aryl linkage giving $(Br_3Te)_2(CH_2)_n$. The good solubility of the products suggests that they be monomeric, the coordination requirements of the tellurium atoms being satisfied by their mutual interaction via bromo bridges in a manner similar to that observed in **127**. The halide derivatives of bis(organyltelluro)-methanes, $CH_2(Te(X)_2R)_2$, where X = Cl, Br, I, and R = Me or Ph, also fall in this category [145].

## 3. STRUCTURAL AND SPECTRAL DATA OF INTRAMOLECULAR COORDINATION COMPOUNDS OF TELLURIUM

Over the last few years there has been a considerable interest in the crystallographic studies of *ortho*-tellurated compounds. Particularly, compounds containing a Te---N bond have been extensively studied. The intramolecular Te---X distances (X = N or O), certain intermolecular Te···X distances and angles at tellurium of intramolecular coordination compounds are tabulated in Tables 1 and 2

$^{125}$Te Mössbauer spectroscopy is a powerful means by which the fundamental nature of bonding and structure in organotellurium compounds may be investigated [147]. The chemical isomer shift $\delta$ is a measure of the electron density at the nucleus and provides information on oxidation states, coordination number and bonding characteristics. The symmetry of the electronic and ligand arrangement around tellurium is obtained by measuring the quadrupole splitting $\Delta$. The $^{125}$Te Mössbauer data of a few *ortho*-tellurated compounds are listed in Table 3. In the azobenzene series [51] $\delta$ is expected to become more positive from RTeX to $RTeX_3$ since the s electrons should be more shielded in the Te(IV) case. The quadrupole splitting ($\Delta$) of RTeX (X = Cl, NCS, dithiocarbamate or $O_2CMe$) are lower than expected. A

TABLE 1

X-ray crystal structure data for intramolecular coordination compounds of tellurium having a Te–N bond

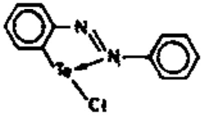
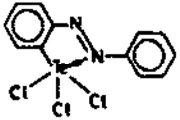
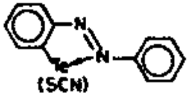
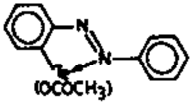
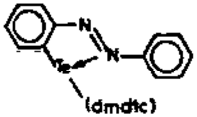
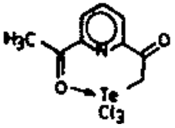
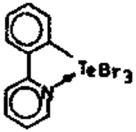
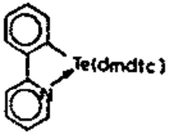
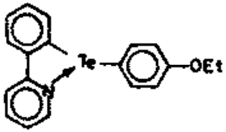
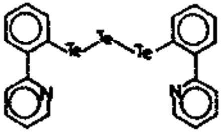
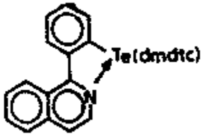
| Reference | Compound | Intramolecular Te–N distances (Å) | Intermolecular Te ··· X distances (Å) | Angle and geometry at tellurium (°) |
|---|---|---|---|---|
| [42] |  | Te–N(A) 2.23(2)<br>Te–N(b) 2.19(2) | Te(A) ··· Cl(B) 3.66<br>Te(B) ··· Cl(A) 3.67 | N(1)–Te–C(2) 72.8(9) (A)<br>N(1)–Te–C(2) 76.8(9) (B) |
| [49] |  | Te–N 2.417 | — | N(1)–Te–C(2) 72.3(2) |
| [50] |  | Te–N 2.243(3) | Te ··· N 3.535(3) | N(2)–Te–C(2) 74.2(2) |
| [50] |  | Te–N 2.260(4)<br>(Te–O(2) 2.953(4) (weak)) | — | N(2)–Te–C(2) 73.9(2) |
| [51] |  | Te–N 2.340(7)<br>(Te–S 3.225(3) (weak)) | | N(2)–Te–C(22) 72.5(3) |
| [61] |  | Te–N 2.402<br>(Te–O(2) 2.878) | Cl(3) ··· H(1) 2.88 | N–Te–C(1) 75.1(1)<br>N–Te–O(2) 61.02(8)<br>Cl(1)–Te–O(2) 100.59(6)<br>Cl(2)–Te–O(2) 81.37(7)<br>Cl(3)–Te–O(2) 135.56(6) |

TABLE 1 (continued)

| Reference | Compound | Intramolecular Te–N distances (Å) | Intermolecular Te···X distances (Å) | Angle and geometry at tellurium (°) |
|---|---|---|---|---|
| [62] |  | Te–N 2.244(14) | Te···Br 3.596(3) | N(1)–Te–C(1) 78.2(7) |
| [62] |  | Te–N 2.354(4)<br>(Te–S(2) 3.667(1)<br>(very weak)) | — | N(1)–Te–C(1) 74.4(2) |
| [62] |  | Te–N 2.695(4) | — | C(1)–Te–C(12) 94.8(2)<br>C(1)–Te–N(1) Not given |
| [63] |  | Te–N 2.554(7) | — | Te(1)–Te(2)–Te(1) 100.4(1)<br>C–Te(1)–Te(2) 99.1(2)<br>N···Te(1)–Te(2) 170.7(2)<br>N···Te(1)–C 71.6(3) |
| [64] |  | Te–N 2.3654(4)(A)<br>Te–N 2.385(4)(B)<br>(Te···S(2) 3.222(1)<br>Te···S(2) 3.230(1) (weak)) | — | N(1)–Te–C(1)<br>N(1)–Te–C(1) |

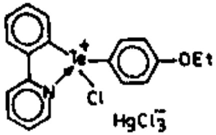
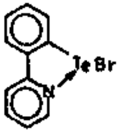
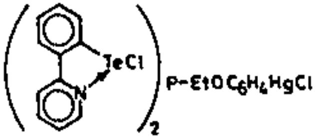
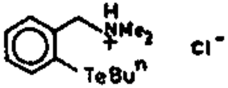
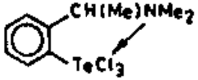
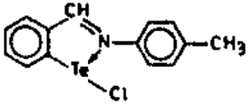
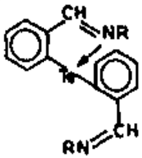
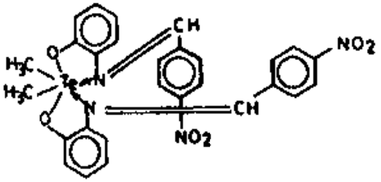
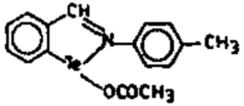
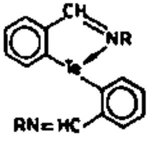
| | | | | |
|---|---|---|---|---|
| [65] |  | Te–N 2.31(2) | — | N–Te–C(7) 78 (1) |
| [70] |  | Te–N 2.236(11) | — | N–Te–C 75.9(5) (1) |
| [70] |  | Te–N 2.236(6) | — | N–Te–C 76.8(8)??? |
| [73] |  | Te–N 2.422(14) | Te ··· Br(1) 3.896(2) | N(1)–Te–C(1) |
| [73] |  | Te–N$^+$ 4.380(4) | Te ··· Cl$^-$ 3.3337(2) | — |
| [74] |  | Te–N 2.411(7) | Te ··· Cl 3.498(4) | N–Te–C(1) 75.6(3) |
| [78] |  | Te–N 2.218 (A)<br>Te–N 2.239 (B) | Te ··· Cl 3.746 | N–Te–C(1) 77.0(2) (A)<br>N–Te–C(1) 76.7(2) (B) |

TABLE 1 (continued)

| Reference | Compound | Intramolecular Te–N distances (Å) | Intermolecular Te···X distances (Å) | Angle and geometry at tellurium (°) |
|---|---|---|---|---|
| [86] | <br>R = P-MeOPh | Te–N 2.702(3) | — | C(1)–Te–C(15) 96.3(2) |
| [82] |  | Te–N(1) 2.923(3)<br>Te–N(2) 2.962(3) | — | N(1)–Te–O(1) 64.8(2)<br>N(1)–Te–O(2) 128.0(2)<br>N(2)–Te–O(1) 129.1(2)<br>N(2)–Te–O(2) 64.1(2) |
| [84] |  | Te–N 2.297(7) | — | N–Te–C(1) 75.8(3) |
| [84] | <br>R = isopropyl | Te–N(1) 2.720(2) | — | — |

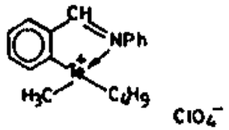
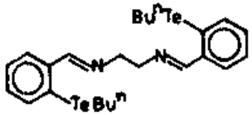
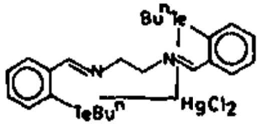
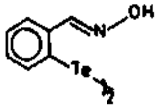
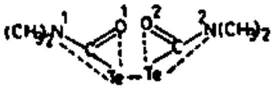
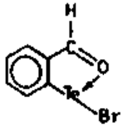
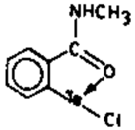
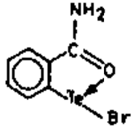
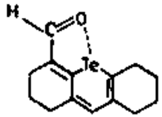
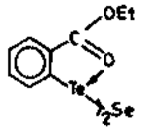
| | | | | |
|---|---|---|---|---|
| [84] |  | Te–N 2.75 | Te · · · O 3.33–3.56 | N–Te–C(1) 71.1 |
| [87] |  | Te–N 2.773 | — | C(4)–Te–C(5) 95.2(4) |
| [87] |  | Te–N 2.786<br>Te–N 2.752 | — | All angles at tellurium in range 96.3(3)–99.7(3) |
| [88] |  | Te–N 2.872(5)<br>Te–N 2.876(5) | Te(1) · · · Te(1) 3.777(4)<br>Te(2) · · · Te(2) 4.041(4) | Te(2)–Te(1)–C(1) 100.3(2)<br>Te(1)–Te(2)–C(8) 100.0(2) |
| [90] |  | Te(1)–O(1) 2.984(11)<br>Te(1)–O(2) 3.341(11)<br>Te(1)–N(1) 3.019(12)<br>Te(2)–O(2) 2.986(10)<br>Te(2)–O(1) 3.505(12)<br>Te(2)–N(2) 3.039(11) | Te · · · Te 4.188 | Te(2)–Te(1)–C(1) 96.1(4)<br>Te(1)–Te(2)–C(2) 92.4(4) |

TABLE 2

X-ray crystal structure data for intramolecular coordination compounds of tellurium having a Te—O bond

| Reference | Compound | Intramolecular Te–O distances (Å) | Intermolecular Te · · · X distances | Angle (deg) and geometry at tellurium |
|---|---|---|---|---|
| [98] |  | Te–O | — | O–Te–C(2) 74.4(0.7)<br>$C_{arom}$–Te–X 94.2(0.6) |
| [99] |  | Te–O 2.250(7) | — | O–Te–C(2) 78.5(4)<br>$C_{arom}$–Te–X 92.7(3) |
| [99] |  | Te–O 2.237(8) | — | O–Te–C(2) 75.6(3)<br>$C_{arom}$–Te–X 95.1(2) |
| [100] |  | Te–O 2.57, 2.58 | — | — |
| [103] |  | Te–O 2.658 | — | — |

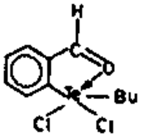
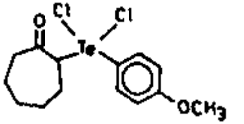
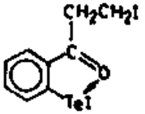
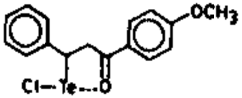
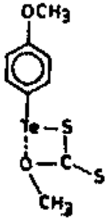
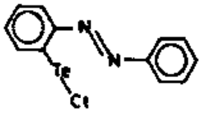
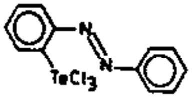
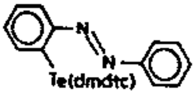
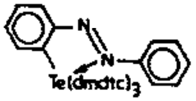
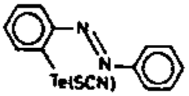
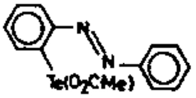
| | | | | |
|---|---|---|---|---|
| [88] |  | Te–O(A) 2.848(4)<br>Te–O(B) 2.830(4) | — | O(1)–Te(1)–C(1)(A) 68.8(4)<br>O(1)–Te(1)–C(1)(B) 69.2(4) |
| [122] |  | Te–O 2.93, 2.94 | — | — |
| [133] |  | Te–O 2.368(6) | $I^1 \cdots I^2$ 4.019(1) | O–Te–C(1) 74.7(3) |
| [134] |  | Te–O(1) 2.206, 2.175 | Te(A) ··· Te(B) 4.289(1)<br>Te(B) ··· C(4)(A) 3.654(4) | O(1)–Te–C(7) 76.37, 76.73 |
| [146] |  | Te ··· O 3.244(2) | Te ··· S(1) 3.466(8)<br>Te ··· S(2) 3.622(1) | S(2)–Te–C(3) 97.24(8) |

TABLE 3

$^{125}$Te Mössbauer data of intramolecular coordination compounds of tellurium

| Reference | Compound | Isomer shift $\delta$ (mm s$^{-1}$) | Quadrupole splitting $\Delta$ (mm s$^{-1}$) | $\tau_{av}$[a] |
|---|---|---|---|---|
| [51] |  | 0.78[b] | $11.8_c$ | |
| [51] |  | 0.89[b] | 8.1[c] | |
| [51] |  | 0.90[b] | 12.6[c] | |
| [51] |  | 0.99[b] | 11.4[c] | |
| [51] |  | 0.86[b] | 11.9[c] | |
| [51] |  | 0.82[b] | 12.5[c] | |
| [145] | $CH_2[Te(Cl)_2Me]_2$ | 0.66[d] | 9.3[e] | 6.3 |
| [145] | $CH_2[Te(Br)_2Me]_2$ | 0.68[d] | 8.1[e] | 5.7 |
| [145] | $CH_2[Te(I)_2Me]_2$ | 0.55[d] | 6.3[e] | 5.4 |
| [145] | $CH_2[Te(Cl)_2Ph]_2$ | 0.70[d] | 8.4[e] | 6.0 |
| [145] | $CH_2[Te(Br)_2Ph]_2$ | 0.68[d] | 7.5[e] | 5.8 |
| [145] | $CH_2[Te(I)_2Ph]_2$ | 0.68[d] | 6.0[e] | 5.7 |
| [145] | $CH_2(TeCl_3)_2$ | 0.90[d] | 7.6[e] | 6.0 |

[a] $\tau_{av}$ is the average linewidth.

[b] With respect to I(Cu) error ± 0.08 mm s$^{-1}$.

[c] Error ± 0.2 mm s$^{-1}$.

[d] Isomer shift relative to I(Cu) with source and absorber at 4.2 K. The error in $\delta$ is ±0.08 mm s$^{-1}$.

[e] $\Delta \pm 0.1$ mm s$^{-1}$.

possibility is that the tellurium *p* electron density is delocalized into the heterocyclic $C{=}C{-}N{=}N \rightarrow Te$ and further deshielding of s electrons occurs. The $\delta$ values of halide derivatives of bis(organyltelluro)methanes, $CH_2(Te(X)_2R)_2$ (X = Cl, Br, I and R = Me, Ph) are more positive than those in parent telluromethanes corresponding to an increase in the s electron density at the tellurium nucleus [145].

TABLE 4

$^{125}$Te NMR data of some intramolecular coordination compounds of tellurium

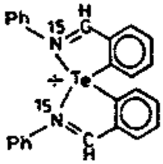
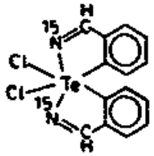
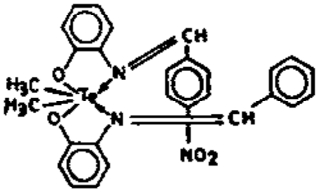
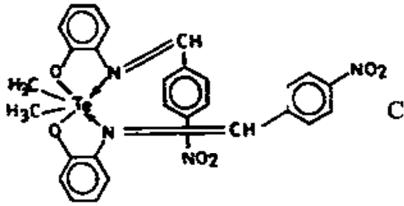
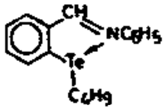
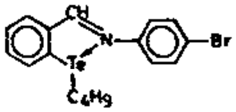
| Reference | Compound | Solvent | $\delta$($^{125}$Te) (ppm$^a$) |
|---|---|---|---|
| [51] | RTeCl | DMSO | 1486.5 |
| [51] | RTeCl$_3$ | CDCl$_3$ | 1278.2 |
| [51] | RTe(dmdtc) | CDCl$_3$ | 1228.6 |
| [51] | RTe(dmdtc)$_3$ | CDCl$_3$ | 1225.4 |
| [51] | RTe(dbdtc) | CDCl$_3$ | 1239.1 |
| [51] | RTe(dbdtc)$_3$ | CDCl$_3$ | 1239.6 |
| [67] | [HgCl$_2$·R′R″Te] | DMSO | 641.5 |
| [67] | [R″–HgCl(R′TeCl)] | CDCl$_3$ | 1323.9 |
| [67] | R′R″Te | CDCl$_3$ | 649.1 |
| [65] | R′R″Te$^+$Cl·HgCl$_3^-$ | DMSO | 1056,4, 1059.1 |
| [79, 86] |  | CDCl$_3$ | 600 |
| [79, 86] |  | CDCl$_3$ | 636 |
| [82] |  | CDCl$_3$ | 1055–1077 |
| [82] |  | CDCl$_3$ | 998–1179 |
| [84] |  | CDCl$_3$ | 483.0 |
| [84] |  | CDCl$_3$ | 484.8 |

TABLE 4 (*continued*)

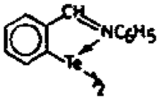
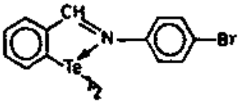
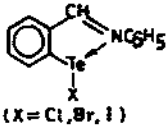
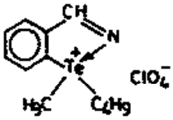
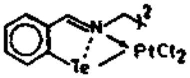
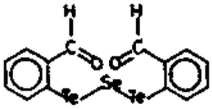
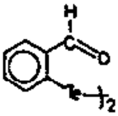
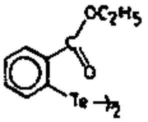
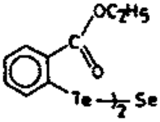
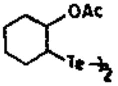
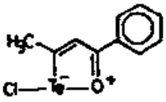
| Reference | Compound | Solvent | $\delta(^{125}\mathrm{Te})$ (ppm$^{a}$) |
|---|---|---|---|
| [84] |  | $CDCl_3$ | 1027.0 |
| [84] |  | $CDCl_3$ | 1036.0 |
| [84] |  | $CDCl_3$ | 1335.0, 1316.0 and 1187.0 (X = Cl, Br, I) |
| [84] |  | $CDCl_3$ | 641.5 |
| [89] |  | DMSO | 512.2, 469.5 |
| [103] |  | $CDCl_3$ | 1120 |
| [103] |  | $CDCl_3$ | 423 |
| [103] |  | $CDCl_3$ | 411 |
| [103] |  | $CDCl_3$ | 907 |
| [117] |  |  | 195.3, 204.2 |
| [134] |  |  | +911.0$^{b}$ |

TABLE 4 (*continued*)

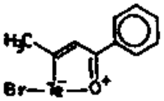
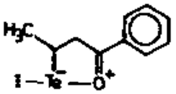
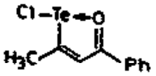
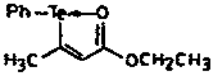
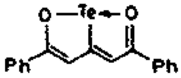
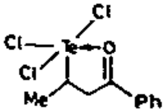
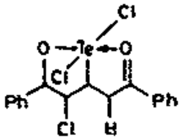
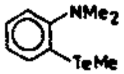
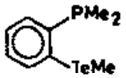
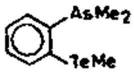
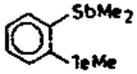
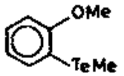
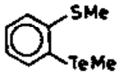
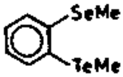
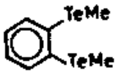
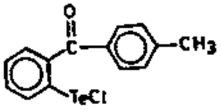
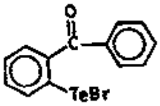
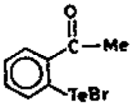
| Reference | Compound | Solvent | $\delta(^{125}Te)$ (ppm[a]) |
|---|---|---|---|
| [134] |  | | +858.0[b] |
| [134] |  | | +677.0[b] |
| [136] |  | $CD_2Cl_2$ | +1726[b] |
| [136] |  | $CD_2Cl_2$ | +807[b] |
| [136] |  | $CD_2Cl_2$ | +1955[b] |
| [136] |  | $CD_2Cl_2$ | +1365[b] |
| [136] |  | $CD_2Cl_2$ | +1444[b] |
| [136] | $CH_2[Te(Cl)_2Me]_2$ | $CDCl_3$ | 834 |
| [144] | $CH_2[Te(Br)_2Me]_2$ | $(CD_3)_2CO$ | 791 |
| | | $(CH_3)_2SO$ | 808 |
| [144] | $CH_2[Te(I)_2Me]_2$ | $CDCl_3$ | 786 |
| [144] | $CH_2[Te(Cl)_2Ph]_2$ | $CDCl_3$ | 858.1 |
| [144] | $CH_2[Te(I)_2Ph]_2$ | $CDCl_3$ | 786 |
| [144] | $CH_2(TeCl_3)_2$ | $CDCl_3$ | 1276.7 |
| [76] |  | $CHCl_3$ | 236 |
| [76] |  | $CHCl_3$ | 258 |
| [76] |  | $CHCl_3$ | 275 |
| [76] |  | $CHCl_3$ | 332 |
| [76] |  | $CHCl_3$ | 206 |

TABLE 4 (*continued*)

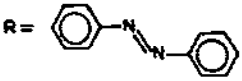
| Reference | Compound | Solvent | $\delta(^{125}Te)$ (ppm[a]) |
|---|---|---|---|
| [76] |  | $CHCl_3$ | 268 |
| [76] |  | $CHCl_3$ | 303 |
| [76] |  | $CHCl_3$ | 372 |
| [125] |  |  | 1226.5[c] |
| [125] |  |  | 1140.2[c] |
| [125] |  |  | 1156.6[c] |

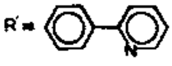
Positive values of $\delta$ indicate a downfield shift.

[a] Relative to $Me_2Te$ unless otherwise indicated.

[b] Relative to bis(diethyldithiocarbamato)tellurium(II).

[c] Relative to $(p\text{-}MeC_6H_4)_2Te_2$.





$^{125}$Te magnetic resonance is a useful addition to other spectroscopic methods for the study of organotellurium compounds [148]. In general, progress in $^{125}$Te NMR spectroscopy has lagged behind that in $^{77}$Se NMR spectroscopy because spin lattice relaxation times for $^{125}$Te are approximately 6–7 times shorter than those of $^{77}$Se in analogous compounds [149]. Spin rotation mechanism has been shown to be dominant for small Te-containing molecules. The $^{125}$Te chemical shifts of intramolecular coordination compounds of tellurium are tabulated in Table 4.

## NOTE ADDED IN PROOF

We list below relevant papers which appeared after submission of the main text: (a) Synthesis and characterization of new organotellurium compounds containing an *ortho*-amino group [150].

(b) Reactions of some *ortho*-tellurated compounds with intramolecular coordinate bonds [151].
(c) Synthesis and characterization of the novel cadmium tellurolate, Cd[Te(*o*-$C_6H_4CH_2NMe_2$)]$_2$ [152].
(d) Transmetallation reaction of Schiff-base type arylmercury compounds with 4-ethoxyphenyltellurium(IV)trichloride and the structure of (4-ethoxyphenyl)-[2-(benzylideneamino-5-methyl)phenyl]tellurium(IV)dichloride [153].
(e) Ligand chemistry of tellurium [154].
(f) Aspects of the chemistry of diorgano tritellurides [155].

## ACKNOWLEDGEMENT

The authors wish to thank Council of Scientific and Industrial Research (CSIR) New Delhi for financial support.

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