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Stable tellurols and their metal derivatives

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Abstract. Data on the synthesis, reactions and structures of stable aromatic tellurols and sterically hindered tellurols containing E – TeH bonds (E = C, Si or Ge) are systematised and generalised. Methods for the preparation of various metal derivatives of tellurols as well as applications of these derivatives in the low-temperature synthesis of metal tellurides are considered. The bibliography includes 90 references.

I. Introduction

Tellurium analogues of alcohols and phenols, *viz*., tellurols (RTeH), belong to a class of organotellurium compounds which are rather poorly studied. First representatives of these compounds, *viz*., alkanetellurols, were synthesised back in 1926,[1] while rather stable aromatic tellurols, *viz*., 2,4,6-trialkylbenzenetellurols and tris(trimethylsilyl)silanetellurols, were prepared only in 1991.[2] Based on these compounds and their analogues and derivatives, a wide range of tellurolates of various metals have been synthesised in recent years. Tellurolates of sterically hindered organoelement tellurols $(Me_3Si)_3ETeH$ (E = C, Si or Ge) are of particular interest because these compounds can be used in the pyrolytic synthesis of metal tellurides. Since these compounds contain E – Te – H bonds (E = Si or Ge), they do not formally belong to tellurols. However, it is reasonable to consider here methods of their preparation, reactions and spectral characteristics, because these derivatives possess unusual properties, in particular, enhanced stability in the crystalline state and in solutions compared to true tellurols. In addition, tellurolates based on the above-mentioned compounds allow one to prepare metal tellurides at relatively low temperatures.[3–7]

II. Synthesis, reactions and structures of tellurols

1. Synthesis and reactions of tellurols

The first alkanetellurol, *viz*., ethanetellurol **1a**, was prepared by high-temperature alcoholysis of Al_2Te_3 at 250 °C.[1] Later on, this method was modified by Baroni.[8] Oxidation of the resulting alkanetellurols can be prevented if the process is performed under an atmosphere of hydrogen. Apparently, the overall reaction is described by the following equation:

$$Al_2Te_3 + 3\,ROH \xrightarrow{\Delta} \underset{\mathbf{1a-d}}{3\,RTeH} + Al_2O_3$$

R = Et (**a**), Me (**b**), Pr (**c**), Bu (**d**).

Alkanetellurols **1c**,**d** were also prepared by the reactions of the corresponding alkyl halides with a solution of sodium ethoxide saturated with hydrogen telluride at low temperature.[8] However, attempts at synthesising methane- and ethanetellurols **1a**,**b** according to this procedure have failed.

$$EtONa + H_2Te \rightleftharpoons EtOH + NaHTe \xrightarrow[-NaBr]{RBr} \underset{\mathbf{1c,d}}{RTeH}$$

R = Pr (**c**), Bu (**d**).

The method which is most generally used for the preparation of different types of tellurols involves the reactions of their lithium and sodium salts (methods for their synthesis are discussed in Section III.1) with protic acids. Thus treatment of sodium methanetellurolate, which has been prepared from dimethyl ditelluride upon cleavage of the Te – Te bond with sodium in liquid ammonia, afforded methanetellurol **1b**.[9–11] Trideuteriomethanetellurol **1e** was prepared analogously.[11]

$$R_2Te_2 + Na \longrightarrow RTeNa \xrightarrow[-NaX]{HX} \underset{\mathbf{1b,e}}{RTeH}$$

R = Me (**b**), CD_3 (**e**); HX = H_2SO_4, H_3PO_4.

The acid H_3PO_4 is a protonating agent of choice [11] because the use of even dilute H_2SO_4 leads to partial oxidation of tellurol **1b** to dimethyl ditelluride.

Alkanetellurols **1** are liquids with an unpleasant odour. The yellowish colour of these compounds is caused by the presence of dialkyl ditellurides, which were formed either upon thermal decomposition of tellurols or upon their oxidation with atmospheric oxygen.[9–11] Tellurols can be stored at the temperature of liquid nitrogen with exclusion of air because they readily decompose at room temperature.[11]

Decomposition of methanetellurol under UV irradiation occurs in two stages. First, dimethyl ditelluride and hydrogen are formed and then more profound decomposition occurs to form methane, higher hydrocarbons and tellurium.[11]

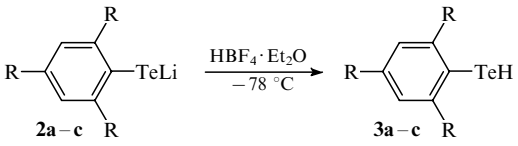
Attempts to synthesise benzene- and thiophene-2-tellurols by protonation of their lithium salts with trifluoroacetic acid in THF or of their sodium salts in an ethanol – ethyl acetate mixture have been unsuccessful.[12] Attempts to prepare benzenetellurol upon

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methanolysis of (phenyltelluro)trimethylsilane have also failed.[13–15] However, benzenetellurol[12,14,15] and thiophene-2-tellurol,[12] which are prepared according to the above-described methods *in situ*, are efficient reducing agents for organic compounds.[12,15] In the presence of ZnI_2, they are used for converting carbonyl compounds into asymmetrical ethers.[14]

Arenetellurols were synthesised by protonolysis of suspensions of sterically hindered lithium arenetellurolates **2** (prepared by reducing the corresponding diaryl ditellurides with lithium triethylborohydride) with HBF_4 etherate in light petroleum. Compounds **3** were obtained in nearly quantitative yields.[2]



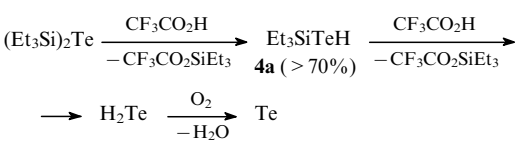
2a–c **3a–c**

R = Me (**a**), Pr^i(**b**), Bu^t (**c**).

Arenetellurols **3** are colourless crystalline compounds, which can be recrystallised from light petroleum at −110 °C. However, these compounds are light-sensitive and begin to decompose at −40 to −30 °C to form metallic tellurium.[2] The thermal stability of arenetellurols **3** is independent of the bulkiness of the substituents. In particular, tellurol **3a** is more stable than **3c**.[2]

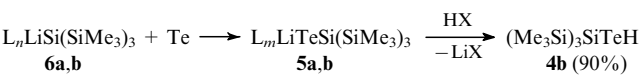
The most stable tellurols are organoelement tellurols $(Me_3Si)_3ETeH$ (E = C, Si or Ge). Due to the presence of bulky substituents, metal tellurolates prepared from these tellurols are readily soluble in nonpolar organic solvents and exist as monomers or weakly associated aggregates. These properties together with the volatility and high thermal stability allow one to use salts of organoelement tellurols in the pyrolytic synthesis of metal tellurides (see Section III).

The first tellurol containing the Si–TeH bond to be synthesised was triethylsilanetellurol **4a**.[16] This compound was prepared by treatment of bis(triethylsilyl) telluride with an equimolar amount of trifluoroacetic acid at 20 °C and was isolated by vacuum distillation.



Under the action of an excess of CF_3CO_2H, the Si–Te bond in the tellurol **4a** was cleaved and triethylsilyl trifluoroacetate and elemental tellurium were formed as the final reaction products.[16] Apparently, the latter was formed upon oxidation of intermediate H_2Te.

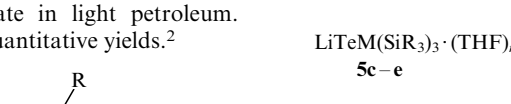
Sterically hindered tris(trimethylsilyl)silanetellurol (**4b**) was synthesised by protonolysis of lithium salts **5a**[17–19] or **5b**[20] with trifluoroacetic acid in hexane[17–19] or with HCl in toluene.[20] The salts **5a**[21] and **5b**[22] were prepared according to a standard procedure for the synthesis of these salts, which involves the insertion of the Te atom at the Si–Li bond in the complexes of tris(trimethylsilyl)silyllithium with THF (**6a**)[21] or with dimethoxyethane (DME) (**6b**).[22]



L = THF: n = 3 (**6a**), m = 2 (**5a**); L = DME: n = 1.5 (**6b**), m = 1 (**5b**); HX = HCl, CF_3CO_2H.

Colourless crystalline tellurol **4b** is stable under an argon atmosphere in the dark for at least several days. In sunlight, solid tellurol **4b** turns dark but the spectral characteristics remain unchanged. In solutions, the tellurol **4b** rapidly decomposes under exposure to light to form a tellurium mirror.[17,18]

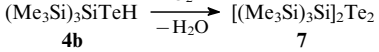
Protonolysis of lithium tris(trimethylsilyl)methanetellurolate (**5c**),[23] tris(trimethylsilyl)germanetellurolate (**5d**)[19] and tris(triphenylsilyl)silanetellurolate (**5e**),[24] which have been preliminarily isolated and purified, with trifluoromethanesulfonic acid in ether[17–19] or with trifluoroacetic acid in hexane[24] afforded tellurols **4c–e** in 57%–81% yields. Protonolysis of lithium salts **5e** in diethyl ether, which is more polar than hexane, was accompanied by partial decomposition of the tellurol **4e** resulting also in bis(triphenylsilyl) telluride and H_2Te.[24]



M = C, R = Me, n = 2 (**5c**); M = Ge, R = Me, n = 3 (**5d**); M = Si, R = Ph, n = 3 (**5e**).

Tellurols **4c–e** are crystalline compounds the colour of which varies from yellow to orange. These compounds melt at temperatures above 120 °C. Compounds **4c**,**d**, like tellurol **4b**, were isolated and purified by sublimation under high vacuum, while tellurol **4e** was purified by recrystallisation from hexane at low temperature. The stability of tellurols **4c**,**d** is similar to that of tellurol **4b**,[19] whereas tellurol **4e** is more sensitive to atmospheric oxygen.[24]

The reactions of tellurols governed by the presence of the hydrotelluride function are poorly studied. Oxidation of the tellurol **4b** with oxygen afforded ditelluride **7**. Compound **7** can be more easily synthesised by the oxidation of the tellurolate **5a** with oxygen or CuCl[17,18] or by the oxidation of the tellurolate **5b** with iodine, because these procedures exclude the stages of isolation and purification of the tellurol.[20]



The pK_a values of tellurols **4b–d** and of a number of related thiols and selenols were determined (photometrically, for solutions in isobutyl methyl ketone).[19] The following values were obtained: 7.3 for $HTeSi(SiMe_3)_3$ (**4b**), 9.3 for $HTeC(SiMe_3)_3$ (**4c**), 7.4 for $HTeGe(SiMe_3)_3$ (**4d**), 8.3 for $HSe(SiMe_3)_3$, 10.7 for $HSSi(SiMe_3)_3$ (the synthesis was described in Ref. 25) and 10.8 for $HSeC(SiMe_3)_3$ (the synthesis was described in Ref. 26).

The acid strengths of silane- and germanetellurols **4b**,**d** are approximately 100 times higher than that of their carbon analogue **4c**. This is also true for the corresponding selenium derivatives. This tendency for the change in the pK_a values was attributed[19] to the lower electronegativity of Si (1.9) and Ge (2.0) compared to C (2.5). For compounds $HM(SiMe_3)_3$ (M = S, Se or Te), the pK_a values increase in the series Te > Se > S.[19] Thus the tellurol **4b** is a stronger acid than the corresponding selenol and thiol by a factor of 10 and 1000, respectively. The same tendency for the change in the acidity is typical of inorganic hydrides of the corresponding elements.[27]

2. X-Ray diffraction analysis and ^{1}H and ^{125}Te NMR spectra of tellurols

The molecular and crystal structure of tris(triphenylsilyl)silanetellurol **4e** was established by X-ray diffraction analysis.[24] The Te–Si bond length is 2.511 Å and the Te–Si–C angles are in the range of 106.0–109.6°. Unlike Ph_3SiOH, which exists in the crystal as an H-bound tetramer,[28] the tellurol **4e** exists as a monomer (like triphenylsilanethiol Ph_3SiSH[29]). In the crystal, there are no shortened or specific intermolecular contacts smaller than the sum of the van der Walls radii of the elements. Thus the Te···Te distances are 4.64 Å (the sum of the van der Waals radii is 4.40 Å).[30] Evidently, hydrogen bonds in the crystal of the tellurol **4e** are absent due to the low electronegativity of the tellurium atom.

The ^{1}H and ^{125}Te NMR spectroscopic data are given in Table 1.

Table 1. Data of ^1H and ^{125}Te NMR spectroscopy of tellurols **2** ($CDCl_3$, −20 °C), tellurols **4** (PhH, 20 °C) and their analogues.

Compound	^1H NMR δ (see[a])	^{125}Te NMR δ (see[b])	J_{Te-H}/ Hz	Ref.
2,4,6-$Me_3C_6H_2TeH$ (**2a**)	−2.68	−91.4	63	2
2,4,6-$Pr^i_3C_6H_2TeH$ (**2b**)	−2.95	−134.8	48.6	2
2,4,6-$Bu^t_3C_6H_2TeH$ (**2c**)	−1.25	153.8	51.9	2
$(Me_3Si)_3SiTeH$ (**4b**)	−8.82	−955	74	17–19
	−8.83	−955.1	74.6	20
$(Me_3Si)_3CTeH$ (**4c**)	−5.1	−63	101	19
$(Me_3Si)_3GeTeH$	−9.02	−940	95	19
Ph_3SiTeH	−6.45	−684	27.4	24
H_3SiTeH [c]	−7.46	–	58	31
H_3GeTeH [c]	−7.44	–	52	31

[a] The chemical shifts of the protons bound to the Te atoms are given; [b] the chemical shifts relative to Me_2Te; [c] the spectra were recorded in $CDCl_3$ at 20 °C.[31]

The signals for the protons bound to the Te atoms in the tellurols **4b**–**e** containing the trimethylsilyl group are observed at substantially higher field (at δ from −6.45 to −8.82) than the analogous signals in the ^1H NMR spectra of the aromatic tellurols **2a**–**c** (at δ from −1.25 to −2.95). A comparison of the chemical shifts of the protons bound to the chalcogen atoms in the ^1H NMR spectra of tris(trimethylsilyl)silanechalcogenols $(Me_3Si)_3EH$ (E = S, Se or Te) are indicative of successive downfield shifts of these signals in the series Te < Se < S.[19]

The resonance signals for the ^{125}Te nuclei are observed as doublets in a very broad region (more than 1100 ppm), *viz*., from δ 153.8 for the aromatic tellurol **2c** (see Ref. 2) to δ −955 for tris(trimethylsilyl)silanetellurol **4b**.[17–20] A substantial upfield shift for the compound **4b** was related to the lower electronegativity of the silyl substituents compared to that of aromatic substituents.[18]

III. Synthesis, reactions and structures of metal tellurolates

Until recently, alkane- or arenetellurolates of alkali metals, *viz*., of lithium, sodium, and, to a lesser degree, of potassium, were the best studied representatives of metal tellurolates. These compounds were prepared either by reduction of the corresponding ditellurides or by insertion of the tellurium atom at the C–Li bond of organolithium derivatives.[32–36] However, they are unstable and are readily oxidised; therefore, none of these tellurolates was isolated in the individual form and structurally characterised. These compounds prepared *in situ* find wide use in the synthesis of various classes of organotellurium compounds and primarily of ditellurides and tellurides. Mercury(II) tellurolates $Hg(TePh)_2$,[37,38] $Hg(TeC_6H_4Me\text{-}4)_2$,[38] $Hg(TeC_6H_4\text{-}OEt\text{-}4)_2$,[39] $Hg(TeBu^t)_2$,[40] $Hg(TeBu^n)_2$,[41] $Hg(TeC_2F_5)_2$ (see Ref. 42) and $Hg(TeCF_3)_2$ (see Ref. 43) were isolated in the individual state. However, these compounds in the solid state exist as polymers, which precluded their studies by X-ray diffraction analysis. Only the structure of a complex mercury tellurolate **8** was established by this method[45] (the synthesis was described in Ref. 44).

$$PhTeM + Hg(TePh)_2 \longrightarrow M[Hg(TePh)_3] \xrightarrow[-MCl]{Ph_4PCl} (Ph_4P)[Hg(TePh)_3]$$

8

M = Na, K.

Mercury tellurolates are soluble in coordinating solvents such as 1,2-bis(diethylphosphino)ethane (DEPE) or 1,2-bis(dimethylphosphino)methane (DMPE).[41] When the tellurolate and the solvent were taken in a ratio of 1:2 or 1:1, coordination polymers or dimeric compounds of the $[Hg(TePh)_2(DEPE)]_2$ type, respectively, were formed.[41] The structure of the latter compound was established by X-ray diffraction analysis.[41] When heated in the solid state, the complexes of this type decompose to form mercury telluride, phosphine and the corresponding diorganyl ditelluride.[41] The dimeric complexes decompose upon heating in solution.

Rather stable tellurols containing bulky organic radicals have been synthesised recently, which made it possible to carry out systematic studies of their reactivities and the properties of the respective metal tellurolates (these data were most completely surveyed in a review[4]).

In this section, we consider methods for the synthesis, reactions and crystal structures of metal tellurolates containing bulky organic radicals. We restrict ourselves to consideration of tellurolates in which metal atoms are bound only to tellurium atoms. Tellurolates of other types, for example, tellurolates of metal cyclopentadienyl derivatives are not considered in detail (the data on these compounds were reported in the review[4]).

1. General methods for the synthesis of metal tellurolates

Presently, four major procedures for the preparation of metal tellurolates are known. These tellurolates were isolated in the individual state and in some cases were characterised by X-ray diffraction analysis.

1. Tellurolysis of the M–N bond in metal *N*-trimethylsilylamides with stable free tellurols (most widely used).

$$RTeH + M[N(SiMe_3)_2]_n \xrightarrow[-(Me_3Si)_2NH]{} (RTe)_nM$$

This method was used for the preparation of tellurolates of Li,[18,19] Na,[18] K,[18] Ca,[46–48] Sr,[46,47] Ba,[46,47] Zn,[17,49,50] Cd,[2,49] Hg,[49,51] Mn(II),[52,53] Sn(II),[54] Pb(II),[54] Fe(II),[52] divalent lanthanides (Eu,[55] Sm[55] and Yb[55]) and trivalent lanthanides (La[56] and Ce[56]) as well as of Al(III),[57] Sb(III)[57] {$Sb(NMe_2)_3$ was used in the synthesis of $Sb[TeSi(SiMe_3)_3]_3$} and Bi(III).[57] Tellurolates of Mg,[46,47] Zn,[17] In(III),[57] Tl(I),[57] Zr(IV)[58] and Hf(IV)[58] were prepared by tellurolysis of the M–C bonds in metal alkyls or metal cyclopentadienyl derivatives with the use of tris(trimethylsilyl)silanetellurol (**4b**).

$$R_nM + HTeSi(SiMe_3)_3 \xrightarrow[-RH]{} M[TeSi(SiMe_3)_3]_n$$

2. Exchange reactions of metal tellurolates (most often, of lithium derivatives) with metal halides. These reactions are of a rather general character as well.

$$RTeM + M'X_n \xrightarrow[-M'X]{} (RTe)_nM$$

M = Li, Na; X = Cl, Br.

This method was used for the preparation of tellurolates of Cu(I),[59] Au(I),[60] Cd,[61] Hg,[49,51] Mn(II),[52] Fe(II),[52] Co(I),[52] Cr(II),[52] Ga(III)[57] and In(I).[57] Sodium tellurolates were used in the synthesis of Zn and Cd tellurolates.[62] Tellurolates of divalent lanthanides (Yb, Sm and Eu,[63,64]) were synthesised with the use of potassium derivatives of sterically hindered tellurols because it is impossible to separate lanthanide tellurolates from lithium or sodium halides formed in the exchange reactions with the use of lithium or sodium salts.

3. Reduction of the corresponding ditellurides with lithium triethylborohydride,[61,65] sodium amalgam,[18,61,66] potassium amalgam[18] or potassium tris(*sec*-butyl)borohydride[61,66] allows one to synthesise alkali metal tellurolates with sterically hindered ligands. The insertion of some metals (Hg,[37–39,41–43,51] Cd[43] or Yb[67]) at the Te–Te bond of tellurides also belongs to reduction reactions. This method was used primarily for the preparation of metal tellurolates **9a**–**f**, **i**, **j** containing not-very-bulky substituents at the tellurium atom. However, tellurolates **9g**, **h**, **j** were also synthesised by this method.[51]

$$RTe—TeR + M \longrightarrow \underset{\mathbf{9a-j}}{(RTe)_2M}$$

Compound **9**	M	R	Ref.
a	Hg	Ph	37, 38
b	Hg	4-MeC_6H_4	38
c	Hg	4-$EtOC_6H_4$	39
d	Hg	Bu	41
e	Hg	C_2F_5	42
f	Hg	CF_3	43
g	Hg	2,4,6-$Me_3C_6H_2$	51
h	Hg	2,4,6-$Pr^i_3C_6H_2$	51
i	Cd	CF_3	43
j	Yb	Ph	67

It should be noted that dimesityl ditelluride readily reacts with metallic mercury in toluene at room temperature without a solvent to form mercury mesitylenetellurolate **9g**,[51] while the reaction of bis(2,4,6-triisopropylphenyl) ditelluride is performed in a polar solvent, such as methanol, at room temperature. The latter reaction is reversible and the tellurolate **9h** decomposes to the corresponding ditelluride and metallic mercury upon heating in methanol or upon recrystallisation from nonpolar solvents. Attempts to prepare mercury bis(2,4,6-tri-*tert*-butylphenyl)tellurolate by the reaction of the corresponding ditelluride with metallic mercury have been unsuccessful.[51]

Ytterbium di(benzenetellurolate) was synthesised in liquid ammonia. After evaporation of the solvent and extraction with pyridine, the complex with composition $(PhTe)_2Yb(Py)_5$ was isolated.[67] Attempts to prepare Yb(III) tellurolate by the reaction of Yb(III) chloride with sodium benzenetellurolate have failed because Yb(III) was reduced to Yb(II) and the same complex of divalent Yb, *viz*., $(PhTe)_2Yb(Py)_5$, has been obtained as the only product.[67]

The only copper(I) tellurolate prepared by insertion of the copper atom at the Te—Te bond was Cu(I) trifluoromethanetellurolate.[43]

$$CF_3Te—TeCF_3 + Cu \longrightarrow CF_3TeCu$$

Boiling of diaryl ditellurides with a copper powder in dioxane resulted in elimination of one tellurium atom to form diaryl tellurides in virtually quantitative yields.[35, 36]

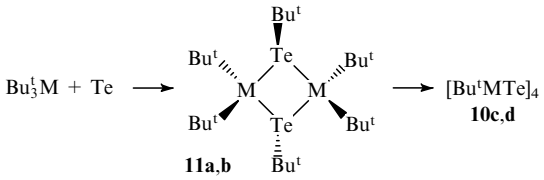
4. Insertion of the tellurium atom at the C—Li bond of the corresponding lithium derivatives was used for the preparation of lithium derivatives of some sterically hindered tellurols.[17–20, 23, 61, 68]

Thus the reactions of organic derivatives of Al(I)[69] and In(I)[70] with elemental tellurium in toluene or hexane gave compounds **10a**, **b** in yields of > 80%. The structures of both compounds contain distorted heterocubane molecular cores M_4Te_4 (M = Al or In) (data from X-ray diffraction analysis).[69, 70]

$$M_4R_4 + Te \longrightarrow \underset{\mathbf{10a,b}}{[RMTe]_4}$$

M = Al, R = C_5Me_5 (**a**); M = In, R = $(Me_3Si)_3C$ (**b**).

The insertion of the Te atom at the M—C bond of tris(*tert*-butyl)gallium[71, 72] or -aluminium[71] occurs on stirring of a mixture of the reagents in toluene at room temperature. In this case, tellurolates **11a**, **b** were obtained in ~ 60% yields. In boiling toluene, compounds **10c**, **d** were formed. These compounds were also formed upon heating of dimers **11a**, **b**.[72] The structure of aluminium tellurolate **11b** was established by X-ray diffraction analysis.[71]



M = Ga (**10c**, **11a**), Al (**10d**, **11b**).

The two latter methods are less common because they allow one to prepare tellurolates of only a limited number of metals.

2. Alkali metal tellurolates

Alkali metal tellurolates were synthesised according to methods 1, 3 and 4 (primarily, according to methods 3 and 4). Tellurolysis of lithium and sodium bis(trimethylsilyl)amides with tris(trimethylsilyl)silanetellurol **4b** afforded lithium tellurolate **5f**[18] and sodium tellurolate **5g**.[18] The reactions performed in hexane yielded alkali metal tellurolates, which are not coordinated by solvent molecules or donor ligands.

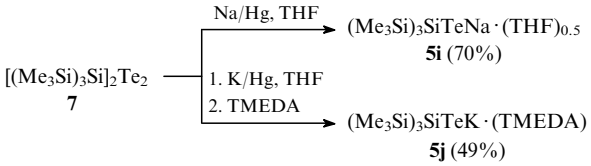
$$\underset{\mathbf{4b}}{(Me_3Si)_3SiTeH} + MN(SiMe_3)_2 \xrightarrow[-(Me_3Si)_2NH]{C_6H_{14}} \underset{\mathbf{5f,g}}{MTeSi(SiMe_3)_3}$$

M = Li (**f**, 54%), Na (**g**, 61%).

Potassium tellurolate **5h** was prepared by the reaction of the tellurol **4b** with Bu^{t}OK.[18]

$$\mathbf{4b} \xrightarrow{Bu^tOK} \underset{\mathbf{5h}}{(Me_3Si)_3SiTeK}$$

Alkali metal tellurolates containing the bulky tris(trimethylsilyl)silyl or aryl substituents were prepared by reducing the corresponding ditellurides (method 3). The reactions are generally carried out in THF at room temperature. The resulting tellurolates are isolated as complexes with THF or with other donor ligands. Thus reduction of the ditelluride **7** with potassium or sodium amalgam gave tellurolates **5i**, **j** as complexes with THF or tetramethylethylenediamine (TMEDA).[18]



The reactions of ditellurides **12** (R = Me or Pr^i) with lithium triethylborohydride in THF,[61] with sodium amalgam in the presence of TMEDA[61, 66] or DME[61] as well as with potassium tris(*sec*-butyl)borohydride either in THF[61] or followed by treatment with crown ether (18-C-6)[66] afforded complexes of tellurolates **13a**–**f**.

$$\underset{\mathbf{12}}{(2,4,6\text{-}R_3C_6H_2)_2Te_2} \longrightarrow \underset{\mathbf{13a-f}}{(2,4,6\text{-}R_3C_6H_2)_2TeML_n}$$

Compound **13**	Reducing agent	R	M	L	*n*	Yield (%)
a	$LiBEt_3H$	Me	Li	THF	1.5	80
b	$LiBEt_3H$	Pr^i	Li	THF	2.5	48
c	Na/Hg	Me	Na	TMEDA	2	80
d	Na/Hg	Pr^i	Na	DME	1	64
e	KBu^s_3BH	Pr^i	K	THF	1.33	40
f	KBu^s_3BH	Pr^i	K	18-C-6	1	47

Complexes of lithium tellurolates were also prepared by the reactions of elementary tellurium with organolithium compounds.

Complexes **5b**,**k** were synthesised by the reaction of powdered tellurium with organolithium compound **14**.[18]

$$(THF)_3LiSi(SiMe_3)_3 \xrightarrow{Te,\ THF} (THF)_2LiTeSi(SiMe_3)_3 \xrightarrow{L} LiTeSi(SiMe_3)_3 \cdot L$$
14 **5a** **5b**,**k**

L = DME (**5b**, 82%), 12-C-4 (**k**, 79%).

The reaction of the lithium derivative **14** with Te in DME gave the complex **5b** in 72% yield.[20] Complexes of tellurolates **5c**,**d**,[19] **15**[61,68] and **16**[61] were synthesised analogously.

$$(THF)_nLiM(SiMe_3)_3 \xrightarrow{Te,\ THF} (THF)_2LiTeM(SiMe_3)_3$$
14 **5c**,**d**

M = C (**c**, 56%), Ge (**d**, 48%).

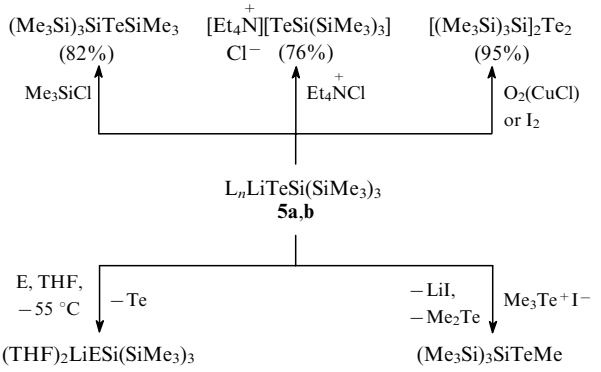
$$2,4,6\text{-}Bu^t_3C_6H_2Li + Te \xrightarrow{THF} 2,4,6\text{-}Bu^t_3C_6H_2TeLi(THF)_3$$
15 (56%)

$$2\text{-}Me_2NCH_2C_6H_4Li \xrightarrow[2.\ DME]{1.\ Te,\ THF} 2\text{-}Me_2NCH_2C_6H_4TeLi \cdot DME$$
16 (91%)

Complexes of alkali metal tellurolates containing bulky substituents are thermally stable at room temperature and can be stored without decomposition under an inert atmosphere for a long period of time. However, these compounds are readily oxidised in the solid state and in solution with atmospheric oxygen to give the corresponding ditellurides. As can be seen from the above-considered reactions, THF in the complexes is readily replaced by stronger donor ligands such as DME, TMEDA, 18-C-6 or 12-C-4.

Some reactions which were studied using alkali metal tellurolates **5a**[17–19] and **5b**[20] as examples are shown in Scheme 1.

Scheme 1



E = Se (93%), S (90%).

It is known[36] that lithium and sodium alkane- and arenetellurolates are oxidised to the corresponding ditellurides. In this respect, the behaviour of lithium tris(triphenylsilyl)silanetellurolate (**5e**) is unusual.[24] Its oxidation with atmospheric oxygen or the reaction with CuCl afforded only $(Ph_3Si)_2Te$.[24]

The exchange reactions of tellurium atoms in diaryl ditellurides[36] and in some tellurium-containing heterocycles[73] for sulfur or selenium atoms have long been known. These reactions proceed at high temperature. The tellurolate **5a** reacts with S or Se at −55 °C. Based on this fact, Bonasia *et al.*[19] considered the reactions of the tellurolate **5a** with selenium and sulfur (metathesis) yielding lithium tris(trimethylsilyl)silaneselenolate and -thiolate to be a new type of reactions in the chemistry of chalcogens.

$$(Me_3Si)_3SiTeLi(THF)_2 \xrightarrow{X} (Me_3Si)_3SiXLi(THF)_2 + Te$$
5a

X = Se, S.

Reactions of the tellurolate **5a** with chalcogens occur as the replacement of tellurium by a lighter chalcogen. It is known that in the reactions of lithium alkane- and arenechalcogenolates, lighter chalcogens are inserted into the bond between heavier chalcogen and lithium atoms to form lithium chalcogenylchalcogenolates **17**.[74]

$$RE^1Li + E^2 \longrightarrow RE^1E^2Li$$
17

E^1 = Te; E^2 = Se, S; E^1 = Se, E^2 = S.

Unlike with lithium tris(trimethylsilyl)silanetellurolate **5a**, the reaction of the carbon analogue of this compound, *viz*., lithium tris(trimethylsilyl)methanetellurolate **5c**, with selenium at −55 °C resulted in a dark-red solution containing, according to the ^{125}Te NMR spectrum, lithium tellurenylselenolate **18**. Attempts at isolating this compound in the solid state have led to its decomposition into a mixture of nonidentified compounds.[19]

$$(THF)_2LiTeC(SiMe_3)_3 \xrightarrow{Se,\ THF,\ -55\ ^\circ C} (THF)_2LiSeTeC(SiMe_3)_3$$
5c **18**

The exchange reactions of tellurolates **5a** and **5e** with cyclopentadienyl complexes of Ti, Zr and Hf made it possible to synthesise new tellurium-containing complexes **19a**–**j**.[24,75] The structures of the compounds **19d**, **g**[75] and **19f**[24] were established by X-ray diffraction analysis.

$$Cp_2MCl_2 + (THF)_nLiTeSi(SiR_3)_3 \longrightarrow Cp_2M[TeSi(SiR_3)_3]_2$$
5a,**e** **19a**–**j**

Compound **19**	Cp	M	R	Yield (%)
a	C_5H_5	Ti	Ph	75
b	C_5Me_5	Ti	Ph	55
c	C_5H_5	Ti	Me	86
d	C_5Me_5	Ti	Me	70
e	C_5H_5	Zr	Ph	71
f	$C_5H_4Bu^t$	Zr	Ph	74
g	C_5H_5	Zr	Me	75
h	C_5H_5	Hf	Ph	67
i	$C_5H_4Bu^t$	Hf	Ph	33
j	C_5H_5	Hf	Me	72

Compounds of the type **19** were also formed in the reactions of lithium tellurolate **5c** with metal complexes.[75] However, the resulting products rapidly decomposed to give eventually Te, $HC(SiMe_3)_3$ and a mixture of nonidentified metal-containing compounds.

In the reactions of Ti, Zr and Hf cyclopentadienyl complexes with the tellurolate **5a**, the nature of the solvent is of considerable importance. Thus the reactions in hexane afforded tellurolates **19**, while the reaction of the compound **5a** with titanium complex in THF yielded the dimeric complex **20** and the ditelluride **7**.[75]

$$Cp_2TiCl_2 + (THF)_2LiTeSi(SiMe_3)_3 \xrightarrow{THF,\ 25\ ^\circ C} [Cp_2TiCl]_2 + [(Me_3Si)_3SiTe]_2$$
20 **7**

The reactions of tellurolates **13a**, **b** with *cis*-bis(triphenylphosphine)platinum dichloride resulted in displacement of one chloride ligand to form tellurium-containing platinum complexes **21a**, **b**. The structure of the complex **21b** was established by X-ray diffraction analysis.[61]

$$2,4,6\text{-}R_3C_6H_2TeLi(THF)_n + (PPh_3)_2PtCl_2 \xrightarrow[-LiCl]{THF} (PPh_3)_2Pt[Te(2,4,6\text{-}R_3C_6H_2)]Cl$$

13a,b → *cis*-**21a,b**

R = Me (**a**), Pr^i (**b**).

The structures of many complexes of alkali metal tellurolates with Lewis bases were established by X-ray diffraction analysis. Below are considered the characteristic structural features of these compounds. In the crystal, lithium tellurolate $(THF)_2LiTe-Si(SiMe_3)_3$ (**5a**) exists as dimers and contains the Li_2Te_2 core. The Te–Li bond lengths in the ring (2.82 and 2.88 Å) are close to the values predicted based on the ionic radii (Li^+, 0.73 Å; Te^{2-}, 2.07 Å).[76] The Te–Si and Li–O bond lengths are 2.48 and 1.90 Å, respectively. The Li–Te–Li and Te–Li–Te bond angles are 90.4 and 89.6°, respectively.[18]

In lithium tellurolate **16**, the Li atom is tetrahedrally coordinated by two oxygen atoms of DME, the nitrogen atom and the tellurium atom.[61] The Te–Li distance in this compound (2.717 Å) is smaller than that in the tellurolate **5a**. The Te–C bond length (2.142 Å) has the standard value.[77] The Te–Li–O bond angles are 125.8 and 118.2° and the Te–Li–N angle is 99.6°. However, it remains unclear whether this molecule retains N → Te coordination, which has been observed in analogous compounds with tellurium-containing substituents in the *ortho* position with respect to the $CH(R)NMe_2$ group (R = H or Me) in the aromatic rings [the N → Te bond lengths are 2.366[78] and 2.406 Å[79] in 2-iodotellurenylbenzyldimethylamine and 2-(1-dimethylaminoethyl)benzenetellurium trichloride, respectively, which are substantially smaller than the sum of the van der Waals radii of Te and N (3.70 Å)[30]].

In the complex **15**[61] containing a bulky aryl substituent, the C–Te–Li angle is 99.1°, whereas the corresponding angles in the structurally similar sodium tellurolate **13c**[66] and potassium tellurolate **13f**[66] are 102.2° and 77.7°, respectively. The aryl ligand in the tellurolate **15** is planar. The Te atom deviates from the plane by 0.56 Å. The Te–Li bond length (2.82 Å) is close to the corresponding bond length in the tellurolate **5a**. The Te–C and Li–O bond lengths are 2.184 and 1.95 Å, respectively. The Te–Li–O angles are in the range of 108.8–115.2°.

In the crystal, potassium tellurolate **13f** exists as monomers. The Te–K distance (3.499 Å) is indicative of a weak interaction between the alkali metal atom and the tellurolate anion.[66] The Te–C distance is 2.15 Å and the C–Te–K angle is 77.68°. The average K–O bond length is 2.849 Å.

3. Alkaline-earth metal tellurolates

The major method for the preparation of alkaline-earth metal tellurolates **22** involves tellurolysis of di[bis(trimethylsilyl)amides] of the corresponding metals with tris(trimethylsilyl)silanetellurol **4b** in hexane at room temperature (the amide : tellurol ratio is 1 : 2). In most cases, the resulting tellurolates were isolated as adducts with different Lewis bases.[46,47]

$$M[N(SiMe_3)_2]_2 + \underset{\mathbf{4b}}{(Me_3Si)_3SiTeH} \xrightarrow[-(Me_3Si)_2NH]{} M[TeSi(SiMe_3)_3] \xrightarrow{L} \underset{\mathbf{22a-i}}{[(Me_3Si)_3SiTe]_2M\cdot L_n}$$

Compound **22**	M	L	*n*	Yield (%)
a	Mg	THF	2	68
b	Mg	Py	2	73
c	Mg	12-C-4	2	50
d	Ca	THF	4	46
e	Ca	Py	4	66
f	Sr	THF	4	25
g	Sr	Py	4	75
h	Ba	THF	4	52
i	Ba	Py	5	73

The reaction performed in toluene afforded compound **22d** in 85% yield.[48]

Magnesium tellurolate **22j**, which does not contain coordinating solvents, was synthesised by tellurolysis of the Mg–C bond of dibutylmagnesium.[46,47]

$$MgBu_2 + HTeSi(SiMe_3)_3 \xrightarrow[-BuH]{C_6H_{14}} \underset{\mathbf{22j}\ (77\%)}{[(Me_3Si)_3SiTe]_2Mg}$$

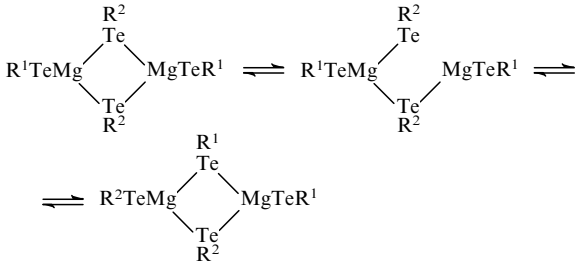
A complex of magnesium **22a** with tetrahydrofuran was prepared[47] by the reaction of mercury bis[tris(trimethylsilyl)silanetellurolate][49] with an excess of powdered Mg in THF (the yield was 44%).

Tellurolates **22a–j** are yellow crystalline compounds, which are readily soluble in hydrocarbons and ether. These compounds are sensitive to atmospheric oxygen and moisture but can be stored under an inert atmosphere at room temperature for a long period of time. The reactions of tellurolates **22** with oxygen afforded ditelluride **7** and the reactions with water yielded the tellurol **4b**.

The tetrahydrofuran complexes slowly lose coordinated solvent molecules at room temperature and are readily converted into the pyridine complexes upon recrystallisation from pyridine.[46,47] Treatment of magnesium tellurolates **22a,b** with 12-crown-4 resulted in replacement of both the coordinated solvent molecules (pyridine or THF) and the tellurolate ligands to form the ionic complex **22c**.[46,47]

$$\underset{\mathbf{22a,b}}{[(Me_3Si)_3SiTe]_2Mg\cdot L_2} + 12\text{-}C\text{-}4 \xrightarrow[-2L]{} \underset{\mathbf{22c}}{[Mg(12\text{-}C\text{-}4)_2][TeSi(SiMe_3)_3]_2}$$

The ^{1}H NMR spectra of magnesium tellurolate **22j** in toluene-d_8 are indicative of the stereochemical flexibility of the latter in solutions.[47] At 20 °C, the ^{1}H NMR spectrum has a singlet signal, which is broadened as the temperature is decreased and is split into two peaks at −90 °C.[47] Apparently, this is due to a slow (within the NMR time scale) intramolecular exchange of the bridging and terminal ligands in the dimeric structure of the tellurolate at low temperature.[47]



In the ^{125}Te NMR spectra of pyridine adducts **22b,e,g,i**, the signals for the ^{125}Te nuclei are observed in a rather narrow region from δ −1578 to −1405 [46,47] (Table 2).

The molecular and crystal structures of the tellurolates **22a**,[46,47] **22d**[46–48] and **22i**[47] were established by X-ray diffraction analysis.

In magnesium tellurolate **22a**, the Mg atom is tetrahedrally coordinated by two oxygen atoms of two THF molecules and two tellurium atoms.[46,47] The Mg–Te bond lengths have similar values (2.720 and 2.714 Å), the Mg–O bond lengths are in the range of 2.035–2.038 Å and the Te–Mg–Te and O–Mg–O angles are 135.48 and 94.8°, respectively. The Te–Mg–O angles are nonequivalent, one angle at each tellurium atom being large (111.77 and 144.37°) and one angle being small (96.37 and 94.79°). This may be due to steric repulsions from the lone electron pairs of the tellurium atoms although a crystal packing effect is not ruled out.[46,47]

The results of two independent crystallographic studies[46,48] of calcium tellurolate **22d** agree with each other. The coordination polyhedron about the Ca atom is a distorted octahedron. The Ca–Te distance is 3.19 Å and the Ca–O distances are 2.36 and

Table 2. Data of ^{125}Te NMR spectroscopy of metal tellurolates.[a]

Compound	Solvent	δ	Ref.
$(Me_3Si)_3SiTeLi(THF)_2$ (**5a**)	C_6D_6	−1622	18, 19
$(Me_3Si)_3SiTeLi(THF)$	C_7D_8	−1578	19
$(Me_3Si)_3SiTeLi(DME)$ (**5b**)	C_6D_6	−1641	20
$(Ph_3Si)_2TeLi(THF)_3$ (**5e**)	C_6D_6	−1337	24
$(Me_3Si)_3CTeLi(THF)_2$ (**5c**)	C_7D_8	−287	19
$(Me_3Si)_3GeTeLi(THF)_2$ (**5d**)	C_6D_6	−1515	19
2,4,6-$Me_3C_6H_2TeLi(THF)_{1.5}$ (**13a**)	THF	−383.7	2
2,4,6-$Pr^i_3C_6H_2TeLi(THF)_{2.5}$ (**13b**)	THF	−478.5	2
2,4,6-$Bu^t_3C_6H_2TeLi(THF)_3$ (**15**)	THF	9.2	2
2,4,6-$Me_3C_6H_2TeK(THF)_{1.3}$	THF-d_8	−296	63
$[(Me_3Si)_3SiTe]_2Mg(Py)_2$ (**22b**)	C_6D_6	−1578	46, 47
$[(Me_3Si)_3SiTe]_2Ca(Py)_4$ (**22e**)	C_6D_6	−1458	46, 47
$[(Me_3Si)_3SiTe]_2Ca(THF)_4$ (**22d**)	THF-d_8	−2204	48
$[(Me_3Si)_3SiTe]_2Sr(Py)_4$ (**22g**)	C_6D_6	−1482	46, 47
$[(Me_3Si)_3SiTe]_2Ba(Py)_5$ (**22i**)	C_6D_6	−1405	46, 47
$[(Me_3Si)_3SiTe]_3Sb$ (**23d**)	C_6D_6	−584	57
$[(Me_3Si)_3SiTe]_3Bi$ (**23c**)	C_6D_6	−627	57
$\{[(Me_3Si)_3SiTe]_2Zn\}_2$ (**22k**)	C_7D_8	−783, −1215	49
$\{[(Me_3Si)_3SiTe]_2Cd\}_2$ (**22l**)	C_7D_8	−933,[b] −1338[c]	49
$[(Me_3Si)_3SiTe]_2Hg$ (**22m**)	C_7D_8	−850	49
$[(Me_3Si)_3SiTe]_2Zn(Py)_2$ (**31a**)	$CDCl_3$	−1469	49
$[(Me_3Si)_3SiTe]_2Cd(DMPE)$ (**31d**)	CD_2Cl_2	−1565[d]	49
$[(Me_3Si)_3SiTe]_2Sn(DMPE)_2$ (**33b**)	C_7D_8	−1175[e]	54
$[(Me_3Si)_3SiTe]_2Sn(PMe_3)$ (**33a**)	C_7D_8	−1165[f]	54
$[(Me_3Si)_3SiTe]_2Fe(DMPE)_2$ (**34c**)	C_6D_6	−1189[g]	52
$[(Me_3Si)_3SiTe]_2Fe(Cl)(DMPE)$ (**36**)	C_6D_6	−1350[h]	52
$[(Me_3Si)_3SiTe]_4Zr$ (**46a**)	see[i]	459	4
$[(Me_3Si)_3SiTe]_4Hf$ (**46b**)	see[i]	193	4
$[(Me_3Si)_3SiTe]_4Zr(NCC_6H_3Me_2\text{-}2,6)_2$ (**48a**)	see[i]	203	4
$[(Me_3Si)_3SiTe]_4Hf(NCC_6H_3Me_2\text{-}2,6)_2$ (**48b**)	see[i]	−14	4
$[(Me_3Si)_3SiTe]_4Zr(DMPE)$ (**49a**)	see[i]	151, −116	4
$[(Me_3Si)_3SiTe]_4Hf(DMPE)_2$ (**49b**)	see[i]	128, −349	4
$[(Me_3Si)_3SiTe]_2Te{=}Zr(DMPE)_2$ (**50a**)	see[i]	−706, −1173,[j] −1197	4
$[(Me_3Si)_3SiTe]_2Te{=}Hf(DMPE)_2$ (**50b**)	see[i]	−701, −1212,[k] −1250	4
$[(Me_3Si)_3SiTe]Au$ (**41b**)	C_6D_6	−1112	60
$[(Me_3Si)_3GeTe]Au$ (**41c**)	C_6D_6	−1093	60
$[(Me_3Si)_3CTe]_4Au_4$ (**41a**)	C_6D_6	−302	60
$[(Me_3Si)_3CTe]Au(PPh_3)$ (**42a**)	C_6D_6	−148	60
$[(Me_3Si)_3SiTe]_2Yb(TMEDA)_2$ (**55a**)	C_6D_6	610	55
$[(Me_3Si)_3SiTe]_2Sm(TMEDA)_2$ (**55b**)	C_6D_6	3243	55
2,4,6-$Me_3C_6H_2Te)_2Yb(THF)_2$ (**54a**)	THF-d_8	−280	64
2,4,6-$Me_3C_6H_2Te)_2Yb(THF)_3$ (**54a**)	THF-d_8	−270	63
2,4,6-$Me_3C_6H_2Te)_2Yb(diglym)_2$ (**54d**)	THF-d_8	−260	64
$[(Me_3Si)_3SiTe]_3La$ (**58a**)	C_7D_8	1018	56
$[(Me_3Si)_3SiTe]_3La(DMPE)_2$ (**59a**)	C_7D_8	−894, −1074	56
$[(Me_3Si)_3SiTe]_2$ (**7**)	C_6D_6	−678	18
$(Ph_3Si)_2Te$	C_6D_6	−851	24
$(Me_3Si)_3SiTeSiMe_3$ (**44**)	C_6D_6	−1081	18
$(Me_3Si)_3SiTeMe$	C_6D_6	−637.7	18

[a] The chemical shifts are given relative to Me_2Te; [b] J_{Te-Cd} = 1059 Hz; [c] J_{Te-Cd} = 1821 Hz; [d] J_{Te-Cd} = 744 Hz, J_{Te-P} = 137 Hz; [e] J_{Te-P} = 64 Hz; [f] J_{Te-P} = 79 Hz; [g] J_{Te-P} = 80 Hz; [h] J_{Te-P} = 78 Hz; [i] the solvent is not mentioned; [j] t, J_{Te-P} = 166 Hz; [k] t, J_{Te-P} = 190 Hz.

2.41 Å. The tellurium ligands are in *trans* positions. The Ca−Te−Si angle is 128.5°.

In barium tellurolate **22i**, the five pyridine ligands are located in the equatorial plane and the two tellurium ligands are in axial positions. The Ba−Te distances are 3.38 Å, the Ba−N distance (average value) is 2.888 Å and the Ba−Te−Ba angle is 171.9°.[47]

4. Aluminium, gallium, indium, antimony and bismuth tellurolates

In this section, we discuss methods for the synthesis of aluminium, gallium and indium tellurolates containing bulky substituents at the tellurium atom.

Tellurolates of Group IIIA elements were synthesised by tellurolysis of the N−M and C−M bonds with the tellurol **4b** (method 1).[57] This procedure was used for the preparation of tellurolates of Al **23a**, In(III) **23b** and Bi(III) **23c**.

$$Al[N(SiMe_3)_2]_3 \xrightarrow[-(Me_3Si)_2NH]{\mathbf{4b},\ C_6H_{14},\ 20\ ^\circ C} \underset{\mathbf{23a}\ (44\%)}{Al[TeSi(SiMe_3)_3]_3}$$

$$Cp_3In \xrightarrow[-CpH]{\mathbf{4b},\ C_6H_{14},\ 20\ ^\circ C} \underset{\mathbf{23b}\ (60\%)}{In[TeSi(SiMe_3)_3]_3}$$

$$Bi[N(SiMe_3)_2]_3 \xrightarrow[-(Me_3Si)_2NH]{\mathbf{4b},\ C_6H_{14},\ -78\ \text{to}\ 0\ ^\circ C} \underset{\mathbf{23c}\ (68\%)}{Bi[TeSi(SiMe_3)_3]_3}$$

Tellurolysis of the C−M bonds afforded tellurolates of In(I) **24a** and Tl(I) **24b**. Compound **24b** was isolated as a solvate with composition $Tl[TeSi(SiMe_3)_3](C_6H_{14})_{0.125}$.

$$CpM + HTeSi(SiMe_3)_3 \xrightarrow[-CpH]{C_6H_{14},\ 20\ ^\circ C} \underset{\mathbf{24a,b}}{M[TeSi(SiMe_3)_3]}$$

M = In (**a**, 43%), Tl (**b**, 80%).

The synthesis of Sb(III) tellurolate **23d** was performed by the tellurolysis of tris(dimethylamino)antimony (**25**) instead of the antimony trimethylsilylamide derivative.[57]

$$\underset{\mathbf{25}}{Sb(NMe_2)_3} \xrightarrow[-Me_2NH]{\mathbf{4b},\ C_6H_{14},\ -78\ \text{to}\ 20\ ^\circ C} \underset{\mathbf{23d}\ (75\%)}{Sb[TeSi(SiMe_3)_3]_3}$$

It should be noted that tris(dimethylamino) derivatives of Sb and Bi are convenient starting compounds in the low-temperature synthesis of tellurides of the corresponding elements. Thus polycrystalline Sb_2Te_3 and Bi_2Te_3 were prepared in high yields by the reactions of $(Me_2N)_3M$ (M = Sb and Bi, respectively) with bis(trimethylsilyl) telluride.[80]

$$M(NMe_2)_3 + (Me_3Si)_2Te \xrightarrow[-Me_3SiNMe_2]{C_6H_{14},\ -30\ ^\circ C} M_2Te_3$$

M = Sb, Bi.

Method 2 consisting in the exchange reaction of metal tellurolates with metal halides is of lesser importance due to lower yields and lesser purity of the compounds formed. Thus tellurolates of Ga(III) **23e** and In(I) **24b** were synthesised by the reactions of the corresponding chlorides with lithium tris(trimethylsilyl)silanetellurolate **5a**.[57]

$$GaCl_3 \xrightarrow[-LiCl]{\mathbf{5a},\ C_6H_{14},\ 20\ ^\circ C} \underset{\mathbf{23e}\ (67\%)}{Ga[TeSi(SiMe_3)_3]_3}$$

$$InCl \xrightarrow[-LiCl]{\mathbf{5a},\ C_6H_{14},\ 20\ ^\circ C} \underset{\mathbf{24b}\ (65\%)}{In[TeSi(SiMe_3)_3]}$$

Attempts to prepare Tl(III) tellurolate by the exchange reaction have been unsuccessful because the tellurolate **5a** was oxidised to the ditelluride **7** in the course of the reaction.[57]

The tellurolates **23a**,**b**,**e** are coloured (from yellow to orange) air- and light-sensitive crystalline compounds, which are readily soluble in hydrocarbons. Tellurolates of Sb(III) and Bi(III) are particularly light-sensitive and thermally unstable. Because of this, these compounds are stored at low temperature in the dark.[57]

The In(I) and Tl(I) derivatives **24a**,**b** form solvates with the solvents (including hexane) from which they were recrystallised. The solvates are stable and lose solvent molecules with difficulty upon heating *in vacuo*.[57]

Reactions of tellurolates **23** remain virtually unknown. It was noted[57] that In(III) tellurolate **23b** reacted with different Lewis bases. However, in all cases, the compound **23b** underwent substantial decomposition to form $[(Me_3Si)_3Si]_2Te$ and $[(Me_3Si)_3Si]_2Te_2$ (**7**). The reaction of Al tellurolate **23a** with Cp_2TiCl_2 afforded the above-described titanocene tellurolate **19c** (the yield was 44%).[57]

The molecular and crystal structure of one of the tellurolates discussed in this section, *viz*., of Ga(III) tellurolate **23e**, was established by X-ray diffraction analysis.[57]

5. Zinc, cadmium and mercury tellurolates

Zinc, cadmium and mercury tellurolates containing both ordinary alkyl and aryl substituents and bulky aryl and trimethylsilyl substituents at the tellurium atom were synthesised.

The most general procedure for the preparation of zinc, cadmium and mercury tellurolates involves tellurolysis of metal di[bis(trimethylsilyl)amides] with sterically hindered tellurols **3a**[2, 50, 51] and **4b**.[17, 49]

$$M[N(SiMe_3)_2]_2 + \underset{\mathbf{3a}}{2,4,6\text{-}Me_3C_6H_2TeH} \xrightarrow[\text{light petroleum}]{-78 \text{ to } 20\ ^\circ C} \longrightarrow \underset{\mathbf{26a-c}}{[(2,4,6\text{-}Me_3C_6H_2Te)_2M]_n}$$

Compound **22**	M	Yield (%)	Ref.
a	Zn	52	50
b	Cd	50	2
c	Hg	65	51

$$M[N(SiMe_3)_2]_2 + \underset{\mathbf{4b}}{HTeSi(SiMe_3)_3} \xrightarrow{C_6H_{14},\ 20\ ^\circ C} \underset{\mathbf{22k-m}}{[(Me_3Si)_3SiTe]_2M}$$

Compound **22**	M	Yield (%)	Ref.
k	Zn	75	17, 49
l	Cd	69	49
m	Hg	82	49

Tellurolysis of the C–Te bond was used only for preparing Zn tellurolate **22k** (in quantitative yield).[17]

$$Et_2Zn + \underset{\mathbf{4b}}{HTeSi(SiMe_3)_3} \xrightarrow[-C_2H_6]{C_6H_{14},\ 20\ ^\circ C} \underset{\mathbf{22k}}{[(Me_3Si)_3SiTe]_2Zn}$$

Dealkystannylation (dealkylsilylation) reactions are not so common. For example, these reactions were used for the preparation of sterically hindered cadmium tellurolate **26b**[2] and its benzene analogue **27**.[81]

$$\underset{\mathbf{26b}}{2,4,6\text{-}Me_3C_6H_2TeSnBu_3} + CdCl_2 \xrightarrow[-Bu_3SnCl]{} \underset{\mathbf{26b}}{[(2,4,6\text{-}Me_3C_6H_2Te)_2Cd]_n}$$

$$PhTeSiMe_3 + CdMe_2 \xrightarrow[-Me_4Si]{} \underset{\mathbf{27}}{(PhTe)_2Cd}$$

Stuczynski *et al*.[81] stated that aryl stannyl(silyl) tellurides offer advantages over tellurols in the synthesis of different types of metal arenetellurolates. In fact, compounds containing the Te–E–C bonds (E = Si or Sn) are substantially more stable than tellurols. These compounds are obtained in high yields from readily available initial compounds and can be stored without decomposition over a long period of time.

So far, the exchange reactions have not been used for the preparation of Zn, Cd and Hg tellurolates with sterically hindered aryl substituents. However, Cd and Zn bis(2-aminophenyl)tellurolates **28a**,**b**[62] and Cd tellurolate **29**[61] were synthesised by these reactions. These compounds were obtained in rather high yields by the reactions of the corresponding lithium arenetellurolates[61] or sodium arenetellurolates[62] with Cd(II) and Zn(II) salts and are the first examples of intracomplex compounds with an MN_2Te_2 coordination unit.

$$2\text{-}H_2NC_6H_4TeNa + M(OAc)_2 \xrightarrow[-AcONa]{} \underset{\mathbf{28a,b}}{(2\text{-}H_2NC_6H_4Te)_2M}$$

M = Cd (**a**), Zn (**b**).

$$2\text{-}Me_2NCH_2C_6H_4TeLi \xrightarrow[-LiCl]{CdCl_2} \underset{\mathbf{29}}{(2\text{-}Me_2NCH_2C_6H_4Te)_2Cd}$$

The exchange reactions are not commonly used for the preparation of Zn, Cd and Hg tellurolates containing the $TeSi(SiMe_3)_3$ group. The reaction of $HgCl_2$ with the tellurolate **5a** afforded Hg tellurolate **22m** in lower yield than in the tellurolysis.[49] The reactions of $ZnCl_2$ and $CdBr_2$ with the tellurolate **5a** gave the respective Zn and Cd complexes with the solvent.[49]

Tellurolate complexes **26c**,**d** were prepared by insertion of the Hg atom at the Te–Te bond of diaryl ditellurides **12a**,**b** in methanol or toluene.[51]

$$\underset{\mathbf{12a,b}}{(2,4,6\text{-}RC_6H_2)_2Te_2} + Hg \longrightarrow \underset{\mathbf{26c,d}}{[(2,4,6\text{-}RC_6H_2Te)_2Hg]_n}$$

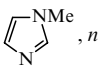
R = Me (**26c**), Pr^i (**26d**, 90%).

Mercury tellurolate **26c** was synthesised by the reaction of the ditelluride **12a** with $Hg[N(SiMe_3)_2]_2$ in light petroleum at 20 °C (the yield of the product was not reported).[51] The mechanism of this sluggish reaction remains unclear. The assumption that $N_2(SiMe_3)_4$ was formed as a by-product was not confirmed. Zinc and cadmium silylamides do not enter into analogous reactions.[51]

The tellurolates **26a–d** are virtually insoluble in polar solvents because they have the polymeric structures in the solid state. However, these compounds are readily soluble in strongly coordinating solvents such as DMSO, DMF and pyridine.[50, 51]

The reactions of zinc tellurolate **26a** with strong Lewis bases afforded four-coordinate monomeric adducts **30a–e**, which were isolated in the individual state in 49%–62% yields.[50] Adducts **30a–e** are more soluble than the tellurolate **26a**. These compounds rather readily lose ligand molecules upon heating.

$$\underset{\mathbf{26a}}{[Zn(TeMes)_2]_n} + L \longrightarrow \underset{\mathbf{30a-e}}{(Mes_2Te)_2Zn \cdot L_n}$$

L = PMe_3: n = 1 (**30a**), 2 (**30b**); L = , n = 2 (**30c**);

L = DMPE, n = 1 (**30d**); L = Py, n = 2 (**30e**).

Unlike zinc tellurolate **26a**, neither cadmium tellurolate **26b** nor mercury tellurolate **26c** form stable adducts with pyridine due to the lower Lewis acidity of cadmium and mercury compared to that of zinc.[50]

Zinc tellurolate **26a** and the complexes **30a–e** decompose upon heating in the solid state[50] and cadmium tellurolate **26b** decomposes upon boiling in mesitylene[2] to form the corresponding tellurides, *viz*., microcrystalline ZnTe and polycrystalline CdTe, respectively. Cadmium telluride was also prepared by heating cadmium tellurolate **29** at 180 °C *in vacuo*.[61]

$$\underset{\mathbf{26a,b}}{M(TeMes)_2} \xrightarrow{\Delta} Mes_2Te + MTe$$

$$\underset{\mathbf{29}}{(2\text{-}Me_2NCH_2C_6H_4Te)_2Cd} \xrightarrow[-CdTe]{} (2\text{-}Me_2NCH_2C_6H_4)_2Te$$

Mercury tellurolate **26c** decomposed upon heating to form metallic mercury and bis(2,4,6-trimethylphenyl) ditelluride.[51] Tellurolates **26** are of limited utility as precursors of metal tellurides due to their polymeric structures, low volatilities and stability.[51,82]

Zinc, cadmium and mercury tris(trimethylsilyl)silanetellurolates **22k–m** are yellow-green crystalline compounds, which are stable under a nitrogen atmosphere at room temperature for a long period of time.[17,49] Their ability to undergo oxidation is determined by the Lewis acidity of the metal atoms. Thus, zinc tellurolate **22k** was almost immediately oxidised to ditelluride **7** when exposed to air, while mercury derivative **22m** remained unchanged on exposure to air for at least 45 min.[49] The tellurolates **22k–m** are thermally stable compounds, sublime without decomposition under reduced pressure,[49] are readily soluble in different organic solvents and are stable in solutions in the absence of atmospheric oxygen.

According to the data of mass spectrometry, the compounds **22k–m** exist in the gas phase as monomers. In solutions, zinc and cadmium tellurolates (**22k** and **22l**, respectively) exist as dimers with the bridging and terminal RTe ligands (the data of multinuclear NMR spectroscopy[49]) analogous to those suggested for magnesium tellurolate **22j**.[47] The exchange between the bridging and terminal RTe ligands is rapid within the NMR time scale at 20 °C and is slow at low temperatures. The ^{1}H NMR spectra of the tellurolates **22k,l** in toluene-d_8 at 20 °C have singlet signals of the $Si(SiMe_3)_3$ groups at δ 0.43–0.45 (see Table 2). These signals are gradually broadened as the temperature decreases and are split into two signals with equal intensities at −50 °C and −34 °C for zinc tellurolate **22k** and cadmium tellurolate **22l**, respectively. The temperatures of coalescence indicate that the rate of exchange in the tellurolates **22k,l** is substantially smaller than that in Mg tellurolate **22j** (the coalescence temperature is −90 °C). The data of ^{125}Te NMR spectroscopy (see Table 2) and ^{113}Cd NMR spectroscopy support this conclusion.[49] Thus in the ^{125}Te NMR spectrum of zinc tellurolate **22k**, the signal which is observed as a singlet at room temperature is split at −60 °C into signals at δ −1215 [the terminal $(Me_3Si)_3SiTe$ group] and −783 [the bridging $(Me_3Si)_3SiTe$ group].[49]

In the temperature range from +80 to −80 °C, the ^{1}H and ^{125}Te NMR spectra of mercury tellurolate **22m** have singlet signals, which does not allow one to choose between the monomeric structure and the dimeric structure with rapid (within the NMR time scale) exchange between the terminal and bridging ligands.[49]

The reactions of the tellurolates **22k,l** with different Lewis bases afforded four-coordinate complexes **31a–d** in high yields.[49]

$$\underset{\textbf{22k,l}}{[(Me_3Si)_3SiTe]_2M} + L \longrightarrow \underset{\textbf{31a–d}}{[(Me_3Si)_3SiTe]_2M\cdot L_n}$$

M = Zn: L = Py, n = 2 (**31a**, 90%); L = bipy, n = 1 (**31b**, 71%);
M = Cd: L = bipy, n = 1 (**31c**, 76%); L = DMPE, n = 1 (**31d**, 77%).

The complexes **31a–d** are substantially more resistant to air and are less soluble in hydrocarbons compared to the initial tellurolates.

Tris(trimethylsilyl)silanetellurolates have considerable advantages over metal arenetellurolates in the pyrolytic synthesis of metal tellurides owing to their high thermal stability, solubility in inert solvents and ability to sublimation leading to monomeric molecules. Thus Zn tellurolate **22k** gave cubic ZnTe at 250–300 °C and Cd tellurolate **22l** gave hexagonal CdTe at 280–350 °C. The only organic reaction product was bis[tris(trimethylsilyl)silyl] telluride **32**.[83]

$$[(Me_3Si)_3SiTe]_2M \xrightarrow{\Delta} MTe + \underset{\textbf{32}}{[(Me_3Si)_3Si]_2Te}$$

M = Zn, Cd.

The molecular and crystal structures of the tellurolates **26b**[2] and **22k**[49] and some complexes, in particular, **30e**,[50] **31a**[49] and **31d**,[49] were established by X-ray diffraction analysis.

In the crystal, the compound **26b** exists as a polymer with the tetrahedrally coordinated cadmium atom and the bridging mesitylenetellurolate ligands.[2] The average Cd–Te and C–Te bond lengths are 2.837 and 2.164 Å, respectively. The Cd–Te–Cd bond angles are in the range of 84.0–116.7° and the C–Te–Cd angle is 107°.

In the crystal, zinc bis(tristrimethylsilyl)silanetellurolate **22k** exists as dimers.[49] The Zn_2Te_2 fragment is nonplanar; the Zn–Te–Zn and Te–Zn–Te angles are 79.29° and 95.62°, respectively. The bridging tellurium atoms have a pyramidal configuration. The coordination environment about each zinc atom is planar-trigonal. The bond lengths in the Zn_2Te_2 core (2.628–2.650 Å) are substantially larger than the $Zn-Te_{termin}$ bond lengths (2.50 Å). The average Te–Si bond lengths in the bridging and terminal ligands have similar values (2.552 and 2.516 Å, respectively).

The pyridine complex of zinc tellurolate **30e** has a distorted tetrahedral geometry.[50] The Te–Zn–Te angle (126.9°) is larger than the standard value due to steric repulsions between the bulky substituents, while the N–Zn–N angle is 89.2°. The Zn–Te bond length (2.573 Å) is equal to that in the pyridine complex of zinc silanetellurolate **31a** (2.574 Å[49]). The Te–C and Zn–N bond lengths are 2.140 and 2.110 Å, respectively.

6. Tin, lead, manganese, chromium, iron and cobalt tellurolates

Most of tin, lead, manganese, chromium, iron and cobalt tellurolates that have been synthesised contain the $TeSi(SiMe_3)_3$ fragment. These compounds were prepared according to two procedures, *viz*., by tellurolysis of the N–metal bonds in metal silylamides (method *a*) and by the exchange reactions of metal halides with lithium tellurolate **5a** (method *b*).

Method *a* was used for the preparation of Sn(II) tellurolate **22n** and Pb(II) tellurolate **22o**.[54]

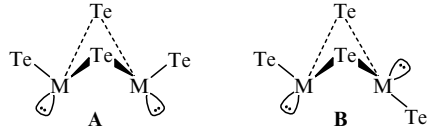
$$\underset{}{M[N(SiMe_3)_2]_2} + \underset{\textbf{4b}}{HTeSi(SiMe_3)_3} \xrightarrow[-(Me_3Si)_2NH]{C_6H_{14},\ 20\ ^\circ C} \underset{\textbf{22n,o}}{[(Me_3Si)_3SiTe]_2M]}$$

M = Sn (**22n**, 81%), Pb (**22o**, 82%).

Method *b* is less suitable for the preparation of tellurolates **22n,o**. Thus the exchange reaction of $SnCl_2$ with tellurolate **5a** afforded the tellurolate **22n** in substantially lower yield than that obtained by tellurolysis. The reaction of $PbCl_2$ with lithium tellurolate **5a** was accompanied by reduction of $PbCl_2$ to metallic lead and oxidation of the compound **5a** to the ditelluride **7**.[54]

The tellurolates **22n,o** are orange or red crystalline compounds, which are stable under nitrogen for a long period of time and are rapidly oxidised in air to form the ditelluride **7**.[54]

The structures of the tellurolates **22n,o** in solution cannot be unambiguously described on the basis of the ^{1}H NMR spectral data. Seligson and Arnold[54] assumed that the presence of nonequivalent signals for the $TeSi(SiMe_3)_3$ groups in the low-temperature ^{1}H NMR spectra may be ascribed either to a monomer–oligomer equilibrium or to *cis–trans* isomerisation in dimeric structures A and B.



A **B**

Like other Sn(II) complexes, the tellurolate **22n** forms adducts with phosphines (**33a**, **b**) in high yields.[54]

$$\underset{\textbf{22n}}{[(Me_3Si)_3SiTe]_2Sn} + L \longrightarrow \underset{\textbf{33a,b}}{\{[(Me_3Si)_3SiTe]_2Sn\}L_n}$$

n = 1, L = PMe_3 (**33a**, 80%); n = 2, L = DMPE (**33b**, 75%).

The tellurolate **22n** forms analogous adducts with a number of other monodentate phosphorus-containing ligands, *viz*., with Me_2PPh, Et_3P and (cyclo-$C_6H_{11})_3P$. However, these adducts were not isolated in the individual state. Their formation was judged from the presence of high-field signals in the ^{31}P NMR spectra of solutions. Weak Lewis bases, such as Ph_3P and $(MeO)_3P$, do not form complexes with **22n**.[54]

Pyrolysis of the tellurolates **22n**,**o** under a stream of nitrogen at 250 °C afforded cubic tellurides SnTe and PbTe. However, these compounds contained admixtures of small amounts of carbon and hydrogen.[54] Thermolysis of the tellurolates **22n**, **o** can be performed by heating them in aromatic hydrocarbons. Thus PbTe was prepared by heating the tellurolate **22o** in toluene at 100 °C for 22 h. The addition of Lewis bases to solutions of the tellurolates **22n**, **o** promotes their decomposition to form metal tellurides. Thus the tellurolate **22o** was quantitatively converted into PbTe upon addition of an excess of MeCN to an ethereal solution.

Like silylamides of other metals, Fe(II) and Mn(II) di[bis(trimethylsilyl)amides] reacted with the tellurol **4b** in hexane at room temperature. However, attempts to purify the resulting tellurolates failed because of their very high solubility.[52] Tellurolysis of Fe(II) and Mn(II) silylamides in the presence of Lewis bases afforded stable crystalline adducts **34a**–**c**.[52]

$$M[N(SiMe_3)_2]_2 + \underset{\mathbf{4b}}{HTeSi(SiMe_3)_3} + L \xrightarrow[-(Me_3Si)_2NH]{C_6H_{14},\ 20\ ^\circ C} \underset{\mathbf{34a-c}}{[(Me_3Si)_3SiTe]_2M \cdot L_n}$$

M = Mn: n = 1, L = DMPE (**34a**, 79%);

n = 2, L = Bu^t––N (**34b**, 81%);

M = Fe, n = 2, L = DMPE (**34c**, 71%).

The reaction of manganese silylamide with the sterically hindered arenetellurol **3a** was performed in the usual fashion and gave Mn(II) arenetellurolate **26e** in 95% yield.[53]

$$Mn[N(SiMe_3)_2]_2 + \underset{\mathbf{3a}}{2,4,6\text{-}Me_3C_6H_2Te_2H} \xrightarrow[-(Me_3Si)_2NH]{\text{light petroleum, 20 °C}} \underset{\mathbf{26e}}{[(2,4,6\text{-}Me_3C_6H_2Te)_2Mn]_n}$$

Fe(II), Mn(II) and Cr(II) tellurolates **34a**, **c**, **d** were also prepared by the exchange reactions.[52] Since the reactions of dihalides of these elements with lithium tellurolate **5a** afford the ditelluride **7** and insoluble pyrophoric products with unidentified structures, the exchange reactions are carried out either in the presence of Lewis bases or starting from adducts of metal halides with DMPE.[52]

$$MX_2(DMPE)_2 + \underset{\mathbf{5a}}{(THF)_2LiTeSi(SiMe_3)_3} \xrightarrow{-LiX,\ -THF} \underset{\mathbf{34a,c,d}}{[(Me_3Si)_3SiTe]_2M \cdot (DMPE)_n}$$

X = Cl, I; M = Mn, n = 1 (**34a**, 80%); M = Fe, n = 2 (**34c**, 79%); M = Cr, n = 2 (**34d**, 74%).

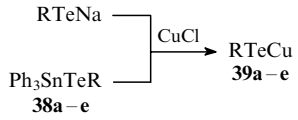
The reaction of lithium tellurolate **5a** with $CoBr_2$ yielded Co(I) tellurolate **35** as the final product due to strong reducing properties of the compound **5a**.[52]

$$CoBr_2(PMe_3)_3 + \underset{\mathbf{5a}}{(THF)_2LiTeSi(SiMe_3)_3} \xrightarrow[-LiBr,\ -THF]{PhMe,\ 20\ ^\circ C} [(Me_3Si)_3SiTe]Co \cdot (PMe_3)_3 + \underset{\mathbf{35}\ (64\%)}{\mathbf{7}}$$

The reaction of the adduct $FeCl_2(DMPE)_2$ with the tellurolate **5a** (taken in an equimolar ratio) afforded tellurolate **36** with mixed ligands (the yield was 88%).[52] This compound was also prepared in 82% yield by ligand exchange between the tellurolate **34c** and $FeCl_2(DMPE)_2$.

$$\left.\begin{array}{l} FeCl_2(DMPE)_2 + \underset{\mathbf{5a}}{(THF)_2LiTeSi(SiMe_3)_3} \\ [(Me_3Si)_3SiTe]_2Fe(DMPE)_2 + FeCl_2(DMPE)_2 \\ \quad\quad\quad\

The latter method is a procedure of choice because it allows one to obtain analytically pure tellurolates **39a–e** in higher yields.



R = Et (**a**), Bu (**b**), C_5H_{11} (**c**), Ph (**d**), 4-$EtOC_6H_4$ (**e**).

The synthesis of Cu(I) benzenetellurolate **39d** was performed with the use of the corresponding germanium and lead derivatives, *viz*., $Ph_3GeTePh$ and $Ph_3PbTePh$, instead of $Ph_3SnTePh$.[87]

The tellurolates **39a–d** are brown insoluble powders, which have apparently the polymeric structures.[85,86]

Attempts to prepare Cu(I) and Ag(I) tellurolates with bulky organic radicals by the exchange reactions of metal chlorides with lithium tellurolate **5a** have been unsuccessful.[59] Since tris(trimethylsilyl)silanetellurolate **5a** is a stronger reducing agent than the usual lithium and sodium tellurolates, it is readily oxidised by Cu(I) and Ag(I) chlorides to the ditelluride **7**.

$$\underset{\mathbf{5a}}{(THF)_2LiTeSi(SiMe_3)_3} + MCl \xrightarrow[-THF]{-LiCl,} \underset{\mathbf{7}}{[(Me_3Si)_3Si]_2Te_2} + M$$

M = Cu, Ag.

However, the reactions with the use of a weaker reducing agent, *viz*., lithium [tris(trimethylsilyl)]methanetellurolate (**5c**), instead of the tellurolate **5a** afforded Cu and Ag tellurolates **40a, b** with the bulky organic substituent at the tellurium atom.[59] The tellurolates **40a, b** were synthesised by the reactions of the tellurolate **5c** with tricyclohexylphosphine complexes of metal halides in toluene at room temperature and were isolated as the complexes with P(cyclo-C_6H_{11})$_3$.[59]

$$\underset{\mathbf{5c}}{(THF)_2LiTeC(SiMe_3)_3} + MX\cdot P(\text{cyclo-}C_6H_{11})_3 \xrightarrow{-LiX} \underset{\mathbf{40a,b}}{[(Me_3Si)_3CTe]M\cdot P(\text{cyclo-}C_6H_{11})_3}$$

M = Cu, X = BF_4 (**a**, 51%); M = Ag, X = Br (**b**).

The synthesis of Au(I) tellurolates with sterically hindered radicals was carried out only by the exchange reactions.[60] Thus free Au tellurolates **41a–c** were prepared by the reactions of AuCl·THF with lithium tellurolates **5a, c, d**. The conditions for the preparation of Au(I) tellurolates are determined by the stability of the resulting compounds. Alkane-type tellurolate **41a** was synthesised in benzene at room temperature, while thermally unstable analogues, *viz*., silane analogue **41b** and germane analogue **41c**, were prepared in ether at −78 °C. The latter two tellurolates were contaminated by LiCl. Attempts to purify these compounds led to their decomposition.

$$\underset{\mathbf{5a,c,d}}{(THF)_nLiTeE(SiMe_3)_3} + AuCl\cdot THF \xrightarrow{-LiCl,\ -THF} \underset{\mathbf{41a-c}}{[(Me_3Si)_3ETe]Au}$$

E = C (**41a**, 42%), Si (**41b**), Ge (**41c**).

Complexes of tellurolates **41a–c** with Ph_3P were synthesised by the exchange reactions between tellurolates **5a, c, d** and the AuCl triphenylphosphine complex.[60] The reactions were carried out under conditions identical with those used in the reactions with free tellurolates. The difference was that alkanetellurolate complex **42a** was also prepared in ether. The complex **42a** was synthesised by the reaction of the tellurolate **41a** with Ph_3P in benzene.[60]

$$\underset{\mathbf{5a,c,b}}{(THF)_nLiTeE(SiMe_3)_3} + AuCl\cdot PPh_3 \xrightarrow{Et_2O} \underset{\mathbf{42a-c}}{[(Me_3Si)_3ETe]Au\cdot PPh_3}$$

$$\underset{\mathbf{41a}}{[(Me_3Si)_3CTe]_4Au_4} + PPh_3 \xrightarrow{PhH} \mathbf{42a}$$

E = C (**42a**, 65%), Si (**42b**), Ge (**42c**).

The tellurolates **41a–c** are crystalline compounds, which differ substantially in thermal stabilities. Of these compounds, Au(I) alkanetellurolate **41a** is most stable, it decomposes only on melting and is resistant to water and air. Tellurolates **41b, c** decompose in solution even at −40 °C, which precludes their recrystallisation and purification. In the solid state, these compounds are resistant to water and air for at least 1–3 h.[60]

The nature of the element bound to three trimethylsilyl groups affects the composition of thermal decomposition products of Au(I) tellurolates and their triphenylphosphine complexes. Only alkanetellurolate **41a** decomposes analogously to tellurolates of other metals containing the bulky $(Me_3Si)_3SiTe$ group [Zn, Cd,[83] Sn, Pb,[54] lanthanides(II),[55] lanthanides(III)[56] and Zr[58]] to form bis[tris(trimethylsilyl)methyl] telluride **43** and, apparently, gold telluride.

$$\underset{\mathbf{41a}}{Au[TeC(SiMe_3)_3]} \xrightarrow{\Delta} \underset{\mathbf{43}}{[(Me_3Si)_3C]_2Te} + AuTe$$

Decomposition of silane- and germanetellurolates proceeded in a different manner. Thus the tellurolate **41b** gave compound **44** as the major product. The analogous mixed germyl silyl telluride **45** was obtained from the tellurolate **41c**.

$$\underset{\mathbf{41b}}{Au[TeSi(SiMe_3)_3]} \xrightarrow{\Delta} \underset{\mathbf{44}}{Me_3SiTeSi(SiMe_3)_3} + (Me_3Si)_2Te + \underset{\mathbf{32}}{[(Me_3Si)_3Si]_2Te} + Au$$

$$\underset{\mathbf{41c}}{Au[TeGe(SiMe_3)_3]} \xrightarrow{\Delta} \underset{\mathbf{45}}{Me_3SiTeGe(SiMe_3)_3} + Au$$

In the ^{125}Te NMR spectra of the tellurolates **41a–c** (see Table 2), the signals are substantially shifted upfield on going from alkanetellurolate **41a** (δ −302) to silanetellurolate **41b** (δ −1112) and germanetellurolate **41c** (δ −1093). Bonasia *et al*.[60] attributed this fact to stronger shielding of the tellurium atom in the compounds **41b, c**.

The molecular and crystal structures of the tellurolate **41a**[60] and its complex with triphenylphosphine **42a**[60] were established by X-ray diffraction analysis. The structure of the tellurolate **41a** comprises a nonplanar-square Au_4Te_4 core. The tellurium atoms occupy the vertices, each Te atom being bound to two Au atoms. The Au_4Te_4 core adopts a butterfly conformation with both wings of the butterfly being nearly coplanar. One wing comprising Te(1), Au(1), Te(2), Au(4) and Te(4) is coplanar to within 0.04Å, while the second half consisting of Te(3), Au(2), Te(2), Au(3) and Te(4) is coplanar to within 0.09 Å.[60] The dihedral angle between these two mean planes is 144.98(6)°. All Au–Te bond lengths are 2.56 Å (average values). The Te–Au–Te fragments are almost linear; the Te–Au–Te angle is 175° (the average value). The Au–Te–Au angles vary in the range of 87–90°. The Te–C bond length in the tellurolate **41a** (2.23 Å) is virtually equal to that in the triphenylphosphine complex **42a** (2.224 Å).[60]

In the complex **42a**, the Te–Au–P fragment is almost linear. The Te–Au–P and Au–Te–C angles are 174.3 and 104.1°, respectively. The Au–Te bond length (2.566 Å) is equal to that in the tellurolate **41a**. The intermolecular Au–Te contacts (3.74 Å) virtually coincide with the sum of the van der Waals radii of the elements (3.72 Å).

8. Zirconium and hafnium tellurolates

Zirconium tellurolate **46a** and hafnium tellurolate **46b** were prepared in 70%–85% yields by tellurolysis of the M–C bonds of metal tetraalkyl derivatives **47** with the tellurol **4b**.[58]

$$\underset{\mathbf{47}}{MR_4} + \underset{\mathbf{4b}}{(Me_3Si)_3SiTeH} \xrightarrow[-RH]{} \underset{\mathbf{46a,b}}{[(Me_3Si)_3SiTe]_4M}$$

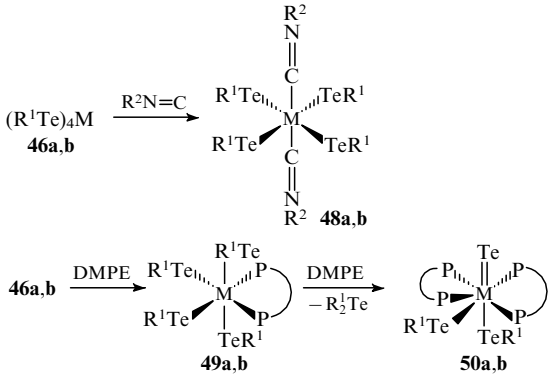
R = Bn, Bu^tCH_2; M = Zr (**a**), Hf (**b**).

The tellurolates **46a**,**b** are high-melting crystalline compounds (**46a** is green and **46b** is red), which can be recrystallised from hexane. These compounds readily react with water and oxygen to give the tellurol **4b** and the ditelluride **7**.[58]

Heating of zirconium tellurolate **46a** *in vacuo* from 200 to 375 °C afforded zirconium telluride $ZrTe_3$ contaminated by admixtures of carbon and hydrogen. In this case, volatile organic thermolysis products, *viz*., bis[tris(trimethylsilyl)silyl] telluride (**32**) and tris(trimethylsilyl)silyl trimethylsilyl telluride (**44**), as well as nonidentified compounds containing the $SiMe_3$ group were obtained.[58]

$$\underset{\mathbf{46a}}{[(Me_3Si)_3SiTe]_4Zr} \xrightarrow{200\text{ to }375\ ^\circ C} ZrTe_3 + \underset{\mathbf{32}}{[(Me_3Si)_3Si]_2Te} + \underset{\mathbf{44}}{Me_3SiTeSi(SiMe_3)_3} +$$

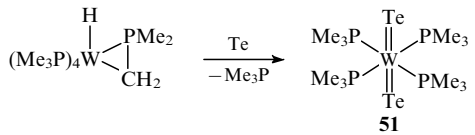
The reactions with Lewis bases are typical of the compounds **46a**,**b**, as of other tellurolates. Thus the reactions with 2,6-dimethylphenyl isocyanide afforded six-coordinate complexes **48a**,**b** of 1 : 2 composition.[58] The reactions with the bidentate DMPE ligand gave complexes **49a**,**b** of 1 : 1 composition.[58]



$R^1 = (Me_3Si)_3Si$, R^2 = 2,6-$Me_2C_6H_3$; M = Zr (**a**), Hf (**b**).

Treatment of the complexes **49a**, **b** with 1 equiv. of DMPE afforded seven-coordinate complexes **50a**,**b** in 50% – 80% yields as well as the telluride **32**.[58]

An analogous tungsten complex **51** containing the terminal W = Te bonds was synthesised.[87]



Later, complexes containing the Nb = Te,[88] Ta = Te[89] and Ge = Te[90] bonds were synthesised.

The complexes **50a**, **b** are red-brown crystalline air-sensitive compounds.[58] In solutions, these compounds are stereochemically fluxional. The ^1H and ^{31}P NMR spectra recorded in toluene at −85 °C have sharp singlets. The signals for the $SiMe_3$ groups are broadened as the temperature is increased to 20 °C and coalesce at a temperature above 40 °C. The ^{125}Te NMR spectrum of the compound **50a** (see Table 2) has three signals at δ −706, −1173 and −1197. The high-field signals were assigned to two non-equivalent $TeSi(SiMe_3)_3$ groups and the low-field signal was assigned to the tellurium atom of the Zr = Te bond.

The structures of the tellurolate **46a** and the telluride **50a**[58] were established by X-ray diffraction analysis. The zirconium atom in the molecule of the compound **46a** is bound to four tellurium atoms and has a pseudotetrahedral coordination environment. The Te – Zr bond lengths are in the range of 2.724 – 2.751 Å and the Te – Zr – Te angles vary in a rather wide range from 101.6 to 115.9 °, which is apparently due to repulsions between the bulky $(Me_3Si)_3SiTe$ groups.[58]

In the complex **50a**, the coordination polyhedron about the zirconium atom is a distorted pentagonal bipyramid. Two DMPE ligands and one [tris(trimethylsilyl)]silanetellurolate ligand lie in the equatorial plane. The second $(Me_3Si)_3SiTe$ ligand and the tellurium atom of the Zr = Te bond occupy axial positions. The Zr – $TeSi(SiMe_3)_3$ bond lengths (2.939 and 3.028 Å for the axial and equatorial ligands, respectively) are substantially larger than those in the tellurolate **46a**, while the Zr = Te bond is substantially shorter (2.650 Å).[58]

9. Lanthanide tellurolates

Recently, considerable attention has been focused on the synthesis of lanthanide tellurolates because these compounds can serve as precursors of lanthanide tellurides, which are of interest from the viewpoint of magnetic and luminescent properties.[64] The synthesis of lanthanide tellurides from elements is performed at high temperatures and is accompanied by formation of substantial amounts of admixtures due to the high oxophilicity of rare-earth elements. In this connection, the low-temperature synthesis of lanthanide tellurides from the corresponding tellurolates, which can be readily purified according to different procedures, is of particular interest.

One of the simplest tellurolates of this type, *viz*., Yb(II) tellurolate **9j**, was synthesised by the reaction of diphenyl ditelluride with Yb in liquid ammonia.[67] Since the tellurolate **9j** is insoluble in usual organic solvents, it was isolated as a complex **52** after evaporation of ammonia and extraction of the residue with pyridine. The complex **52** is unstable and eliminates pyridine yielding the complex **53**.[67]

$$PhTeTePh + Yb \xrightarrow{NH_3\,(liq.)} \underset{\mathbf{9j}}{(PhTe)_2Yb} \xrightarrow{Py} \underset{\mathbf{52}}{(PhTe)_2Yb(Py)_5} \xrightarrow[-4\,Py]{} \underset{\mathbf{53}}{(PhTe)_2Yb(Py)}$$

An attempt to prepare Yb(III) tellurolate by the exchange reaction of $YbCl_3$ with sodium benzenetellurolate led only to Yb(II) derivative **53**.

$$YbCl_3 \xrightarrow[2.\ Py]{1.\ PhTeNa} \underset{\mathbf{53}}{Yb(TePh)_2(Py)} + Ph_2Te_2$$

The structure of the complex **52** was established by X-ray diffraction analysis.[67] The coordination polyhedron about the Yb atom is a pentagonal bipyramid. The equatorial positions are occupied by five pyridine ligands and the axial positions are occupied by two benzenetellurolate ligands. The Te – Yb – Te and Yb – Te – C angles are 175.5 and 103.6 °, respectively. The average Yb – Te, Te – C and Yb – N bond lengths are 3.282, 2.192 and 2.618 Å, respectively.

Lanthanide(II) tellurolates **54a** – **c** containing the bulky mesitylenetellurolate residue were synthesised by the exchange reactions of lanthanide(II) halides **55** with potassium 2,4,6-trimethylbenzenetellurolate.[63,64] When the reactions are carried out with the use of sodium or lithium tellurolates, lithium and sodium halides formed in the reactions cannot be completely separated from the major reaction products. Potassium bromide and iodide are readily precipitated from the reaction mixtures because they are less soluble in THF than the corresponding lithium and sodium halides.[64]

$$\underset{\mathbf{55}}{LnX_2(THF)_2} + MesTeK \xrightarrow[-KX]{THF} \underset{\mathbf{54a-c}}{Ln(TeMes)_2(THF)_n}$$

Ln = Yb, n = 2–3 (**54a**, 85%–93%); Ln = Sm, n = 2 (**54b**, 67%); Ln = Eu, n = 2, (**54c**, 71%), X = Br, I.

The complexes of Yb(II) tellurolate with diglyme and DME (**54d**,**e**, respectively) were prepared analogously.[64]

$$YbI_2L_2 + MesTeK \xrightarrow[-KI]{} \underset{\mathbf{54d,e}}{Yb(TeMes)_2L_2}$$

L = diglyme (**d**), DME (**e**).

An alternative approach to the synthesis of lanthanide tellurolates, which makes it possible to prevent the formation of alkali metal halides, involves the reactions of lanthanide alkoxides (aryloxides) with mesityl trimethylsilyl telluride. The driving force for these reactions is the formation of Si—O bonds. For example, this procedure was used for the preparation of the tellurolate **54a**.[64]

$$Yb(OMes)_2(THF)_3 + MesTeSiMe_3 \xrightarrow[-ArOSiMe_3]{} \underset{\mathbf{54a}}{Yb(TeMes)_2(THF)_2}$$

The preparative usefulness of this procedure is impaired because the resulting trimethylsilyl ethers cocrystallise with, or coordinate, tellurolates **54** and are removed with difficulty.

The tellurolates **54a–e** are coloured crystalline compounds (**54a**, **b**, **d** are orange and **54c** is dark-green). These compounds are very air- and moisture-sensitive; Yb tellurolate **54a** is diamagnetic and the tellurolates **54c**, **d** are paramagnetic. The effective magnetic moments are 3.06 and 6.95 μ_B, respectively.[64]

Pyrolysis of the complex **54a** in boiling toluene at 250–300 °C *in vacuo* afforded dimesityl telluride and a black insoluble precipitate. Annealing of the precipitate at 900 °C for 24 h gave cubic YbTe.[63]

$$\underset{\mathbf{54a}}{(MesTe)_2Yb} \longrightarrow YbTe + Mes_2Te$$

Representatives of lanthanide(II) tellurolates of yet another type, *viz*., bis[tris(trimethylsilyl)silane]tellurolates **55a–c**, were synthesised by a slightly modified procedure of tellurolysis of silylamides of the corresponding metals **56a–c**. The reaction in diethyl ether in the presence of an excess of TMEDA afforded six-coordinate complexes **55a–c** in 40%–63% yields.[55]

$$\underset{\mathbf{56a-c}}{Ln[N(Me_3Si)_2]_2} + \underset{\mathbf{4b}}{HTeSi(SiMe_3)_3} + TMEDA \xrightarrow[-(Me_3Si)_2NH]{Et_2O,\ 20\ ^\circ C} \underset{\mathbf{55a-c}}{[(Me_3Si)_3SiTe]_2Ln(TMEDA)_2}$$

Ln = Yb (**a**), Sm (**b**), Eu (**c**).

The reaction performed with DMPE as a Lewis base yielded a seven-coordinate dimer **57**[55] containing the bridging DMPE ligand. The formation of the Eu(II) complex with the coordination number as large as seven is a consequence of the longer Eu—P bond compared to the Eu—N bond.[55]

$$Eu[N(Me_3Si)_2]_2 + \underset{\mathbf{4b}}{HTeSi(SiMe_3)_3} + DMPE \xrightarrow[-(Me_3Si)_2NH]{Et_2O,\ 20\ ^\circ C} \underset{\mathbf{57}\ (50\%)}{\{[(Me_3Si)_3SiTe]_2Eu(DMPE)_2\}_2(\mu\text{-DMPE})}$$

In the reaction with Eu(III) silylamide, the tellurol **4b**, which is a strong reducing agent, converted Eu(III) into Eu(II). The tellurol **4b** also reduced Yb(III) and Sm(III) silylamides.[55]

The tellurolates **55a–c** are deeply coloured air- and moisture-sensitive crystalline compounds. After storage under nitrogen at room temperature for 12 h, these compounds begin to decompose. At −40 °C, these compounds remain unchanged within several weeks.[55] The large magnetic moments of the complexes **55c** and **57** ($\sim$ 8.0 μ_B) preclude the use of NMR spectroscopy.

Like most of trimethylsilanetellurolates of other metals, the tellurolate **55a** decomposes upon heating (150–200 °C, 10^{-2} Torr) to form the telluride **32** and YbTe contaminated by a carbon admixture.[55]

$$\underset{\mathbf{55a}}{[(Me_3Si)_3SiTe]_2Yb(TMEDA)_2} \xrightarrow[-TMEDA]{\Delta} YbTe + \underset{\mathbf{32}}{[(Me_3Si)_3Si]_2Te}$$

The molecular and crystal structure of the tellurolate **57** was established by X-ray diffraction analysis.[55]

Unlike ytterbium, samarium and europium tris[di(trimethylsilyl)amides], which gave lanthanide(II) derivatives upon tellurolysis,[55] La(III) and Ce(III) silylamides were converted into lanthanide(III) tellurolates upon treatment with 3 equiv. of the tellurol **4b** [56] as evidenced by the data of ^1H and ^{125}Te NMR spectroscopy of the reaction mixtures. However, free La(III) and Ce(III) tellurolates **58a**,**b** are thermally unstable. Because of this, these compounds are isolated as complexes with DMPE **59a**,**b**, which are formed upon addition of an excess of the ligand to the reaction mixture. The yields of the complexes **59a**, **b** were no higher than 75%.[56]

$$Ln[N(Me_3Si)_2]_3 + \underset{\mathbf{4b}}{(Me_3Si)_3SiTeH} \xrightarrow[-(Me_3Si)_2NH]{} \underset{\mathbf{58a,b}}{[(Me_3Si)_3SiTe]_3Ln} \xrightarrow{DMPE} \underset{\mathbf{59a,b}}{[(Me_3Si)_3SiTe]_3Ln(DMPE)_2}$$

Ln = La (**a**),Ce (**b**).

Crystalline complexes **59** are coloured, *viz*., **59a** is yellow and **59b** is orange. The complex **59a** is diamagnetic and the complex **59b** is paramagnetic (μ_{eff} = 2.28 μ_B). The data of dynamic multinuclear spectroscopy (^1H, ^{13}C, ^{31}P and ^{125}Te) are indicative of the stereochemical fluxionality of the compounds **59a**, **b** in solutions. Thus the ^1H NMR spectrum of the complex **59a** at 23 °C has a broad singlet of three equivalent tellurolate ligands and broad peaks of the methyl and methylene groups of the phosphorus-containing ligands. When the temperature is decreased to −84 °C, the tellurolate ligands give two peaks with the intensity ratio of 2:1 and the methyl groups of DMPE give two broad peaks with equal intensities. The ^{125}Te NMR spectra at −70 °C have two signals with the intensity ratio of 2:1. An analogous temperature dependence is also typical of the ^{13}C and ^{31}P NMR spectra.[56]

As mentioned above, lanthanide(III) tellurolates in the absence of donor ligands decomposed to form bis[tris(trimethyl)silyl] telluride **32** and a complex mixture of products from which compounds **60a**, **b** were isolated in low yields. The metal–tellurium clusters **60a**, **b** were considered [56] as intermediates in the pyrolytic conversions of the tellurolates **59a**,**b** into lanthanide tellurides. Pyrolysis of the compounds **59a**, **b** and **60a**, **b** *in vacuo* at 600 °C afforded lanthanide tellurides.[56]

$$\underset{\mathbf{59a,b}}{Ln[TeSi(Me_3Si)_3]_3(DMPE)_2} \xrightarrow{20\ ^\circ C} \underset{\mathbf{60a,b}}{Ln_5Te_3[TeSi(Me_3Si)_3]_9} \xrightarrow{600\ ^\circ C} Ln_2Te_3$$

The structures of the compounds **59a** and **60b** were established by X-ray diffraction analysis.[56] The La atom in the complex **59a** has a pseudopentagonal-bipyramidal environment. Both phosphine ligands and one tellurolate ligand lie in the equatorial plane and two other tellurolate ligands are located in the axial plane. The $La-Te_{eq}$ bond length is 3.141 Å and the $La-Te_{ax}$ bond lengths are 3.168 and 3.170 Å, respectively. The $Te_{ax}-La-Te_{ax}$ angle is 145.7°. Steric interactions between the equatorial tellurolate and phosphine ligands result in the difference in the La—P bond lengths (3.127, 3.143 Å and 3.208, 3.216 Å).

The molecule of the compound **60b** contains a six-membered —[Te—Ce]$_3$— ring with the μ_3-bridging Ce(TeR)$_3$ fragments located above and below this ring. The Ce—Te$_{termin}$ bond lengths are smaller (3.026 Å) than the Ce—Te$_{bridg}$ bond lengths (3.183 and 3.235 Å). The Ce_3Te_3 bond lengths vary from 3.124 to 3.278 Å.

IV. Conclusion

As is evident from the present review, the synthesis of new metal tellurolates and their pyrolysis to the corresponding tellurides are of prime interest. It is in this field that the progress should be expected. Yet another line of investigation involves the synthesis of new stable tellurols. The stability of aromatic tellurols is determined by steric factors. Two-coordinate tellurium derivatives can be stabilised also by introducing substituents, such as COR, CH=N or N=N, which can form intramolecular coordination bonds with the tellurium atom, at the *ortho* position with respect to the tellurium-containing function. This method has not been applied in the chemistry of tellurols so far. Apparently, the synthesis of stable tellurols and intracomplex metal compounds based on these tellurols will be developed and will be the subject of further studies.

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