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Organic derivatives of monocoordinated tellurium

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Abstract. Data on the methods of synthesis, structures, and reactivity of organic derivatives of monocoordinated tellurium, namely, compounds with C = Te bonds and phosphine tellurides $R_3P=Te$, are described systematically and generalised. The use of the latter compounds as synthetic equivalents of elemental tellu rium for the preparation of metal tellurides is considered. The bibliography includes 139 references.

I. Introduction

Organic derivatives of monocoordinated tellurium, namely, compounds with C = Te bonds and phosphine tellurides $R_3P=Te$, constitute a relatively little studied class of organotellurium compounds. In fact, the first phosphine telluride, tributylphosphine telluride, was synthesised in 1963,[1] while the first and still the only one known stable telluroketone, 1,1,3,3-tetramethylindanetellone, which is stable only in solution, was synthesised only in 1993.[2] The synthesis, structure, and chemical properties of tellurocarbonyl compounds and phosphine tellurides have been considered most comprehensively in a monograph devoted to the chemistry of organic derivatives of selenium and tellurium.[3,4] However, during more than a decade, which has passed after the publication of this monograph, the number of studies dealing with the derivatives of monocoordinated tellurium has approximately doubled. New fields of application of tellurocarbonyl compounds have been discovered, for example, as dienophiles in the syntheses of six- and seven-membered tellurium-containing heterocycles. Of special interest is the use of phosphine tellurides as synthetic analogues of elemental tellurium for the synthesis of some organotellurium compounds, which undergo thermal decomposition under relatively mild conditions to give metal tellurides [5] possessing semiconductor and other valuable properties.

II. Synthesis and reactions of compounds containing C = Te bonds

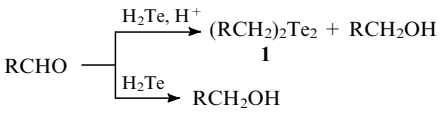
Up to now, four types of tellurocarbonyl compounds have been described in the literature: telluroketones (telluroaldehydes) $R_2C=Te$ (R = H, Alk, or Ar), tellurocarboxylic acids $RC(=Te)OH$, *O*-alkyl tellurocarboxylates $RC(=Te)OR^1$, and telluroamides $RC(=Te)NR^1R^2$ and their analogues (tellurohydrazides and telluroureas). These compounds sharply differ in stability. Only representatives of the two latter types have been isolated in a pure state. The formation of telluroketones (telluroaldehydes) and tellurocarboxylic acids is judged either from the NMR spectra of reaction mixtures or from the products of their chemical transformations. However, the stability of tellurocarbonyl compounds of all these types is substantially enhanced when the tellurocarbonyl carbon atom carries bulky organic substituents or relatively strong π-electron-donating groups (OR, NR_2, $NR^1NR^2_2$) or upon coordination to transition metal compounds. It should be noted that one of the most efficient methods used to increase the stability of other classes of organotellurium derivatives, such as tellurenyl halides, azides, acetates, and isothiocyanates, diorganyl tritellurides, *etc*., has not been used so far in the chemistry of tellurocarbonyl compounds. This method consists in the introduction, into appropriate positions of aryl or alkenyl substituents of functional groups (CHO, COR, CO_2R, NO_2, N = N, CH = N, CH_2NMe_2, *etc*.) containing sp^2 (or, more rarely, sp^3) hybridised O or N atoms, which form strong intramolecular coordination bonds with Te atoms.[6]

1. Telluroaldehydes and telluoroketones

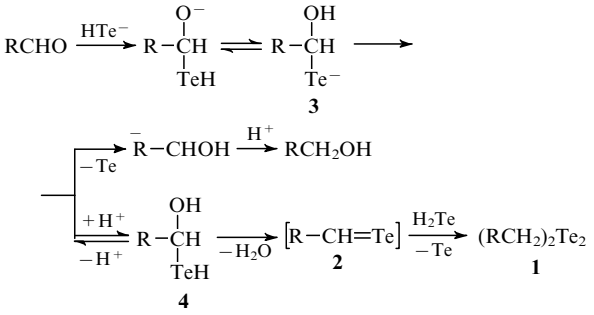
Despite the apparent similarity of chalcogens (S, Se, Te),[7] their properties are appreciably different; therefore, in some cases, methods that are used successfully for the synthesis of organic derivatives of sulfur and selenium cannot be used to prepare their tellurium analogues. For example, 'dialkyl telluroketones' have been described in a study,[10] which is cited in monographs dealing with the chemistry of organotellurium compounds.[8,9] They were synthesised by a method similar to a method used to prepare thioketones, namely, by the reaction of the corresponding ketones with H_2Te in a strongly acidic medium. However, in reality, the reactions of H_2Te, generated *in situ* from aluminium telluride and water, with aldehydes and ketones afford alcohols [11] or mixtures of dialkyl ditellurides with alcohols.[12] Alcohols are formed in 50% – 100% yields when H_2Te is passed through solutions of carbonyl compounds in THF.[11] When solutions of aldehydes contain strong acids (CF_3COOH, $PhSO_3H$, H_2SO_4), dialkyl ditellurides **1** are formed as the main reaction products (yields 34% – 56%); in this case, only traces of primary aliphatic alcohols are formed.[12] Ketones react in a similar way, but the yields of the corresponding dialkyl and di(cycloalkyl) ditellurides are lower.[12]

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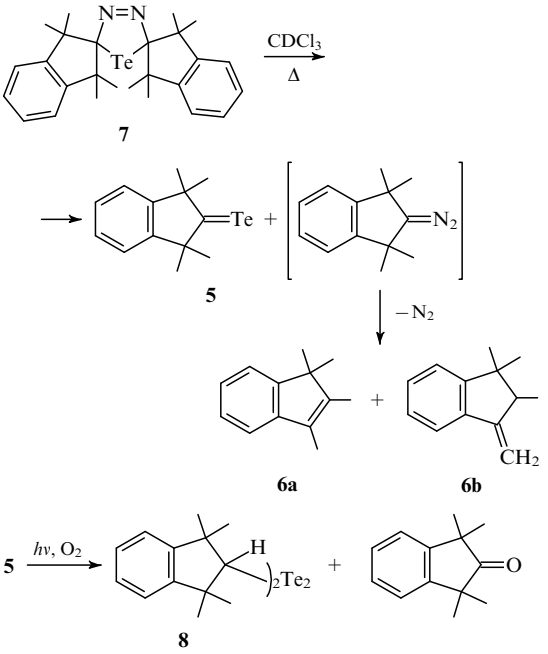


According to the scheme proposed by the researchers cited,[12] the ditellurides **1** result from the reduction of telluroaldehydes **2** with hydrogen telluride. The influence of pH on the outcome of these reactions is due to the fact that in strongly acidic media the acid–base equilibrium **3**⇌**4** is almost entirely shifted to the right:



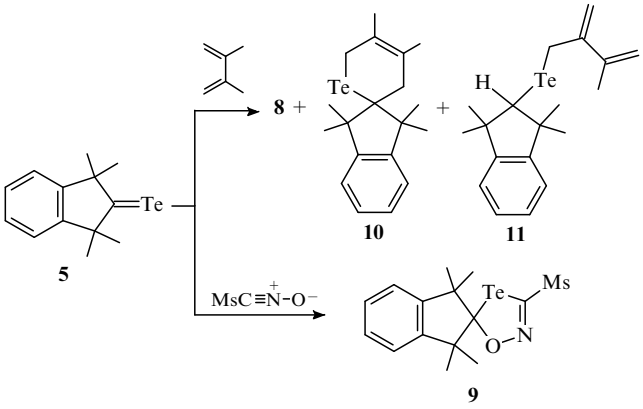
a. Stable telluroketones

As noted above, 1,1,3,3-tetramethylindanetellone **5** is the only stable, although only in solution, telluroketone that has been characterised by various spectroscopic methods.[2] This compound was obtained in an almost quantitative yield, together with alkenes **6a** and **6b**, upon thermolysis of 1,3,4-tellurodiazoline **7**; the compound **7** was synthesised in 26% yield by treating the hydrazone of 1,1,3,3-tetramethylindanone with tellurium dichloride in the presence of Et_3N.[13]

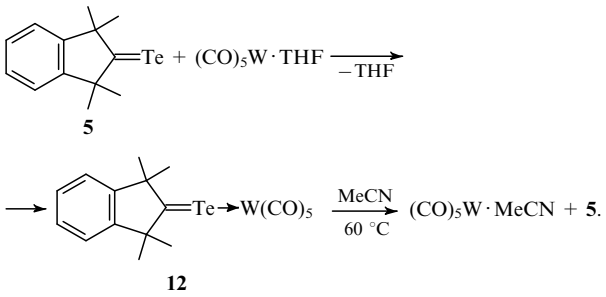


The telluroketone **5** is very sensitive to oxygen and light; on exposure to UV radiation, it is converted into a mixture of ditelluride **8** and 1,1,3,3-tetramethylindanone.[2] The ^{13}C NMR signal for the C=Te-group carbon atom (δ 301 ppm) is substantially shifted downfield with respect to the signals for other C=X groups (C=O, δ 226.0 ppm; C=S, δ 282.1 ppm, C=Se, δ 294.0 ppm). The same is true for the ^{125}Te signal (δ 2858.3 ppm in relation to Me_2Te), which is the lowest-field signal in the series of organotellurium compounds known. The long-wave absorption band (λ = 825 nm) in the UV spectrum of the ketone **5** undergoes substantial bathochromic shift with respect to the bands of the corresponding selenium (λ = 667 nm) and sulfur (λ = 527 nm) derivatives.

The compound **5** enters into 1,3-dipolar cycloaddition with mesitylnitrile oxide yielding a derivative of a new heterocyclic system, oxatellurazole **9**. Like other tellurocarbonyl compounds (see below), the ketone **5** enters into the Diels–Alder reaction with 2,3-dimethylbutadiene[2] to give compounds **11** and **8** in addition to 1-telluracyclohex-3-ene derivative **10**.



The complex **12** was synthesised in a yield of more than 70% by the reaction of the telluroketone **5** with the complex $(CO)_5W\cdot THF$.[14] Earlier, complexes of this type had been obtained only by insertion of a Te atom into C=M bonds in transition metal complexes.

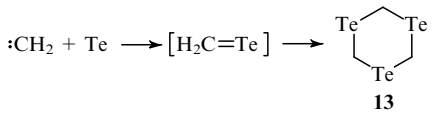


The compound **12** was isolated as dark-violet crystals. Unlike the initial telluroketone, it is resistant to heating and exposure to light. The signals for the C=Te-group atoms in the ^{13}C and ^{125}Te NMR spectra are shifted upfield with respect to the corresponding signals in the spectra of **5**; they are manifested at δ 285 and 1783 ppm, respectively. The C=Te bond length in the complex **12** found by X-ray diffraction analysis[14] amounts to 1.987 Å, which is close to the length of the similar bond in S=C=Te (1.904 Å);[15] this indicates that the order of the C=Te bond in **12** is closer to two. The telluroketone **5** is a relatively weak donor; in fact, when the complex **12** is heated in MeCN at 60 °C, the tellurium-containing ligand is quantitatively replaced by MeCN.

b. Methods for the generation of unstable telluroaldehydes and telluroketones. Dimerisation and the Diels–Alder reaction

All the telluroaldehydes and telluroketones, except for the ketone **5**, are unstable. Conclusions about the formation of these compounds are based on the structures of products of their subsequent chemical transformations, first of all, dimerisation (or trimerisation in the case of telluroformaldehyde) and the Diels–Alder reaction.

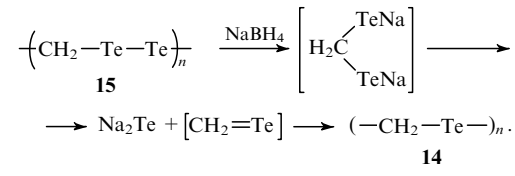
Telluroformaldehyde was the first telluroaldehyde reported in the literature. It was obtained by treatment of tellurium mirrors with the carbene generated by thermal decomposition of diazomethane[16–18] or by photodissociation of ketene.[17] On cooling, the gaseous monomeric telluroformaldehyde trimerises to yield 1,3,5-tritelluracyclohexane **13**.



13

The structure of the heterocyclic compound **13** was confirmed by IR spectroscopy and mass spectrometry.[18] The reactions of the compound **13** with bromine or iodine give the corresponding dihalomethanes.[17]

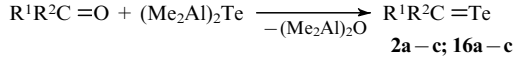
Apart from the trimer **13**, telluroformaldehyde can also exist as a polymeric form, poly(methylene telluride) **14**. Disodium methaneditellurolate resulting from reduction of poly(methylene ditelluride) **15**[19] with sodium tetrahydridoborate in ethanol disproportionates into sodium telluride and telluroformaldehyde, which then polymerises to give the polytelluride **14**.[20]



15 **14**

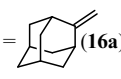
It has been suggested[21] that the synthesis of poly(methylene telluride) occurs according to a scheme which includes reduction of the polyditelluride **15** with sodium tetrahydridoborate in methanol and alkylation of sodium methyleneditellurolate with dibromo(or diiodo)methane. In our opnion, this mechanism is erroneous. We believe that the polymer **14** results from disproportionation of the dianion as described above rather than from the alkylation.

Although in recent years several methods for the generation of telluroaldehydes and telluroketones have been developed, it is fairly difficult to judge their synthetic potential, because their chemical properties have not been extensively studied. The most efficient method for the preparation of telluroaldehydes **2** and telluroketones **16** is the reaction of bis(dimethylaluminium) telluride with aldehydes or ketones in boiling dioxane.[22,23] The driving force of these reactions is the formation of thermodynamically favourable Al–O bonds.

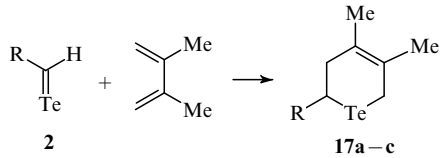


2a–c; 16a–c

R^1 = H; R^2 = Ph (**2a**), Pr (**2b**), Bu^t (**2c**);[22]

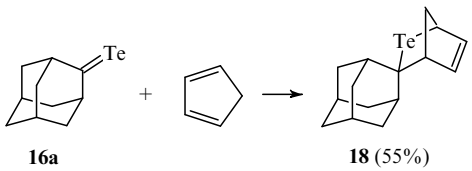
R^1, R^2 =  (**16a**),  (**16b**);[22] $R^1 = R^2$ = $C_5H_5FeC_5H_4$ (**16c**).[23]

The tellurocarbonyl compounds **2** and **16** formed initially can be trapped by 2,3-dimethylbutadiene or cyclopentadiene; this gives Diels–Alder adducts **17**–**19** in 44%–62% yields.[22] These reactions are the only methods known to date for the synthesis of 1-telluracyclohex-3-enes[24] and 2-tellurabicyclo[2.2.1]hept-5-enes. The formation of the telluroketone **16c** is indicated by the blue colouration of the solution. Owing to the low stability of this compound, it was impossible to determine its spectral characteristics. Unlike the sulfur and selenium analogues which form complexes with pentacarbonylchromium and -tungsten, the reaction of the ketone **16c** with $(CO)_5M \cdot THF$ (M = Cr, Mo, W) occurs as detelluration and affords tetraferrocenylethylene in a quantitative yield.[23]

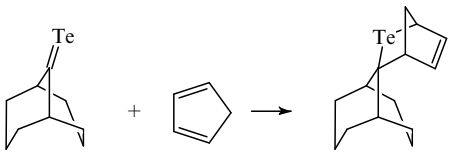


2 **17a–c**

R = Ph [**17a**, (49%)]; Pr [**17b**, (44%)]; Bu^t [**17c**, (62%)].

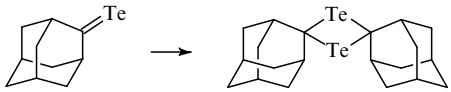


16a **18** (55%)



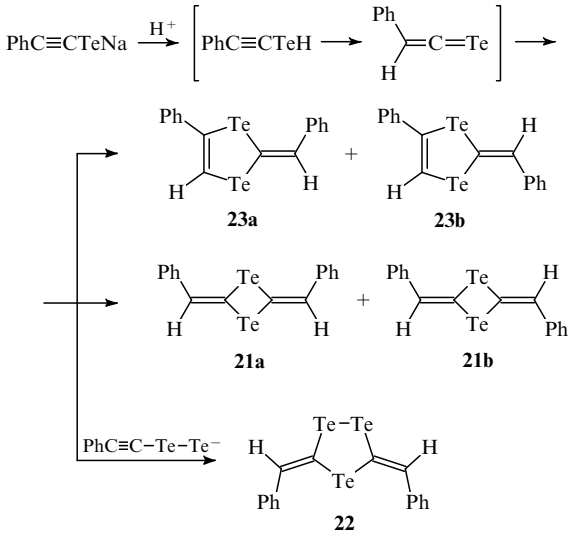
16b **19** (52%)

In the absence of dienes, the ketone **16a** dimerises to give 1,3-ditelluretane derivative **20** (yield 28%);[22] reactions of this type for other ketones have not been reported.



16a **20**

It is noteworthy that the first ditelluretanes, *cis*- (**21a**) and *trans*- (**21b**) 2,4-dibenzylidene-1,3-ditelluretanes (the structure of the *trans*-isomer was confirmed by X-ray diffraction analysis[25]), were obtained in low yields upon protonation of sodium phenylethynyltellurolate with a solution of HCl in ether.[25,26] It has been reported[27] that ditelluretane **21a** and *cis*-3,5-dibenzylidene-1,2,4-tritellurole **22** are the main products of this reaction; the structure of the latter was determined by X-ray diffraction analysis.[27] The protonation of sodium phenylethynyltellurolate with CF_3COOH affords a mixture consisting of **21a** and *cis*- and *trans*-2,6-diphenyl-1,4-ditellurafulvalene, **23a** and **23b**, respectively.[28] Apparently, these reactions involve intermediate formation of a telluroketone, which either dimerises yielding the compounds **21** or **23**, or reacts with phenylethynylditellurolate anion being thus converted into the tritellurole **22**.[27]



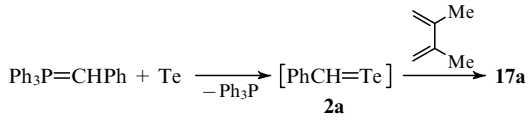
23a **23b**

21a **21b**

22

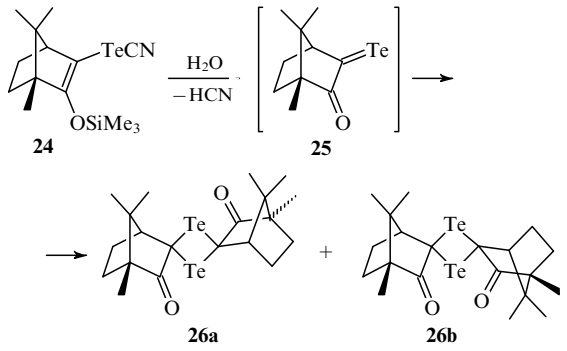
Tellurium-containing heterocycles have also been synthesised from tellurocarbonyl compounds generated by other methods. One of these methods, which has been used previously in the chemistry of selenoaldehydes,[29] is based on the reaction of benzylidenetriphenylphosphorane with powdered tellurium in boiling toluene.[30] The resulting tellurobenzaldehyde **2a** is trapped by 2,3-dimethylbutadiene to give the heterocyclic derivative **17a** in a yield of only 11%. This way of generation of telluroaldehydes is much less efficient than the method described above in which bis(dimethylaluminium) telluride acts as the tellurating reagent.

In view of the fact that phosphine tellurides (see below) are efficient synthetic analogues of elemental Te, it would be of interest to check whether these compounds could be used in this reaction instead of elemental Te.

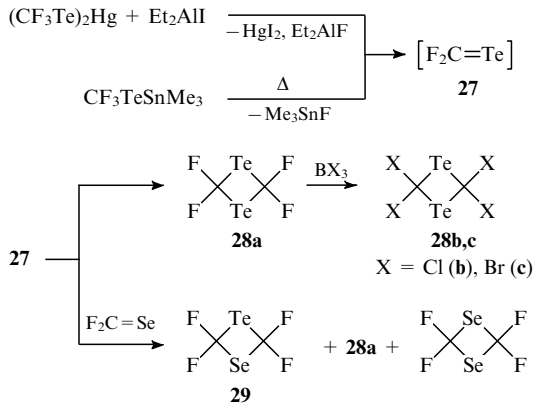


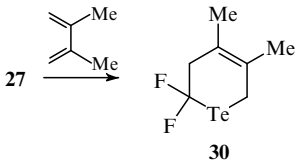
The reaction of the phosphorane with an equimolar or catalytic amount of tellurium in the absence of a diene affords only *trans*-stilbene in a yield of more than 60%.[30]

Yet another way of generating telluroketones, which has also been borrowed from the chemistry of organoselenium derivatives,[31] consists in the elimination of HCN from tellurocyanate **24**.[32] Hydrolysis of this compound under anaerobic conditions gives rise to a mixture of the *anti*- and *syn*-isomers of 1,3-ditelluretane **26a** and **26b** (yields 45% and 6%, respectively) resulting from dimerisation of the intermediate telluroketone **25**.



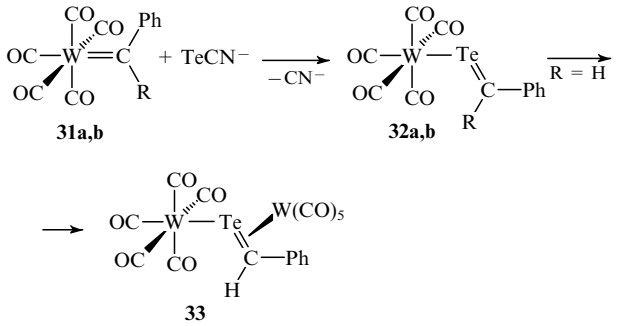
One more approach to the generation of tellurocarbonyl compounds reported in the literature, which is not associated with their formation from transition metal complexes, has been studied in relation to tellurocarbonyl difluoride **27**.[33,34] This compound is formed in a fairly low yield upon treatment of bis(trifluoromethyltelluro)mercury with diethylaluminium iodide and rapidly dimerises to give 2,2,4,4-tetrafluoro-1,3-ditelluretane **28a**.[33,34] The telluretane **28a** was obtained in higher yields (50%–60%) by pyrolysis of trifluoromethyltellurotrimethylstannane.[34] Co-condensation of the compound **27** with selenocarbonyl difluoride results in the formation of 2,2,4,4-tetrafluoro-1-selena-3-telluretane **29**.[34] The reaction of the compound **27** with 2,3-dimethylbutadiene gives 6,6-difluoro-3,4-dimethyl-1-telluracyclohex-3-ene **30**. This heterocyclic derivative was prepared in 48% yield by heating trifluoromethyltellurotrimethylstannane with 2,3-dimethylbutadiene in a sealed tube. The synthesis of dichloro- and dibromotelluretanes **28b,c** by treatment of the tetrafluoride **28a** with boron halides also deserves attention.[34]





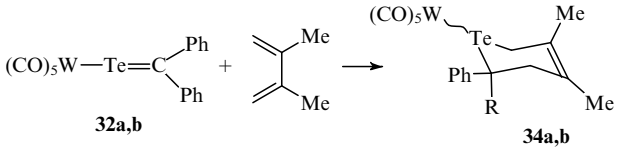
c. Telluration of transition metal complexes

Yet another method for stabilisation of telluroaldehydes and telluroketones is the formation of complexes with transition metal compounds. These complexes, unlike the complex of telluroketone with pentacarbonyltungsten (**12**) described above,[14] are formed upon interaction of metal complexes of various structures with tellurium-containing nucleophiles or elemental tellurium, $TeCN^-$ and HTe^- being usually employed as the tellurium-containing nucleophiles. For example, complexes **32a**[35] and **32b**[36] have been obtained in 18% and 12% yields, respectively, by the reaction of complexes **31** with $TeCN^-$. The complex **32a** is thermally fairly unstable and is readily converted into binuclear complex **33** (the yield given above refers to **33**).



R = H (**a**), Ph (**b**).

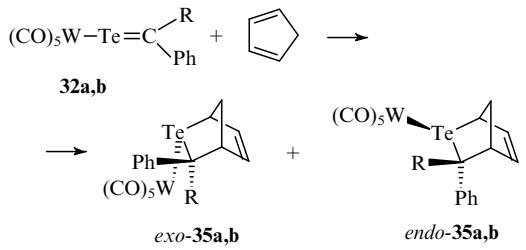
The complexes **32** enter into reactions typical of tellurocarbonyl derivatives, in particular, into the Diels–Alder reaction, *i.e.* they behave similarly to 'free' tellurocarbonyl compounds. Their reaction with 2,3-dimethylbutadiene leads to pentacarbonyltungsten complexes of 1-tellura-3,4-dimethylcyclohex-3-enes **34a,b** in 12%[37] and 8%[36] yields, respectively. It has been reported[37] that the reactivity of complexes of the $(CO)_5W-X=CPh_2$ type, where X = S, Se, and Te, sharply increases in the series S < Se < Te. In fact, whereas the reaction of **32b** with 2,3-dimethylbutadiene at −25 °C is completed over a period of 45 min, the reaction of the selenium analogue with the same diene requires 10 hours at room temperature. Finally, pentacarbonyl(diphenylthione)tungsten does not react with this diene at all under these conditions.



R = H (**a**), Ph (**b**).

The complex **34a** exists in solution as an equilibrium mixture of two conformers in which the Ph group occupies an equatorial position.[36]

The reactions of the complexes **32** with cyclopentadiene occur faster than with 2,3-dimethylbutadiene and afford tungsten complexes of 2-tellurabicyclo[2.2.1]hept-5-enes **35a,b**[36,37] in 31% and 24% yields, respectively. The formation of the complex **35a** is highly stereoselective: the ratio of the *exo*- and *endo*-isomers is 11 : 1.[36] The structure of the major isomer, *exo*-**35a**, was established by X-ray diffraction analysis.[36]

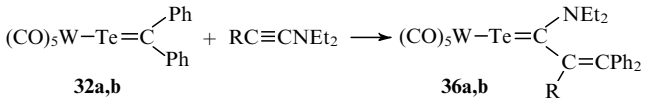


32a,b

exo-**35a,b** *endo*-**35a,b**

R = H (**a**); Ph (**b**).

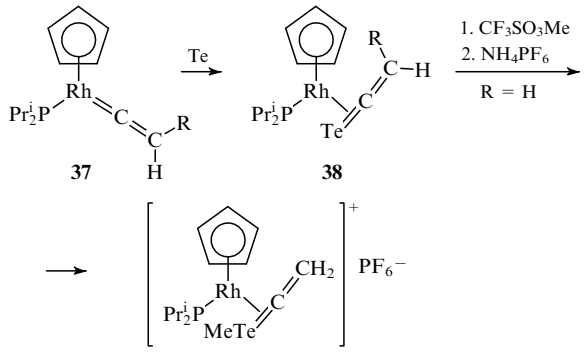
Reactions of the complex **32b** with 1-diethylaminoprop-1-yne and bis(diethylamino)acetylene have also been studied.[38] They occur as [2 + 2]-cycloaddition followed by electrocyclic ring opening and give rise to telluroacrylamide complexes **36a,b**.[38] The complex **36b** decomposes on prolonged heating in an ethereal solution under a CO atmosphere to give $W(CO)_6$, Te, and $Et_2NCH=C(NEt_2)CHPh_2$.



32a,b **36a,b**

R = Me (**36a**), NEt_2 (**36b**).

Metal complexes have also been used to stabilise chalcogenoketenes including telluroketenes.[39] Complexes **38** as well as their sulfur and selenium analogues have been synthesised in relatively high yields (68%–87%) by the reaction of vinylidene rhodium complexes **37** with chalcogens in benzene. Methylation of **38** (R = H) with methyl triflate and subsequent treatment with NH_4PF_6 results in the formation of an ionic complex **39**.[39]

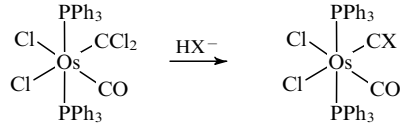


37 **38**

39

R = H, Me, Ph.

Finally, we would like to mention the synthesis of tellurocarbonyl complex **41a** (X = Te) in which the C=Te group acts as a carbonyl ligand.[40] The complex **41a** as well as its sulfur (**41b**) and selenium (**41c**) analogues were obtained as crystals, stable in air, on treatment of osmium dichlorocarbene complex **40** with HX^- anions (X = S, Se, Te).

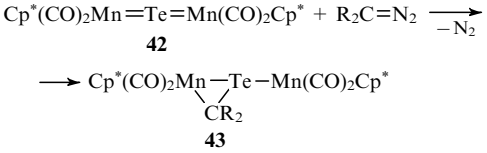


40 **41a–c**

X = Te (**a**), S (**b**), Se (**c**).

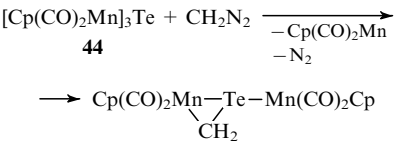
The ν(C=X) absorption frequencies in the IR spectra of the complexes **41a–c** regularly decrease in the order S (1315 cm^{-1}) > Se (1156 cm^{-1}) > Te (1056 cm^{-1}).[40]

The tellurium-containing groups in the complexes **32** and **38** are bound to metal atoms either through the Te atom or by the C=Te double bond, *i.e.* these compounds are η^1-complexes. At the same time, a number of heterobinuclear μ-alkylidene complexes of the dimetallacyclopropane type containing C and M in three-membered rings have also been described. Complexes of this type, for example, **43** and **45**, have been prepared as blue crystalline compounds by treatment of the manganese complexes **42**[41] or **44**[42] with diazoalkanes.[41,43]



42 **43**

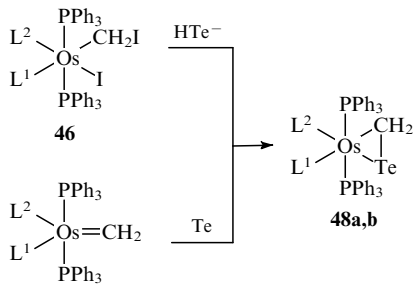
R = H, Me; Cp^* is C_5Me_5.



44 **45**

Cp is C_5H_5.

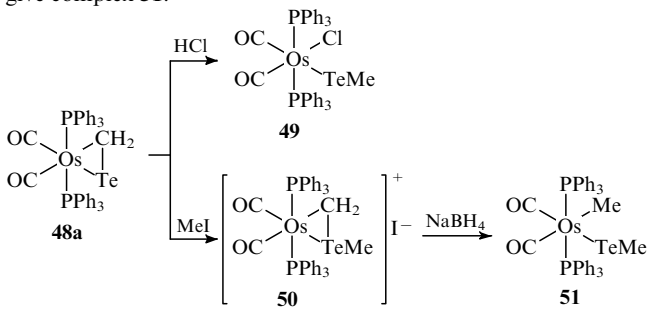
The reactions of osmium complexes **46**[44] and **47**[45] with hydrogentelluride anions[44] or elemental tellurium[45] resulted in the formation of telluroformaldehyde complexes **48a,b**.



46 **47** **48a,b**

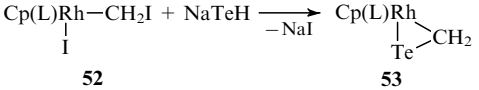
$L^1 = L^2 = CO$ (**46**, **48a**);
L^1 = NO, L^2 = Cl (**47**, **48b**).

The reaction of the complex **48a** with HCl involves the Os–CH_2 bond and gives rise to complex **49**.[43] In the reaction with methyl iodide, the attack is directed at the tellurium atom; the cationic complex **50** thus formed is easily reduced by sodium tetrahydridoborate with opening of the three-membered ring to give complex **51**.[44]



48a **49** **50** **51**

Rhodium complexes **53** containing rigid three-membered rings have been synthesised in relatively low yields by reaction of rhodium complexes **52** with sodium hydrogentelluride.[46,47]

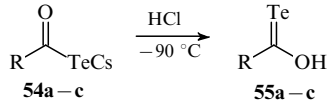


52 **53**

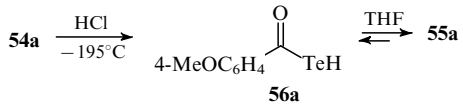
L = Me_3P,[46,47] Pr^i_3P,[47] CO.[47]

2. Telluronic acids

The synthesis and some reactions of tellurocarboxylic acids have been described only quite recently. These acids were prepared by acidolysis of the corresponding cesium tellurocarboxylates **54** with an ethereal solution of HCl.[48] At low temperatures in a polar solvent like THF, they exist mostly as the telluroxo form **55** (telluronic acids).[48]



54a–c **55a–c**



56a

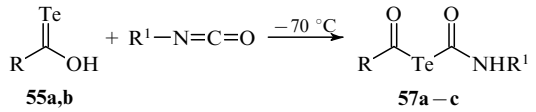
R = 4-$MeOC_6H_4$ (**a**), 4-MeC_6H_4 (**b**), Me_3C (**c**).

The structure of the acids **55** has been confirmed by their spectral characteristics. The ^1H and ^{13}C NMR spectra of these compounds recorded at −90 °C contain no signals corresponding to the TeH and C=O groups present in the isomeric tellurolic acids **56**. The singlets observed at δ 16.02, 16.48 and at δ 222.9, 223.1 ppm were attributed to the OH and C=Te fragments of the acids **55a** and **55b**, respectively. When the temperature was raised to −70 °C, the signals mentioned above were markedly broadened; this was attributed [48] to a dynamic exchange process involving the formation and rupture of hydrogen bonds (Te–H···O, O–H···O) in the above equilibrium. The telluroxo structure of these compounds is also supported by the magnitudes of ^{125}Te chemical shifts (δ 952 ppm for **55a** and δ 1024 ppm for **55b**). The acids of the aromatic series are coloured dark-green (λ_{max} = 652 and 673 nm for **55a** and **55b**, respectively), whereas tellurotrimethylacetic acid **55c** is blue-violet (λ_{max} = 594 nm).

The isomeric tellurobenzoic *Te*-acid **56a** was prepared by treatment of the salt **54a** with liquid hydrogen chloride at −195 °C followed by raising the temperature to −90 °C. At −110 °C, the dark-brown salt **54a** was converted into the solid yellow acid **56a**, which is soluble in toluene at −90 °C. The signal observed in the ^{125}Te NMR spectrum of this compound at δ 535 ppm was assigned to the TeH group. When THF was added to the resulting solution, the acid **56a** was converted into the isomeric acid **55a**.[48]

Tellurocarboxylic acids of both types are unstable at ambient temperature and are very sensitive to oxygen; on exposure to air even at −90 °C, they immediately decompose with liberation of elemental Te. The tellurolic acids **56** are appreciably less stable than telluronic acids **55**.[48]

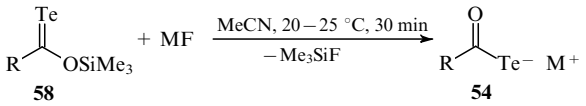
Tellurocarboxylic acids **55a,b** react with aryl isocyanates in THF or CH_2Cl_2 at −70 °C to give stable acyl carbamoyl tellurides **57a–c**, their yields exceeding 80%.[48]



55a,b **57a–c**

R = 4-$MeOC_6H_4$: R^1 = Ph (**57a**), 4-MeC_6H_4 (**57b**);
R = 4-MeC_6H_4: R^1 = Ph (**57c**).

The synthesis of free acids from their salts proved to be possible only for cesium salts.[49] These salts, which are relatively stable (for R = Ar) under an inert atmosphere, as well as their rubidium analogues, have been prepared in 40%–60% yields by the reactions of *O*-trimethylsilyl tellurocarboxylates **58** (see Section II.3) with cesium and rubidium fluorides.[49]

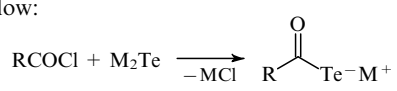


58 **54**

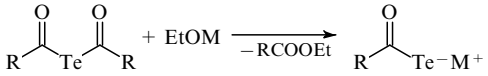
M = Cs, Rb; R = Me, Bu^t, Ph, 2-MeC_6H_4, 4-MeC_6H_4, 2-$MeOC_6H_4$, 4-$MeOC_6H_4$, 4-ClC_6H_4.

The presence of a carbonyl group in the compounds **54** was confirmed by an X-ray diffraction study of *Te*-cesium 2-methoxytellurobenzoate **54a**.[49]

It should be noted that salts of type **54** containing lighter alkali metal cations, that is, lithium,[50] sodium [51,52] and potassium,[53] have been synthesised earlier using one of the reactions presented below:



M = Li, Na.

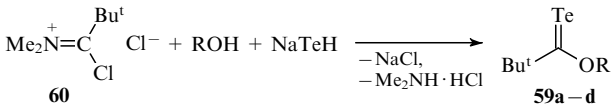


M = Na, K.

However, it was impossible to carry out X-ray diffraction analyses of these salts, because they were sensitive to oxygen and thermally unstable and, hence, it was difficult to purify them. The same features precluded preparation of the corresponding acids from these salts.

3. *O*-Alkyl and *O*-trimethylsilyl tellurocarboxylates

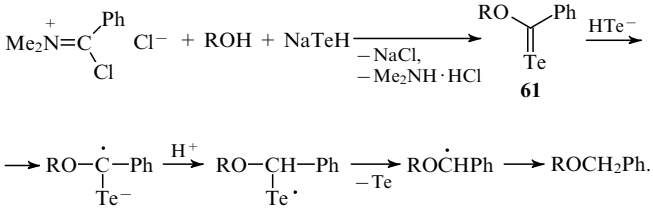
O-Alkyl tellurocarboxylates **59** were the first representatives of organotellurium compounds with the C=Te bond to be isolated in a pure state. These compounds were prepared by Barton *et al.*[54,55] by the reaction of (1-chloro-2,2-dimethylpropylidene)dimethylammonium chloride **60** with alcohols and sodium hydrogentelluride, synthesised from $NaBH_4$ and Te in ethanol in the absence of air and light.



60 **59a–d**

R = CH_2Bu^t (**a**), (−)-menthyl (**b**), adamantylmethyl (**c**), 5α-cholestan-3β-yl (**d**), Δ^9-tigogenyl-3 (**e**).

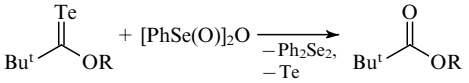
The yields of the compounds **59** varied over wide limits, namely, from 6% in the case of **59b** to 91% for **59c**. Evidently, the higher stability of the compound **59a** is due to the presence of bulky *tert*-butyl groups in their molecules. In fact, when the analogous phenyl derivative is used instead of the chloride **60**, the reactions with alcohols and sodium hydrogentelluride afford the corresponding benzyl ethers as the final products. Tellurobenzoates **61** were postulated as intermediate compounds.[56,57]



Since these reactions occur under relatively mild conditions, it was proposed [56,57] to use them for protecting hydroxy groups in carbohydrates and other compounds, labile in alkaline media.

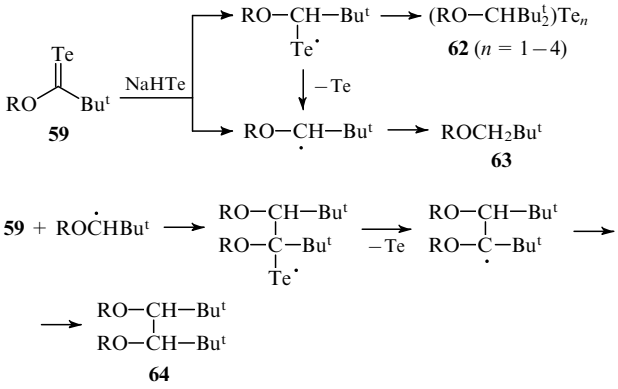
The compounds **59** are coloured violet, which is due to absorption of the tellurocarbonyl chromophore with λ_{max} = 584 – 596 nm; the ^{13}C NMR signals for the carbon nuclei of the C = Te group occur at δ 229 ppm.[54, 55]

The esters **59** are quite stable to atmospheric oxygen in the dark. However, they are readily oxidised by phenylseleninic anhydride; in the case of **59d**, the ester of the corresponding carboxylic acid is formed in an almost quantitative yield.[54, 55]



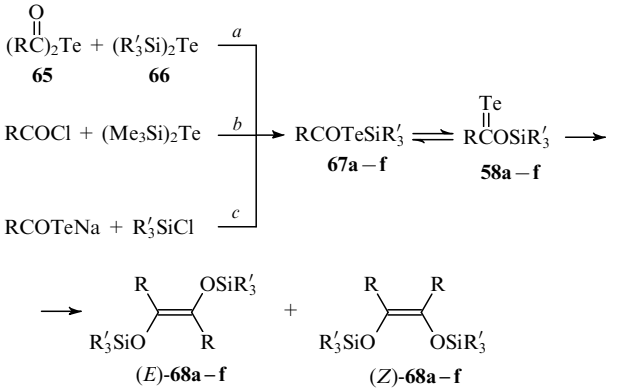
59d

The reaction of the telluroesters **59** with excess sodium hydrogentelluride initially yields a mixture of oligotellurides **62** and finally gives esters **63** and **64**. The formation of these compounds was explained in terms of the scheme given below.[55]



64

The silyl esters **58** represent yet another type of telluroesters with C = Te bonds. They have been synthesised by reactions of bis(acyl) tellurides **65** with bis(trialkylsilyl) tellurides **66** [pathway (*a*)], of acyl chlorides with equimolar amounts of bis(trimethylsilyl) tellurides [pathway (*b*)],[58–61] and of sodium tellurocarboxylates with trialkylchlorosilanes [pathway (*c*)].[52]

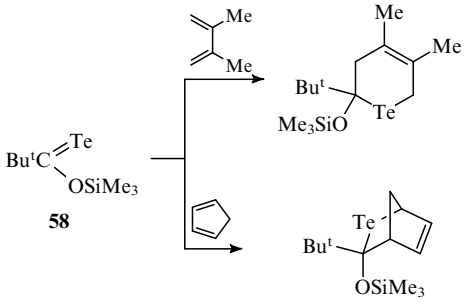


Compound	R	R'_3	Pathway
a	Me	Me_3	*a*, *b*
b	Bu^t	Me_3	*a*, *b*
c	Me	Pr^iMe_2	*a*
d	2-MeC_6H_4	Me_3	*c*
e	2-MeC_6H_4	Bu^tMe_2	*c*
f	Ph	Bu^tMe_2	*a*

The compounds **58** gradually decompose in solutions with liberation of tellurium giving mixtures of *E*- and *Z*-isomers of alkenes **68**[58–61] (when R = R′ = Me, the *E*:Z ratio amounts to 55 : 45[57]). The stability of the esters **58** increases with increase in the size of the substituents R and R′. For example, in the reaction of bis(acetyl) telluride with bis(trimethylsilyl) telluride, the mixture of alkenes **68a** is formed in almost quantitative yield over a period of 30 min, whereas the reaction of bis(acetyl) telluride with bis[(dimethyl)isopropylsilyl] telluride giving rise to a mixture of the alkenes **68c** is completed only over a period of 12 h.[58, 61]

Te-Silylated derivatives **67** are the precursors of the esters **58**; they either completely isomerise into *O*-silylated esters **58** (for R = Ar[52]) or exist as equilibrium mixtures with them. Thus the reaction of pivaloyl chloride with silyl telluride **66** (R^1 = Me) affords an equilibrium mixture of the compounds **67b** (35%) and **58b** (65%),[60] as indicated by the spectral parameters of the blue liquid formed in this reaction (λ_{max} = 624 nm[58, 60]). The ^{13}C NMR spectrum exhibits signals at δ 207.5 (C = O) and δ 251.2 ppm (C = Te); the ^{125}Te NMR signal corresponding to the compound **58b** is manifested at δ 1418 ppm.[60]

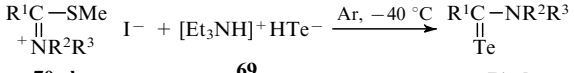
Similarly to telluroaldehydes and telluroketones (see Section II.1), the esters **58** enter into [2 + 4]-cycloaddition to 2,3-dimethylbutadiene and cyclopentadiene giving the corresponding tellurium-containing heterocycles.[60]



58

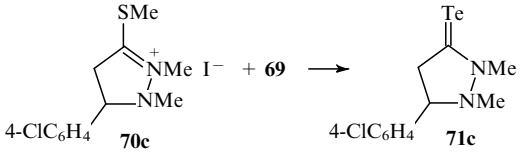
4. Telluroamides and their analogues

The first telluroamides and tellurohydrazides **71** were synthesised at about the same time as telluroesters, in 1979.[62] They have been prepared similarly to selenium analogues,[63] namely, by treating the salts **70** with the hydrogentelluride anion **69** generated from Et_3N and H_2Te in CH_2Cl_2.[62] The yields of the compounds **71** were low (5% – 19%).



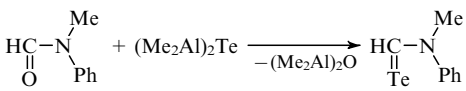
70a,b **69** **71a,b**

R^1 = Ph: $R^2 = R^3$ = Me (**a**); R^2 = Me, $R^3 = NMe_2$ (**b**).



70c **71c**

Telluroamides have also been synthesised from bis(dimethylaluminium) telluride, which had been used previously to prepare telluroaldehydes and telluroketones.[22, 23] (see Section II.1). Treatment of *N*-methylformanilide with this tellurating reagent resulted in the synthesis of telluroformanilide **71d** in a yield of about 90%.[64]



71d

However, other telluroformanilides could not be isolated because they decomposed during purification.

The compounds **71** are stable at room temperature in the absence of water. They are rapidly hydrolysed in moist air or in wet solvents to give the corresponding amides and elemental tellurium resulting from fast oxidation of H_2Te.[62] The hydrolysis is catalysed by alumina and silica gel; this apparently accounts for the fact that other telluroformanilides could not be isolated. The relatively high stability of telluroamides (hydrazides) **71a – c** is caused by the presence of strong electron-donating substituents

(NR_2, $NR^1NR_2^2$) at the tellurocarbonyl carbon atom. Evidently, the stability of telluroamides, like that of telluroesters **59**, could be increased by introducing bulky substituents into their molecules. However, compounds of this type have not yet been synthesised.

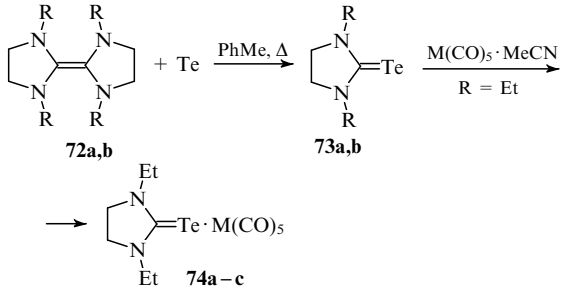
The long-wave absorption bands associated with the $n \rightarrow \pi^*$ transition in the C=Te fragment in the UV spectra of the telluroamides **71a,d** shift bathochromically with respect to those in the spectra of the analogous selenium derivatives by more than 100 nm and are located at 540 nm.[62,64]

The ^{1}H NMR data imply that the barriers (ΔG) to rotation of the NMe_2 groups in the amides $PhC(X)NMe_2$ vary in the following sequence:

$$C=O\,(62.3\ kJ\ mol^{-1}) < C=S\,(77.0\ kJ\ mol^{-1}) < < C=Te\,(80.5\ kJ\ mol^{-1}) < C=Se\,(80.8\ kJ\ mol^{-1}).^{65}$$

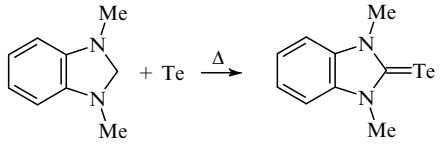
The deviation of the ΔG value for the telluroamide **71a** from the general tendency was attributed [65] to the increase in the steric strain in the ground state caused by the repulsion between the bulky Te atom and the (*Z*)-*N*-methyl group.

The stability of telluroureas **73** and **75** is also associated with the presence of electron-donating substituents at the tellurocarbonyl group. These compounds have been synthesised by the oxidation of alkenes **72** [66] or 1,3-dimethylbenzimidazoline with elemental Te. The compounds **73** were formed in 42%–45% yields, and the tellurourea **75** was obtained in ~ 9% yield.



72a,b **73a,b** **74a–c**

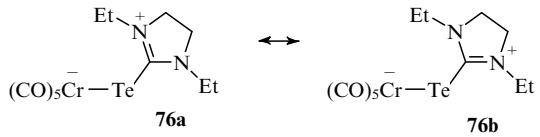
R = Me (**a**), Et (**b**); M = Cr (**74a**), Mo (**74b**), W (**74c**).



75

The properties of the tellurourea **75** have scarcely been studied. It has been reported [67] that the long-wave absorption bands in the UV spectra of 1,3-dimethylbenzimidazolinechalcogenones shift bathochromically in the series: thione (λ = 310 nm), selone (λ = 318 nm), tellurone (λ = 372 nm).

The properties of the telluroureas of type **73** have been studied somewhat more extensively.[66] These compounds are sensitive to air and decompose with the liberation of tellurium both in solutions and in the solid state. Complexes **74**, which are formed in 50%–75% yields in the reaction of the tellurourea **73b** with Cr, Mo, and W carbonyls, are more stable to air. The length of the C–Te bond in the complex **74a** corresponds to the length of a single C–Te bond and is equal to 2.12 Å; this is much longer than a similar bond in the complex **12** formed from the telluroketone **5** and tungstenpentacarbonyl (1.987 Å [14]). This was explained [66] by the assumption that the resonance-stabilised zwitter-ionic structures **76** make the predominant contributions to the ground state of the complexes.

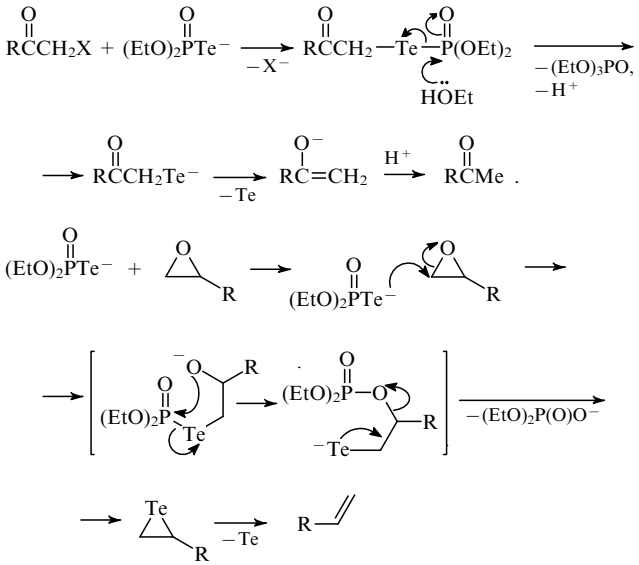


76a **76b**

III. Synthesis, reactions, structures, and spectroscopic characteristics of phosphine tellurides $R_3P=Te$

1. Synthesis of phosphine tellurides

The first compound with the P–Te bond was synthesised by Foss about 50 years ago.[68] The reaction of elemental Te with an ethanolic solution of potassium diethyl phosphite has resulted in the synthesis of $(EtO)_2P(O)TeK$. Later, the corresponding sodium derivative was used as an efficient dehalogenating reagent for α-chloro- and α-bromoketones,[69] and also for deoxygenation of epoxides.[70]



As mentioned above, the first phosphine telluride, tributyl phosphine telluride, was synthesised by Zingaro in 1963.[1] This compound and similar compounds **77** have been prepared by the interaction of triorganylphosphines with elemental tellurium in anhydrous toluene.[1,71,72] The yields of the compounds **77** varied from 5% to 45%. However, the reaction of tris(*tert*-butyl)-phosphine with tellurium carried out under the same conditions gave the corresponding phosphine telluride in an almost quantitative yield.[73] Phosphine tellurides have been synthesised in substantially higher yields (75%–80%) by heating trialkyl(cycloalkyl)phosphines with tellurium without a solvent.[74]

$$R_3P + Te \longrightarrow R_3P{=}Te$$

77a–i

R = Me (**a**),[72] Et (**b**),[71] Pr (**c**),[71,74] Bu (**d**),[1,71,74] Bu^t (**e**),[73] C_5H_{11} (**f**),[74] cyclo-C_6H_{11} (**g**),[74] C_8H_{17} (**h**),[74] R_3 = $PhBu_2$ (**i**).[71]

It should be noted that there is no direct correlation between the solubility of tellurium in phosphines and the capability of the latter of being converted into phosphine tellurides. In fact, the solubility of tellurium in dimethyl(phenyl)phosphine (defined as the ratio of the number of moles of dissolved Te to the number of phosphine moles multiplied by 100) [71] is 16.7, and that for dibutyl(phenyl)phosphine is 9.1; however, only the latter compound yields phosphine telluride upon interaction with tellurium. No triorganylphosphine tellurides containing more than one phenyl group have been obtained so far. For example, all attempts to prepare triphenylphosphine telluride failed. However, this compound has been obtained as a complex with triphenylphosphine (**78**) by detelluration of $TeCN^-$ with triphenylphosphine in acetonitrile in the presence of lithium perchlorate.[75]

$$Ph_3P + NCTe^- \xrightarrow[-CN^-]{} [Ph_3P{=}Te] \xrightarrow{Ph_3P} Ph_3P{=}Te\cdot PPh_3.$$

78

The structure of the adduct **78** was determined by X-ray diffraction analysis.[75] It contains a linear P–Te–P fragment with non-equivalent P–Te bonds. The length of one of these bonds is 2.27–2.42 Å; this falls into the range of typical P=Te bonds in phosphine tellurides (2.31–2.37 Å [76–80]); the other bond, which is 3.41–3.95 Å long, corresponds to a 'secondary interaction'[81] between the Te atom and the phosphorus atom in triphenylphosphine.

The reversible reaction between triorganylphosphines and $NCTe^-$ anions was used to estimate quantitatively the 'tellurophilicity' of phosphines;[78] for this purpose, the equilibrium constants (K) for the reaction

$$R_3P + NCTe^- \rightleftharpoons R_3P{=}Te + CN^-$$

were measured. The following results were obtained:

R			Me_2N	Et_2N	Bu	
K	8.000	0.600	0.540	0.270	0.170	0.009

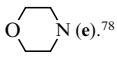
R	Pr^i_3N	EtO	MeO	BuO	Ph
K	0.048	~ 0.003	~ 0.001	~ 0.003	0

The K values are in fairly good agreement with other findings. Thus the fact that Ph_3P does not form phosphine tellurides is consistent with the K value found (0.000). At the same time, various triaminophosphines characterised by relatively large K readily react with elemental tellurium giving tris(dialkylaminophosphine) tellurides **79** in high yields.[78,82–85]

$$(R_2N)_3P + Te \longrightarrow (R_2N)_3P{=}Te$$

79

R_2N = Me_2N (**a**),[82,84,85] Et_2N (**b**),[83]  (**c**),[78]

 (**d**),[78]  (**e**).[78]

Amidophosphine tellurides of type **80**[83,86–88] and **81**[88] have been obtained in a similar way.

$$R^1_nP(NR^2R^3)_{3-n} + Te \longrightarrow R^1_nP(Te)(NR^2R^3)_{3-n}$$

80

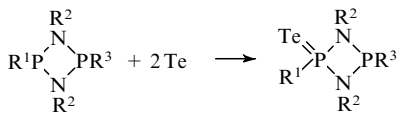
n = 1: $R^1 = R^2 = Me$;[83,87] $R^1 = Me$, $R^2 = R^3 = Et$;[88] $R^1 = Ph, Et$; $R^2 = R^3 = Me$;[82]

n = 2: $R^1 = Bu^t$; $R^2 = H$, $R^3 = Pr^i$, cyclo-C_6H_{11}.[86]

$$(Et_2N)_2P(CH_2)_4P(NEt_2)_2 + 2Te \longrightarrow (Et_2N)_2P(Te)(CH_2)_4P(Te)(NEt_2)_2.$$

81

Cyclic phosphine tellurides, which are relatively resistant against water and air compared to other phosphine tellurides, have been synthesised by the reactions of the corresponding diazadiphosphetidines with tellurium.[89–91] Depending on the ratio of the reactants, these reactions gave diazadiphosphetidine monotellurides **82**[89–91] and ditellurides **83**.[89]

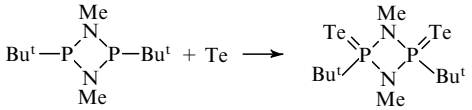


82a–c

82a: R^1 = Me, $R^2 = Bu^t$, R^3 = Cl;[89]

82b: $R^1 = R^3 = NMe_2$, $R^2 = Bu^t$;[90]

82c: $R^1 = R^3 = Bu^t$, R^2 = Me.[91]



83

Dichloro(methyl)phosphine does not react with tellurium,[92] although the chloro-substituted diazadiphosphetidine forms the corresponding telluride **82a** in 17% yield.[89]

The fairly low tellurophilicity of trialkyl phosphites accounts for the fact that no trialkyl phosphotelluroates $(RO)_3P{=}Te$ have been synthesised so far. However, phosphonites $RP(OR')_2$ are able to form compounds **84** with a P=Te bond. The stability of these compounds is largely determined by the nature of the hydrocarbon substituents attached directly to the phosphorus atom. For example, **84a** resulting from reaction of diethyl ethylphosphonite with Te decomposes during distillation,[93] whereas phosphonotelluroate **84b** formed from diethyl allylphosphonite is relatively stable under an inert atmosphere.[94]

$$RP(OR')_2 + Te \longrightarrow RP(Te)(OR')_2$$

84a,b

R = R′ = Et (**a**); R = $CH_2CH{=}CH_2$, R′ = Et (**b**).

Phosphonotelluroate **85** was obtained in 44% yield by the reaction of bis(trimethylsilyl) hydrogenphosphonite with Te in dioxane.[95]

$$(Me_3SiO)_2PH + Te \longrightarrow (Me_3SiO)_2P(Te)H$$

85

Finally, it should be noted that *N*-diphenyltellurophosphinoyl(triphenyl)phosphazene **86** is formed in a yield of 87% when the corresponding phosphazene is heated with elemental tellurium in benzene.[96]

$$Ph_3P{=}N{-}PPh_2 \longrightarrow Ph_3P{=}N{-}P(Te)Ph_2$$

86

Thus, synthesis of all types of compounds containing P=Te bonds is based on the reactions of P(III) derivatives with elemental tellurium. Other sources of tellurium do not afford phosphine tellurides, although their sulfur and selenium analogues are used to prepare the corresponding phosphine chalcogenides. For example, unlike diorganyl disulfides and diselenides, which react with triorganylphosphines to give triorganylphosphine sulfides or selenides,[97] diorganyl ditellurides subjected to photolysis in the presence of tertiary phosphines yield only mixtures of organyl tellurides and elemental tellurium.[98]

2. Reactions of phosphine tellurides

Triorganylphosphine tellurides $R_3P{=}Te$ are golden-yellow crystalline compounds, which partially decompose in air or during recrystallisation. Therefore, they are normally recrystallised in the presence of the corresponding phosphines. In many cases, heating of solutions of phosphine tellurides in hydrocarbon solvents results in the formation of tellurium mirrors.[71] Only tris(*tert*-butyl)phosphine telluride is thermally stable both in the solid state and in solutions.[73] Tris(dialkylaminophosphine) tellurides are also quite sensitive to air and decompose with liberation of elemental Te.[82] Phosphine tellurides containing residues of cyclic nitrogen-containing compounds at the phosphorus atom are more stable.[78] Diazadiphosphetidine tellurides **82** and **83** are very stable both in the crystalline state and in solutions.[88–90]

a. Exchange reactions

The ^1H, ^{31}P and ^{125}Te spectra of mixtures of phosphine tellurides with phosphines recorded at room temperatures indicate that the Te atom migrates rapidly, on the NMR time scale, between the

phosphine molecules.[73,98–101] Apparently, this reaction occurs *via* a transition state like **87**.[99]

$$R^1_3P{=}Te + R^2_3P \rightleftharpoons [R^1_3\overset{+}{P}{-}Te^{-}\overset{\cdot\cdot}{P}R^2_3] \rightleftharpoons$$

87

$$\rightleftharpoons R^1_3P + Te{=}PR^2_3$$

$R^1 = R^2 = Bu^t$,[73,99,100] Me_2N,[99] Bu;[100]
$R^1 = Bu^t$, $R^2 = Me_2N$.[73,99]

However, in the $Bu^t_3P{=}Te/Bu^t_2PSiMe_3$ system, the Te atom is rapidly and irreversibly transferred to the silylphosphine; the intermediate phosphine telluride **88** immediately rearranges into compound **89** containing a Te–Si bond.[101] However, this compound and also similar derivatives with Te–Ge and Te–Sn bonds have not been isolated in an analytically pure state due to disproportionation, which is described by the following scheme:[101]

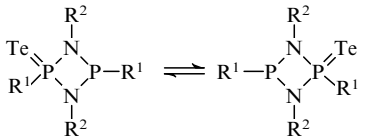
$$Bu^t_3P{=}Te + Bu^t_2PSiMe_3 \xrightarrow[-Bu^t_3P]{} \left[Bu^t_2P(Te){-}SiMe_3\right] \longrightarrow$$

88

$$\longrightarrow Bu^t_2P{-}TeSiMe_3 \longrightarrow (Me_3Si)_2Te + (Bu^t_2P)_2Te.$$

89

Fast, on the NMR time scale, transfer of a tellurium atom between phosphorus atoms has been observed for cyclic phosphine tellurides **82b**,**c**.[90,91]



82b,c

$R^1 = Me_2N$, $R^2 = Bu^t$ (**b**);[90] $R^1 = Bu^t$, $R^2 = Me$ (**c**).[91]

The concentration dependence of the coalescence temperature indicates that this process can occur not only as intramolecular exchange, which is facilitated by the non-planarity of the diazadiphosphetidine ring,[76] but also intermolecularly.

b. Protonation and alkylation

The protonation of phosphine tellurides with strong acids affords cations $[R_3PTeH]^+$.[102] However, no salts with these cations have been isolated in a pure state; their formation in solutions has been judged only by NMR spectra.

Under mild conditions (benzene, room temperature), phosphine tellurides are alkylated with methyl iodide to give methyltellurophosphonium salts **90**, their yields being about 90%.[103] The salts **90** are soluble in nitromethane but decompose soon after dissolution.

$$R_3P{=}Te + MeI \longrightarrow [R_3PTeMe]^+I^-$$

90

R = Me, Pr^i, Bu, Bu^t, Me_2N.

It is of interest that not only phosphine tellurides but also their complexes with metal carbonyls can be methylated.[104] Thus the reaction of the complex **91** with methyl iodide gave cationic complex **92**.[4]

$$(CO)_5W{-}Te{-}PBu^t_3 + MeI \longrightarrow \left[(CO)_5W{-}\overset{Me}{Te}{-}PBu^t_3\right]^+ I^-$$

91 **92**

The P–Te bonds in the salts **90** tend to be cleaved by strong nucleophiles. For instance, treatment of these salts with methyllithium affords dimethyl telluride and triorganylphosphines.[103]

$$[R_3PTeMe]^+I^- + MeLi \xrightarrow[-LiI]{} R_3P + Me_2Te$$

90

c. Oxidation

The phosphine tellurides **77c,d** are oxidised with the ferrocenium salts $Cp_2Fe^+X^-$ (X = BF_4, PF_6, SbF_6) at low temperatures to give dications **93**, the yields of which are about 30%, and ferrocene.[105]

$$R_3P{=}Te + (C_5H_5)_2Fe^+X^- \xrightarrow[-Cp_2Fe]{}$$

77c,d

$$\longrightarrow [R_3P{-}Te{-}Te{-}Te{-}PR_3]^{2+}2X^-$$

93

R = Pr^i (**c**), Bu^t (**d**); X = BF_4, PF_6, SbF_6.

The salt **93** (R = Bu^t, X = SbF_6) was studied by X-ray diffraction analysis.[105] Based on the bond lengths Te–Te (2.71 Å) and P–Te (2.50 Å, which corresponds to a single bond between Te and P atoms) and on the Te–Te–Te (109 °) and Te–Te–P (108.6 °) bond angles, this compound was described [105] as a Te_3^{2+} dication stabilised by complex formation with Bu^t_3P.



In a more recent study,[106] tributylphosphine telluride has been used to stabilise the tellurenyl cations RTe^+. These species were generated by oxidation of diorganyl ditellurides with the nitrosonium salts NO^+X^- (X = BF_4, ClO_4) and isolated as stable complexes $[Bu_3P \rightarrow TeP]^+X^-$.

d. Complex formation

Phosphine tellurides form complexes with some metal salts. Like their sulfur and selenium analogues, phosphine tellurides act as donors in complex formation. Moreover, since in this case the bipolar character of the ($P{=}Te \leftrightarrow P^+{-}Te^-$) bond is more pronounced, phosphine tellurides are stronger donors than phosphine sulfides or phosphine selenides.

Thus tributylphosphine telluride reacts with mercury(II) bromide to give a complex of the composition $(HgBr_2)_4(TePBu_3)_3$, which is fairly sensitive to oxygen and heating.[107] According to X-ray diffraction data, this complex consists of dimeric $[(HgTePBu_3)_3Br_5]_2^{2+}$ cations and binuclear $[Hg_2Br_6]^{2-}$ anions. The reactions of trimethylphosphine telluride with nickel and cobalt salts follow a different pathway, which includes decomposition of phosphine telluride and liberation of elemental tellurium even at −30 °C.[72]

The first phosphine telluride complexes **91a**–**c** were prepared in almost quantitative yields on irradiation of mixtures of Cr, Mo, and W carbonyls with tris(*tert*-butyl)phosphine telluride in THF.[104] They appear as dark-red crystals fairly stable in air and at elevated temperatures.

$$M(CO)_6 + Te{=}PBu^t_3 \xrightarrow[-CO]{h\nu} (CO)_5M{-}TePBu^t_3$$

91a–c

M = Cr (**a**), Mo (**b**), W (**c**).

The relatively high donor ability of the phosphine telluride ligands is indicated by the substantial upfield shift of the signals of the CO groups in the ^{13}C NMR spectra of the complexes **91**. This is also confirmed by the fact that the phosphine telluride ligands in the complexes **91**, unlike those in similar complexes derived from phosphine sulfides $(CO)_5M{-}S{=}PR_3$,[108] are not replaced by Ph_3P or CO on heating in solutions at 80 °C.[104] The length of the P–Te bond in the complex **91c** is 2.439 Å, which corresponds to a single P–Te bond.[104]

The results of NMR studies of complexes **94** also indicate that phosphine tellurides are stronger donors than other phosphine

chalcogenides. These compounds have been synthesised [109] by a reaction similar to that used earlier [110] to prepare the corresponding sulfur and selenium derivatives. The dark-brown complexes **94** were formed in almost quantitative yields on the interaction of salts **95** with phosphine tellurides in dichloromethane at room temperature.

$$[CpFe(CO)_2\cdot THF]^+BF_4^- + Te{=}PR_3 \xrightarrow{-THF}$$
95

$$\longrightarrow [CpFe(CO)_2TePR_3]^+BF_4^- \xrightarrow{-Te}$$
94a–e

$$\longrightarrow [CpFe(CO)_2PR_3]^+BF_4^-$$
96a–e

R = Me (**a**), Pr^i (**b**), Bu^t (**c**), Me_2N (**d**),  (**e**).

The compounds **94** are stable in air in the solid state but slowly decompose in solutions with liberation of tellurium to give complexes **96**.[109] The complex **94e**, which is the least stable in this series, decomposes yielding $[CpFe(CO)_3]^+BF_4^-$ and the corresponding phosphine telluride. The attempts to replace one of the CO groups in the cation **94** by a second R_3PTe molecule, which would have resulted in the formation of the cations $[CpFe(CO)(TePR_3)_2]^+$, failed; heating or irradiation of mixtures of **94** with $R_3P{=}Te$ was accompanied by intense decomposition. Meanwhile, treatment of the cations **94** with iodine resulted in the rupture of the Fe–Te bonds and in the formation of $[CpFe(CO)_2I]_2$.[109]

It should be noted that the reaction of the uranium cyclopentadienyl complex **97** with tributylphosphine telluride, unlike the reactions of the salts **95**, is accompanied by elimination of tributylphosphine giving rise to compound **98**.[111]

$$(MeC_5H_4)_3U\cdot THF + Bu_3P{=}Te \xrightarrow[-Bu_3P]{-THF,} [(MeC_5H_4)_3U]_2Te\,.$$
97 **98**

Triphenylphosphine sulfide and selenide react with the complex **97** yielding compounds with similar structures. In the case of triphenylphosphine oxide, this gives the complex $(MeC_5H_4)_3U\cdot OPPh_3$.[111]

e. Phosphine tellurides as synthetic equivalents of elemental tellurium. Preparation of metal tellurides

The use of phosphine tellurides as synthetic equivalents of elemental tellurium to introduce tellurium into molecules of organic and organoelement compounds is based on the fact that phosphine tellurides readily dissociate on heating. In some cases, phosphine tellurides are preferred over elemental tellurium, since the reactions can be carried out at lower temperatures and the products can be obtained in higher yields. Moreover, some telluration reactions can occur only with phosphine tellurides. Low-temperature synthesis of metal tellurides is among the most significant synthetic applications of phosphine tellurides. Thus triethylphosphine telluride reacts with metallic mercury in toluene at room temperature to give mercury telluride in an almost quantitative yield.[112]

$$Et_3P{=}Te + Hg \xrightarrow[-Et_3P]{} HgTe.$$

Phosphine tellurides eliminate metallic tellurium at lower temperatures than the majority of widely used sources of tellurium such as Me_2Te and Et_2Te, which generate tellurium at temperatures above 200 °C.[5,113]

The easy thermal dissociation of phosphine tellurides has served as the basis for the recently developed synthesis of semiconductor nanosized crystals [114] by pyrolysis of a mixture of organometallic substrates upon their injection into a hot coordinating solvent. Thus cadmium telluride with a size of crystals ranging from 12 to 115 Å was obtained by the introduction of $(C_8H_{17})_3P{=}Te$ and Me_2Cd into $(C_8H_{17})_3P{=}O$ at 240 °C followed by keeping the reaction mixture at 190–220 °C to grow the crystals.[114]

The reactions of phosphine tellurides with some organoelement compounds result in insertion of tellurium into C–element bonds. For example, the formation of mercury telluride in the reaction of $Et_3P{=}Te$ with diorganylmercury derivatives occurs according to the following scheme:[112]

$$RHgR + Et_3P{=}Te \xrightarrow[-Et_3P]{PhMe,\ \Delta} RTe{-}HgR \xrightarrow[-Et_3P]{Et_3P{=}Te}$$

$$\longrightarrow RTe{-}Hg{-}TeR \xrightarrow[-R_2Te]{} HgTe$$

R = Et, Ph.

It should be noted that various Ar_2Hg react with elemental tellurium only under fairly drastic conditions (> 200 °C) to give diaryl tellurides.[8,9]

Insertion of Te atoms into Sc–C(sp^3) or Sc–C(sp^2) bonds occurs relatively easily when permethylscandoceno-alkyls or -aryls are made to react with tributylphosphine telluride or elemental tellurium.[115–118] The reactions of scandocenes with phosphine telluride occur faster than the reactions with elemental tellurium, and compounds **99** are formed in higher yields (31%–71%).

$$(C_5Me_5)_2Sc{-}R \xrightarrow[\text{or Te}]{Bu_3P{=}Te} (C_5Me_5)_2Sc{-}TeR$$
99

R = Me_3SiCH_2, $PhCH_2$, *erythro*-CHDCHDBu^t, $CH_2CHDCH_2CH_2CH{=}CMe_2$, Ph, cyclo-$C_5H_9CH_2$.

The dimeric scandium μ-telluride **100** has been prepared in a similar way;[115,117] its structure was determined by X-ray diffraction analysis.

$$(C_5Me_5)_2Sc{-}D \xrightarrow[-D_2]{Bu_3P{=}Te \text{ or } Te} [(C_5Me_5)_2Sc]_2Te.$$
100

The advantages of $Bu_3P{=}Te$ over elemental tellurium are illustrated by the synthesis of the scandocene derivative **101**.[118] When elemental tellurium is used, the reaction is completed over 4–5 h, whereas in the case of $Bu_3P{=}Te$, this reaction occurs immediately after mixing the reactants.

$$[Me_2Si(Bu^tC_5H_3)_2]Sc{-}CH_2SiMe_3 \xrightarrow[-Bu_3P]{Bu_3P{=}Te}$$

$$\longrightarrow [Me_2Si(Bu^tC_5H_3)_2]Sc{-}TeCH_2SiMe_3\,.$$
101

Yet another example of the insertion of a Te atom into a C–element bond is the reaction of complexes **102** with trialkylphosphine tellurides yielding alkyltelluride manganese complexes **103**.[119,120] Pyrolysis of one of these products (**103b**) gives rise to manganese telluride.

$$RMn(CO)_5 \xrightarrow[PhMe,\ \Delta]{R'_3P{=}Te} RTeMn(CO)_3(PR'_3)_2 \xrightarrow[R' = Et]{300\ ^\circ C,\ 45\ min} MnTe$$
102 **103a,b**

R = CH_2Ph: R′ = Me (**103a**), Et (**103b**);

$$MeMn(CO)_5 \xrightarrow[PhMe,\ \Delta]{Et_3P{=}Te} MeTeMn(CO)_3(PEt_3)_2 + MeMn(CO)_3(PEt_3)_2.$$
103c

A series of metal tellurides including manganese telluride have been prepared using complexes of metals in low oxidation states. Depending on the reaction conditions, the reactions involving these compounds either directly afford metal tellurides or initially

afford clusters the pyrolysis of which under relatively mild conditions leads to tellurides. Manganese [121] and cobalt [122, 123] tellurides have been obtained using carbonyls of the corresponding metals **104** the reactions of which with triethylphosphine telluride in toluene give rise to binuclear complexes **105**; these products result from the insertion of two tellurium atoms into metal–metal bonds in the initial complexes.

$$(CO)_nM{-}M(CO)_n + Et_3P{=}Te \xrightarrow[-Et_3P]{} \underset{\mathbf{104}}{\longrightarrow} [(Et_3P)_2(CO)_{n-2}MTe]_2 \xrightarrow{\Delta} MnTe$$

105a,b

M = Mn, n = 5 (**a**); M = Co, n = 4 (**b**).

The dimeric molecules of **105** are built like diorganyl ditellurides R–Te–Te–R, but contain $(Et_3P)_2(CO)_{n-2}M$ groups instead of the organic radicals. The Te–Te bond lengths (2.763 Å in **105a** [121] and 2.765 Å in **105b** [122]) are somewhat larger than that in diphenyl ditelluride (2.712 Å [124]). The pyrolysis of the complex **105a** giving crystalline manganese telluride occurs under substantially milder conditions (300 °C, 16 h) than does the synthesis of this telluride from the elements (heating to 800 °C followed by keeping the reaction mixture at 500 °C [121]).

When the $Co_2(CO)_8$: $(Et_3P{=}Te)$: Et_3P ratio was varied, clusters **106** [122] and **107a** [122, 123] were isolated in addition to the compound **105b**. The former of these clusters can also be obtained from **105b**, $Co_2(CO)_8$, and Et_3P;[122] treatment of the complex **105b** with $Et_3P{=}Te$ and Et_3P affords the cluster **107a**.[122]

$$\mathbf{105b} \xrightarrow{Co_2(CO)_8,\ Et_3P} \underset{\mathbf{106}}{(Et_3P)_4(CO)_6Co_4Te_2}$$

$$\mathbf{105b} \xrightarrow{Et_3P{=}Te,\ Et_3P} \underset{\mathbf{107a}}{(Et_3P)_6Co_6Te_8} \xrightarrow{\Delta} CoTe$$

The chromium-containing cluster **107b**, similar to the cobalt derivative **107a**, was prepared by treatment of bis(triethylphosphinediallyl)chromium or bis(2,4-dimethylpentadienyl)chromium with triethylphosphine telluride.[125]

$$(Et_3P)_2Cr(C_nH_m)_2 + Et_3P{=}Te \longrightarrow \underset{\mathbf{107b}}{(Et_3P)_6Cr_6Te_8} \xrightarrow{315\ ^\circ C,\ 19\ h} Cr_3Te_4$$

n = 3, m = 5; n = 7, m = 11.

According to X-ray diffraction data, the clusters **107a,b** are built of octahedra consisting of six cobalt (the Co–Co bond length is 3.23 Å [122]) or chromium (the Cr–Cr bond length is 2.94 Å [125]) atoms; the octahedra are incorporated into a cube combining 8 tellurium atoms; the triethylphosphine groups are bound only to metal atoms.

Pyrolysis of the clusters **107a** (300 °C, 45 min [122, 123]) and **107b** (315 °C, 19 h [125]) gives rise to polycrystalline β-CoTe and Cr_3Te_4, respectively. In a relatively recent study,[126] the cluster $(Ph_2PPr)_6Co_6Te_8$ the composition of which is close to that of **97a** was synthesised by the reaction of $CoCl_2$ with Ph_2PPr and trimethyl(phenyltelluro)silane.

The complexes bis(cyclooctadiene)nickel **108a** [127] and (cyclooctatetraene)iron **108b** [128] served as the starting compounds for the preparation of the tellurides of these metals. Thus heating of bis(cyclooctadiene)nickel **108a** in boiling toluene, which normally results in its dissociation to Ni and cyclooctadiene, affords polycrystalline nickel telluride when carried out in the presence of $Et_3P{=}Te$.[127] The synthesis of this telluride from the elements is possible only upon prolonged heating at 400–600 °C.

$$\underset{\mathbf{108a}}{NiL_2} + R_3P{=}Te \xrightarrow[-L,\ -R_3P]{PhMe,\ \Delta} NiTe$$

L = cyclooctadiene.

Nickel telluride [127] as well as a mixture of β- and γ-FeTe [128] have been synthesised by pyrolysis of clusters **109**–**111** formed initially. These clusters, like those considered above, are intermediate compounds on the way from organic substrates to inorganic solid materials. The nickel clusters **109** and **110** contain $Et_3P-Ni-Te$ fragments with tetracoordinated nickel and tellurium atoms;[127] in the cluster **111**, the tellurium atoms are tricoordinated, and the iron atoms are tetracoordinated.[128]

$$\underset{\mathbf{108a,b}}{ML_2} + Et_3P{=}Te \xrightarrow[-L]{Et_3P,\ C_6H_{14},\ 20-25\ ^\circ C} \underset{\mathbf{109}}{Ni_9Te_6(PEt_3)_8}$$

$$\underset{\mathbf{108a,b}}{ML_2} + Et_3P{=}Te \xrightarrow[-L]{Et_3P,\ PhMe,\ 20-25\ ^\circ C} \underset{\mathbf{110}}{Ni_{20}Te_{18}(PEt_3)_{12}}$$

$$\underset{\mathbf{108a,b}}{ML_2} + Et_3P{=}Te \xrightarrow[-L]{PhMe,\ 20-25\ ^\circ C} \underset{\mathbf{111}}{(Et_3P)_4Fe_4Te_4} \xrightarrow[18\ h]{280\ ^\circ C} FeTe$$

M = Ni, L = cyclooctadiene (**108a**);
M = Fe, L_2 = cyclooctatetraene (**108b**).

Like nickel telluride, palladium telluride was synthesised using two procedures: by heating of an equimolar mixture of $Pd(PPh_3)_4$ and $Et_3P{=}Te$ in toluene [129] and *via* the clusters **112** and **113**; however, the clusters were isolated in fairly low yields (10% and 2%, respectively).

$$Pd(PPh_3)_4 + Et_3P{=}Te \longrightarrow$$

$$\xrightarrow[20-25\ ^\circ C]{C_7H_{16}-PhMe} \underset{\mathbf{112}}{(Et_3P)_4Pd_2Te_2} + \underset{\mathbf{113}}{(Et_3P)_8Pd_6Te_6} \xrightarrow[14\ h]{250\ ^\circ C} PdTe$$

$$\xrightarrow[]{PhMe,\ \Delta} PdTe$$

To complete the discussion of the methods for synthesis of metal tellurides, we shall mention a new approach developed recently,[130] which is based on the use of phosphine tellurides other than $R_3P{=}Te$. Complexes **114**, which have been obtained in almost quantitative yields by the reaction of phosphine tellurides **80** with zinc and cadmium bis[*N*-di(trimethylsilyl)amides], provide an example.[130, 131]

$$M[N(SiMe_3)_2]_2 + 2\ Bu^t_2P(Te)NHR \xrightarrow{-HN(SiMe_3)_2}$$

80

$$\longrightarrow \underset{\mathbf{114a-d}}{Bu^t_2P(Te)\text{–}N(R)\text{–}M\text{–}N(R)\text{–}(Te)PBu^t_2}$$

M = Zn: R = Pr^i (**114a**), cyclo-C_6H_{11} (**114b**);
M = Cd: R = Pr^i (**114c**), cyclo-C_6H_{11} (**114d**).

The complexes **114** are crystalline compounds readily soluble in toluene. Based on the results of X-ray diffraction analysis of the selenium analogue of **114a**,[131] a distorted tetrahedral structure has been ascribed to these complexes. Pyrolysis of the complexes **114a,b** at 300 °C and **114d** at 320 °C gives rise to cubic zinc telluride with an admixture of elemental tellurium and to cubic cadmium telluride, respectively.[130]

Phosphine tellurides have also been used to synthesise compounds containing M – Te – M fragments. For example, the reaction of tributyltinhydride with tributylphosphine telluride in the presence of catalytic amounts of $(C_5Me_5)_2TiH$ resulted in the formation of bis(tributylstannyl) telluride **115**.[132] We shall not discuss the mechanism of the catalytic action of $(C_5Me_5)_2TiH$;[132] however, it should be noted that without this compound, the formation of the telluride **115** proceeds very slowly.

$$Bu_3SnH + Bu_3P{=}Te \xrightarrow[-Bu_3P,\ -H_2]{(C_5Me_5)_2TiH} \underset{\mathbf{115}}{(Bu_3Sn)_2Te}.$$

Compounds **116** containing the M – Te – M′ fragment (M and M′ are atoms of different elements) were prepared by the reactions of dimetal derivatives **117** with tributylphosphine telluride.[132] However, unlike **116a**, which rapidly disproportionates to give symmetrical tellurides **118a** and **119a**, its phenyl analogue disproportionates quite slowly.

$$\underset{\mathbf{117a,b}}{(C_5Me_5)_2Ti{-}SnR_3} + Bu_3P{=}Te \xrightarrow{-Bu_3P} \underset{\mathbf{116a,b}}{(C_5Me_5)_2Ti{-}TeSnR_3} \longrightarrow$$

$$\longrightarrow \underset{\mathbf{118a,b}}{[(C_5Me_5)_2Ti]_2Te} + \underset{\mathbf{119a,b}}{(Bu_3Sn)_2Te}$$

R = Bu (**a**), Ph (**b**).

The reaction of the telluride **118** with tributylphosphine telluride giving rise to compound **120** is the only example of transformation of a telluride into a ditelluride known at present.[132, 133] It is of interest to verify whether diorganyl tellurides R_2Te would be converted into diorganyl ditellurides R_2Te_2 upon treatment with tributylphosphine telluride. The compound **120** can be regarded as a synthetic equivalent of Te_2^{2-}, because its interaction with benzyl chloride affords dibenzyl ditelluride.[133]

$$\underset{\mathbf{118}}{[(C_5Me_5)_2Ti]_2Te} + Bu_3P{=}Te \xrightarrow{-Bu_3P}$$

$$\longrightarrow \underset{\mathbf{120}}{(C_5Me_5)_2Ti\begin{smallmatrix}Te\\|\\Te\end{smallmatrix}} \xrightarrow[-(C_5Me_5)_2TiCl_2]{PhCH_2Cl} (PhCH_2)_2Te_2.$$

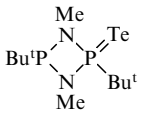
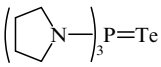
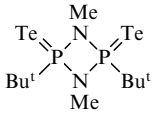
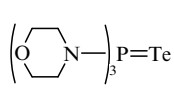
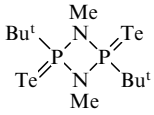
3. X-Ray diffraction analysis and spectroscopic characteristics of phosphine tellurides.

a. X-Ray diffraction analysis of phosphine tellurides

The data considered in this Section are mostly concerned with the lengths of P – Te bonds. Detailed information about the fine structure of phosphoryl groups R_3P can be found in original publications. The molecular and crystal structures of six compounds with P = Te bonds have been studied by X-ray diffraction analysis. The corresponding bond lengths are listed in Table 1.

It can be seen from Table 1 that the P = Te bond lengths vary over a narrow range and are intermediate between the theoretically predicted lengths of single (2.48 Å [134]) and double (2.27 Å [134]) P = Te bonds. These lengths have been reported [80] to correspond to a bond order of 1.5; this implies a substantial contribution of the bipolar $P^+ - Te^-$ structure to the ground state of phosphine telluride molecules. Comparison of the P – chalcogen bond lengths in tris(morpholinophosphine) telluride **79e** and its selenium analogue [78] with the sums of the radii of double bonds formed by the corresponding elements indicates that the contribution of the bipolar structure to the resonance hybrid in compounds with the P = Te bonds is larger than that in compounds with the P = Se bonds. This is indirectly supported by the conclusion, based on measurements of the dipole moments of phosphine chalogenides, that the polarity of compounds increases in the sequence oxide < sulfide < selenide.[135] However, the values of the bond dipole moments of P = X bonds (X = O, S, Se, Te) calculated from the dipole moments of $(C_8H_{17})_3P{=}X$ [136] do not confirm this conclusion.

Table 1. Lengths of the P = Te bonds in phosphine tellurides.

Compound	Bond length /Å	Ref.	Compound	Bond length /Å	Ref.
$Bu^t_3P{=}Te$	2.368	80	 **82c**	2.354	76
 **79c**	2.355	79	 *cis*-**83**	2.305	77
 **79e**	2.357	78	 *trans*-**83**	2.327	77

The diazadiphosphetidine rings in the compounds **82c** [76] and *cis*-**83** [77] are markedly non-planar, whereas *trans*-**83** [77] is planar.

Although tellurium atoms in other types of organotellurium compounds tend to form both intramolecular [6] and intermolecular bonds with atoms of other elements,[137] none of the phosphine tellurides has been found to contain any intermolecular contacts between tellurium and phosphorus atoms that would be shorter than the sum of their van der Waals radii.

b. Spectroscopic characteristics of phosphine tellurides.

Ultraviolet spectra of phosphine tellurides have been relatively little studied, which is apparently due to the fact that these compounds readily decompose in solutions. Therefore, the UV spectra have been reported only for the most stable compounds **79** in which the phosphorus atom is bound to nitrogen atoms incorporated into heterocycles. The absorption maxima of these compounds are observed at 280 nm.[78] Although the nature of the electronic transition responsible for this absorption is not known exactly, presumably,[78] it is the $n \rightarrow \pi^*$ transition. Particular interest is aroused by comparison of the UV spectra of compounds of the $Ph_3P{=}X$ type containing O, S, Se, and Te atoms. The data for these derivatives presented in Table 2 indicate that the absorption bands shift bathochromically in the series O, S, Se, and Te.

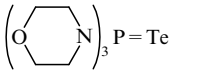
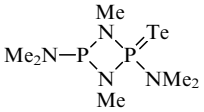
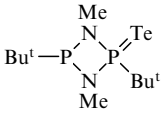
Table 2. Data of the UV spectra for compounds $R_3P{=}X$.[78]

R	X	λ_{max}/ nm	lg ε
	O	< 205	
	S	~ 210	~ 3.70
	Se	~ 225	~ 3.56
	Te	286	2.79
	Te	288	2.85
	Te	281	2.80

According to several publications,[73, 74, 78, 84, 96] the P=Te stretching bands lie in the range of 445–526 cm^{-1}. However, Watari,[138] who studied the IR and Raman spectra of $Me_3P=Te$ and $(CD_3)_3P=Te$, did not find any absorption bands between 400 and 450 cm^{-1}; the bands for the P=Te stretching vibrations were observed at 376 cm^{-1}. It should be noted that the order of variation of the force constants of the P=X bonds in the series of phoshphine chalcogenides $R_3P=X$ differs depending on R. For R = Me_2N, the force constants change in the order O > Te > Se > S,[84] whereas in the case of R = Me, this order is O > S > Se > Te.[138]

Data on the ^{31}P and ^{125}Te NMR spectra of phosphine chalcogenides of various types are listed in Table 3.

Table 3. Chemical shifts (δ, ppm) and spin-spin coupling constants (J/ Hz) in the ^{31}P and ^{125}Te NMR spectra of phosphine tellurides.

Compound	$\delta(^{31}P)$ [a]	$\delta(^{125}Te)$ [b]	$J(^{31}P-^{125}Te)$	Ref.
$Me_3P=Te$		−513.4		80
$Et_3P=Te$		−875.2	1743	80
$Pr^i_3P=Te$		−1000.3	1735	80
$Bu_3P=Te$	+11.0		1720	83
		−807.0	1730	80
		−803.2	1732	139
$Bu^t_3P=Te$	+75.2			99
		−836.5	1663	139
	+77.5		1600	73
$(Me_2N)_3P=Te$	+54.5		2003	85
	+58.8			99
		−826.4	2105	80
		−821.7	2095	139
$(Et_2N)_3P=Te$	+48.0		2037	83
			2040	80
		−812.6	2153	139
			1821	80
$Me(Me_2N)_2P=Te$	+51.8		1950	83, 87
	+16.7			90
	+119.5			91
$Et_2(EtO)P=Te$	+83.0		1964	83

[a] In relation to 85% H_3PO_4; [b] in relation to Me_2Te.

The ^{125}Te NMR spectra (provided that the solution contains no free phosphine) are well resolved doublets arising due to $^{31}P-^{125}Te$ spin-spin coupling.[139] In the case of triphenylphosphine telluride which exists, as shown above, as a complex with triphenyl phosphine, the ^{125}Te signal is exhibited as a broad singlet at δ −491.8 ppm, owing to rapid migration of the Te atom between the Ph_3P groups.[139]

The ^{125}Te chemical shifts range from δ −513 to −1000 ppm (in relation to Me_2Te) indicating that the Te nuclei are appreciably shielded and that the bipolar structures $R_3P^+-Te^-$ make substantial contributions to the ground states of phosphine telluride molecules.

The $^{31}P-^{125}Te$ spin-spin coupling constants are 1660–2150 Hz, the values for tris(dialkylaminophosphine) tellurides being approximately 300–400 Hz greater than those for phosphine tellurides $R_3P=Te$.

IV. Conclusion

The data presented in this review demonstrate certain progress in the chemistry of organic derivatives of monocoordinated tellurium achieved over the past decade. Efficient methods for the generation of telluroaldehydes and telluroketones have been developed and the first relatively stable telluroketone was synthesised. Dimerisation and Diels–Alder reactions of these compounds have led to the synthesis of ditelluretanes, 1-telluracyclohex-3-enes and 2-tellurabicyclo[2.2.1]hept-5-enes. New complexes of tellurocarbonyl derivatives with transition metal compounds have been prepared and their chemical transformations have been studied. It has been shown that at low temperatures in polar solvents like THF, tellurocarboxylic acids exist in the telluroxo-form. The chemistry of telluroesters and telluroamides has been developed to a lesser extent. Development of new methods for the synthesis of compounds with C=Te bonds, study of the possibility of using these derivatives in the preparation of tellurium-containing heterocycles, and attempts to synthesise stable telluroaldehydes and telluroketones by introducing substituents, able to form intramolecular coordination bonds with the C=Te groups, into their molecules appear to be promising lines of research in this field.

As regards phosphine tellurides, the main progress has been achieved in the investigation of their reactivity towards alkylation, complex formation, oxidation, and other types of transformation. However, the discovery and study of reactions in which phosphine tellurides act as synthetic substitutes of elemental tellurium is the most important achievement. This property of phosphine tellurides forms the basis for using them in low-temperature syntheses of metal tellurides and new types of tellurium-containing clusters. In addition to further development of these studies, it appears of interest to attempt using phosphine tellurides as tellurating reagents in the synthesis of some organotellurium derivatives (the transformation of diorganyl tellurides into diorganyl ditellurides, reactions with halogen-containing substrates, *etc*.)

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References

1. R A Zingaro *J. Organomet. Chem.* **1** 200 (1963)
2. M Minoura, T Kawashima, R Okazaki *J. Am. Chem. Soc.* **115** 7019 (1993)
3. F S Guziec, in *The Chemistry of Organic Selenium and Tellurium Compounds* Vol. 2 (Eds S Patai, Z Rappoport) (New York: Wiley-Interscience, 1987) p. 215
4. W W DuMont, R Hensel, S Kubiniok, L Lange, in *The Chemistry of Organic Selenium and Tellurium Compounds* Vol. 2 (Eds S Patai, Z Rappoport) (New York: Wiley-Interscience, 1987) p. 591
5. H B Singh, N Sudha *Polyhedron* **15** 745 (1996)
6. W R McWhinnie, I D Sadekov, V I Minkin *Sulfur Rep.* **18** 295 (1996)
7. I D Sadekov, V I Minkin *Usp. Khim.* **64** 527 (1995) [*Russ. Chem. Rev.* **64** 491 (1995)]
8. K J Irgolic *The Organic Chemistry of Tellurium* (New York: Gordon and Breach, 1974)
9. I D Sadekov, A A Maksimenko, V I Minkin *Khimiya Tellurorganicheskikh Soedinenii* (The Chemistry of Organotellurium Compounds) (Rostov-on-Don: Rostov State University, 1983)
10. R E Lyons, E D Scudder *Chem. Ber.* **64** 530 (1931)
11. N Kambe, K Kondo, S Morita, S Murai, N Sonoda *Angew. Chem., Int. Ed. Engl.* **19** 1009 (1980)
12. N Kambe, T Inagaki, N Miyoshi, A Ogawa, N Sonoda *Chem. Lett.* 1171 (1987)
13. R Okazaki, M Minoura, T Kawashima *Chem. Lett.* 1047 (1993)

14. M Minoura, T Kawashima, N Tokitoh, R Okazaki *J. Chem. Soc. Chem. Commun*. 123 (1996)
15. G Silvey, W Hardy, C H Townes *Phys. Rev*. **87** 236 (1952)
16. F O Rice, A L Glasebrook *J. Am. Chem. Soc*. **56** 2381 (1934)
17. T G Pearson, R H Purcell, G S Saigh *J. Chem. Soc*. 409 (1938)
18. F D Williams, F X Dunbar *J. Chem. Soc., D* 459 (1968)
19. C W Dirk, D Nalewajek, G B Blanchet, H Schaffer, F Moraes, R M Boyse, F Wudl *J. Am. Chem. Soc*. **107** 675 (1985)
20. I D Sadekov, B B Rivkin, A A Maksimenko, V I Minkin *Zh. Org. Khim*. **22** 2615 (1986) [a]
21. T Nogami, Y Tasaka, K Inoue, H Mikawa *J. Chem. Soc., Chem. Commun*. 269 (1985)
22. M Segi, T Koyama, Y Takata, T Nakajima, S Suga *J. Am. Chem. Soc*. **111** 8749 (1989)
23. P Denilf, B Bildstein *J. Organomet. Chem*. **453** 53 (1993)
24. I D Sadekov, V I Minkin *Adv. Heterocycl. Chem*. **63** 2 (1995)
25. S L Bender, N F Haley, H R Luss *Tetrahedron Lett*. **22** 1495 (1981)
26. V Z Laishev, M L Petrov, A A Petrov *Zh. Org. Khim*. **17** 2064 (1981) [a]
27. M V Lakshmikantham, M P Cava, M Albeck, L Engman, P Carroll, J Bergman, F Wudl *Tetrahedron Lett*. **22** 4199 (1981)
28. M V Lakshmikantham, M P Cava, M Albeck, L Engman, F Wudl, E Aharon-Shalom *J. Chem. Soc., Chem. Commun*. 828 (1981)
29. G Erker, R Hock, R Nolte *J. Am. Chem. Soc*. **110** 624 (1988)
30. G Erker, R Hock *Angew. Chem*. **101** 181 (1989)
31. T G Back, B P Dyck, M Parvez *J. Org. Chem*. **60** 703 (1995)
32. T G Back, B P Dyck, M Parvez *J. Org. Chem*. **60** 4657 (1995)
33. P Boese, A Haas, C Limberg *J. Chem. Soc., Chem. Commun*. 1378 (1991)
34. P Boese, A Haas, C Limberg *J. Chem. Soc., Dalton Trans*. 2547 (1993)
35. H Fisher, S Zeuner *J. Organomet. Chem*. **252** C63 (1983)
36. H Fisher, A Fruh, C Troll *J. Organomet. Chem*. **415** 211 (1991)
37. H Fisher, U Gerbing *J. Organomet. Chem*. **299** C7 (1986)
38. H Fisher, J Pashalidis *J. Organomet. Chem*. **348** C1 (1988)
39. J Wolf, R Zolk, U Schubert, H Werner *J. Organomet. Chem*. **340** 161 (1988)
40. G R Clark, K Mardsen, W R Roper, L J Wright *J. Am. Chem. Soc*. **102** 1206 (1980)
41. W A Herrmann, C Hecht, M L Ziegler, B Balbach *J. Chem. Soc., Chem. Commun*. 686 (1984)
42. M Herberhold, D Reiner, D Neugebauer *Angew. Chem*. **95** 46 (1983)
43. W A Herrmann, J Weichmann, R Serrano, K Blechschmitt, H Pfisterer, M L Ziegler *Angew. Chem., Int. Ed. Engl*. **22** 314 (1983)
44. C E L Headford, W R Roper *J. Organomet. Chem*. **244** C53 (1983)
45. A F Hill, W R Roper, J M Waters, A H Wright *J. Am. Chem. Soc*. **105** 5939 (1983)
46. W Paul, H Werner *Angew. Chem., Int. Ed. Engl*. **22** 316 (1983)
47. H Werner, W Paul, W Knaup, J Wolf, G Muller, J Riede *J. Organomet. Chem*. **358** 95 (1988)
48. S Kato, Y Kawahara, H Kageyama, R Yamada, O Niyomura, T Murai, T Kanda *J. Am. Chem. Soc*. **118** 1262 (1996)
49. Y Kawahara, S Kato, T Kanda, T Murai, M Ebihara *Bull. Chem. Soc. Jpn*. **68** 3507 (1995)
50. S Kato, H Sasaki, M Yagihara *Phosphorus Sulfur Silicon Relat. Elem*. **67** 27 (1992)
51. T Kanda, S Nakaiida, S Murai, S Kato *Tetrahedron Lett*. **30** 1829 (1989)
52. S Kato, H Kageyama, T Kanda, T Murai, T Kawamura *Tetrahedron Lett*. **31** 3587 (1990)
53. T Kakigano, T Kanda, M Ishida, S Kato *Chem. Lett*. 178 (1987)
54. A G M Barrett, D H R Barton, R W Read *J. Chem. Soc., Chem. Commun*. 645 (1979)
55. A G M Barrett, R W Read, D H R Barton *J. Chem. Soc., Perkin Trans. 1* 2191 (1980)
56. D H R Barton, S W McCombie *J. Chem. Soc., Perkin Trans. 1* 157 (1975)
57. A G M Barrett, R W Read, D H R Barton *J. Chem. Soc., Perkin Trans. 1* 2184 (1980)
58. T Severengiz, W W DuMont, D Lenoir, H Voss *Angew. Chem*. **97** 1051 (1985)
59. S Kato, T Murai, M Ishida *Org. Prep. Proc. Int*. **18** 369 (1986)
60. T M Severengiz, W W DuMont *J. Chem. Soc., Chem. Commun*. 820 (1987)
61. W W DuMont, D Seuring, H U Meyer, R Martens, M Ostrowski, A M Salzen *Phosphorus Sulfur Silicon Relat. Elem*. **67** 11 (1992)
62. K A Lerstrup, L Henriksen *J. Chem. Soc., Chem. Commun*. 1102 (1979)
63. D L Klayman, R J Shine *J. Org. Chem*. **34** 3549 (1968)
64. M Segi, A Kojima, T Nakajima, S Suga *Synlett* 105 (1991)
65. U Berg, L Henriksen, K A Lerstrup, J Sandstrom *Acta Chem. Scand., Ser B* **36** 19 (1982)
66. M F Lappert, T R Martin, G M McLaughlin *J. Chem. Soc., Chem. Commun*. 635 (1980)
67. M Z Girshovich, A V El'tsov *Zh. Org. Khim*. **39** 941 (1969) [a]
68. O Foss *Acta Chem. Scand*. **4** 1241 (1950)
69. D L J Clive, P L Beauliew *J. Org. Chem*. **47** 1124 (1982)
70. D L J Clive, S M Menchen *J. Chem. Soc., Chem. Commun*. 658 (1977)
71. R A Zingaro, B H Steeves, K Irgolic *J. Organomet. Chem*. **4** 320 (1965)
72. A M Brodie, G A Rodley, C J Wilkins *J. Chem. Soc., A* 2927 (1969)
73. W W DuMont *Z. Naturforsch., B Chem. Sci*. **40** 1453 (1985)
74. G N Chremos, R A Zingaro *J. Organomet. Chem*. 22 637 (1970)
75. T Austad, T Rod, K Ase, J Songstad, A H Norbury *Acta Chem. Scand*. **27** 1939 (1973)
76. S Pohl *Z. Naturforsch., B Chem. Sci*. **33** 610 (1978)
77. S Pohl *Z. Naturforsch., B Chem. Sci*. **34** 256 (1979)
78. C Romming, A J Iversen, J Songstad *Acta Chem. Scand., Ser. A* **34** 333 (1980)
79. C Romming, K Maartmann-Moe, J Songstad *Acta Chem. Scand., Ser. A* **38** 349 (1984)
80. N Kuhn, H Schumann, G Wolmershauser *Z. Naturforsch., B Chem. Sci*. **42** 674 (1987)
81. R W Alcock *Adv. Inorg. Chem. Radiochem*. **15** 1 (1972)
82. N P Grechkin, I A Nuretdinov, N A Buina *Izv. Akad. Nauk SSSR, Ser. Khim*. 169 (1969) [b]
83. I A Nuretdinov, E I Loginova *Izv. Akad. Nauk SSSR, Ser. Khim*. 2827 (1973) [b]
84. F Rauchle, W Pohl, B Blaich, J Goubeau *Ber. Bunsenges. Phys. Chem*. **75** 66 (1971)
85. P A W Dean *Can. J. Chem*. **57** 754 (1979)
86. M Bochmann, G S Bwembya, N T Whilton, X Song, M B Hursthouse, S J Coles, A Karaulov *J. Chem. Soc. Dalton Trans*. 1887 (1995)
87. E I Loginova, I A Nuretdinov, Yu A Petrov *Teor. Eksp. Khim*. **10** 75 (1974) [c]
88. K Diemert, W Kuchen, J Kutter *Phosphorus Sulfur Relat. Elem*. **15** 155 (1983)
89. O J Scherer, G Schnabl *Chem. Ber*. **109** 2996 (1976)
90. R Keat, D G Thompson *J. Organomet. Chem*. **141** C13 (1977)
91. O J Scherer, G Schnabl *Angew. Chem*. **89** 500 (1977)
92. M Wieber, H U Werther *Monatsh. Chem*. **99** 1153 (1968)
93. E Gryszkiewicz-Trochimowski, J Quinchon, O Gryszkiewicz-Trochimowski *Bull. Soc. Chim. Fr*. 1794 (1960)
94. A I Razumov, B G Liorber, M B Gazizov, Z M Khammatova *Zh. Obshch. Khim*. **34** 1851 (1964) [d]
95. K Issleib, W Mogelin, A Balszuweit *Z. Anorg. Allg. Chem*. **530** 16 (1986)
96. H G Mardersteig, H Noth *Z. Anorg. Allg. Chem*. **375** 272 (1970)
97. D Purdela, R Vilceanu *Khimiya Organicheskikh Soedinenii Fosfora* (The Chemistry of Organic Compounds of Phosphorus) (Translated from Rumanian; Moscow: Khimiya, 1972)
98. D H Brown, R J Cross, D Millington *J. Organomet. Chem*. **125** 219 (1977)
99. W W DuMont, H J Kroth *J. Organomet. Chem*. **113** C35 (1976)
100. W W DuMont, H J Kroth *Z. Naturforsch., B Chem. Sci*. **36** 332 (1981)
101. W W DuMont *Angew. Chem., Int. Ed. Engl*. **19** 554 (1980)
102. C Glidewell, E J Leslie *J. Chem. Soc., Dalton Trans*. 527 (1977)
103. N Kuhn, H Schumann *Phosphorus Sulfur Relat. Elem*. **26** 199 (1986)
104. N Kuhn, H Schumann, G Wolmershäuser *J. Chem. Soc., Chem. Commun*. 1595 (1985)
105. N Kuhn, H Schumann, R Boese *J. Chem. Soc., Chem. Commun*. 1257 (1987)
106. C Kollemann, F Sladky *J. Organomet. Chem*. **396** C1 (1990)

107. L Huang, R A Zingaro, E A Meyers, J F Reibenspies *Heteroatom. Chem.* **7** 57 (1996)
108. E W Aiscough, A M Brodie, A R Furness *J. Chem. Soc., Dalton Trans.* 2360 (1973)
109. N Kuhn, H Schumann *J. Chem. Soc., Dalton Trans.* 541 (1987)
110. N Kuhn, H Schumann *J. Organomet. Chem.* **304** 181 (1986)
111. J Brennan, R Andersen, A Zalkin *Inorg. Chem.* **25** 1761 (1986)
112. M L Steigerwald, C R Sprinkle *Organometallics* **7** 245 (1988)
113. G N Pain, G I Christiancz, R S Dickson, G B Deacon, B O West, K McGregor, R S Rowe *Polyhedron* **9** 921 (1990)
114. C B Murray, D J Norris, M G Bawendi *J. Am. Chem. Soc.* **115** 8706 (1993)
115. W E Piers, L R McGillivray, M Zaworotko *Organometallics* **12** 4723 (1993)
116. W E Piers *J. Chem. Soc., Chem. Commun.* 309 (1994)
117. W E Piers, D J Parks, L R McGillivray, M J Zaworotko *Organometallics* **13** 4547 (1994)
118. W E Piers, G Ferguson, J F Gallagher *Inorg. Chem.* **33** 3784 (1994)
119. K McGregor, G B Deacon, R S Dickson, G D Fallon, R S Rowe, B O West *J. Chem. Soc., Chem. Commun.* 1293 (1990)
120. A P Colemann, R S Dickson, G B Deacon, G D Fallon, M Ke, K McGregor, B O West *Polyhedron* **13** 1277 (1994)
121. M L Steigerwald, C E Rice *J. Am. Chem. Soc.* **110** 4228 (1988)
122. M L Steigerwald, T Siegrist, S M Stuczynski *Inorg. Chem.* **30** 4940 (1991)
123. M L Steigerwald, T Siegrist, S M Stuczynski *Inorg. Chem.* **30** 2256 (1991)
124. G Llabres, O Dideberg, L Dupont *Acta Crystallogr., Sect. B* **28** 2438 (1972)
125. B Hessen, T Siegrist, T Palstra, S M Tanzler, M L Steigerwald *Inorg. Chem.* **32** 5165 (1993)
126. J F Corrigan, S Balter, D Fenske *J. Chem. Soc., Dalton Trans.* 729 (1996)
127. J G Brennan, T Siegrist, S M Stuczynski, M L Steigerwald *J. Am. Chem. Soc.* **111** 9240 (1989)
128. M L Steigerwald, T Siegrist, S M Stuczynski, Y U Kwon *J. Am. Chem. Soc.* **114** 3155 (1992)
129. J G Brennan, T Siegrist, S M Stuczynski, M L Steigerwald *J. Am. Chem. Soc.* **112** 9233 (1990)
130. G S Bwembya, X Song, M Bochmann *Adv. Mater.* **7** 11 (1995)
131. M Bochmann, G S Bwembya, M B Hursthouse *J. Chem. Soc., Dalton Trans.* 2813 (1995)
132. J M Fisher, W E Piers, S D Batchilder, D P Susan, M J Zaworotko *J. Am. Chem. Soc.* **118** 283 (1996)
133. J M Fisher, W E Piers, L R McGillivray, M J Zaworotko *Inorg. Chem.* **34** 2499 (1995)
134. A Bondi *J. Phys. Chem.* **68** 441 (1964)
135. R R Carlson, D W Meek *Inorg. Chem.* **13** 1741 (1974)
136. Yu Ya Borovikov, E V Ryl'tsev, I E Boldeskul, N G Feshchenko, Yu P Makovetskii, Yu P Egorov *Zh. Obshch. Khim.* **40** 1957 (1970) [d]
137. I D Sadekov, L E Rybalkina, D Ya Movshovich, S B Bulgarevich, V A Kogan *Usp. Khim.* **60** 1229 (1991) [*Russ. Chem. Rev.* **60** 628 (1991)]
138. F Watari *Inorg. Chem.* **20** 1776 (1981)
139. C H W Jones, R D Sharma *Organometallics* **6** 1419 (1987)

[a] — *Russ. J. Org. Chem. (Engl. Transl.)*
[b] — *Russ. Chem. Bull. (Engl. Transl.)*
[c] — *Teor. Exp. Chem. (Engl. Transl.)*
[d] — *Russ. J. Gen. Chem. (Engl. Transl.)*