Russian Chemical Reviews **68** (5) 415 – 433 (1999) © 1999 Russian Academy of Sciences and Turpion Ltd

UDC 546.24.07 + 546.711 + 547.8

Synthesis, reactions and structures of complexes of metal carbonyls and cyclopentadienyl carbonyls with organotellurium ligands †

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Abstract. Published data on the synthesis, reactivity and structure of complexes formed in the reactions of organic derivatives of tellurium with metal carbonyls and cyclopentadienyl carbonyls are described systematically and generalised. The bibliography includes 142 references.

I. Introduction

The substantial progress achieved in synthetic organotellurium chemistry has stimulated studies dealing with metal complexes with organotellurium ligands.[1–11] In recent years, considerable attention has been paid to metal complexes, in particular, complexes of metal carbonyls and cyclopentadienyl carbonyls with organochalcogens, including organotellurium, ligands. Study of these complexes has allowed researchers to elucidate the influence of the nature of donor atoms (sulfur, selenium and tellurium) on the reactivity and structural and spectral features of compounds of the same type containing these atoms. Compounds prepared by the reactions of metal carbonyls with phosphine tellurides[12–14] and diphenyl ditelluride[15] and of tetracarbonylmanganese complexes with tellurium-containing ligands[16,17] are convenient precursors of metal tellurides, the synthesis of which can be performed at relatively low temperatures.

This review is concerned with the synthesis, structures and reactivity of complexes formed by metal carbonyls and cyclopentadienyl carbonyls with organotellurium ligands. Various tellurium-containing clusters which contain either telluride (–Te–) or ditelluride (–Te–Te–) bridges have been considered in earlier reviews;[2–4,18] therefore, we do not dwell on them here.

II. Complexes with organic derivatives of monocoordinated tellurium

This Section contains data on the reactions of metal carbonyls and cyclopentadienyl carbonyls with organic derivatives of monocoordinated tellurium. This type of derivative includes phosphine tellurides $R_3P = Te$ and compounds with C=Te bonds. Since organyltellurolate anions RTe^- can also be formally classified as derivatives of monocoordinated tellurium, this Section also presents data concerning complexes with bridging and terminal RTe groups.

1. Phosphine tellurides

Methods for the synthesis and some reactions of complexes of phosphine tellurides with metal carbonyls and cyclopentadienyl carbonyls have been considered fairly comprehensively in a review.[19] Therefore, here we present only recent data concerning the structure, synthesis and transformations of some of these compounds (Table 1). Spectral characteristics of complexes **1a–c** are listed in Table 2.

Table 1. Some complexes of phosphine tellurides with metal carbonyls and cyclopentadienyl carbonyls.

Initial compounds		Reaction products	Ref.
$R_3P=Te$	Metal complexes		
$Bu^t_3P=Te$	$M(CO)_6$ (M = Cr, Mo, W)	$(CO)_5M-Te=PBu^t_3$ (**1a–c**) [a] (M = Cr (**a**), Mo (**b**), W (**c**))	20
$Et_3P=Te$	$Co_2(CO)_8$	$[(Et_3P)_2(CO)_2CoTe]_2$ (**2**) $(Et_3P)_4(CO)_6Co_4Te_2$ (**3**) $(Et_3P)_6Co_6Te_8$ (**4**) [b]	13, 14
	$Mn_2(CO)_{10}$	$[(Et_3P)_2(CO)_3MnTe]_2$ (**5**)	12
$Me_3P=Te$	$BnMn(CO)_5$	$BnTeMn(CO)_3(PMe_3)_2$ (**6a**)	16, 17
$Et_3P=Te$	$BnMn(CO)_5$	$BnTeMn(CO)_3(PEt_3)_2$ (**6b**)	16, 17
	$MeMn(CO)_5$	$MeTeMn(CO)_3(PEt_3)_2$ (**6c**) [c,d] $MeMn(CO)_3(PEt_3)_2$ (**7**)	16, 17
$R_3P=Te$	$[CpFe(CO)_2THF]^+ . BF_4^-$ (**9**)	$[CpFe(CO)_2TePR_3]^+BF_4^-$ (**10**) [e]	23, 24

[a] As opposed to thiophosphorane complexes of a similar structure, phosphine telluride in the complexes **1a–c** cannot be replaced by Ph_3P or CO even at 80 °C.[21] [b] A complex with a similar structure, $(Ph_2PrP)_6Co_6Te_8$, was prepared by the reaction of Ph_2PrP with PhTeSiMe$_3$ and $CoCl_2$.[22] [c] A mixture of **6c** and **7** is formed. [d] The complex **6c** can also be prepared by the reaction of $BrMn(CO)_3(PEt_3)_2$ (**8**) with MeTeLi.[17] [e] Decomposition of the complex **10** affords the complex $[CpFe(CO)_2PR_3]^+BF_4^-$ (**11**), while the reaction of **10** with I_2 gives $[CpFe(CO)_2I]_2$ (**12**).[23]

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Received 22 July 1998
Uspekhi Khimii **68** (5) 454 – 473 (1999); translated by Z P Bobkova

† Dedicated to the blessed memory of Doctor of Chemical Sciences Gusein Kurban-Ismailovich Magomedov.

Table 2. Spectral characteristics of the complexes **1a**–**c**.[20]

Compound	$\delta_{^{31}P}$	$\delta_{^{125}Te}$[a]	$\delta_{C=O}$		$J_{^{31}P-^{125}Te}$ /Hz	$\nu_{C=O}$ / cm^{-1}
			cis	*trans*		
1a	53.5 (744)[b]	−635 (−839)[b]	218.5	224.9	1502 (1600)[b]	2052, 1927, 1986, 1913, 1937
1b	54.7	−749	206.8	213.1	1602	2055, 1937, 1988, 1912, 1941
1c	49.9	−770	199.4	200.4	1600	2063, 1927, 1982, 1909, 1932

[a] With respect to Me_2Te. [b] The chemical shifts for the free ligand are given in parentheses.

According to X-ray diffraction analysis,[20] complex **1c** has an octahedral structure, the P–Te bond length being equal to 2.439 Å. Comparison of this value with the lengths of the P = Te bonds in phosphine tellurides, which range from 2.305 to 2.371 Å,[25–31] shows that the P–Te bond in the complex **1c** is mainly a single bond. This finding was explained[20] by assuming that the bipolar ionic structure $Bu^t_3\overset{+}{P}-Te=M^{2-}(CO)_5$ makes the predominant contribution to the ground electronic state of the complex **1**.

The structures of clusters **2**–**5** have been studied by X-ray diffraction analysis. Here we shall briefly describe only the structures of the compounds **2**[14] and **5**[12] closest to compounds that constitute the subject of this review. The molecules of the clusters **2** and **5** contain ditelluride bridges, Te–Te, the tellurium atoms of these bridges being bound to the Co and Mn atoms, respectively. The Te–Te bonds (2.765 Å in the cluster **2** and 2.763 Å in the compound **5**) are somewhat longer than those in diaryl ditellurides [2.697 Å in di(4-methylphenyl) ditelluride,[32] 2.702 Å in di(4-chlorophenyl) ditelluride,[33] 2.710 Å in di(4-methoxyphenyl) ditelluride[34] and 2.712 Å in diphenyl ditelluride[35]]. The Co–Te–Te and Mn–Te–Te bond angles (101.7° and 105.5°, respectively) are also somewhat greater than the C–Te–Te angle in diaryl ditellurides [for example, in di(4-methoxyphenyl) ditelluride, this angle is 99.8°]. The coordination polyhedron about the Co atom is a distorted trigonal bipyramid in which the apical positions are occupied by the Et_3P groups; the environment of the Mn atoms is a distorted octahedron with *trans*-arranged phosphine ligands.

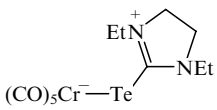
According to X-ray diffraction data,[16,17] the crystal unit cell in the complex $BnTeMn(CO)_3(PEt_3)_2$ **6a** contains two crystallographically independent molecules, which differ in the conformation of the ethyl groups at the phosphorus atoms. The bond geometry about the manganese atom is a slightly distorted octahedron with *trans*-arrangement of the Et_3P groups. The Mn–Te bond length (2.702 Å) is close to the bond length in the cluster **5** (2.763 Å),[12] and the C–Te bond length is within the range normal for this type of bond.[36]

2. Tellurocarbonyl compounds

Synthesis and reactions of complexes of metal carbonyls with tellurocarbonyl compounds have been described in detail in a review.[19] Here we present only some examples of these complexes for which X-ray diffraction data have been obtained or chemical reactions have been studied (Tables 3, 4).

The bond lengths in the complex **17**, determined by X-ray diffraction analysis,[42] point to the presence of a weak coordination bond W–Te, the length of which (2.808 Å) is close to the upper limit of the lengths of single W–Te bonds (2.88 Å).[46] The C=Te bond length amounts to 1.987 Å, which is close to the length of this bond in S=C=Te (1.904 Å[47]). This indicates that the carbon–tellurium bond in the complex **17** is close to a double bond. The fact that upon heating of the complex **17** in a MeCN solution, the solvent displaces the telluroketone **16c** to give the complex $(CO)_5W\cdot MeCN$ confirms the conclusion that the coordination in this complex is weak.[42]

The molecular and crystal structures of the complex **19a** were studied by X-ray diffraction analysis.[43] The geometry of bonds about the chromium atom corresponds to a distorted octahedron. The C–Te bond length (2.12 Å) falls into the range of lengths typical of single C–Te bonds,[36] while the Cr–Te–C bond angle is 96.1°. The Cr–Te bond length (2.765 Å) differs only slightly from



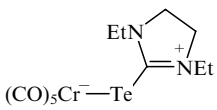
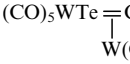
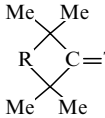
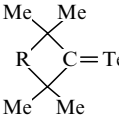
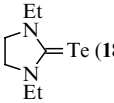
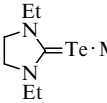
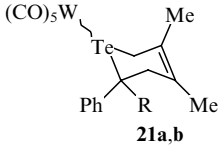
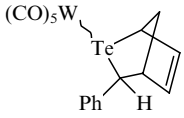
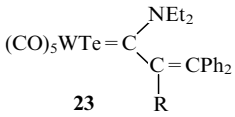


Table 3. Complexes of transition metal carbonyls with monocoordinated tellurium.

Initial compounds		Reaction products	Ref.
metal carbonyls	tellurium derivatives		
$(CO)_5W=CPhR$ (**13a**,**b**) [R = Ph (**a**), H (**b**)]	$(Ph_3P=N=PPh_3)^+(TeCN)^-$	$(CO)_5W-Te=CPhR$ (**14a**,**b**)	37, 38
		$(CO)_5WTe=CPhH$ (**15**)  $W(CO)_5$	
$(CO)_5W\cdot THF$	 Te (**16a**–**c**)	 $Te\cdot W(CO)_5$ (**17**)[b,c]	40–42
	[R = $(CH_2)_2$ (**a**), CH=CH (**b**), *o*-C_6H_4 (**c**)[a]]	(R = *o*-C_6H_4)	
$M(CO)_5\cdot MeCN$ [M = Cr (**a**), Mo (**b**), W (**c**)]	 Te (**18**)	 $Te\cdot M(CO)_5$ (**19a**–**c**)[d]	43

[a] Spectral characteristics of the compound **16c**: $\delta_{^{13}C}$ = 301 (C=Te), $\delta_{^{125}Te}$ = 2858, λ_{max} = 825 nm.[40]
[b] Diferrocenyl telluroketone does not form complexes with metal carbonyls.[39]
[c] Spectral characteristics of the compound **17**: $\delta_{^{13}C}$ = 285 (C=Te), $\delta_{^{125}Te}$ = 1783, λ_{max} = 525 nm.[42]
[d] The complex **19a** (M = Cr) decomposes on exposure to light to give complex $Et\underline{N(CH_2)_2N(Et)}Cr(CO)_5$ (**20**).

Table 4. Products of the addition of the complexes **14a**,**b** to unsaturated compounds.

Complex	Unsaturated compound	Product	Ref.
$(CO)_5WTe=CPhR$ (**14a**,**b**) (R = Ph (**a**), H (**b**))		 **21a**,**b**	39, 44
$(CO)_5WTe=CHPh$ (**14b**)		 *exo*-**22**, *endo*-**22**	34, 44
$(CO)_5WTe=CPh_2$ (**14a**)	$RC\equiv CNEt_2$	 **23**	45

those in other complexes containing chromium and tellurium. The C–Te bond in the complex **19a** is much longer than the carbon–tellurium bond in the compound **17** (1.987 Å), which is due to the predominant contribution of polar resonance structures to the ground state of the molecule.[43]

3. Organyltellurolate complexes

An important method for the synthesis of the complexes **24**, containing metal carbonyl fragments and organyltellurolate (mainly, aryltellurolate) bridging groups is based on reactions of various metal carbonyls **25** with diaryl ditellurides.[48–54]

Dodecacarbonyltriiron,[48–51] dodecacarbonyltriruthenium,[49] dodecacarbonyldimanganese [53,54] and hexacarbonylmolybdenum [52] enter into this reaction. The number of diaryl ditellurides that have been involved in this reaction is quite limited. The use of diphenyl ditelluride,[49,52–54] bis(pentafluorophenyl) ditelluride [50,51] and di(4-methoxyphenyl) ditelluride [48] has been reported.

$$\underset{\textbf{25a–d}}{M_x(CO)_y} + Ar_2Te_2 \xrightarrow[-CO]{} \underset{\textbf{24a–f}}{[M(CO)_zTeAr]_2}$$

$M_x(CO)_y$	$[M(CO)_zTeAr]_2$	Ref.
$Fe_3(CO)_{12}$ (**25a**)	$[Fe(CO)_3TeC_6F_5]_2$ (**24a**)	50, 51
	$[Fe(CO)_3TePh]_2$ (**24b**)	49
	$[Fe(CO)_3Te\ C_6H_4OMe\text{-}4]_2$ (**24c**)	48
$Ru_3(CO)_{12}$ (**25b**)	$[Ru(CO)_3TePh]_2$ (**24d**)	49
$Mo(CO)_6$ (**25c**)	$[Mo(CO)_4TePh]_2$ (**24e**)	52
$Mn_2(CO)_{10}$ (**25d**)	$[Mn(CO)_4TePh]_2$ (**24f**)	53, 54

These reactions occur under relatively mild conditions Whereas in the case of $Fe_3(CO)_{12}$ **25a**, the complexes **24a–c** are the only reaction products, the reaction of ruthenium carbonyl **25b** with diphenyl ditelluride yields, depending on the ratio of the reactants, either a mixture of **24d** and $[Ru(CO)_2(TePh)_2]_n$ (n = 6, 7, 12) **26** or only the latter compound.[49] When a molar excess of diphenyl ditelluride is used, only the complex **26** is formed, whereas with a **25b** : Ph_2Te_2 ratio of 3 : 2, a mixture containing the compound **26** (~90%) and the complex **24d** (~10%) is produced.[49]

Variation of the reaction temperature has a substantial influence on the composition of manganese complexes. Indeed, UV irradiation of a tetrahydrofuran solution of $Mn_2(CO)_{10}$ **25d** and diphenyl ditelluride at room temperature affords the bis-bridged complex **24f**,[53] whereas refluxing of the initial solution yields paramagnetic compound **27**, containing three bridging PhTe groups.[53]

$$\underset{\textbf{25d}}{Mn_2(CO)_{10}} + Ph_2Te_2 \xrightarrow[-CO]{THF,\ \Delta} \underset{\textbf{27}}{Mn_2(CO)_6(TePh)_3}$$

Unlike other carbonyls, $Co_2(CO)_8$ reacts with diaryl ditellurides in an atmosphere of CO (pressure 10–100 atm) to give telluroesters.[55,56] It was assumed [56] that these reactions yield complexes **28** as intermediates.

$$Ar_2Te_2 + Co_2(CO)_8 \xrightarrow[125-200\ ^\circ C]{MeCN,\ 10-100\ atm} \underset{\textbf{28}}{[ArTeCo(CO)_4]} \longrightarrow ArC(O)TeAr$$

Ar = Ph, 4-$MeOC_6H_4$.

In the case of dialkyl ditellurides, no telluroesters are formed, the corresponding dialkyl tellurides being the only reaction products.[56]

Diaryl tellurides can be used instead of diaryl ditellurides as the sources of bridging ArTe ligands in the preparation of complexes of the type **24**. Thus the complex **24f** is formed when a mixture of manganese carbonyl **25d** and diphenyl telluride is heated under rigorous conditions.[48]

$$\underset{\textbf{25d}}{Mn_2(CO)_{10}} + Ph_2Te \xrightarrow{p\text{-xylene},\ 130\ ^\circ C,\ 125\ h} \underset{\textbf{24f}}{[Mn(CO)_4TePh]_2}$$

Yet another approach to the synthesis of binuclear manganese complexes of type **24**, containing various bridging ligands TeR [R = Ph, Alk, $(Me_3Si)_3Si$] is based on the nucleophilic replacement of the bromine atom in bromo(pentacarbonyl)manganese by lithium organyltellurolates.[17,53] The reaction products **29** formed initially are quite unstable; they eliminate a CO molecule being thus converted into the binuclear complexes **24** in 10%–52% yields.[17] The attempts to stabilise the mononuclear complexes **29** by introducing the bulky tris(trimethylsilyl)silyl group failed.[16]

$$BrMn(CO)_5 + RTeLi \xrightarrow[-LiBr]{} \underset{\textbf{29}}{[RTeMn(CO)_5]} \xrightarrow[-CO]{} \underset{\textbf{24f–k}}{[Mn(CO)_4TeR]_2} \xrightarrow{\Delta} MnTe$$

R = Ph (**f**), Me (**g**), Et (**h**), Pr^i (**i**), CH_2SiMe_3 (**j**), $(Me_3Si)_3Si$ (**k**).

The reductive thermolysis of the complexes **24g**, **h** carried out by heating them under a hydrogen atmosphere at 300 and 200 °C, respectively, affords films containing manganese telluride in addition to manganese and tellurium.[17]

The attempts to convert the complexes **24** into the complexes **6** (*cf*. Section II.1) by substituting triorganylphosphines for the CO groups were unsuccessful.[17] At room temperature, the reaction proceeded very slowly, while at an elevated temperature, it gave a complex mixture of non-identified products.

Nucleophilic substitution of chlorine in iridium complex **30** occurring on treatment of this complex with relatively stable lithium 2,4,6-tris(*tert*-butylphenyl)tellurolate has been used to prepare complex **31** the structure of which was studied by X-ray diffraction analysis.[57]

$$\underset{\textbf{30}}{(Ph_3P)_2Ir(CO)Cl} + 2,4,6\text{-}Bu^t_3C_6H_2TeLi \xrightarrow[-LiCl]{} \underset{\textbf{31}\ (80\%)}{(Ph_3P)_2Ir(CO)TeC_6H_2Bu^t_3\text{-}2,4,6}$$

Recently the complex **24g** was synthesised [58] by virtue of a new tellurium-containing reagent, dimethyl(methyltelluro)telluronium tetrafluoroborate **32** (which was prepared by alkylation of dimethyl ditelluride by trimethyloxonium tetrafluoroborate in acetonitrile). Treatment of a THF solution of the compound **32** with salt **33** gives initially, like the reaction of bromo(pentacarbonyl)manganese with lithium methyltellurolate described

above,[17] the mononuclear complex **29** (R = Me), the existence of which in solution at 0 °C was proved by spectroscopy (IR, ^{1}H NMR). This product rapidly dimerises with abstraction of CO to give the complex **24g**.

$$\underset{\mathbf{32}}{Me_2\overset{+}{T}e{-}TeMe}\ BF_4^- + \underset{\mathbf{33}}{(PPN)[Mn(CO)_5]} \xrightarrow[-(PPN)BF_4,\ -Me_2Te_2]{THF} MeTeMn(CO)_5 \xrightarrow[-CO]{} \underset{\mathbf{24g}}{[(CO)_4MnTeMe]_2}$$

$$\underset{\mathbf{29}}{MeTeMn(CO)_5}$$

PPN = $Ph_3P{=}\overset{+}{N}{=}PPh_3$.

Since the natures of both components can be varied, this reaction can become a convenient method for the synthesis of binuclear complexes of type **24**. The prospects for using the salt **32** and its analogues in preparative organic chemistry are not less important. Sulfonium salts with similar structures containing alkyl and aryl radicals at the disulfide bridge[59–61] and also dimethyl(phenylseleno)sulfonium tetrafluoroborate[62] are used in the synthesis of episulfonium salts, S-arylation (alkylation) of alkenes, phenylselenation of aromatic compounds and in other reactions.

Manganese complexes of the type **24** have also been obtained using tellurium-containing anionic compounds **34a**,**b** (their synthesis is described below).[63] Treatment of the salt **34a** with triphenylmethyl tetrafluoroborate gave the complex **24f** in 34% yield. The same complex was isolated in 30% yield together with anionic complex **35** when salt **36a** (M = Te) was made to react with 'pentacarbonyl(bromo)manganese.[58]

$$\underset{\mathbf{34a,b}}{(PPN)[(CO)_3Mn(TeR)_3Mn(CO)_3]} \xrightarrow[-(PPN)BF_4]{Ph_3C^+BF_4^-} \underset{\mathbf{24f}}{[(CO)_4MnTePh]_2}$$

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

$$\underset{\mathbf{36a}}{(PPN)[Mn(CO)_4(MPh)_2]} + BrMn(CO)_5 \xrightarrow{\mathbf{36a}} (PPN)[(CO)_3BrMn(MPh)_2Mn(CO)_4] + \mathbf{24f}$$

M = Te. **35**

Now we shall briefly describe two other reactions resulting in the formation of complexes with bridging aryltellurolate groups. Thus the compound **24f** has been synthesised by refluxing complexes **37**, prepared by the reaction of octacarbonyldihalomanganeses (for details, see Section III.2) with diphenyl ditelluride, in heptane[64] or benzene.[53]

$$\underset{\mathbf{37a,b}}{Mn_2X_2(CO)_6\cdot Te_2Ph_2} \xrightarrow[-MnX_2,\ -CO,\ -Ph_2Te_2]{\Delta} \underset{\mathbf{24f}}{[(CO)_4MnTePh]_2}$$

X = Br (**a**), I (**b**).

Osmium complex **38** (yield 7%) has been obtained, together with non-identified compounds, on treatment of complex **39** with di(4-methoxyphenyl)tellurium dichloride at room temperature.[65] Thermolysis of the complex **38** (refluxing in octane for 2 h) affords cluster **40** (yields 6%). The mechanism of transformation of the compound **39** into **38** has not been discussed.

$$\underset{\mathbf{39}}{(PPN)[HOs_3(CO)_{11}]} + (4\text{-}MeOC_6H_4)_2TeCl_2 \longrightarrow [HOs_3(CO)_{10}TeC_6H_4OMe\text{-}4] \xrightarrow{\Delta} \underset{\mathbf{40}}{Os_3Te_2(CO)_9}$$

$$\underset{\mathbf{38}}{[HOs_3(CO)_{10}TeC_6H_4OMe\text{-}4]}$$

The molecular and crystal structures of the complexes **24e**,[52] **24f**,[53,63] and **24g**[58] have been studied by X-ray diffraction analysis (Fig. 1). The structure of the molecules **24e**–**g** is a planar rhombus M_2Te_2, in which the methyl groups occupy *syn*-positions;[58] the phenyl groups in the complex **24f** occupy *trans*-positions. The most important bond lengths and bond angles in the complexes **24e**–**g** are presented in Table 5.

The ^{1}H, ^{13}C and ^{125}Te NMR spectra of the complex **24g** indicate the presence of two different TeMe groups, which is

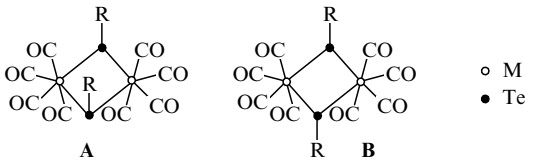


Figure 1. Molecular geometry of **24e**–**g**; **A** is the *syn*-isomer, **B** is the *anti*-isomer.

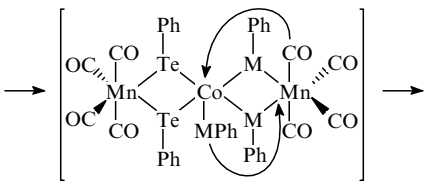
Table 5. Bond lengths and bond angles in the complexes **24e**–**g**.[58]

Complex	Bond lengths/ Å		Bond angles/ deg.	
	M–Te	C–Te	M–Te–M	Te–M–Te
$[Mo(CO)_4TePh]_2$ **24e**	2.756	2.133	68.8	111.2
$[Mn(CO)_4TePh]_2$ **24f**	2.661	2.129	95.96	84.04
$[Mn(CO)_4TeMe]_2$ **24g**	2.661	2.183	95.71	83.66

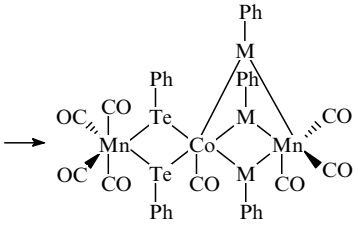
consistent with the finding that two conformers (**A** and **B**, see Fig. 1) exist in solution in a ratio of 4 : 5.[17] The signals of the two TeMe groups in this complex coalesce at 361 K, and those for **24j** coalesce at 343 K, although the ^{125}Te NMR spectrum of the latter compound exhibits only one ^{125}Te signal. The data of multinuclear NMR spectroscopy for solutions of the complexes **24h**,**i** also point to the presence of two isomers. Judging by the fact that ^{125}Te NMR spectra of the complexes **24f**,**k** exhibit singlet ^{125}Te signals, these complexes exist as a single, more stable, isomer due to fast interconversion of the isomers.[17]

The binuclear manganese complex **27**,[53] which contains three bridging PhTe groups, has been described above. Recently,[63,66] trinuclear complexes containing either five PhTe bridges (**42a**, M = Te) or two PhTe bridges and three PhSe bridges (**42b**, M = Se) have been prepared. The complex **42a** was synthesised by the reaction of cobalt perchlorate hexahydrate with diphenyl ditelluride in the presence of the anionic complex **36a**; the reaction is accompanied by oxidation of Co^{2+} to Co^{3+}.[63] The mixed selenium-and-tellurium complex was prepared from cobalt perchlorate hexahydrate, diphenyl diselenide and the anionic complexes **36a** and **36b**.[66] Evidently, the compounds **42a**,**b** result from rearrangement of the complexes **41a**,**b** formed intermediately.

$$\underset{\mathbf{36a}}{(PPN)[Mn(CO)_4(TePh)_2]} + \underset{\mathbf{36a,b}}{(PPN)[Mn(CO)_4(MPh)_2]} + Co(ClO_4)_2\cdot 6H_2O + Ph_2M_2 \longrightarrow$$



41a,**b**



42a,**b** (> 90%)

M = Te (**a**), Se (**b**).

According to X-ray diffraction data,[63,66] the complexes **42a**,**b** contain linear chains of atoms Mn – Co – Mn. The Co(III) ion is bound either to five PhTe bridging ligands and a terminal CO group (**42a**) or to two PhTe bridging groups, three PhSe bridging groups and a carbonyl group (**42b**). Thus, the coordination environment of the Co(III) atom in both complexes is a distorted octahedron. One Mn atom in **42a**,**b** is coordinated to two PhTe bridging ligands and four terminal carbonyl groups; the other manganese atom is linked to three carbonyls and three PhTe (**42a**) or PhSe (**42b**) bridges. Thus, the coordination polyhedron formed about each manganese is also a distorted octahedron. The Te – metal bond lengths in **42a** are the following: Co – Te (Mn – Te) 2.657 Å;[62] in **42b**, they are 2.576 and 2.654 Å, respectively; the Co – Se bond length is 2.450 Å.[66]

Unlike octacarbonyldihalo-manganese[64] and -rhenium,[67] which react with diphenyl ditelluride with retention of the Te – Te bond (for details, see Section III.2), oxidative addition of diaryl ditellurides to the carbonyl chloro iridium complex **43** occurs with rupture of the Te – Te bond and gives complexes **44** containing terminal ArTe ligands. Spectral characteristics of the complexes (shift of the singlet signal in the ^{31}P NMR spectrum by ~ 100 ppm in relation to that in the spectrum of the initial complex **43** and the ^{125}Te chemical shifts) are consistent with the structure **44**; however, the exact geometry of these complexes is unknown. During the reaction, a broad EPR signal typical of tellurium-centred radicals was observed; based on this fact, a reaction mechanism was proposed which includes the initial addition of the ditelluride to the Ir(I) complex **43** followed by homolytic cleavage of the Te – Te bond to give the Ir(III) complexes **44**.[68]

$$\underset{\mathbf{43}}{IrCl(CO)(PPh_3)_2} + Ar_2Te_2 \xrightarrow[2\ h]{PhMe,\ \Delta} \underset{\mathbf{44}}{IrCl(TeAr)_2(CO)(PPh_3)_2}$$

Ar = 4-$EtOC_6H_4$, 4-MeC_6H_4, Ph, 4-ClC_6H_4.

Among other halo carbonyl complexes containing ArTe ligands, rhodium complex **45** should be noted. It was synthesised in a yield of more than 50% by passing CO through a benzene solution of complex **46**.[69]

$$\underset{\mathbf{46}}{(Ph_2Te)_2RhTePhCl_2} + CO \longrightarrow \underset{\mathbf{45}}{(Ph_2Te)_2Rh(CO)TePhCl_2}$$

In addition to the neutral carbonyl and halo carbonyl complexes described above, anionic carbonyl complexes with terminal RTe ligands have been reported. The synthesis of these compounds is based on a reaction typical of diorganyl ditellurides, namely, cleavage of the Te – Te bond by various nucleophiles: organolithium and organomagnesium compounds, alkalis, cyanide anion, *etc*.[70] When anionic metal carbonyls such as $[Mn(CO)_5]^-$ (see Refs 58, 63) and $[HFe(CO)_4]^-$ (see Refs 71 – 74) are used as nucleophiles, the reactions with diorganyl ditellurides result in the synthesis of the anionic tellurium-containing complexes **36a**, **47a**,**b**,[58,63] and **48**,[71–74] the yields of the complexes being higher than 90%. The reactions occur under mild conditions (THF, room temperature) at a reactant molar ratio of 1 : 1. Dimethyl ditelluride reacts with $[Mn(CO)_5]^-$ similarly to diphenyl ditelluride but the reaction occurs more slowly. The formation of an intermediate complex of the type **36b** was judged only by the IR spectra of the reaction mixture; the reaction with dimethyl ditelluride yields the complex **34b** as the final product.[63]

$$\underset{\mathbf{33}}{X[Mn(CO)_5]} + R_2Te_2 \xrightarrow[-CO]{THF,\ 20\ ^\circ C} \underset{\mathbf{36a},\ \mathbf{47a},\mathbf{b}}{X[Mn(CO)_4(TeR)_2]}$$

X = PPN: R = Ph (**36a**), Me (**47a**); X = Na-18-C-6, R = Ph (**47b**).

$$(PPN)[HFe(CO)_4] + Ph_2Te_2 \xrightarrow[-PhTeH]{THF,\ 20\ ^\circ C} \underset{\mathbf{48}}{(PPN)[PhTeFe(CO)_4]}$$

The complexes **36a**, **47a**,**b**, and **48** are crystalline compounds, stable in the absence of air and readily soluble in polar solvents.

The molecular and crystal structures of the complexes **47b**[63] and **48**[72] were studied by X-ray diffraction analysis. The crystal lattice of the former compound contains separate [Na^+ 18-C-6 · 2 THF] cations and *cis*-$[Mn(CO)_4(TePh)_2]^-$ anions. As was to be expected, the manganese ion has an octahedral configuration of bonds; the average Mn – Te bond length is 2.673 Å.

The complex **48**[72] has a trigonal-bipyramidal configuration of bonds about the Fe atom; the TePh group occupies the axial position. The Fe – Te bond length is 2.630 Å. The Fe – CO_{ax} bond (1.83 Å) is substantially longer than the Fe – CO_{eq} bond (1.73 Å).

The transformation of the compounds **36a** and **47a** on refluxing in a THF solution and the transformation of the complex **47b** at room temperature afford the complexes **34a**,**b** and **49** in high yields.[63]

$$\mathbf{36a},\ \mathbf{47a},\mathbf{b} \xrightarrow[-CO]{\Delta} \underset{\mathbf{34a},\mathbf{b},\ \mathbf{49}}{X[(CO)_3Mn(TeR)_3Mn(CO)_3]}$$

X = PPN: R = Ph (**34a**), Me (**34b**); X = Na-18-C-6, R = Ph (**49**).

According to X-ray diffraction data,[63] the crystals of **34a**,**b** consist of discrete cations and anions with slightly distorted octahedral configurations of bonds about each manganese atom (three bridging RTe ligands and three terminal carbonyl groups). The Mn – Te bond lengths are 2.674 Å in **34a** and 2.688 Å in **34b**.[63]

It is noteworthy that the Mn – Te bond in the neutral binuclear triply bridged compound **27** (2.638 Å)[53] is on the average somewhat shorter than the corresponding bonds in the anionic complexes **34a**,**b**. The Mn – Te – Mn bond angles (average values) are also appreciably different; in the neutral derivative **27**, this angle (70.9 °)[53] is much smaller than those in the anionic complexes **34a** and **34b** (82.8 ° and 81.0 °, respectively).[63]

The complex **36a** is detellurated upon the reaction with iodine[58] or $NOPF_6$ in acetonitrile[63] to give complexes **50** and *cis*-**51**.

$$\underset{\mathbf{36a}}{(PPN)[Mn(CO)_4(TePh)_2]} \begin{cases} \xrightarrow[MeCN]{NOPF_6} \underset{\mathbf{50}}{(PPN)[Mn(CO)_3(MeCN)_3]} \\ \xrightarrow[-Ph_2Te_2]{I_2,\ THF} \underset{cis\text{-}\mathbf{51}}{(PPN)[Mn(CO)_4I_2]} \end{cases}$$

The reaction of the complex **34a** with $Ph_3C^+BF_4^-$ giving rise to the complex **24f**[63] and the reaction of the complex **36a** with pentacarbonyl(bromo)manganese giving a mixture of **24f** and **35**[58] have been described previously.

The anionic iron complex **52**, containing three terminal PhTe groups, is formed in the reaction of the anionic iron carbonyl derivative with two moles of Ph_2Te_2 in THF at room temperature.[71] The reaction rate markedly increases when the amount of Ph_2Te_2 in the reaction mixture increases. The complex **48** is formed as the intermediate compound.

$$(PPN)[HFe(CO)_4] + Ph_2Te_2 \xrightarrow[-CO]{} [\mathbf{48}] \xrightarrow[-CO]{} \underset{\mathbf{52}}{fac\text{-}(PPN)[Fe(CO)_3(TePh)_3]}$$

It should be noted that the complex **52** is formed in the reaction of $(PPN)[HFe(CO)_3PPh_3]$ with diphenyl ditelluride instead of the expected complex $(PPN)[Fe(CO)_2PPh_3(TePh)_3]$, *i.e*. in this case, the triphenylphosphine ligand rather than CO is replaced.[71]

The crystal structure of the solvate **52** · 0.5THF is formed from separate cations and anions.[71] The coordination polyhedron around the iron atom is a distorted octahedron with a Fe – Te bond length of 2.630 Å.

The complex **48** is a convenient starting compound for the synthesis of both new and known neutral[72,73] and anionic

tellurium-containing metal carbonyl complexes.[74] Thus its alkylation with methyl iodide gives rise to an oily telluride complex **53**,[72,73] while the reaction with HBF_4 affords the binuclear compound **24b**, described above.[72]

$$(PPN)[PhTeFe(CO)_4] \xrightarrow[-CO,\ -H_2,\ -(PPN)BF_4]{HBF_4} [Fe(CO)_3TePh]_2$$
48 **24b**

$$(PPN)[PhTeFe(CO)_4] \xrightarrow[-(PPN)I]{MeI} PhTeMeFe(CO)_4$$
48 **53**

It follows from published data[71,74] that the complex **48** undergoes oxidative addition to diphenyl ditelluride to give the complex **52**. The reaction of the complex **48** with Ph_2Se_2 follows a similar pattern and gives rise to complex **54**.[74] Diphenyl disulfide does not react with **48**.

$$(PPN)[PhTeFe(CO)_4] + Ph_2Se_2 \xrightarrow[-CO]{THF,\ 20\ ^\circ C} (PPN)[Fe(CO)_3TePh(SePh)_2]$$
48 **54** (90%)

Thus, the ability of diphenyl chalcogenides to enter into oxidative addition reactions with the complex **48** decreases in the sequence $Ph_2Te_2 > Ph_2Se_2 > Ph_2S_2$ due to the decrease in the nucleophilicity of the chalcogens.

Complex **55**, in which the ratio of PhTe to PhSe groups is the opposite to that in the complex **54**, was prepared by the reaction of the selenium analogue of the complex **48** with diphenyl ditelluride.[74]

$$(PPN)[PhSeFe(CO)_4] + Ph_2Te_2 \xrightarrow[-CO]{THF,\ 20\ ^\circ C} (PPN)[Fe(CO)_3SePh(TePh)_2]$$
55 (90%)

The molecular and crystal structures of the complexes **54** and **55** were studied by X-ray diffraction analysis.[74]

The reactions of diaryl ditellurides with metal cyclopentadienyl carbonyls are mostly accompanied by rupture of the Te–Te bonds and give complexes containing terminal or bridging ArTe ligands. Depending on the conditions (temperature, solvent, the presence or absence of UV radiation), the reactions of diaryl ditellurides with molybdenum,[75–77] chromium[78] and iron[79,80] cyclopentadienyl carbonyls give rise to complexes of four types. Under relatively mild conditions (room temperature or short-term refluxing in benzene), mononuclear complexes **56** with terminal ArTe ligands are formed.

$$[\eta^5\text{-}C_5R_5M(CO)_n]_2 + Ar_2Te_2 \longrightarrow \eta^5\text{-}C_5R_5M(CO)_nTeAr + [\eta^5\text{-}C_5R_5M(CO)_{n-1}TeAr]_2$$
56a–e **57a–e**

Compound **56**	*n*	R	M	Ar	Ref.
a	3	H	Mo	Ph	75
b	3	H	Cr	Ph	78
c	3	Me	Mo	Ph	76
d	2	H	Fe	Ph	79
e	2	H	Fe	4-$EtOC_6H_4$	80

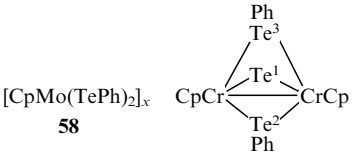
An X-ray diffraction study showed that the Te–C and Te–Cr bond lengths in the complex **56b** are 2.117 and 2.763 Å, respectively; the C–Te–Cr bond angle is 105.4°.[78]

In some cases, in addition to the complexes **56**, binuclear complexes **57** with bridging ArTe groups were also isolated. They become the major products when the reaction is carried out under more drastic conditions (many-hour heating in toluene at 60 °C or under reflux for chromium and molybdenum complexes or refluxing in benzene for iron compounds). The complexes **57** can also be obtained on heating or exposure to UV radiation of solutions of the compounds **56**.

The complex **57a** is formed in 50% yield when $[CpMo(CO)_2]_2$ is made to react with diphenyl ditelluride in toluene at room temperature.[77]

Refluxing of bis(tricarbonylcyclopentadienyl)molybdenum with diphenyl ditelluride in xylene results in the formation of completely decarbonylated complex **58**.[75] When bis(tricarbonylcyclopentadienyl)chromium reacts with diphenyl ditelluride in toluene at 80°C, complex $[CpCr(TePh)]_2Te$ **59**, containing three telluride bridges, is produced.[78]

$[CpMo(TePh)_2]_x$ **58**



59

It should be noted that the reaction of tricarbonyl(cyclopentadienyl)molybdenum with diphenyl diselenide occurs under milder conditions than that with diphenyl ditelluride.[75] In this case, the complexes $CpMo(CO)_3SePh$ and $[CpMo(SePh)_2]_x$ were isolated, although judging by the IR spectra, the solution contained the selenium analogue of the complex **57**. The reaction with diphenyl disulfide gave the completely decarbonylated complex of the type **58** as the only product.[75] Thus, the capability of ArE groups (E = S, Te, Te) of stabilising mono- and binuclear complexes decreases in the series Te > Se > S.[75] The same series of the stability of complexes as a function of the chalcogen nature holds for iron mononuclear complexes **56**.[79]

Several geometric isomers are possible for the complexes **57a**,**c**. However, the ^1H NMR spectrum of the complex **57a** contains only one set of signals of cyclopentadienyl protons, indicating that only one isomer is present in the solution.[75] The binuclear complexes of iron **57d**,**e** can exist as five geometric isomers (**A**–**E**, Fig. 2).

Judging by the ^1H NMR spectra, the complex **57d** exists in solution as a mixture of two isomers; the attempts to separate the mixture into components failed.[79]

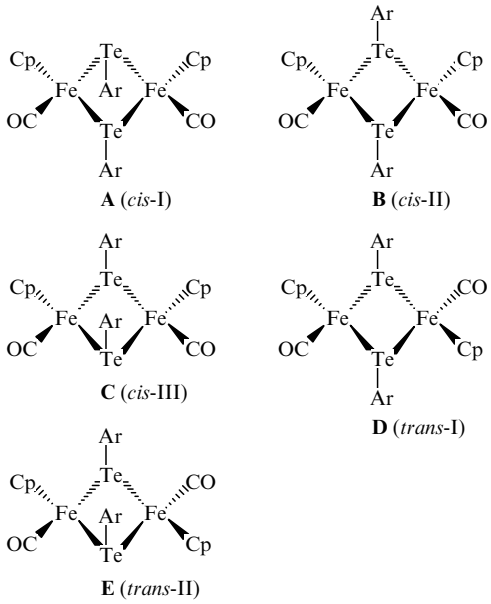


Figure 2. Geometric isomers of the complexes **57d**,**e**. The given nomenclature is proposed in Ref. 80.

In the case of **57e**, crystals of two isomers (**A** and **D**, see Fig. 2) have been isolated in < 5% yields.[80] The molecular structures of these isomers were studied by X-ray diffraction analysis.[80] Both isomers contain Fe_2Te_2 rings, which are slightly bent along the axis connecting the iron atoms. The Te – Fe bond lengths (average) are 2.541 Å for isomer **A** and 2.547 Å for isomer **D**; the Fe – Te – Fe angles are 82.88° and 94.16°, respectively. The environments of the iron and tellurium atoms in both isomers are approximately the same. Each iron atom is situated at the centre of a distorted tetrahedron and the tellurium atoms are at a vertex of a trigonal pyramid. The difference between the isomers is that identical substituents (cyclopentadienyl, *p*-ethoxyphenyl, and carbonyl groups) in isomer **A** (Ar = *p*-$EtOC_6H_4$) occupy *cis*-positions with respect to each other, whereas in isomer **D** (Ar = *p*-$EtOC_6H_4$), they are *trans*-arranged. According to a proposed nomenclature,[80] the former compound is defined as the *cis*-I isomer and the latter one is referred to as *trans*-I.

The molecular structures of binuclear molybdenum (**57a**)[81] and chromium (**57b**)[78] complexes have also been studied by X-ray diffraction analysis.

The structure of the complexes **57a**,**b** is close to the structure of the corresponding sulfur derivatives. Both compounds incorporate non-planar four-membered M_2Te_2 rings with Mo – Te distances of 2.822 Å and Cr – Te distances of 2.721 Å. The Te – Mo – Te and Mo – Te – Mo bond angles are 70.18° and 97.05°, respectively, and Te – Cr – Te and Cr – Te – Cr, are 70.39° and 98.12°. The Te – Te distance in the complex **57a** is 3.24 Å, while that in **57b** is 3.14 Å. Taking into account the fact that the sum of the van der Waals radii of tellurium atoms is 4.4 Å,[82] it can be considered that there exist weak bonds between the tellurium atoms in these complexes. In the molybdenum complex **57a**, the phenyl groups, the cyclopentadienyl rings, and the carbonyl groups occupy *trans*-positions with respect to each other.[81]

The bond lengths and bond angles in compound **59** (X-ray diffraction data[78]) are listed in Table 6.

Table 6. Average bond lengths and angles in the complex **59**.[78]

Bond	Length/ Å	Bond angle	Size/ deg
Te^2-C	2.15	$Cr-Te^1-Cr$	68.47
Te^3-C	2.13	$Cr-Te^2-Cr$	67.06
Te^1-Cr	2.609	$Cr-Te^3-Cr$	67.34
Te^2-Cr	2.65		
Te^3-Cr	2.647		

The heteronuclear cyclopentadienyl carbonyl complexes **60** and **61** with bridging PhE ligands (E = S, Se, Te) have been synthesised by the reaction of bis(phenylchalcogeno)niobocenes with nitrosyl carbonyl mercury complexes.[83]

$$Cp_2Nb(EPh)_2 + Hg[Fe(CO)_3NO] \longrightarrow \underset{\mathbf{60}\ (70\%-80\%)}{Cp_2Nb(EPh)_2Fe(NO)CO}$$

E = S, Se, Te.

Niobium-and-cobalt-containing complexes **61** were prepared according to the following scheme:

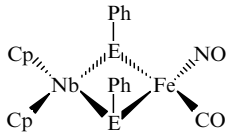
$$Cp_2Nb(EPh)_2 + Hg[Co(CO)_4] \longrightarrow \underset{\mathbf{61}}{Cp_2Nb(EPh)_2Co(CO)_2}$$

E = S, Se, Te.

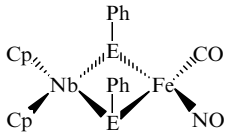
The rate of formation of the complexes **60** and **61** increases in the sequence S < Se < Te, which was attributed[83] to the increase in the nucleophilicity of chalcogens in the same series.

The complexes **60** and **61** are more stable than the initial cyclopentadienyl derivatives of niobium. They are stable in DMSO solutions under an inert atmosphere but rapidly decompose in air.[83]

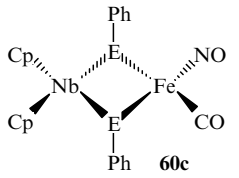
The IR spectra of the complexes **60** exhibit bands at 1610 (NO) and 1840 cm^{-1} (C = O). The complexes **61** are characterised by two bands, 1850 and 1910 cm^{-1}. The ^1H NMR spectra of the compounds **61** (E = Se, Te)‡ contain three singlets for the cyclopentadienyl protons, which was explained by *cis* – *trans* isomerism. The ^1H NMR spectra of the complexes **60** exhibit six singlets due to the cyclopentadienyl protons, which correspond to two *cis*-(**60a**,**b**) and one *trans*-isomer (**60c**).[83]



60a

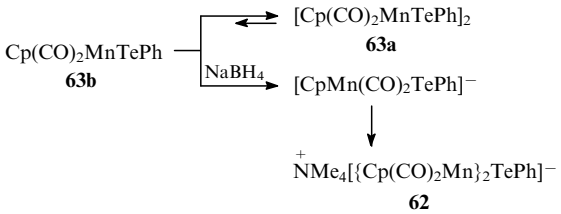


60b



60c

Apart from the neutral complexes described above, which contain bridging and terminal RTe groups, several anionic and cationic cyclopentadienyl carbonyl complexes with organyl telluride ligands have been synthesised. Thus anionic complex **62** is formed when paramagnetic monomeric complex **63b**, which occurs in solution in equilibrium with diamagnetic dimer **63a**, is reduced by sodium borohydride.[84]



The coordination polyhedron around the tellurium atom in the complex **62** is a pseudo-tetrahedron, the Mn – Te bond length being 2.556 Å.[84]

Anionic complex **64**, containing a bridging MeTe ligand, is formed in 85% yield when complex **65**[85] is made to react with methyllithium.[86, 87]

$$\underset{\mathbf{65}}{[CpMn(CO)_2]_3Te} \xrightarrow[\text{2. (PPN)Cl}]{\text{1. MeLi}} \underset{\mathbf{64}}{[\{CpMn(CO)_2\}_3TeMe](PPN)}$$

Oxidation of neutral cyclopentadienyl carbonyl complexes **63a** and **66** by silver hexafluorophosphate has given rise to cationic complexes **67a**[84] and **67b** (yield 56%).[88] In the cation **67a**, the tellurium atom forms a pyramidal configuration of bonds; the Mn – Te bond length is 2.513 Å.[84]

$$\underset{\mathbf{63a},\ \mathbf{66}}{[\eta^5\text{-}R_5C_5(CO)_2MnTeAr]_2} \xrightarrow{AgPF_6} \underset{\mathbf{67a},\mathbf{b}}{[\eta^5\text{-}R_5C_5(CO)_2MnTeAr]^+PF_6^-}$$

R = H, Ar = Ph (**63a**, **67a**); R = Me, Ar = Mes (**66**, **67b**).

Cationic chromium complex **68** has been prepared in a nearly quantitative yield by methylation of the corresponding neutral complex with methyl trifluoromethanesulfonate followed by treatment of the reaction mixture with NH_4PF_6.[86]

‡ The spectrum of the sulfur analogue could not be recorded due to its low solubility.

$$[CpCr(CO)_3]_2Te \xrightarrow[2.\ NH_4PF_6]{1.\ CF_3SO_3Me} [\{CpCr(CO)_3\}_2TeMe]^+PF_6^-$$
68

III. Complexes with organic derivatives of dicoordinated tellurium

This Section surveys data on the synthesis, structure and reactions of carbonyl and cyclopentadienyl carbonyl complexes of transition metals containing as ligands organic derivatives of dicoordinated tellurium such as diorganyl tellurides R^1TeR^2, tellurium-containing heterocycles, diorganyl ditellurides RTe–TeR and organoelement compounds with C–Te–E and E–Te–E fragments (E is a Group IV or V element). For tellurols RTeH, tellurenyl halides RTeHal and tellurocyanates RTeCN, complexes of this type are unknown.

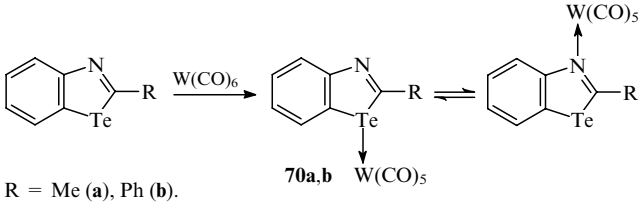
1. Complexes of diorganyl tellurides

Several types of complexes of metal carbonyls and cyclopentadienyl carbonyls with acyclic and cyclic (tellurium-containing heterocycles) diorganyl tellurides have been obtained.

Thus heating or UV irradiation of solutions of diorganyl tellurides and hexacarbonyls of Group VI metals [or complexes $(CO)_5M \cdot THF$, which can be readily prepared from them] results in the formation of pentacarbonyl complexes **69a**,[89] **70a**,**b**[90] and **69b**.[91]

$$R_2Te + M(CO)_6 \xrightarrow[-CO]{THF} (CO)_5M \cdot TeR_2$$
69a,**b**

M = Cr, R = 2-$Me_2NCH_2C_6H_4$ (**a**);
M = W, R = 2,4,4-tris(trimethylsilyl)cyclopenta-2,5-dien-1-yl (**b**).

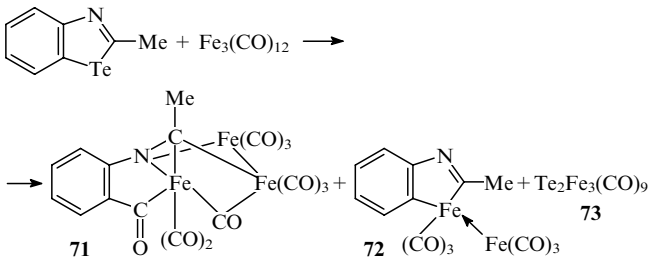


R = Me (**a**), Ph (**b**).

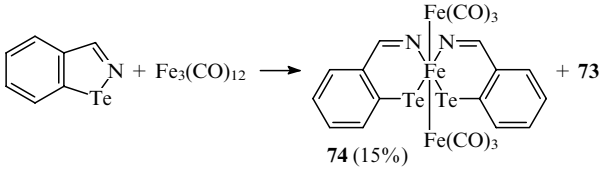
The structure of the complexes **69a**,**b** was proved by X-ray diffraction analysis.[90,91] However, in another study,[92] the product of reaction between chromium hexacarbonyl and dimethyl telluride was identified as $[Cr(CO)_5]_2TeMe_2$ (IR spectroscopy and elemental analysis data).

The results obtained by ^1H NMR spectroscopy indicate that in solutions of the compounds **70a**,**b** [in C_6D_6 or $(CD_3)_2CO$], an equilibrium between Te- and N-centered complexes exists, as in the case of metal carbonyl complexes of benzothiazoles and benzoselenazoles.[93]

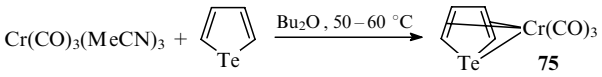
When examining the formation of benzotellurazole complexes of the type **70**, one can follow the influence of the nature of the metal carbonyl on the structure of the final product, which has been repeatedly noted for other ligands. Thus the reaction of 2-methylbenzotellurazole with $Fe_3(CO)_{12}$ in boiling toluene gives rise to a mixture, formed in a low yield (6%–13%), of detellurated complexes **71** and **72** and tellurium-containing cluster **73**.[94]



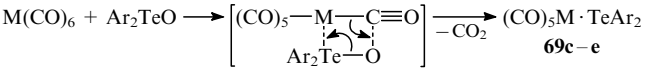
The reaction of benzoisotellurazole with $Fe_3(CO)_{12}$ is also accompanied by the destruction of the heterocycle and gives complex **74** and the cluster **73**.[94]



Whereas in **69a**,**b** and **70a**,**b** the metal is coordinated only by the tellurium atom, the reaction of tellurophene, possessing heteroaromatic properties, with the chromium acetonitrile complex affords a different type of product, namely, π-complex **75** (yield 80%).[95] Similar complexes are formed with thiophene and selenophene.[95]



Recently,[96,97] a new approach to the synthesis of the complexes **69c**–**e** has been proposed, which is based on the reaction of metal hexacarbonyls with diaryl telluroxides in THF. Presumably,[97] the reaction occurs *via* a four-membered transition state.



Compound **69**	Ar	M	Yield (%)	Ref.
c	4-$MeOC_6H_4$	Cr	50	96
d	4-$MeOC_6H_4$	Mo	42	97
e	4-$MeOC_6H_4$	W	29	97

It should be noted that in the presence of pyridine, chromium hexacarbonyl reacts with di(4-methoxyphenyl) telluroxide to give the corresponding telluride and a complex of pyridine with chromium pentacarbonyl.[96]

$$Cr(CO)_6 + (4\text{-}MeOC_6H_4)_2TeO + Py \xrightarrow[-CO_2]{CHCl_3} (CO)_5Cr \cdot Py + (4\text{-}MeOC_6H_4)_2Te$$

The reaction of hexacarbonyls of Group VI metals and iron pentacarbonyl with organoelement oxides R_nEO (n = 2, 3; E = Se, Te, As, Sb) is a fairly general process. It has been reported[96] that the reactions of chromium hexacarbonyl with the oxides obey second-order kinetics and that their relative rates decrease in the sequence TeO > SeO > SbO > AsO. Meanwhile, the least basic compounds among Group V and VI element oxides — triphenylphosphine oxide and diphenyl sulfoxide — do not react with hexacarbonyls of chromium group metals at all. It has been shown[97] that the rates of reactions of di(4-methoxyphenyl) telluroxide with metal hexacarbonyls $M(CO)_6$ decrease in the series W > Mo > Cr (the relative rates are 9.4, 4.4 and 1.0, respectively).

It follows from the above data that in order to prepare complexes of the type **69**, metal carbonyls should be made to react with diorganyl tellurides . Diorganyl tellurides can arise as intermediates in the reactions of metal hexacarbonyls with other organotellurium compounds and then react with excess metal hexacarbonyls, present in the reaction mixture, to give complexes of the type **69**. This idea has been confirmed by the synthesis of complexes **76a**,**b**, containing a dimethyl telluride ligand, from an organic compound containing tetracoordinated tellurium (dimethyltellurium diiodide) and salts **77**.[98] However, these complexes exist only in solution and rapidly decompose when the solvent is removed *in vacuo*.[98]

$$\underset{\mathbf{77}}{Na[M(CO)_n]} + Me_2TeI_2 \longrightarrow \underset{\mathbf{76a,b}}{[M(CO)_n]_2TeMe_2}$$

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

The vigorous reaction of octacarbonyldicobalt with dimethyltellurium diiodide affords polymeric complex **78**.[98] However, the mechanism of this reaction is unknown.

$$Co_2(CO)_8 + Me_2TeI_2 \xrightarrow[-CO]{} \underset{\mathbf{78}}{[Co(CO)_5TeMe_2]_n}$$

It is of interest that the photoinduced reaction of Me_2TeI_2 with decacarbonyl-dimanganese and -dirhenium affords iodo carbonyls **79** in 60% – 80% yields.[98]

$$M_2(CO)_{10} + Me_2TeI_2 \xrightarrow[-CO]{h\nu} \underset{\mathbf{79a,b}}{IM(CO)_4TeMe_2}$$

M = Mn (**a**), Re (**b**).

The chromium complex **69f** has been synthesised using a specific method for the synthesis of diethyl telluride derivatives, namely, alkylation of anionic complex **80** with triethyloxonium tetrafluoroborate.[99]

$$Cr(CO)_6 \xrightarrow[2.\ (PPN)Cl]{1.\ Na_2Te,\ EtOH,\ \Delta} \underset{\mathbf{80}}{(PPN)[Cr(CO)_5TeH]} \xrightarrow[-(PPN)BF_4]{Et_3O^+BF_4^-} (CO)_5CrTeEt_2$$

69f (> 60%)

Another example in which alkylation has been used to prepare telluride complexes — the synthesis of the complex **53** [72, 73] — is described in Section II.3. On treatment with iodine, the complex **53** is oxidised to give halo carbonyl complex **81a** (yield 94%), which was characterised by spectroscopy (^{1}H NMR, ^{13}C NMR, IR, UV).[73]

$$\underset{\mathbf{53}}{(MeTePh)Fe(CO)_4} \xrightarrow{I_2} \underset{\mathbf{81a}}{(MeTePh)Fe(CO)_3I_2}$$

The diphenyl analogue of the compound **81a** — complex **81b** — has been synthesised from diphenyltellurium diiodide. This complex reacts with $(CO)_5W \cdot THF$ to give the diphenyl telluride derivative **69g**.[73] The mechanism of formation of this product and the structures of other reaction products have not yet been elucidated.

$$Fe(CO)_5 + Ph_2TeI_2 \xrightarrow[-CO]{THF} \underset{\mathbf{81b}}{Ph_2TeFe(CO)_3I_2} \xrightarrow{W(CO)_5 \cdot THF} (CO)_5W \cdot TePh_2$$

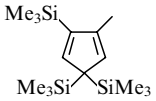
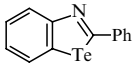
69g (62%)

The molecular and crystal structures of the complexes **69a**–**c**,**g** and **70b** were studied by X-ray diffraction analysis. The most important bond lengths and bond angles are listed in Table 7.

The coordination polyhedron about the metal atom in all the studied complexes is a distorted octahedron; the tellurium atom normally has a pyramidal environment. The secondary intramolecular coordination N → Te, occurring in the free ligand, is retained in the structure **69a**.[89] The N – Te distance (3.096 Å) in **69a** coincides almost completely with the average N – Te distance in the ligand.

In the complex **70b**, formed by a bidentate tellurium-containing heterocycle, 2-phenylbenzotellurazole, with tungsten hexacarbonyl, of the two possible sites of coordination, namely, the 'hard' nitrogen atom and the 'soft' tellurium atom, it is the latter that is involved in coordination with tungsten, in conformity with the principle of hard and soft acid and bases (see Table 7).[100] In all probability, the complex **70b** is the first structurally characterised complex of a benzochalcogenazole with chalcogen – metal coordination.

Table 7. Bond lengths and bond angles in the complexes $(CO)_5M \cdot TeR_2$.

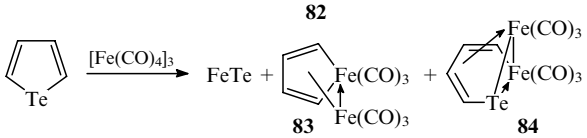
Compound	M	R	Bond lengths /Å		C – Te – C bond angle /deg	Ref.
			M – Te	C – Te [a]		
69a	Cr	2-$Me_2NCH_2C_6H_4$	2.667	2.133	97.2	89
69b	W		2.839	2.139	98.5	91
69c	Cr	4-$MeOC_6H_4$	2.684	2.131	95.5	97
69g	W	Ph	2.809	2.125	94.8	73
70b	W		2.809	2.17	78.0	90

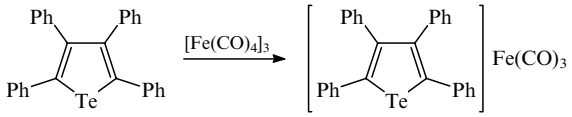
[a] The average bond lengths and angles are given.

The reactions of binuclear and trinuclear metal carbonyls with diorganyl tellurides give different products, depending on the nature of the substrate. The reaction of $Mn_2(CO)_{10}$ with diphenyl telluride, accompanied by rupture of the C – Te bond and yielding the complex **24f** with bridging PhTe ligands,[48] has been described above (see Section II.3). The reaction of the trinuclear complex $Fe_3(CO)_{12}$ with the same telluride gives complex **82** in a moderate yield (25%).[48]

When dodecacarbonyltriiron is made to react with tellurophene in benzene, a mixture of FeTe, ferrole **83** and complex **84** is formed.[101] Based on the mass spectra [molecular ion peak with $m/z = 459$ and peaks due to ions with $m/z = 459 - 28n$ ($n = 0 - 6$)] and the IR spectra (absorption bands for three terminal carbonyl groups in the range 1995 – 2064 cm^{-1}), a metallocene structure was ascribed to **84**.[101] Tetraphenyltellurophene reacts with $Fe_3(CO)_{12}$ to give complex **85** in a low yield.[102]

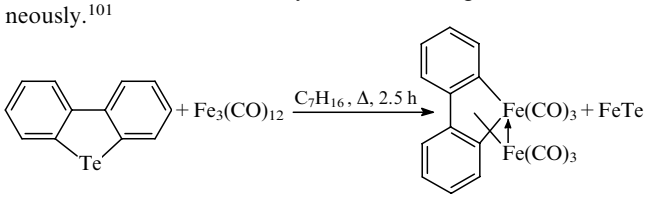
$$[Fe(CO)_4]_3 + Ph_2Te \longrightarrow \underset{\mathbf{82}}{Fe(CO)_4TePh_2}$$





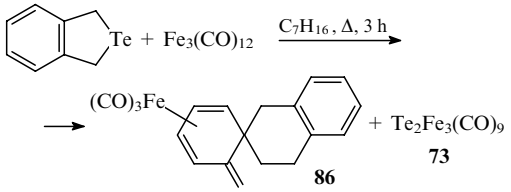
According to the data of McWhinnie *et al.*,[101] when conditions of the reaction of tellurophene with $Fe_3(CO)_{12}$ are changed (refluxing in heptane, 2.5 h), this reaction yields ferrole **83** (45%) and FeTe, which appears to arise upon elimination of CO and $Fe(CO)_5$ molecules from ferrole **83**.

Under the same conditions, dibenzotellurophene is converted into dibenzoferrole in 28% yield, FeTe being formed simultaneously.[101]



The reaction of telluroindan follows a different route. Refluxing a mixture of telluroindan with $Fe_3(CO)_{12}$ gives rise to new

complex **86** (yield 15%) and the cluster **73**. The structure of the compound **86** was confirmed by X-ray diffraction analysis.[101]

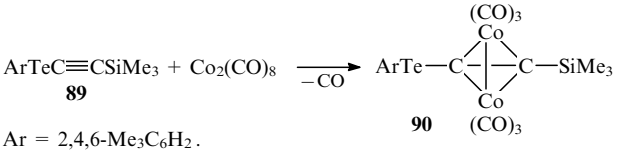


The reaction of $Co_2(CO)_8$ with diphenyl telluride is accompanied by rupture of both C–Te bonds, binuclear complex **87** being the final reaction product.[48] Heating of a mixture of diethyl telluride, $Co_2(CO)_8$ and $Fe_3(CO)_{12}$ affords cluster **88** in 30% yield.[103]

$$Co_2(CO)_8 + Ph_2Te \xrightarrow{PhH,\ \Delta} \underset{\mathbf{87}}{Co_2Te(CO)_5}$$

$$Et_2Te + Fe_3(CO)_{12} + Co_2(CO)_8 \xrightarrow{C_6H_{14},\ \Delta} \underset{\mathbf{88}}{FeCo_2(\mu_3\text{-}Te)(CO)_9}$$

Aryl ethynyl telluride **89** reacts with octacarbonyldicobalt in a different way.[104] The reaction carried out in a 1:1 pentane–toluene mixture at 25 °C gives complex **90** in 45% yield. According to X-ray diffraction data,[104] in this complex, as in other alkynyl complexes, the cobalt atom is coordinated to the multiple-bond carbon atoms rather than to tellurium.



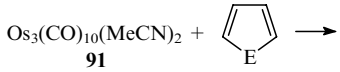
Ar = 2,4,6-$Me_3C_6H_2$.

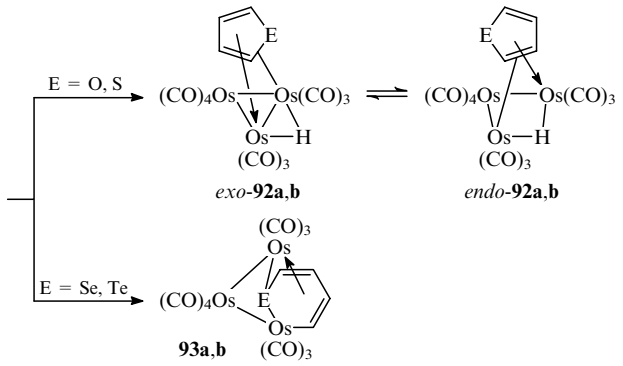
The lengths of the Co–Co, C–C, Ar–Te and C–Te bonds in the complex **90** are 2.465, 1.31, 2.311 and 2.066 Å, respectively.[104]

The reaction of nickel carbonyl with diphenyl telluride, unlike the reactions of manganese and cobalt carbonyls, is accompanied by complete dearylation and decarbonylation, tellurium and nickel being the only reaction products.[48] It is noteworthy that nickel carbonyl reacts with derivatives of tetracoordinated tellurium, $ArTeCl_3$ and Ar_2TeCl_2, to give (after hydrolysis of the reaction mixture) carboxylic acids.[105]

The structure of complexes resulting from the reaction of the osmium carbonyl cluster **91** with five-membered aromatic heterocycles is determined by the nature of the heteroatom.[106,107] Thus when the complex **91** reacts with furan[107] or thiophene,[106] the corresponding hydrido furyl (**92a**) or hydrido thienyl (**92b**) complex is obtained. The complexes **92a**,**b** have similar spectral characteristics. According to the X-ray diffraction data obtained for **92a**,[107] the heterocyclic fragments in these compounds act as μ,η^1,η^2-vinylic ligands. The ^1H NMR spectra imply that the thiophene complex **92b** exists in solution at −55 °C as a mixture of *exo*- and *endo*-isomers (ratio 4:1), which undergo fast interconversion at room temperature.[106]

The reactions of the complex **91** with selenophene and tellurophene in cyclohexane give rise to complexes **93a**,**b**.[106] The spectral characteristics of these compounds are close to each other but sharply differ from those of the complexes **92**. The X-ray diffraction data obtained for the selenophene complex **93a** indicate that it has resulted from insertion of the Os atom into the Se–C rather than C–H bond.[106]

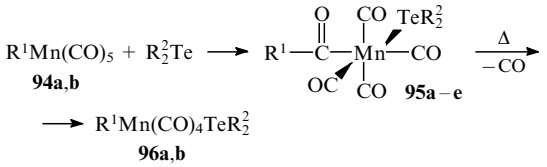




E = O (**92a**, 46%), S (**92b**, 57%), Se (**93a**, 20%), Te (**93b**, 35%).

Carbonyl-containing complexes of various types are also formed in the reactions of diorganyl tellurides with alkyl and acyl manganese carbonyls and manganese, rhenium, ruthenium, rhodium and iridium halo carbonyls.

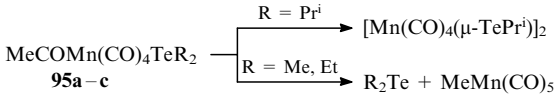
The reactions of pentacarbonyl(methyl)manganese **94a** with dialkyl tellurides in THF at room temperature occur in the same way as reactions with other Lewis bases, giving rise to (acetyl)tetracarbonyl(dialkyl telluride)manganeses **95a**–**c** in yields of more than 80%.[108] The reaction with diisopropyl telluride occurs very slowly; the complex **95c** has not been isolated in an analytically pure state. When dialkyl tellurides are made to react with benzyl(pentacarbonyl)manganese **94b**, the complexes **95d**,**e** are formed together with substantial amounts of decarbonylated products **96**. Thus the reaction of **94b** with dimethyl telluride affords an unseparable mixture consisting of the initial carbonyl (10%), the complex **95d** (80%) and the corresponding decarbonylated product **96a** (10%). The reaction of **94b** with diethyl telluride in boiling pentane yields the decarbonylated complex **96b** as the only product.[108]



Compound	**94a**	**94b**	**95a**	**95b**	**95c**	**95d**	**95e**	**96a**	**96b**
R^1	Me	Bn	Me	Me	Me	Bn	Bn	Bn	Bn
R^2			Me	Et	Pr^i	Me	Et	Me	Et

^1H and ^{125}Te NMR spectra (singlets in the region of 153.0 to 688.6 ppm) and IR spectra indicate that the complexes **95a**–**e** exist in solutions as single isomers with *cis*-arrangement of the acetyl and dialkyl telluride ligands.[108]

The complexes **95a**–**e** decompose when distilled *in vacuo* (0.5 mm Hg, 40–70 °C), the reaction pathway depending on the nature of the substituent at the tellurium atom.[108]



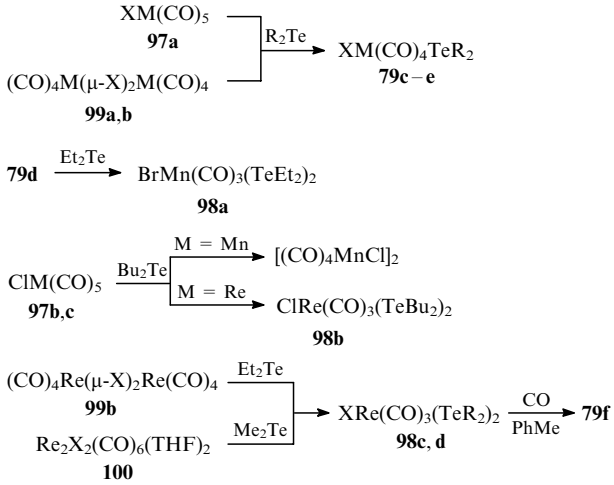
The complexes **95f**, **g** have been synthesised by the reaction of pentacarbonyl(propionyl)manganese with dialkyl tellurides.[108]

$$EtCOMn(CO)_5 + R_2Te \xrightarrow{-CO} \underset{\mathbf{95f,g}\ (>70\%)}{EtCOMn(CO)_4TeR_2}$$

R = Me (**f**), Et (**g**).

The reductive thermolysis of the complexes **95b**,**c**,**g** under a hydrogen atmosphere at 200 °C yields films containing manganese and tellurium.[108]

The reactions of manganese[48,108–111] and rhenium[111–113] halo carbonyls with dialkyl and diaryl tellurides have been studied. Dimethyl and diethyl tellurides react with bromo(pentacarbonyl)manganese **97a** giving rise to dialkyl telluride complexes **79c**,**d**, their yields exceeding 80%.[108] The reaction of pentacarbonylchloromanganese **97b** with dibutyl telluride affords the binuclear complex $[(CO)_4MnCl]_2$.[48] When the complex **79d** is treated with a second mole of diethyl telluride, it is converted into bis(diethyl telluride) complex **98a**.[108] Compounds of this type are formed as the only products in reactions of diphenyl telluride[48,109,110] and phenoxatellurine[48] with manganese[48] and rhenium[111] halo carbonyls. The complex **98b** also arises in the reaction of pentacarbonylchlororhenium **97c** with dibutyl telluride,[112] *i.e.* the rhenium and manganese compounds react in different ways. Evidently, this implies that the rhenium complexes **98** are more stable than the corresponding manganese analogues. Rhenium bis(dialkyl telluride) complexes **98c**,**d** were prepared by the reaction of di-μ-chlorobis[tetracarbonylrhenium(I)] **99b** with diethyl telluride under drastic conditions[113] and by the reaction of complex **100** with dimethyl telluride at room temperature.[111]



Compound	X	M	R
97a, **99a**	Br	Mn	
97b, **99b**	Cl	Re	
97c	Cl	Mn	
79c	Br	Mn	Me
79d, **98a**	Br	Mn	Et
79e	Cl	Re	Me
79f, **98c**	Br	Re	Me
98b	Cl	Re	Br
98d	Cl	Re	Et

The reaction of the binuclear rhenium complex **99b** with dimethyl telluride[113] gives the complexes **79e**, while the reaction of the similar manganese complex **99a** with dimethyl telluride performed under relatively mild conditions affords the complex **79c**. When carbon monoxide is passed through a toluene solution of the complex **98c** at room temperature, the complex **79f** is produced.[111]

The rhenium complexes **79e**,**f** are much more stable than the manganese analogues. Thus it has been found[108] that the manganese complex **79c** exists only in solution, the attempted isolation resulting in its complete decomposition.

Study of the dimethyl chalcogenide ligand exchange in the rhenium complexes **98**[111] shows that the equilibrium in these reactions is shifted towards the formation of complexes containing heavier chalcogen atoms.[111]

$$ReBr(CO)_3(E^1Me_2)_2 + E^2Me_2 \rightleftharpoons ReBr(CO)_3(E^2Me_2)_2 + E^1Me_2$$

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

A new pathway to the iodo carbonyl complexes **79a**,**b** is based on the reaction of decacarbonyl-dimanganese and -dirhenium with dimethyltellurium diiodide.[98] The compounds **79a**,**b** were isolated by sublimation *in vacuo* at 60 °C. The reactions of other dialkyltellurium dihalides with the manganese and rhenium carbonyls have not been studied.

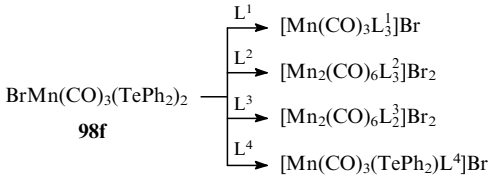
$$M_2(CO)_{10} + Me_2TeI_2 \xrightarrow{h\nu} \underset{\textbf{79a,b}}{IM(CO)_4TeMe_2}$$

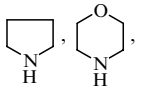
M = Mn (**a**, 80%), Re (**b**, 60%).

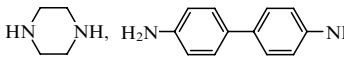
Passing NO through a benzene solution of the complex **98e** gives the nitrosyl complex **101**, which, however, has not been isolated in an analytically pure state.[48]

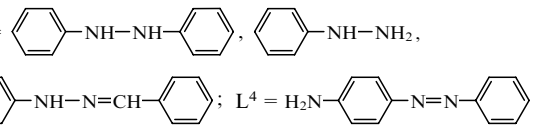
$$\underset{\textbf{98e}}{ClMn(CO)_3(TePh_2)_2} + NO \xrightarrow[-CO]{} \underset{\textbf{101}}{Mn(NO)_3TePh_2} + Ph_2Te + Ph_2TeCl_2$$

The reaction of the manganese complex **98f** with nitrogen-containing ligands results in the replacement of either or both diphenyl telluride ligands, depending on the nature of the reagent used.[110]



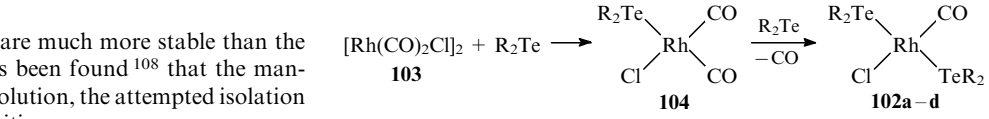
L^1 = ;

L^2 = ;

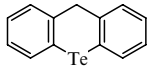
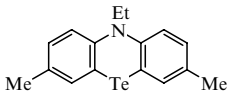
L^3 = ;

L^4 = .

Both Rh(I)- and Rh(III)-containing complexes have been synthesised from rhodium halo carbonyls. Compounds of the former type (**102a**–**d**) were prepared by the reaction of di-μ-chlorobis[dicarbonylrhodium(I)] **103** with diorganyl tellurides,[69,114] including tellurium-containing heterocycles,[115] at room temperature in pentane, hexane or toluene. According to IR spectroscopy, after the isolation of the complex with telluroxanthene **102c** (ν_{CO} 1967 cm^{-1}), the mother liquor contains the intermediate dicarbonyl complex **104** (ν_{CO} 2080, 2033 cm^{-1}), which has resulted from cleavage of the chloride bridges in the complex **103** by the tellurium-containing ligand.[115]

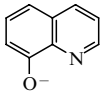


R = Et (**a**), Ph (**b**);

R_2Te =  (**c**),  (**d**).

The reactions of $[Rh(CO)_2Cl]_2$ with tellurium-containing ligands generally resemble its reactions with triorganylphosphines. However, tellurium-containing ligands, in particular, telluroxanthene and 3,7-dimethyl-*N*-ethylphenotellurazine, are weaker donors than phosphines. Indeed, $Rh(acac)(CO)_2$ readily reacts with triphenylphosphine at room temperature to give $Rh(acac)(CO)PPh_3$[116,117] but does not react with telluroxanthene even at 80 °C.[115] However, telluroxanthene and 3,7-dimethyl-*N*-ethylphenotellurazine replace the alkene ligand in the rhodium complex **105**, giving rise to complexes **106** with *trans*-arrangement of organic ligands.[115]

$$\underset{\mathbf{105}}{Rh(Oxq)(C_8H_{14})CO} + R_2Te \xrightarrow[-C_8H_{14}]{} \underset{\mathbf{106}}{Rh(Oxq)(CO)TeR_2}$$

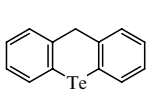
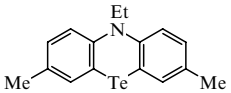
Oxq — , C_8H_{14} — cyclooctene.

The weaker donor properties of diorganyl tellurides compared to those of tertiary phosphines account for the fact that telluride ligands in the complexes **102c**,**d** and **106** are readily substituted by triphenyl- and tributylphosphines.[115]

The rhodium carbonyl complexes **102a**,**b** undergo fast oxidative addition of halogens and thiocyanogen to give octahedral Rh(III) complexes **107a–c**,[114] **107d–f**[69] and **107g**,**h**.[115]

$$\underset{\mathbf{102a,b}}{Rh(CO)(TeR_2)_2Cl} + X_2 \longrightarrow \underset{\mathbf{107a-h}}{Rh(CO)(TeR_2)_2ClX_2}$$

R = Et: X = Cl (**a**), Br (**b**), I(**c**); R = Ph: X = Br (**d**), I (**e**), SCN (**f**);

R_2Te =  (**g**),  (**h**); X = I.

The complex **107a** was also prepared by the reaction of the diethyl ditelluride complex **102a** with hydrogen chloride;[114] **102a** also adds several other reagents to give Rh(III) complexes **108a**,**b**.[114] It is noteworthy that the diphenyl telluride analogue **102b**, unlike the compound **102a**, does not react with methyl iodide.[69]

$$\underset{\mathbf{102a}}{Rh(CO)(TeEt_2)_2Cl} + HCl \xrightarrow[-H_2]{HCl} \underset{\mathbf{107a}}{Rh(CO)(TeEt_2)_2Cl_3}$$

$$\underset{\mathbf{102a}}{Rh(CO)(TeEt_2)_2Cl} + HCl \xrightarrow{XY} \underset{\mathbf{108a,b}}{Rh(CO)(TeEt_2)_2ClXY}$$

XY = MeI (**108a**), $PhSO_2Cl$ (**108b**).

The complex **108a** easily reacts with carbon monoxide; the insertion of CO into the Rh–Me bond gives rise to a rhodium(III) acyl derivative.[114]

$$\underset{\mathbf{108a}}{Rh(CO)(TeEt_2)_2MeICl} + CO \longrightarrow Rh(CO)(TeEt_2)_2(COMe)ICl$$

On passing from the planar rhodium(I) complexes **102** to the octahedral rhodium(III) complexes **107** and **108**, the ν_{CO} value increases by $\sim 100\ cm^{-1}$.[69,114,115]

The CO stretching vibration frequencies in the spectra of the complexes **102c** (1956, 1946 cm^{-1}), **102d** (1962 cm^{-1}), and the analogue of **102d** containing phenothiazine as a ligand (1966 cm^{-1})[115] indicate that the π-dative transfer of electron density from the central atom to a carbonyl group is less significant in the complex with phenothiazine than in the complexes with telluroxanthene and tellurazine. A similar effect, although less pronounced, noted for diethyl chalogenide complexes **102**,[114] may be due to the enhancement of the σ-donor properties of chalcogen atoms in the series S < Se < Te. The substantial increase in ν_{CO} following the transition from the complexes **102c**,**d** to the phenothiazine complex attests that the Rh(I)–S bond is weaker than Rh(I)–Te.[115]

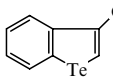
The complex **102a** not only enters into oxidative addition reactions but also reacts with tetracyanoethylene and fumaronitrile to give stable 1 : 1 adducts **109** in almost quantitative yields.[118] In these complexes, the metal is coordinated to the double bond of the cyanoalkene. Similar complexes with acrylonitrile and cinnamonitrile are not formed.[118]

$$\underset{\mathbf{102a}}{Rh(CO)(TeEt_2)_2Cl} + \begin{matrix} R & & CN \\ & \diagdown\!\!\diagup & \\ NC & & R \end{matrix} \xrightarrow[C_5H_{12}]{PhH,} \underset{\mathbf{109}}{R(NC)C{=}C(CN)R\ |\ Rh(CO)(TeEt)_2Cl}$$

R = H, CN.

The rhodium(III) complexes **107** have also been obtained by replacement of one tellurium-containing ligand in complexes **110** by CO, which is attained by passing carbon monoxide through solutions of the complexes **110** in chloroform or toluene.[69,119]

$$\underset{\mathbf{110}}{(R_2Te)_3RhCl_3} + CO \xrightarrow[-R_2Te]{} \underset{\mathbf{107}}{Rh(CO)(TeR_2)_2Cl_3}$$

R_2Te = Ph_2Te, , .

Data on halo carbonyl complexes of iridium with diorganyl tellurides can scarcely be found in the literature. The only representative of this class of compound, complex **111**, has been synthesised by the reaction of polymeric iridium chloro carbonyl with diethyl telluride.[120]

$$[Ir(CO)_3Cl]_n + Et_2Te \xrightarrow[-CO]{} \underset{\mathbf{111}}{ClIr(CO)_2TeEt_2}$$

Only few representatives of complexes of diorganyl tellurides with iron[48] and ruthenium[121,122] halo carbonyls are known. Iron diphenyl telluride complexes **112** were prepared by substituting diphenyl telluride for one carbonyl group in tetracarbonyldihaloirons. The structure of these products was not specially studied; they were identified by analogy with other complexes.[48]

$$Fe(CO)_4X_2 + Ph_2Te \xrightarrow[-CO]{} \underset{\mathbf{112}}{\begin{matrix} & & TePh_2 & & \\ OC & & | & & X \\ & & Fe & & \\ OC & & | & & X \\ & & CO & & \end{matrix}}$$

X = Br, I.

A mixed iron carbonyl nitrosyl complex was synthesised in a similar way.[48]

$$Fe(NO)_2(CO)_2 + Ph_2Te \xrightarrow[-CO]{Et_2O,\ 20-25\ ^\circ C} Fe(NO)_2(CO)TePh_2$$

Complexes **113a–d**, containing two telluride ligands, were prepared by the reactions of polymeric ruthenium halo carbonyls with diorganyl tellurides.[121,122] These reactions also give small amounts of tritelluride complexes **114a–d**.[121] They were not isolated in a pure state and their existence in solution was confirmed by IR spectra.

$$[Ru(CO)_2X_2]_n + R_2Te \xrightarrow{PhH,\ 100\ ^\circ C} \underset{\mathbf{113a-d}}{Ru(CO)_2(TeR_2)_2X_2} + \underset{\mathbf{114a-d}}{Ru(CO)(TeR_2)_3X_2}$$

X = Br: R = Bu (**a**), Ph (**b**); X = I: R = Bu (**c**), Ph (**d**).

The mixture of the compounds **113e** and **114e**, resulting from the reaction of a CO-saturated alcoholic solution of $RhCl_3 \cdot H_2O$ with Ph_2Te, was successfully separated by fractional crystallisation.[121]

$$RuCl_3 \cdot H_2O + CO + Ph_2Te \longrightarrow$$

$$\longrightarrow \underset{\textbf{113e}\ (40\%)}{Ru(CO)_2(TePh_2)_2Cl_2} + \underset{\textbf{114e}\ (25\%)}{Ru(CO)(TePh_2)_3Cl_2}$$

The reactions of complexes of the type **113** with halogens lead to the rupture of the Te–Ru bonds, unlike similar reactions of analogous complexes containing nitrogen and phosphorus ligands, in which less active halogens are replaced by more active ones.[121]

$$\underset{\textbf{113c,d}}{Ru(CO)_2(TeR_2)_2I_2} + X_2 \longrightarrow Ru(CO)_2X_2 + R_2TeX_2 + I_2$$

R = Bu (**c**), Ph (**d**); X = Cl, Br.

Of complexes of metal cyclopentadienyl carbonyls with diorganyl tellurides, compounds of Group V elements, vanadium[123,124] and niobium,[125] have been described. These complexes, having the composition $CpM(CO)_3TeR_2$ **115**, are prepared by exposure of a solution of tetracarbonyl(cyclopentadienyl)-vanadium or -niobium and a large excess of a diorganyl telluride to UV or visible light. Complexes of the type **115** with other diorganyl chalcogenides have also been synthesised.

$$CpM(CO)_4 + ER_2 \xrightarrow[-CO]{THF} \underset{\textbf{115}}{CpM(CO)_3ER_2}$$

Compound **115**	M	R_2E	Ref.
a	V	Me_2S	124
b	V	Me_2Se	124
c	V	Me_2Te	124
d	V	Ph_2S	123
e	V	Ph_2Se	123
f	V	Ph_2Te	123
g	Nb		125
h	Nb		125
i	Nb		125

When other solvents (toluene, heptane) are used instead of THF, the complexes **115g–i** substantially decompose and their yields diminish.[125] The low thermal stability of dimethyl chalcogenide complexes is the obstacle preventing large-scale preparation of these compounds.[124] Niobium complexes with tetrahydrochalcogenophenes are the most stable; they have been isolated as individual crystalline compounds. However, they are still fairly sensitive to air both in the crystalline state and especially in solutions.[125] All complexes of the type **115** tend to decompose in solution to give diorganyl chalcogenides and $CpM(CO)_4$.[124,125] The stability of the diorganyl chalcogenide complexes with the same metal increases in the series S < Se < Te.[123–125] This stability series was attributed[125] to the increase in the σ-donor capacity on passing to heavier chalcogens. This is confirmed by IR spectra, which display a decrease in ν_{CO} in the order S > Se > Te both for the vanadium[124] and niobium[125] diorganyl chalcogenide complexes **115**.

The reaction of formation of the complexes **115a–c** is reversible, the equilibrium constant increasing in the order S < Se < Te (4.5×10^{-3}, 1.8×10^{-2} and 5.8×10^{-1}, respectively). The dimethyl sulfide ligand in the complex **115a** can be displaced by dimethyl selenide and dimethyl telluride ligands; the equilibrium constants for these reactions are 4.0 and 1.3×10^{2}, respectively.[124]

$$\underset{\textbf{115a}}{CpV(CO)_3SMe_2} + Me_2E \rightleftharpoons \underset{\textbf{115b,c}}{CpV(CO)_3EMe_2} + Me_2S$$

The reactions of tetracarbonyl(cyclopentadienyl)-vanadium and -niobium with diorganyl chalcogenides can occur by either dissociative (pathway *a*) or associative (pathway *b*) mechanism.[125]

$$CpM(CO)_4 \xrightarrow[-CO]{a} [CpM(CO)_3] \xrightarrow{R_2E,\ fast} \underset{\textbf{115}}{CpM(CO)_3ER_2}$$

$$CpM(CO)_4 \xrightarrow[R_2E]{b} [CpM(CO)_4ER_2] \xrightarrow[-CO]{fast} \textbf{115}$$

Kinetic measurements[125] indicate that the formation of the niobium complexes **115g–i** occurs according to both mechanisms.

The tetrahydrochalcogenophene ligands in the complexes **115g–i** are easily replaced by various phosphine ligands.[125] The reaction rate increases in the series Te < Se < S, thus confirming the fact that on passing to heavier chalcogens, the complex stability increases, which has been repeatedly noted above.

$$\underset{\textbf{115g–i}}{CpNb(CO)_3ER^1_2} + R^2_3P \xrightarrow[-R^1_2E]{} CpNb(CO)_3PR^2_3$$

R^2 = Bu, Ph, OPh.

In addition to the neutral complexes of diorganyl tellurides with metal cyclopentadienyl carbonyls **115** described above, cationic cyclopentadienyl carbonyl complexes of iron[126,127] and molybdenum[128] and anionic cyclopentadienyl carbonyl complexes of vanadium[129,130] have been synthesised.

When dimethyl chalcogenides react with cationic complexes **116a–c** under mild conditions, they substitute the THF molecule, which results in the formation of cationic complexes **117a–c**, their yields exceeding 90%.[126] On UV irradiation of solutions containing the complexes **117a–c** and dimethyl chalcogenides, the latter replace a CO molecule to give cationic monocarbonyl complexes **118a–c** (yields 47%–82%).[126] The cationic complexes **117a–c** and **118a–c** react with salts containing nucleophilic anions (CN^-, I^-) to give neutral complexes **119**, **120a–c**, in which X is cyano group or iodine.[126]

$$\underset{\textbf{116}}{[CpFe(CO)_2THF]^+BF_4^-} + Me_2E \xrightarrow{CH_2Cl_2} \underset{\textbf{117a–c}}{[CpFe(CO)_2EMe_2]^+BF_4^-} \longrightarrow$$

$$\xrightarrow{a} \underset{\textbf{119}}{CpFe(CO)_2X}$$

$$\xrightarrow{b} \underset{\textbf{118a–c}}{[CpFe(CO)(EMe_2)_2]^+BF_4^-} \xrightarrow{a} \underset{\textbf{120a–c}}{[CpFe(CO)EMe_2]X}$$

E = S (**a**), Se (**b**), Te (**c**); X = CN, M = K; X = I, M = Li;
(*a*) MX, CH_2Cl_2, ~20 °C, Ar; (*b*) Me_2E, CH_2Cl_2, *hν*.

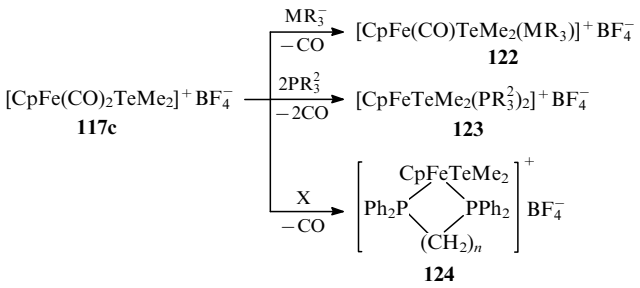
Exposure of solutions of the complexes **117a,b** and dimethyl chalcogenides containing a heavier chalcogen to UV radiation leads to the displacement of a CO molecule and the formation of compounds **121**, which incorporate two different dimethyl chalcogenide ligands.[127]

$$\underset{\textbf{117a,b}}{[CpFe(CO)_2E^1Me_2]^+BF_4^-} + E^2Me_2 \xrightarrow[-CO]{h\nu}$$

$$\longrightarrow \underset{\textbf{121}}{[CpFe(CO)E^1Me_2(E^2Me_2)]^+BF_4^-}$$

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

Treatment of the complex **117c** with organoelement compounds of Group V elements results in the replacement of one or more CO ligands giving rise to compounds **122–124**.[127]



MR^1_3 = PMe_3, $P(NMe_2)_3$, PPh_3, $AsPh_3$, $SbPh_3$; R^2 = Me, OMe, OPh; X = $Ph_2P(CH_2)_nPPh_2$.

The molecular and crystal structures of the complex **117c** have been studied by X-ray diffraction analysis.[131] In this compound, the iron atom is linked to two terminal carbonyl groups, one $TeMe_2$ ligand and one cyclopentadienyl ring, which form a pseudo-octahedral configuration. No tight contacts between the $[CpFe(CO)_2TeMe_2]^+$ cations and the BF_4^- anions were found in the crystals. The Fe–Te distance is 2.533 Å. The dimethyl telluride ligand occupies the *anti*-position in relation to the cyclopentadienyl ring, which minimises steric contacts. The Te–C bond length (2.107 Å) and the C–Te–C bond angle (93.1°) fall within the ranges of these values normal for organic tellurides.

The extended Hückel quantum-chemical calculations[131] for the $[CpFe(CO)_2EMe_2]^+$ cations confirmed the conclusion, based on the study of reactions of the cations **117**, that the stability of the Fe–E bond increases in the series S < Se ≪ Te.

A different approach has been used to prepare molybdenum cyclopentadienyl carbonyl complexes **125**.[128] These monocarbonyl complexes were synthesised in 39%–91% yields by treatment of tricarbonyl(cyclopentadienyl)iodomolybdenum with silver tetrafluoroborate in the presence of the corresponding dimethyl chalcogenides (at a molar ratio of the reactants of 1 : 1 : 1).

$$CpMo(CO)_3I + AgBF_4 + EMe_2 \xrightarrow[-AgI]{CH_2Cl_2} \underset{\mathbf{125}}{[CpMo(CO)_3EMe_2]^+BF_4^-}$$

E = S, Se, Te.

Dicarbonyl molybdenum-containing cations **126** were obtained in 86%–93% yields by oxidation of the dimer of dicarbonyl(cyclopentadienyl)molybdenum with ferrocenium tetrafluoroborate in the presence of dimethyl chalcogenides.[128] These compounds are formed as mixtures of *cis*- and *trans*-isomers the latter being formed in substantially larger amount.[128]

$$[CpMo(CO)_2]_2 + EMe_2 + [Cp_2Fe]^+BF_4^- \xrightarrow[-Cp_2Fe]{CH_2Cl_2} \underset{\mathbf{126}}{[CpMo(CO)_2(EMe_2)_2]^+BF_4^-}$$

E = S, Se, Te.

Anionic vanadium pentacarbonyl complexes **127**, containing diorganyl chalcogenides as ligands, have been synthesised by ligand exchange, namely, by the replacement of the THF molecule in the anionic complexes of vanadium **128** by diorganyl chalcogenide.[129, 130]

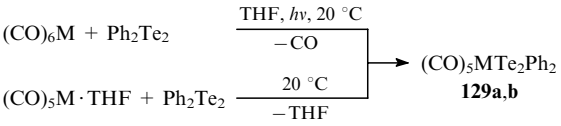
$$\underset{\mathbf{128}}{Et_4N^+[V(CO)_5THF]^-} + R^1R^2E \xrightarrow[-THF]{} \underset{\mathbf{127a-d}}{Et_4N^+[V(CO)_5ER^1R^2]^-}$$

Compound **127**	R^1	R^2	E	Ref.
a	Ph	Ph	S	130
b	Ph	Ph	Se	129, 130
c	Ph	Ph	Te	129, 130
d	Me	Ph	S	129, 130

Among the synthesised compounds, only the tellurium complex **127c** is stable at room temperature.[130] The ^{51}V NMR spectra of the complexes **127a–c** demonstrate that the metal atom becomes more shielded with an increase in the size of the chalcogen atom. The $\delta_{^{51}V}$ values for E = S, Se, Te are −1618, −1658 and −1753 ppm, respectively.[130]

2. Complexes of diorganyl ditellurides

It has been shown in Section II that bi- and trinuclear iron, ruthenium and manganese carbonyls and molybdenum hexacarbonyl react with diaryl ditellurides with cleavage of the Te–Te bond to give complexes containing bridging ArTe ligands. However, when diphenyl ditelluride reacts with chromium and tungsten hexacarbonyls, the Te–Te bond is retained in the resulting complexes.[15, 132] Depending on the ratio of the substrates, this gives either 1 : 1 (**129**)[132] or 2 : 1 (**130**)[15] complexes. Complexes of the former type are produced in 40%–60% yields on UV irradiation of tetrahydrofuran solutions of metal hexacarbonyls and diphenyl ditelluride at room temperature.[132] The use of adducts of metal carbonyls with THF instead of hexacarbonyls makes it possible to prepare the complexes **129** in approximately the same yield without UV irradiation.[132]



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

The complexes **129a,b** are orange crystalline compounds, stable in air and readily soluble in organic solvents.[132]

The structures of complexes of both types were studied by X-ray diffraction analysis.[132] The metal atom is bound only to one tellurium atom; the coordination polyhedron is a slightly distorted octahedron. The Cr–Te and W–Te bond lengths are 2.679 and 2.810 Å, respectively. The complexation has only a slight effect on the Te–Te bond length in the ligand; in the complex **129a**, the length of this bond is 2.737 Å, and in **129b**, it is 2.718 Å (the Te–Te bond length in Ph_2Te_2 is 2.712 Å [32]).

The ^{125}Te NMR spectra of the complexes **129** exhibit, in conformity with the structure proposed for them, two singlet signals due to ^{125}Te nuclei; for the chromium complex **129a**, they occur at 289 and 250 ppm (with respect to Ph_2Te_2), while for the tungsten complex, they are observed at 340 and 34 ppm.[132] Since the positions and shapes of the ^{125}Te signals do not depend on the temperature, no exchange processes occur in solutions. It remains unknown why the difference between the chemical shifts of the two ^{125}Te nuclei in the tungsten complex **129b** ($\Delta\delta$ = 306 ppm) is much greater than that in the chromium derivative **129a** ($\Delta\delta$ = 39 ppm).

Heterometallic complexes **130a–c** have been prepared in 40%–55% yields by the reaction of equimolar amounts of **129a–c** with $(CO)_5M^2 \cdot THF$.[15]

$$\underset{\mathbf{129a-c}}{(CO)_5M^1(Te_2Ph_2)} + (CO)_5M^2 \cdot THF \xrightarrow{THF} \underset{\mathbf{130a-c}}{[(CO)_5M^1][(CO)_5M^2]Te_2Ph_2}$$

$M^1 = M^2$ = Cr (**a**), W (**b**); M^1 = Cr, M^2 = W (**c**).

The complexes **130a–c** can also be synthesised by UV irradiation of a mixture of metal hexacarbonyls and diphenyl ditelluride (taken in a molar ratio of 2 : 1) followed by evaporation of the reaction mixture *in vacuo*.[15]

The compounds **130** form dark lilac crystals, readily soluble in aromatic and chlorinated solvents. They are fairly stable in air but gradually decompose in solutions. In coordinating solvents (acetonitrile, THF), especially in the light or on exposure to UV radiation, they decompose to give the complexes **129**.[15]

According to X-ray diffraction data,[15] each metal atom in the complex **130a–c** is linked to one Te atom. The coordination polyhedron is a distorted octahedron. The Cr–Te bond in **130a** (2.656 Å) and the W–Te bond in **130b** (2.779 Å) are somewhat shorter than the corresponding bonds in the complexes **129**. However, the Te–Te bond lengths in the complexes **130a–c** (2.812, 2.808 and 2.828 Å, respectively) are markedly longer than the corresponding bonds in the complexes **129** and diphenyl ditelluride. The C_2Te_2 fragment is planar, the $M(CO)_5$ groups occupying *trans*-positions with respect to the Te–Te bonds.[15]

This molecular geometry implies one signal in the ^{125}Te NMR spectrum. For the complex **130b**, $\delta_{^{125}Te}$ is 417. However, for the complexes **130a**,**c**, no signals for the ^{125}Te nuclei were detected; this was attributed[15] to weakening of the Te–Te bond and its possible dissociation to give paramagnetic monomers. However, no evidence for such a homolytic bond cleavage (which could be provided, *e.g.*, by EPR spectroscopy) is presented in this study.

Thermal decomposition of the complexes **129a**,**b** and **130a–c** was studied by differential scanning calorimetry.[15] The complexes **129a**,**b** decompose at 185–192 °C to give inorganic ditellurides $CrTe_2$ and WTe_2. The binuclear complexes **130a–c** lose the carbonyl and phenyl groups at 180–234 °C to yield, depending on the composition of the initial compound, CrTe, WTe and $CrWTe_2$.

Metal halo carbonyls, similarly to metal carbonyls, can react with diorganyl ditellurides both with rupture and with retention of the Te–Te bond. The reaction of *trans*-chlorocarbonylbis(triphenylphosphine)iridium **43** with di(4-ethoxyphenyl) ditelluride, accompanied by Te–Te bond rupture and giving the complex **44** with bridging ArTe ligands, was described above (see Section II).[68] Meanwhile, the reactions of the dimeric rhenium bromo carbonyl **100** (PhMe, room temperature) or pentacarbonyl(halo)-manganese **97a**,**d** (Et_2O, Pr^i_2O, Δ)[64] and -rhenium **97e**,**f** (Pr^i_2O, Δ)[67] with Ph_2Te_2 give the binuclear complexes **37a–d** in which the Te–Te bond is retained. The dimeric octacarbonyl halo derivatives $Mn_2X_2(CO)_8$ are formed as intermediate compounds in the reactions of manganese complexes.[64] An intermediate with the same composition has been postulated for the reaction involving pentacarbonyl(iodo)rhenium.[67]

$$\begin{array}{l}[M_2X_2(CO)_6(THF)_2]\\ \textbf{100}\\ \\ XM(CO)_5\\ \textbf{97a,d–f}\end{array}\quad\begin{array}{l}\xrightarrow[-THF]{Ph_2Te_2}\\ \\ \xrightarrow[-CO]{Ph_2Te_2}\end{array}\quad[M_2X_2(CO)_6Te_2Ph_2]\ \textbf{37a–d}$$

M = Mn: X = Br (**37a**, **97a**), I (**37b**, **97d**);
M = Re: X = Br (**37c**, **97e**, **100**), I (**37d**, **97f**).

The complexes **37a–d** are red or red-brown crystalline compounds. The manganese complexes **37a**, **b** exist in air in the crystalline state only for several minutes; in solutions, they are fairly unstable thermally and photochemically unlike the rhenium complexes **37c**,**d**. Thermal decomposition of manganese complexes affords the complexes **24f** with bridging PhTe ligands (see Section II.3).

The molecular and crystal structures of the rhenium complex **37c** were studied by X-ray diffraction analysis.[67] The geometry of bonds about the rhenium atoms is a pseudo-octahedron, each rhenium atom being bound to three carbonyl groups, one tellurium atom of the ditelluride fragment and two bridging bromine atoms. The average length of the Te–Re bond is 2.760 Å, and the Te–Te bond length is equal to 2.794 Å, which is somewhat longer than this bond in diphenyl ditelluride (2.712 Å).[32] The length of the bridging Re–Br bond is 2.642 Å; the Te···Br contact (3.674 Å) is almost 0.5 Å shorter than the sum of the van der Waals radii of the corresponding atoms (3.91 Å) and attests apparently to a weak interaction between them.[82]

The fact that the IR spectra of the rhenium bromo carbonyl **37c** are similar to those of the iodo carbonyl **37d** suggests that they have similar structures.[67] The IR spectra of the complexes **37a–d** and their sulfur and selenium analogues show a regular decrease in the ν_{CO} value following an increase in the atomic mass of the chalcogen. In the opinion of the researchers cited,[67] this regularity is largely due to the increase in the σ-donor capacity of chalcogens in the series S < Se < Te.

The diphenyl ditelluride ligand in the complexes **37a–d** can be substituted by other ligands under mild conditions. Thus, on dissolution in THF, the diphenyl ditelluride molecule is ejected to be replaced by a THF molecule.[64, 67] However, the adduct of bromo(tricarbonyl)manganese with THF, formed from the manganese complex **37a**, is unstable even at room temperature[64] and decomposes to give a mixture of non-identified products.

$$\underset{\textbf{37a}}{Mn_2Br_2(CO)_6Te_2Ph_2} + THF \xrightarrow[-Ph_2Te_2]{} BrMn(CO)_3(THF)_2$$

Dissolution of the rhenium complex **37c** and its S and Se analogues results in the equilibrium

$$Re_2Br_2(CO)_6E_2Ph_2 + 2THF \rightleftharpoons Re_2Br_2(CO)_6(THF)_2 + Ph_2E_2$$

E = S, Se, Te.

The equilibrium constants diminish in the series S (3.15) > Se (7.5×10^{-2}) > Te (5×10^{-4}).[64]

The diphenyl ditelluride ligand in the complexes **37a**,**b** is replaced relatively easily at room temperature by carbon monoxide.[64]

$$\underset{\textbf{37a,b}}{Mn_2Br_2(CO)_6Te_2Ph_2} + 2CO \xrightarrow[-Ph_2Te_2]{} Mn_2Br_2(CO)_8$$

For the manganese complexes of diphenyl dichalcogenides $Mn_2Br_2(CO)_6E_2Ph_2$ (E = Se, Te), the rate of this reaction for E = Se is higher than that for E = Te, which reflects the increase in the bond strength in this series.[64]

A ^{13}C NMR study of the exchange of diphenyl dichalcogenide ligands in the reaction of rhenium complexes **37** enriched in ^{13}C with diphenyl dichalcogenides showed that the strength of the Re–chalcogen bond increases on passing from Se to Te. The ligand containing a heavier chalcogen expels the ligand containing a lighter chalcogen from the complex.

$$Re_2Br_2(^{13}CO)_6E^1_2Ph_2 + E^2_2Ph_2 \overset{CDCl_3}{\rightleftharpoons} Re_2Br_2(^{13}CO)_6E^2_2Ph_2 + Ph_2E^1_2$$

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

Complexes of metal cyclopentadienyl carbonyls with diaryl ditellurides are relatively little studied.[88, 133] The dark lilac complex of diphenyl ditelluride with dicarbonyl(cyclopentadi-enyl)-manganese **131** has been prepared in 70% yield by the reaction of tricarbonyl(cyclopentadienyl)manganese with diphenyl ditelluride in heptane on exposure to UV radiation.[133] This complex was also obtained by the reaction of diphenyl ditelluride with [CpMn(CO)$_2$]THF at room temperature.[133]

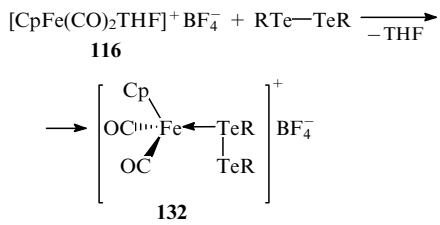
$$\begin{array}{l}CpMn(CO)_3 + Ph_2Te_2\\ [CpMn(CO)_2]THF + Ph_2Te_2\end{array}\quad\begin{array}{l}\xrightarrow[-CO]{C_7H_{16},\,h\nu}\\ \xrightarrow[-THF]{}\end{array}\quad[CpMn(CO)_2]Te_2Ph_2\ \textbf{131}$$

The complex **131** is fairly sensitive to air. It is readily soluble in THF, CH_2Cl_2 and in aromatic hydrocarbons and poorly soluble in alkanes. Its solution in THF does not exhibit signals in the EPR spectrum, and a toluene solution produces no signal in the ^{125}Te NMR spectrum.[133]

The complex $[MeCp(CO)_2Mn]_2(MesTe)_2$ with a similar structure has been synthesised in 33% yield by the reaction of the adduct [MeCp(CO)$_2$Mn]THF with Mes_2Te_2.[88] It follows from X-ray diffraction data[133] that each $CpMn(CO)_2$ fragment in complex **131** is linked to one tellurium atom. The Mn–Te bond length is 2.486 Å. The metal atoms are in the *trans*-positions

relative to the Te–Te bond, the atoms in the Mn–Te–Te–Mn fragment thus formed lying in one plane. The coordination to the metal scarcely influences the Te–C bond length (2.128 Å) but substantially influences the Te–Te bond length, which is equal to 2.884 Å in the complex **131** and 2.712 Å in diphenyl telluride. The Te–Te–C bond angle also considerably changes — it is 88.4° in **131** and 97.4° and 100.3° in free Ph_2Te_2.[32] This was interpreted [133] as being due to the additional dative interaction of the lone electron pairs of manganese with vacant *d* orbitals of tellurium.

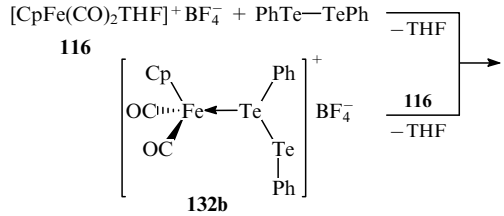
The Te–Te bond in diorganyl ditellurides is retained when they react with the cationic iron complex **116**. The reaction occurs under mild conditions (CH_2Cl_2, ~20 °C) and affords complexes **132a**,**b** in high yields (85%–98%).[134] The sulfur and selenium analogues of the complexes **132** were prepared in a similar way in 89%–98% yields.[134]

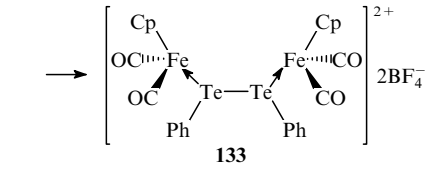


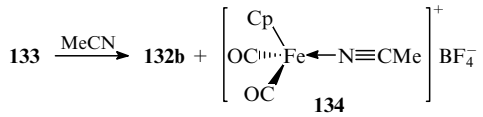
R = Me (**a**), Ph (**b**).

When diphenyl ditelluride reacts with two equivalents of the salt **116** or when the complex **132b** is treated with one equivalent of **116**, complex **133** is formed in 81% yield. Obviously, in this compound, diphenyl ditelluride acts as a bridging ligand, both its Te atoms being linked to iron atoms.[134] The sulfur and selenium analogues of **133** were synthesised in a similar way in 84% and 87% yields, respectively.[134]

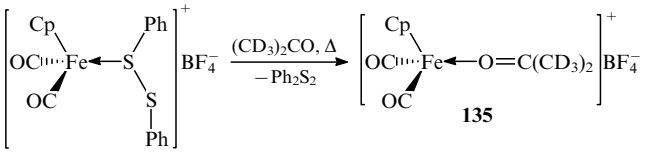
It should be noted that the complex **133** and its chalcogen analogues react with MeCN to give mixtures of complexes **132b** and **134**.



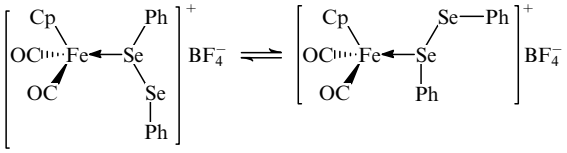




Diphenyl dichalcogenide complexes of the type **132** behave differently on heating in $(CD_3)_2CO$. In the sulfur complex, the solvent displaces the disulfide ligand, which leads to complex **135**.[134]



In the case of the selenium analogue, the data of ^{13}C NMR spectroscopy indicate the occurrence of a dynamic process, which was interpreted as a 1,2-shift of the $CpFe(CO)_2$ fragment.[134]

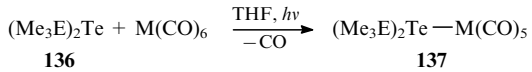


For the tellurium complex **132b**, no splitting of the ^{13}C signals of the phenyl groups is observed even at 200 K.[131]

3. Complexes of metal carbonyls with compounds with tellurium–element bonds

The formation of complexes from metal carbonyls and compounds containing Te–element bonds can, in principle, involve coordination of the metal atom both to tellurium and to the other element.

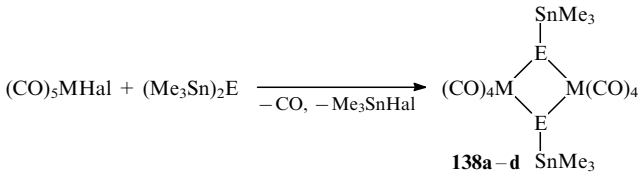
The interaction of metal hexacarbonyls with compounds $(Me_3E)_2Te$ (**136**, E = Ge, Sn, Pb) gives rise to complexes **137**, their yields being 17%–45%.[135,136] The reactions proceed in THF on exposure to UV radiation.



M = Cr, Mo, W; E = Ge, Sn, Pb.

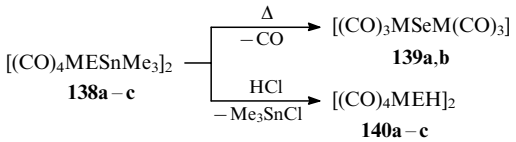
The complexes **137** are rather sensitive to moisture and atmospheric oxygen. Complexes with similar compositions and structures are formed when Cr, Mo and W hexacarbonyls are made to react with bis-element-substituted sulfides [137] and selenides.[135]

The reactions of $Mn(CO)_5Br$ and $Re(CO)_5Cl$ with $(Me_3Sn)_2E$ (E = Se, Te) afford binuclear complexes **138a**–**d**, which contain apparently bridging $(Me_3Sn)E$ ligands.[138] Unlike the selenium derivatives **138a**,**b**, which are formed in high yields, the yields of their tellurium analogues **138c**,**d** are quite low. Thus the manganese complex **138c** was isolated in a yield of only 11%, and the formation of the rhenium derivative **138d** was judged only from the IR spectra of the reaction mixture.[138]



E = Se: M = Mn (**a**), Re (**b**); E = Te: M = Mn (**c**), Re (**d**).

The complexes **138** can be transformed *via* two routes giving either compounds **139** or **140**.[138] The thermal transformation of **138** into **139** can be accomplished only for selenium-containing derivatives **138a**,**b**; the tellurium analogue could not be synthesised. On treatment with HCl, the complexes **138a**–**c** undergo destannylation to give the compounds **140a**–**c**.



E = Se: M = Mn (**a**, 69%), Re (**b**, 66%); E = Te, M = Mn (**c**, 57%).

The proton signals of the EH groups in the ^1H NMR spectra of the complexes **140a**–**c** substantially shift upfield on passing from Se to Te. The chemical shifts of the SeH group in the spectra of **140a**,**b** are −6.20 and −4.13 ppm, respectively, whereas the signal for the TeH group in the spectrum of **140c** occurs at

−12.80 ppm.[138] For comparison, the chemical shifts of protons of the TeH groups in stable tellurols $(Me_3Si)_3ETeH$ are −5.10 (E = C), −8.82 (E = Si), −9.02 (E = Ge).[139]

Unlike complexes formed by metal carbonyls with compounds containing Te–E bonds with Group IV elements, in which the tellurium atom acts as the coordination site, in the case of complexes in which E is a Group V element, both tellurium and this element can be involved in coordination.

The complexes **141a–c** have been prepared in relatively low yields (14%–27%) by reactions of metal carbonyls with compounds **142a–c** at room temperature.[140, 141]

$$M(CO)_5 \cdot THF + \underset{\mathbf{142a-c}}{(CF_3)_2ETeMe} \xrightarrow{THF} \underset{\mathbf{141a-c}}{(CO)_5M(CF_3)_2ETeMe}$$

M = Cr: E = P (**a**), As (**b**); M = Mo, E = P (**c**).

The complexes **141a,c** with phosphorus ligands are relatively stable in the light both in the solid state and in solutions in the absence of atmospheric oxygen. The arsenic analogue **141b** decomposes in solution over a period of several days even in the dark and under an inert atmosphere. Based on the spectroscopy data,[140, 141] it was concluded that in phosphorus complexes, the metal is coordinated only to the P atom, while the arsenic complex exists as two isomers in which the metal is coordinated to either As or Te.

The reaction of the complex **141a** with trimethyltin hydride occurs with rupture of the P–Te bond.[142]

$$\underset{\mathbf{141a}}{Cr(CO)_5(CF_3)_2PTeMe} + Me_3SnH \longrightarrow Cr(CO)_5(CF_3)_2PH + MeTeSnMe_3$$

A common drawback of studies describing metal carbonyl complexes with tellurium-containing ligands with Te–element bonds is that no X-ray diffraction data are presented.

IV. Conclusion

In the last 10–15 years, substantial progress has been achieved in the synthesis and study of complexes of metal carbonyls and cyclopentadienyl carbonyls with organic derivatives of tellurium(II). This includes synthesis of the complexes of metal carbonyls and cyclopentadienyl carbonyls with tellurocarbonyl compounds and triorganylphosphine tellurides, the use of organic derivatives of tricoordinated (diaryl telluroxides) and tetracoordinated (σ-telluranes) tellurium for the synthesis of Te(II) complexes and the possibility of thermolytic synthesis of metal tellurides. The reactions of bidentate N,Te-containing organic ligands also present interest; in particular, this refers to the synthesis of the first structurally characterised complex of benzochalcogenazoles with metal–tellirium coordination. It is significant that many types of complexes of organotellurium compounds considered here are more stable than complexes containing structurally related organic compounds of sulfur and selenium.

Further research in this field should be directed apparently along the following lines: (1) systematic studies of complexes with broad variation of the electronic and spatial structures of organotellurium ligands and metal carbonyls; (2) the search for new preparative methods for the synthesis of complexes of Te(II) organic derivatives using various compounds of tricoordinated (telluronium ylides, tellurimides, telluronium salts) and tetracoordinated (organyltellurium trihalides, aryltellurinic acid derivatives) tellurium as well as organyltellurenyl halides, organyl tellurocyanates, and telluroesters; (3) elucidation of the relationship between the structural and spectral characteristics of complexes and the structures of both initial components and elucidation of the influence of the nature of the chalcogen atom on the structure and reactivity of complexes containing similarly constructed organochalcogen ligands; (4) synthesis of complexes with various ambidentate tellurium-containing ligands; (5) preparation of complexes with organotellurium ligands of various types containing bulky organic substituents $(Me_3Si)_3E$ (E = C, Si, Ge) and the use of these complexes as initial compounds for low-temperature synthesis of metal tellurides.

The review was financially supported by the Russian Foundation for Basic Research (Projects No. 96-03-32502a, No. 96-03-32026a) and by the INTAS (Grant 94-4675).

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