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THE LIGAND CHEMISTRY OF TELLURIUM

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ABBREVIATIONS

πCp	π-$C_5H_5^-$
Ph	C_6H_5
p-tolyl	*p*-CH_3–C_6H_4
Me	CH_3^-
Et	$C_2H_5^-$
n-Pr	n-C_3H_7
n-Bu	n-C_4H_9
R	alkyl
Ar	aryl

DMF	*N*, *N*-dimethylformamide
DMSO	dimethyl sulfoxide
THF	tetrahydrofuran
DCE	1,2-dichloroethane
tu	thiourea
etu	ethylenethiourea
su	selenourea
esu	ethyleneselenourea
fod	1,1,1,2,2,3,3-heptafluorooctane-4,6-dionate
PPN	$[N(PPh_3)_2]^+$

A. INTRODUCTION

Although the coordination chemistry of ligands containing heavier group VA donor atoms [1,2] as well as sulfur [3–9] and selenium [3,9,10] ligands has been widely investigated, the analogous chemistry of tellurium ligands is relatively unexplored [3,10–13]. This has probably been due to the lack of commercial availability of a wide variety of organotellurium ligands, in contrast to, for example, organophosphines, as well as to the generally held belief that organotellurium compounds are extremely toxic and air sensitive. This misconception can probably be traced historically to the early work in this area by Chatt and coworkers [14–23a] dealing with Pd(II) and Pt(II) complexes with diethyl telluride and di(n-propyl) telluride. These latter materials are indeed foul-smelling, air-sensitive liquids. The diaryl derivatives, with the exception of the liquid $TePh_2$, are air-stable solids. Indeed, air-stable dialkyl derivatives are obtained with sufficiently long alkyl chains (e.g., $Te(n\text{-}C_{16}H_{33})_2$ is an air-stable white solid; m.p. 45°C [11]).

In the past few years, however, considerably increased interest in organotellurium chemistry is evidenced by the number of publications [11,12] and patents [23b] in this area. This latter work is related to the use of organotellurium compounds in thermally processed photographic elements. The facile chemical reduction of such compounds at elevated temperatures (i.e., 100–175°C) in both stoichiometric and catalytic modes has resulted in the formulation of a wide variety of nonsilver imaging processes using tellurium chemistry [23b]. The synthetic methodology now exists to prepare a wide variety of organotellurium ligands [11,12].

Indeed, in the past few years an increasing number of papers have appeared describing transition metal complexes with organotellurium ligands. This trend can be expected to accelerate as organotellurium synthetic methodology becomes familiar to the practising coordination chemist. Comparison of the properties of such complexes with those of the large number of complexes with organophosphines [1,2], for example, may lead to useful applications for such complexes. This review is intended to promote interest in this relatively unexplored area of ligand chemistry.

B. TELLURIUM—AN OVERVIEW OF ITS CHEMISTRY

(i) Oxidation states of tellurium

Tellurium exhibits an exceptionally wide variety of formal oxidation states. Its common oxidation states are 2 − (Te^{2-} [24]), 1 − (Te_2^{2-} [24,25], Te^- [26]), 2 + ($Te(S_2X)_2$; $X = NR_2$ [27–29], COR [27,30–32]), 4 + ($TeCl_4$, TeO_2 [33,34]), and 6 + (TeF_6 [33,34]). A number of polynuclear species with fractional formal oxidation states have been reported: 2/3 − (Te_3^{2-}) [35], 1/4 + (Te_8^{2+}) [36,37], 1/3 + (Te_6^{2+}) [36–38], 1/2 + (Te_4^{2+}) [36–40], and 2/3 + (Te_6^{4+}) [41]. Trivalent compounds, $[Et_4N]_2[Te(mnt)_2Cl]$ (mnt = 1,2-dicyanoethylene-1,2-dithiolate) [42] and $(2\text{-biphenylyl})_2Te_2I_4$ [43], and several monovalent compounds (i.e., Te_4^{4+} [36,38,39]) have also been reported.

The 2 − state is readily accessible by the reduction of the metal in aqueous solution by a variety of reducing agents or by sodium in liquid ammonia [24,44]. This oxidation state is very susceptible to aerial oxidation to the metal, and solutions of Te($^{2-}$), which are useful reagents in organotellurium chemistry, are generally prepared in situ. The 6 + state is accessible only with strong oxidizing agents (e.g., F_2, permanganate, chloric acid) [33,34]. The two most common oxidation states in tellurium chemistry are the 2 + and 4 + states. Most tellurium compounds in these oxidation states can be conveniently prepared from Te metal (in some cases with intermediate reduction to Te^{2-}), $TeCl_4$, or TeO_2.

(ii) Te(II) and Te(IV) as Lewis acids

The coordination chemistry of Te(II) as a Lewis acid has been the subject of relatively little detailed investigation with respect to the synthesis and properties of these materials, although several crystal structures of Te(II) complexes with monodentate and bidentate sulfur ligands [27,30,31] have been reported (e.g., $[TeL_2X_2]$ [45,46], $[TeL_4]X_2$ [27,30,31,47,48], $[L_2Te(\mu\text{-}L)_2TeL_2]^{4+}$ [49] where L = thiourea or selenourea and X = halide, pseudohalide; and $Te(S_2X)_2$ where X = COR [27,30–32], CNR_2 [27–29], $P(OR)_2$ [27,50]). Indeed, the coordination chemistry of Te(II) is generally restricted to halo ligands and ligands with sulfur or selenium donor atoms (e.g., thioureas, selenoureas, SCN, 1,1-dithio ligands). The crystal structures of a number of the complexes with 1,1-dithio ligands have shown the presence of intermolecular Te–S interactions to give pseudo five-coordinate complexes [27]. A recent paper [51] reported the crystal structure of the first five-coordinate monomeric Te(II) complex ($[Et_4N][Te(S_2COEt)_3]$) which contains two bidentate and one monodentate xanthate ligands. A number of mixed organotellurium(II) complexes have also been reported, e.g., PhTe(etu)Br [52,53], PhTe(esu)I [52,53], $[Me_4N][PhTe(XCN)_2]$ (X = S, Se) [54], PhTe(su)Cl [55], $[Ph_4As][PhTeXY]$ [X = I, Br; Y = I, Br, Cl) [56].

Although arenetellurenyl halides (ArTeX; X = Cl, Br, I) [57–59] are generally rather unstable materials, a number of stable derivatives of this general type incorporating *ortho* substituents which interact via a Te · · · O or Te · · · N have been recently reported, e.g., *o*-formylphenyltellurenyl bromide [60], 2-(chlorotelluro)-*N*-methylbenzamide [61], 2-(bromotelluro)benzamide [61], (*o*-nitrophenyl)tellurenyl bromide [62], (2-phenylazophenyl-CN′)-tellurium(II) chloride [63].

The coordination chemistry of Te(IV) as a Lewis acid has been the subject of relatively little detailed investigation. Several adducts of TeX_4 (X = Cl, Br) with amines [64–68], sulfides [69–71], tetramethylthiourea [72–75], and 2,6-lutidine-*N*-oxide [76] have been reported. Husebye and co-workers have reported the crystal structures of a few 7- and 8-coordinate complexes with dialkyldithiocarbamates: $PhTe(S_2CNEt_2)_3$ [77], $Te(S_2CNMe(CH_2CH_2OH))_3Br$ [78], $Te(S_2CNMe(CH_2CH_2OH))_4$ [78], $Te(S_2CNC_4H_8O)_4$ [79], $Te(S_2CNEt_2)_4$ [80]. The crystal structure of the mixed O,S chelate bis(monothiopyrocatecholato)tellurium(IV) was recently reported [81], the analogous pyrocatecholato complex having been described earlier [82].

Gysling et al. [83] recently reported a new class of organotellurium(IV) complexes in which the tellurium trichloride moiety is stabilized to aerial hydrolysis by bonding to an organic radical via a carbon atom and some incorporated group VA or VIA donor site. The crystal structure of one such derivative, the condensation product of $TeCl_4$ and 2,6-diacetylpyridine, has been reported [83], the product $TeCl_3(2\text{-}CH_2CO(6\text{-}CH_3CO\text{-}C_5H_3N))$ containing a tridentate (i.e., C,N,O, coordination) organic radical.

C. A SURVEY OF TELLURIUM LIGANDS AND SYNTHESIS OF METAL–TELLURIUM BONDS

The earliest work dealing with the ligand properties of organotellurium derivatives involved the use of mercuric halides to form complexes with various dialkyl [84–88] and diaryl tellurides [89–101], primarily as a method of characterizing the organotellurium compounds. The synthesis of some monomeric and dimeric palladium and platinum halide complexes with the lower dialkyl tellurides was later described by Chatt and co-workers [14–23a] as part of their classic studies of the coordination chemistry of such square planar complexes. In the early 1960s, the use of organotellurium ligands in transition metal carbonyl chemistry was first described by Hieber and Kruck

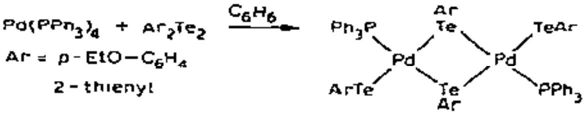
[102]. In addition to the use of dialkyl [103,104] and diaryl [102–105] tellurides as ligands, Hieber and co-workers introduced the use of diaryl ditellurides (ArTeTeAr) as reagents to form bridging M(μ-TeAr)$_2$M linkages via oxidative addition reactions [102,106]

$$\begin{aligned} &\mathrm{Fe_3(CO)_{12}} + 3\ \mathrm{Te_2}(p\text{-}\mathrm{MeO{-}C_6H_4})_2 \rightarrow \\ &\quad 3\mathrm{(OC)_3Fe}(\mu\text{-}\mathrm{Te}(p\text{-}\mathrm{MeO{-}C_6H_4}))_2\mathrm{Fe(CO)_3} + 6\ \mathrm{CO} \end{aligned} \qquad (1)[102]$$

Baddley and co-workers [107,108] later demonstrated that a terminal M–TeAr bond could be formed by analogous reactions, the dimeric complexes with the bridging bonding mode being formed under more forcing conditions

$$\begin{aligned} &[\pi\mathrm{CpFe(CO)_2}]_2 + \mathrm{Te_2Ph_2} \xrightarrow[\text{reflux}]{\mathrm{C_6H_6}} \pi\mathrm{CpFe(CO)_2TePh} \xrightarrow[\text{IR lamp}]{\mathrm{C_6H_6},\ \text{reflux}} \\ &\quad \pi\mathrm{Cp(CO)Fe}(\mu\text{-}\mathrm{TePh})_2\mathrm{Fe(CO)}\pi\mathrm{Cp} \end{aligned} \qquad (2)[107]$$

An interesting complex incorporating both terminal and bridging aryl tellurol ligands was recently reported by Chia and McWhinnie [109]



(3)

In addition to the use of diarylditellurides to form M(μ-TeAr)$_2$M linkages [102,106–114], recent work has shown that ArTeCOAr′ [115] (eqn. 4) and ArTeMPh$_3$ (M = Ge, Sn, Pb) (eqns. 5, 6) [116–119] derivatives are useful reagents for the formation of such linkages.

$$\mathrm{PdCl_2(NCPh)_2} + \mathrm{PhTeCOPh} \xrightarrow{\mathrm{CHCl_3}} [\mathrm{Pd(TePh)_2}]_n \qquad (4)[115]$$

$$\mathrm{CuCl} + \mathrm{Ph_3SnTePh} \xrightarrow{\mathrm{CH_3CN}} [\mathrm{CuTePh}]_n \qquad (5)[116,117]$$

$$\mathrm{PdCl_2(NCPh)_2} + \mathrm{Ph_3GeTePh} \xrightarrow{\mathrm{CHCl_3}} [\mathrm{Pd(TePh)_2}]_n \qquad (6)[119]$$

Two examples have been reported in which such bridging units (i.e., μ-TePh) are formed under forcing conditions using TePh$_2$ [102,120].

A variety of complexes containing both bridge M(μ-TeAr)$_2$M linkages [117,121] (e.g., eqn. 7) and terminal M–TeAr bonds [113,122–125] (e.g., eqns. 8–10) have been prepared by metathetical reactions in which a ditelluride is initially cleaved with a reducing agent to generate ArTe$^-$

$$\begin{array}{l} \mathrm{Na^+TePh^-} + \mathrm{CuCl} \xrightarrow{\mathrm{EtOH}} [\mathrm{CuTePh}]_n \\ \quad \uparrow \mathrm{NaBH_4/NaOH} \\ \quad \mathrm{PhTePh} \end{array} \qquad (7)[117]$$

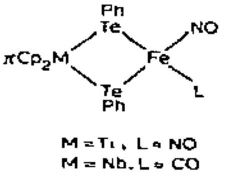
$$[\pi\mathrm{CpNi(P(n\text{-}Bu)_3)_2}]^+\mathrm{Cl}^- + \mathrm{NaTePh} \rightarrow \pi\mathrm{CpNi(P(n\text{-}Bu)_3)TePh} + \mathrm{P(n\text{-}Bu)_3} + \mathrm{NaCl} \qquad (8)[122]$$

$$\pi\mathrm{Cp_2ZrCl_2} + 2\ \underset{\underset{\mathrm{PhLi}}{\uparrow \mathrm{Te(0)/ether}}}{\mathrm{PhTeLi}} \rightarrow \pi\mathrm{Cp_2Zr(TePh)_2} + 2\ \mathrm{LiCl} \qquad (9)[123]$$

$$\mathrm{Hg(TePh)_2} + [\mathrm{Ph_4P}]^+[\mathrm{TePh}]^- \xrightarrow{\mathrm{THF}} [\mathrm{PPh_4}]^+[\mathrm{Hg(TePh)_3}]^- \qquad (10)[113]$$

Dimeric complexes containing TePh^- bridging ligands have also been prepared by use of a mercury reagent [126]

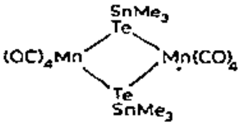
$$\pi\mathrm{Cp_2M(TePh)_2} + 1/2\ \mathrm{Hg[Fe(CO)_3NO]_2} \xrightarrow{\text{acetone}}$$



(11)[126]

A Te–Sn cleavage reaction with the formation of a tellurol bridged dimer occurred in the reaction of $\mathrm{Te(SnMe_3)_2}$ with bromopentacarbonylmanganese(I) [127]

$$\mathrm{Mn(CO)_5Br} + \mathrm{Te(SnMe_3)_2} \xrightarrow[60°\mathrm{C}]{\mathrm{C_6H_6}}$$



(12)[127]

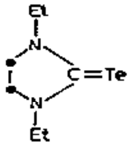
Complexes with diaryl ditellurides (Hg(II) [87,114a,128], Cu(I) [116,117,129], U(V) [130a], and Re(I) [130b]) and dialkyl ditellurides (Cu(I) [116]) in which the Te–Te bond remains intact have also been reported.

Most of the reported transition metal complexes with tellurium ligands involve the above ligand types, although a few examples with tellurium heterocycles [102,131–135] as well as with ligands containing Te–E bonds (E = Ge [136], Sn [127,136,137], Pb [136], P [138a,c], As [138a]) as well as cluster compounds incorporating tellurium [102,139–148] have been reported (see Fig. 1). The first tellurocarbonyl complex [149a] (i.e., $\mathrm{OsCl_2(CO)(CTe)(PPh_3)_2}$), complexes with a tellurourea-type ligand ($\mathrm{M(CO)_5L}$ (M = Cr, Mo, W), *cis*-$\mathrm{Mn(Br)(CO)_4L}$; $\mathrm{L = Te{=}\overline{CNEtCH_2CH_2N}Et}$ [138b]) and $\mathrm{HTe^-}$ (i.e., $\mathrm{C^+[M(CO)_5TeH]^-}$, M = Cr; $\mathrm{C^+ = PPN^+}$; M = W; $\mathrm{C^+ = AsPh_4^+}$ [149b]) have also been recently reported.

Although a large number of coordination complexes of the pseudohalides ($\mathrm{XCN^-}$; X = O [188–190], S [188,189,191,192], Se [188,189,192]) have been reported, to date no transition metal tellurocyanates have been described. The simple alkali metal tellurocyanates can be prepared in nonaqueous solvents (e.g., MeCN, acetone, DMSO) by reacting MCN (M = Na, K) with

Ti c [126] d [123]	**V**	**Cr** a [149b] h [136,137] j [132] k [138a] o [138b] p [149b] q [149b]	**Mn** a [102*] b [102,105] c [102,151] i [127] j [102] o [138b]	**Fe** b [102] c [102,106,110, 107,112,114b, 126,153] d [107] j [132] m [139-146]	**Co** c [126] m [102] j [154b]	**Ni** d [122,159**]	**Cu** b [171,180] c [116,117,119] e [116,117] f [63,116,117, 129] g [116,117]	**Zn**		
Zr d [123]	**Nb** c [126] d [124]	**Mo** c [108,125] d [108,124] k [138c] o [138b]	**Tc**	**Ru** a [104,154a] b [104] c [112] m [147-148]	**Rh** a [155-157] b [120] c [120]	**Pd** a [13,18-20, 160-168] b [109,167, 169-171] c [109,115,168] d [109] j [132]	**Ag** a [135,181,182] b [134,135] j [134,135]	**Cd** h [185]		
Hf	**Ta** o [150]	**W** d [124] h [136,137] o [138b] p [149b] q [149b]	**Re** a [103,152] b [103] g [130b] i [127]	**Os** l [149a] m [148]	**Ir** a [158]	**Pt** a [14,15,17, 21-23a, 160-164, 167,168, 172-179] b [109,171,174] m [139b] n [176]	**Au** a [183] b [184]	**Hg** a [84-88,186] b [89-104,114a] c [111,114a,121 d [113,187] e [115,114a] f [87,114a] j [133]		**U** l [130a]

Fig. 1. Transition metal complexes with tellurium ligands: (a) complex with dialkyl telluride; (b) complex with diaryl telluride; (c) complex with bridging Te(aryl)$^-$; (d) complex with terminal Te(aryl)$^-$; (e) complex with bridging Te(alkyl)$^-$; (f) complex with diarylditelluride; (g) complex with dialkylditelluride; (h) complex with terminal Te(MR$_3$)$_2$ (M=Ge,Sn, Pb); (i) complex with bridging TeSnMe$_3^-$; (j) complex with tellurium heterocycle; (k) complex with (CF$_3$)$_2$ETeMe (E=P, As); (l) complex with tellurocarbonyl (M–CTe); (m) tellurium incorporated in cluster compound; (n) complex with bridging TeMe$_2$ ligand; (o) complex with



(p)complex with terminal TeH$^-$; (q) complex with bridging TeH$^-$. * The complex Mn(CO)$_4$(Te(n-Bu)$_2$)Cl was proposed as an intermediate in the catalytic conversion of Mn(CO)$_5$Cl into [Mn(CO)$_4$Cl]$_2$ in the presence of the telluride in refluxing ether, but no dialkyl telluride complex of Mn has been isolated. ** A complex involving this linkage has been proposed as an intermediate in the conversion of ArTeCl$_3$ and Ar$_2$TeCl$_2$ derivatives into the corresponding carboxylic acids by Ni(CO)$_4$ in DMF.

tellurium, but such solutions deposit the starting materials on evaporation of the solvent [193]. However, salts of tellurocyanate with bulky cations have been isolated (i.e., Et$_4$N$^+$ [194], Me$_4$N$^+$ [195], AsPh$_4^+$ [195], PPN$^+$ [196]), and the crystal structure of PPN[TeCN] has been reported [197].

An analogous situation exists for the trialkyl phosphine tellurides. A series of (alkyl)$_3$PTe derivatives [198–210] have been prepared by reaction of the phosphines with tellurium in nonaqueous solvents. However, unlike the analogs with the lower chalcogens (R_3PX; $X=O$ [211], S [212,213], Se [10,213]), no coordination complexes with these rather unstable derivatives have been reported.

Thus, tellurium ligand chemistry still offers a vast area of interesting synthetic organometallic chemistry as well as coordination chemistry involving studies of new tellurium–metal linkages and fundamental studies of the ligand properties of tellurium bases.

In much of the early work in this area, complexes with tellurium ligands were prepared merely as supplementary examples, the main emphasis being on complexes with group VA ligands, especially organophosphines. In the past few years, however, there has been renewed interest in all the above areas as well as some efforts to understand the fundamental ligand properties of organotellurium compounds. ^{125}Te NMR [168,214] and Mössbauer spectroscopy [114a,b,117,171,215–218] have provided useful information on the properties of tellurium ligands, and the first crystal structure determinations of metal complexes with organotellurium ligands have recently been reported (i.e., *trans*-$Pd(SCN)_2(Te(CH_2CH_2CH_2Si(CH_3)_3)_2)_2$ [13], $[PPh_4][Hg(TePh)_3]$ [187], $[Cr(CO)_5\{Te=\overline{CNEtCH_2CH_2N}Et\}]$ [138b], *cis*-$[\pi CpCOFe(\mu\text{-}Te(p\text{-}EtO-C_6H_4))_2FeCO\pi Cp]$ [114b], and $Re_2(\mu\text{-}Br)_2(\mu\text{-}Te_2Ph_2)(CO)_6$ [130b]. In the sections that follow, coordination complexes with organotellurium ligands will be described according to the central metal and the Te ligand type. At present, complexes with tellurium ligands have been reported for 24 elements (Fig. 1).

D. SYNTHESIS OF ORGANOTELLURIUM LIGANDS

Irgolic [11,12,24] has discussed the synthetic aspects of organotellurium chemistry in several reviews and a monograph. Therefore, only some general aspects of the synthesis of organotellurium ligands will be discussed here, and the reader is referred to the above references for detailed procedures for specific compounds.

The organic chemistry of tellurium has been the subject of study for more than 140 years, the first organometallic compound, $TeEt_2$, having been prepared in 1840 by Wöhler [219]. After this initial work, the area remained relatively dormant until the work of Lederer in 1910–1920 and Morgan and Drew in the 1920s. (See ref. 11 for a summary of this early work.) Since 1960 there has been a steadily increasing interest in organotellurium chemistry, areas of recent emphasis being tellurium heterocycles [220] and coordination complexes with tellurium ligands [13].

The two most generally useful starting materials for organotellurium syntheses are $TeCl_4$ (Fig. 2) and tellurium metal (Fig. 3). Reactions of $TeCl_4$

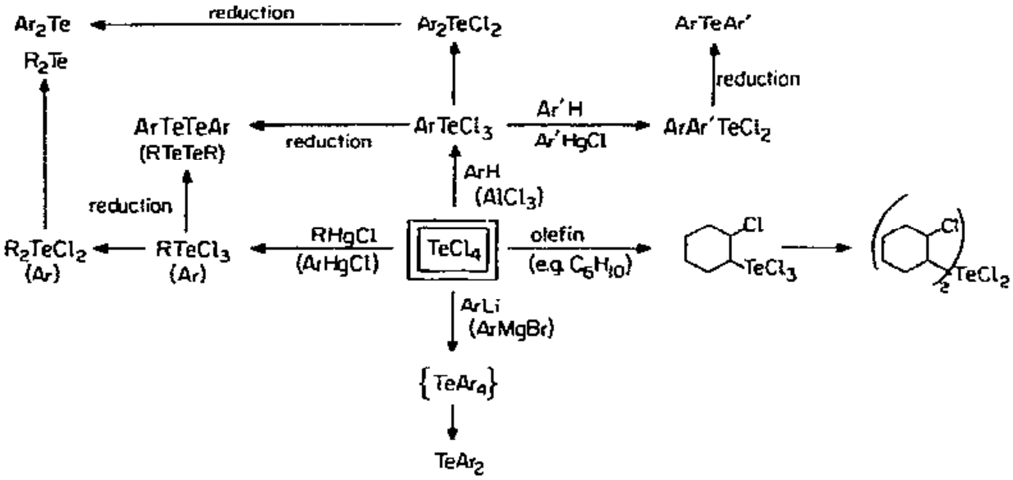


Fig. 2. The use of $TeCl_4$ in organotellurium synthesis.

with aromatics [221], olefins [222,223], and a wide variety of organometallic reagents [224], both aromatic and aliphatic, can be used to prepare organotellurium derivatives (Fig. 2).

Dialkyl tellurides can be prepared starting from $TeCl_4$ by reactions with alkyl mercuric chlorides [225], acetylenes [226], olefins or ketones (e.g., MeCOPh [227], acetylacetone derivatives [228–232]) followed by reduction

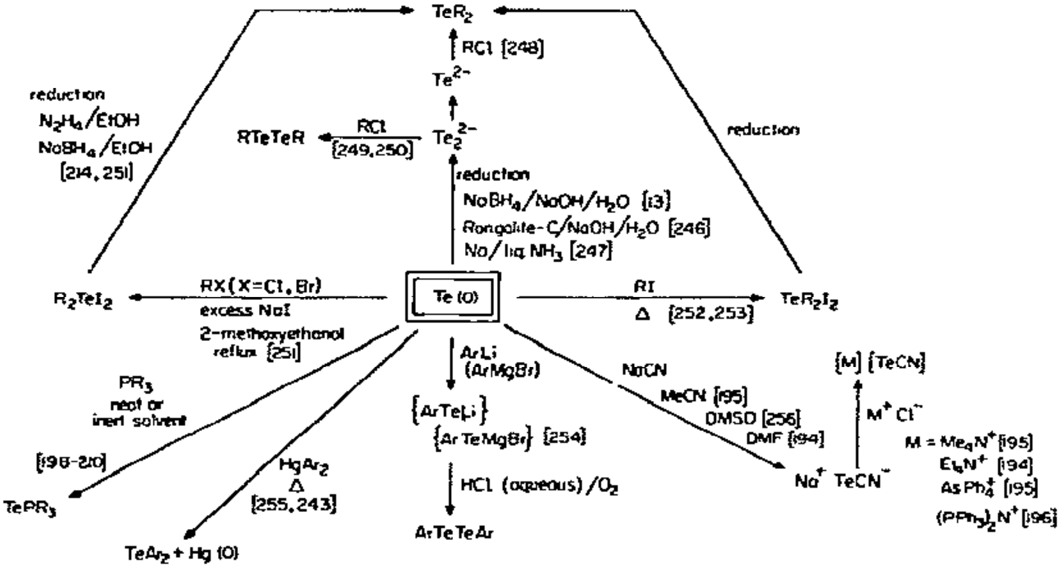


Fig. 3. The use of Te(0) in organotellurium synthesis.

of the initially formed (alkyl)$_2$TeCl$_2$ derivatives. However, reactions with TeCl$_4$ are most commonly used to prepare the aryl derivatives

$$\mathrm{TeCl_4} \xrightarrow[\substack{\mathrm{ArHgCl}\ [224,225,238] \\ \mathrm{Ar_2Hg}\ [224,234] \\ \mathrm{MAr_4}\ (\mathrm{M = Sn}\ [235],\ \mathrm{Pb}\ [236])}]{\substack{\mathrm{ArH}\ [221,237\text{–}239] \\ \mathrm{ArH/AlCl_3}\ [233]}} \mathrm{ArTeCl_3} \qquad (13)$$

Activated aromatics (e.g., PhOMe, PhNMe$_2$) [221] readily condense with TeCl$_4$, and nonactivated aromatics such as benzene itself react in the presence of AlCl$_3$ [233]. Of the organometallic reagents that have been used in reactions with TeCl$_4$ (eqn. 13), the aryl mercuric chlorides are the generally most useful for the preparation of both symmetrical ligands (TeAr$_2$) and unsymmetrical derivatives (TeArAr′), the latter ligands being prepared by sequential reactions with TeCl$_4$ and the isolated Cl$_3$TeAr derivative. Such mercury reagents incorporating a wide variety of functional groups can be readily prepared by Grignard reactions (HgCl$_2$ + ArMgBr) or more conveniently by the diazo method (decomposition of the double salts [ArN$_2$][HgCl$_3$] by Cu(0) in acetone or alcohol) [240,241].

Diaryl tellurides have also been prepared by reaction of TeCl$_4$ with aryl Grignard [241,242] and lithium [243,244] reagents. These reactions are generally carried out with excess organometallic reagent under forcing conditions to decompose the unstable intermediate tetraaryl tellurium derivative [245].

The aryl tellurium trichlorides, which are readily isolated from reactions with TeCl$_4$ (eqn. 13), can be easily reduced to diaryl ditellurides [237]. These, in turn, are very useful reagents for the synthesis of a wide variety of symmetrical and unsymmetrical diorganotellurides (Fig. 4). They are also useful reagents for the formation of terminal metal–TeAr and bridge metal (μ-TeAr)$_2$ metal linkages by direct or indirect routes (Fig. 5). Under forcing conditions, the trichlorides are converted to dichlorides by reaction with a second mole of organic or organometallic reagent. These derivatives can then be easily reduced to the corresponding diaryl tellurides (eqn. 13).

Alkyl derivatives of tellurium* are generally most conveniently prepared starting from Te(0) via reduction to Te$_2^{2-}$ or Te^{2-} followed by alkylation (Fig. 3). Wöhler's [219] original synthesis of diethyl telluride in 1840 involved reacting potassium telluride with ethyl sulfate. He prepared the potassium telluride by reducing tellurium metal with the carbonaceous residue obtained

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* TeMe$_2$, TeEt$_2$ and Te(n-Bu)$_2$ are commercially available.

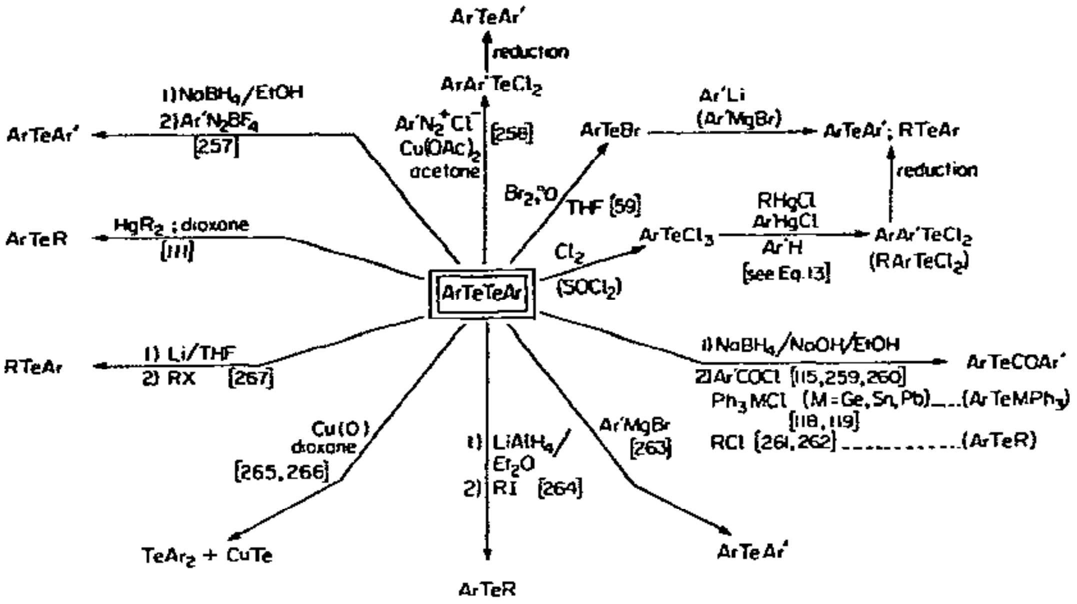


Fig. 4. Synthesis of symmetrical and unsymmetrical diorganotellurides from diarylditellurides.

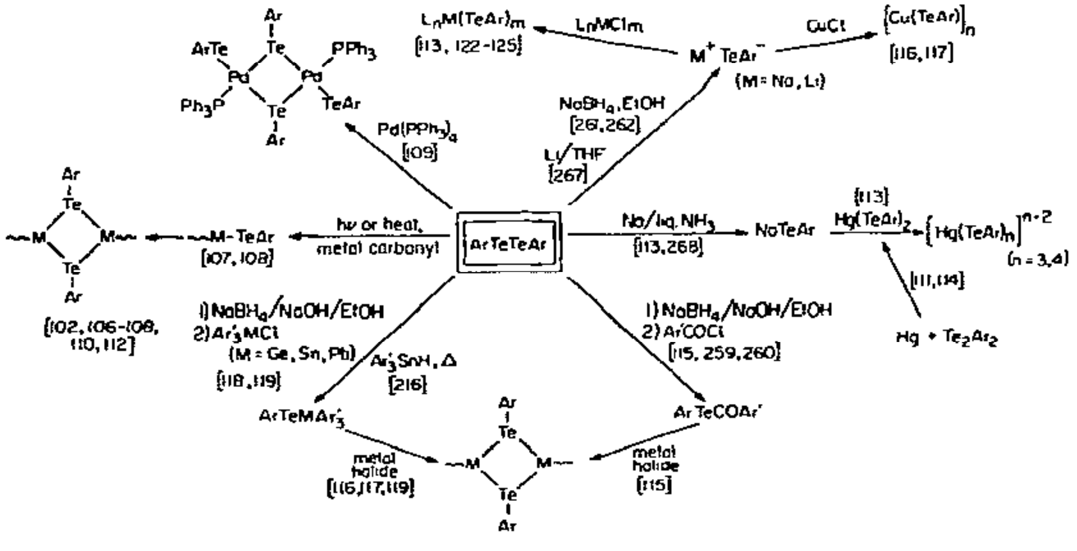
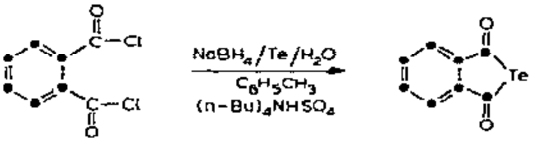


Fig. 5. Generation of ArTe$^-$ ligands from diaryl ditellurides.

by the thermal decomposition of potassium hydrogen D-tartrate at red heat until the carbon monoxide evolution had ceased. However, the reduction of tellurium to Te^{2-} can be carried out more conveniently in aqueous base with a variety of reducing agents (e.g., sodium formaldehyde sulfoxylate (Rongalite-C) [246,248,269,270], sodium dithionite [271], sodium bisulfite [272], thiourea dioxide [271,272], and potassium borohydride [13]).

Reaction of the aqueous Te^{2-} solution (Rongalite-C and borohydride being the most common reducing agents here) with an alkyl halide in a suitable solvent such as methanol gives facile alkylation to the dialkyl telluride (Fig. 3). Alternatively, if the alkyl halide is not stable under such highly alkaline conditions, a suspension of sodium telluride in an organic solvent such as methanol or DMF is used, the telluride being formed by the sodium reduction of tellurium in liquid ammonia followed by evaporation of the ammonia and addition of an appropriate organic solvent [44,273–275].

Bergman and Engman [276] have recently reported a phase-transfer method for the alkylation of sodium telluride. Reaction of a toluene solution of phthaloyl chloride with an aqueous solution of Na_2Te, generated by $NaBH_4$ reduction of tellurium metal, with tetrabutylammonium hydrogen sulfate as the phase-transfer catalyst, gave telluraphthalic anhydride [276a]:



(14)

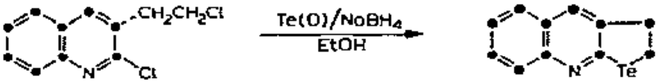
This method may have more general utility in the synthesis of dialkyl tellurides, which are unstable at the high pH used in the conventional methods in aqueous solution [13].

The same authors have also reported [277] a convenient one-step synthesis of symmetrical dialkyl selenides by reacting selenium metal with the appropriate tetraalkyl ammonium borohydride in toluene

$$2\,R_4N^+BH_4^- + Se \rightarrow R_2Se + H_2 + R_3NBH_3 \qquad (15)$$

Here the ammonium salt functions as both the reducing agent [$Se(0) \rightarrow Se^{2-}$] and the alkylating agent. With Te(0), only tetrabutylammonium borohydride was a strong enough reducing agent to give the dialkyl telluride [277].

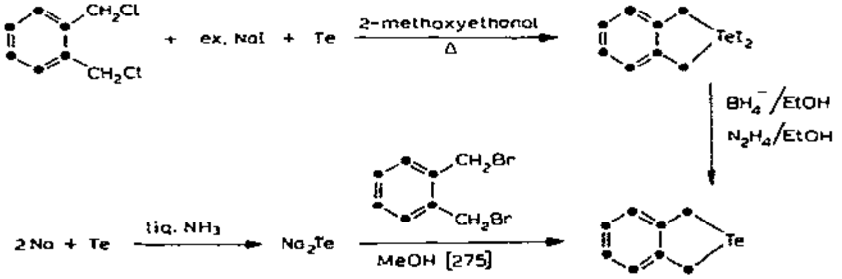
The reduction of tellurium metal in ethanol with $NaBH_4$ has also been reported [278–283].



(16)[56]

Here the reduction product formed in situ was formulated as NaHTe (although the selenium analog is well known [284,285], this species is not well characterized: the only well-documented tellurol derivatives are the very unstable CH_3TeH [286,287a] and PhTeH [287b]).

Another useful route to alkyl tellurides involves reacting tellurium powder at high temperature with an alkyl iodide, the resulting $Te(alkyl)_2I_2$ [252,253] derivative being readily reduced to the dialkyl telluride [214]. The yields in such reactions are generally rather low, although use of tellurium generated in a metal atom reactor has been reported to give improved yields [253]. Ziolo and Günther [251] recently reported a convenient modification of this general method in which tellurium powder is refluxed in a high-boiling solvent (e.g., 2-methoxyethanol) in the presence of a large excess of NaI and an alkyl halide (eqn. 17)

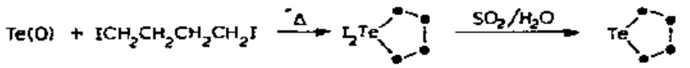


(17)[251]

(18)

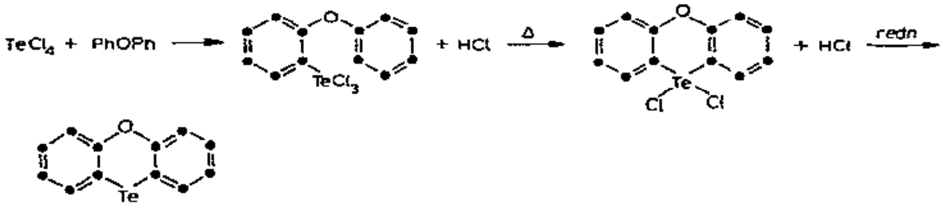
The particular derivative prepared by this new route, 1,1-diiodo-3,4-benzo-1-telluracyclopentane, is a convenient precursor to the Te(II) heterocycle 1,3-dihydrobenzo[c]tellurophene, which has also been prepared [275] by alkylation of Na_2Te formed from the reaction of the elements in liquid ammonia (eqn. 18). This synthetic method may have more general utility in organotellurium chemistry.

The heterocyclic chemistry of tellurium has been the subject of considerable recent interest, a number of new ring-closure reactions having been developed [220]. Most of the tellurium heterocycles that have been used as ligands, however, can be prepared by the general reactions described above.



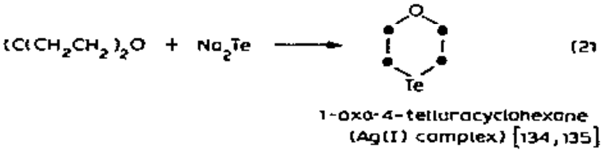
tellurocyclopentane
(Hg(II) complex)

(19) [133]

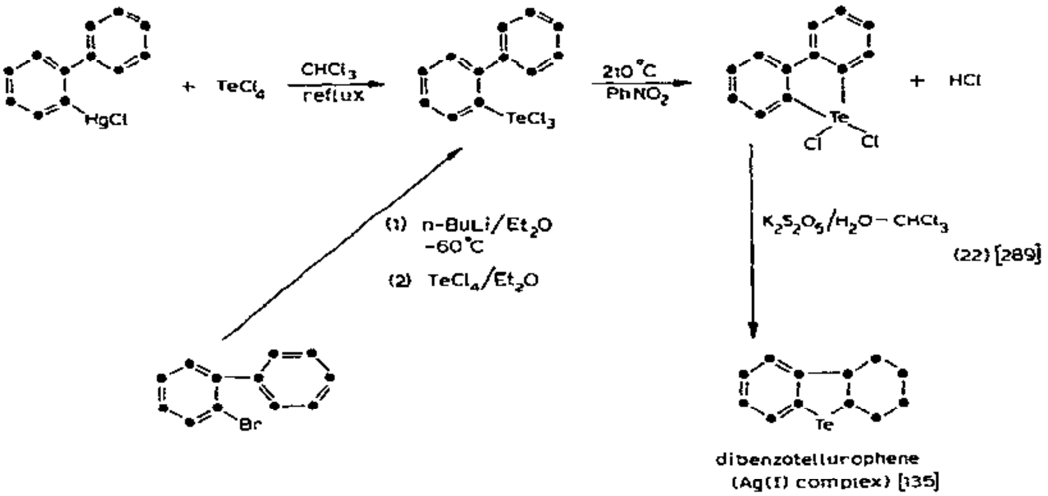


phenoxatellurine
(Mn(I) complex) [102]

(20) [288]

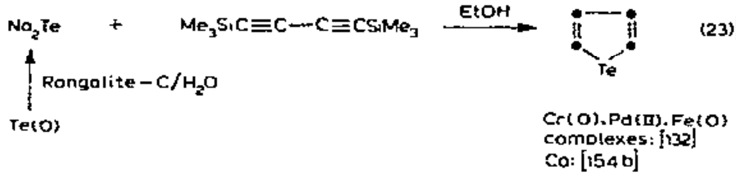


(21) [246]



(22) [289]

Tellurophene itself has been prepared by a variety of routes [11], and its chemistry has been reviewed [290,291]. A recently reported route provides this heterocycle in good yield from readily available starting materials [292].



(23) [292]

E. TRANSITION METAL COMPLEXES WITH TELLURIUM LIGANDS

(i) *Zn, Cd, Hg*

Zn, Cd

No well-characterized complexes of Zn or Cd with organotellurides have been reported. Coates [182] claimed that dimethyl telluride forms a complex with cadmium iodide, but no details were given. However, cadmium complexes with $Te(EEt_3)_2$ ($E = Ge$, Sn) have been prepared and characterized [185]

$$Cd(Ge(C_6F_5)_3)_2 + n\ Te(EEt_3)_2 \rightarrow Cd(Ge(C_6F)_3)_2(Te(EEt_3)_2)_n \qquad (24)$$

$E = Ge$, $n = 1$; $E = Sn$, $n = 1, 2$. The air-sensitive, colorless complexes, which are soluble in common organic solvents, were prepared by reaction of the components in toluene, concentration of the reaction solution, and dilution with hexane. The difficulty in forming 2:1 complexes with these Te ligands has been attributed to both steric and electronic factors (i.e., decreased σ donor properties of the Te as a result of $\mathrm{Te} \rightarrow \mathrm{E}\ d\pi - p\pi$ interactions).

Hg

Dialkyl telluride complexes. Several complexes having the composition $HgX_2(TeR_2)$ (Table I) have been prepared by reacting the telluride with the

TABLE I

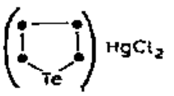
Cd and Hg complexes with tellurium ligands

	M.p. (°C)	Ref.
Cd complexes		
$Cd(C_6F_5)_2(Te(GeEt_3)_2)$	104–106	185
$Cd(C_6F_5)_2(Te(SnEt_3)_2)$	dec. >85	185
$Cd(C_6F_5)_2(Te(SnEt_3)_2)_2$	dec. >80	185
Hg complexes		
(a) Dialkyl telluride complexes		
$[HgCl_2TeEt_2]_2$		186
$HgCl_2TeMe_2$ [a]	179 (dec.)	84–86
$HgBr_2TeMe_2$ [a]	160–161 (dec.)	85, 86
HgI_2TeMe_2 [a]	107 (sl. dec.)	85, 86
$[HgCl_2Te(n\text{-}Bu)_2]_2$	97–98	186
$HgCl_2Te(n\text{-}C_5H_{11})_2$ [a]		88
$HgBr_2Te(n\text{-}C_5H_{11})_2$ [a]	88	88
$HgI_2Te(n\text{-}C_5H_{11})_2$ [a]		88
$Me_2TeBr_2HgI_2$		114a
$Me_2TeI_2HgBr_2$	127–128	114a
$[Me_2TeI_2]_2HgPh_2$ [b]	127–128	114a
(b) Diaryl telluride complexes		
$HgCl_2TePh_2 \cdot 5\ EtOH$	130	89
$HgCl_2TePh_2$	160–161	89
$HgBr_2TePh_2$	148	90
HgI_2TePh_2	146	87
$HgCl_2Te(o\text{-tolyl})_2$	212	188
$HgI_2Te(o\text{-tolyl})_2$	142–143	90
$HgBr_2Te(o\text{-tolyl})_2$	199–200	90
$HgCl_2Te(p\text{-tolyl})_2 \cdot 6\ EtOH$	135–136	89
$HgCl_2Te(p\text{-tolyl})_2 \cdot 3\ EtOH$	132–133	89
$HgBr_2Te(p\text{-tolyl})_2$	85	90
$HgI_2Te(p\text{-tolyl})_2$	65	90

TABLE I (continued)

	M.p. (°C)	Ref.
HgCl$_2$Te(*o*-EtO–C$_6$H$_4$)$_2$	174–175	96
HgBr$_2$Te(*o*-EtO–C$_6$H$_4$)$_2$	160–161	96
HgI$_2$Te(*o*-EtO–C$_6$H$_4$)$_2$	90	96
HgCl$_2$Te(α-naphthyl)$_2$	187–188	97
HgBr$_2$Te(α-naphthyl)$_2$	178–179	97
HgI$_2$Te(α-naphthyl)$_2$	152–153	97
HgCl$_2$Te(*m*-MeO–C$_6$H$_4$)$_2$	89	94
HgBr$_2$Te(*m*-MeO–C$_6$H$_4$)$_2$	115 (dec.)	94
HgI$_2$Te(*m*-MeO–C$_6$H$_4$)$_2$	122	94
HgCl$_2$Te(*m*-Me–C$_6$H$_4$)$_2$·6 EtOH	116–117	92
HgBr$_2$Te(*m*-Me–C$_6$H$_4$)$_2$	53	92
HgI$_2$Te(*m*-Me–C$_6$H$_4$)$_2$		92
HgCl$_2$Te(*p*-EtO–C$_6$H$_4$)$_2$	150–151	100
HgBr$_2$Te(*p*-EtO–C$_6$H$_4$)$_2$	155–156	100
HgI$_2$Te(*p*-EtO–C$_6$H$_4$)$_2$	123–124	100
HgCl$_2$Te(*p*-MeO–C$_6$H$_4$)$_2$	90	98
HgBr$_2$Te(*p*-MeO–C$_6$H$_4$)$_2$	77–78	98
HgI$_2$Te(*p*-MeO–C$_6$H$_4$)$_2$	63	98
HgCl$_2$Te(*o*-MeO–C$_6$H$_4$)$_2$	143–144	95
HgBr$_2$Te(*o*-MeO–C$_6$H$_4$)$_2$	84	95
HgI$_2$Te(*o*-MeO–C$_6$H$_4$)$_2$	80–81	95
HgCl$_2$Te(2,4-Me$_2$–C$_6$H$_3$)$_2$	106	93
HgBr$_2$Te(2,4-Me$_2$–C$_6$H$_3$)$_2$	99	93
HgI$_2$Te(2,4-Me$_2$–C$_6$H$_3$)$_2$	107–108	93
HgCl$_2$Te(2,5-Me$_2$–C$_6$H$_3$)$_2$	179–180	93
HgBr$_2$Te(2,5-Me$_2$–C$_6$H$_3$)$_2$	169–170	93
HgI$_2$Te(2,5-Me$_2$–C$_6$H$_3$)$_2$	166–167	93
(c) Complexes with unsymmetrical diaryl tellurides		
HgI$_2$TePh(*o*-tolyl)	133–134	101
HgCl$_2$TePh(*p*-tolyl)	91	99
HgBr$_2$TePh(*p*-tolyl)	54	99
HgI$_2$TePh(*p*-tolyl)	74	99
(d) Complexes with alkyl aryl tellurides		
HgBr$_2$TeMePh	124	87
(e) Complexes with diaryl ditellurides		
Yellow-HgI$_2$Te$_2$Ph$_2$	101–102	87
(HgCl$_2$)$_2$Te$_2$(*p*-EtO–C$_6$H$_4$)$_2$	110–112	114a
(HgCl$_2$)$_2$Te$_2$(*p*-MeO–C$_6$H$_4$)$_2$	114–115	114a
Yellow-HgBr$_2$Te$_2$(*p*-EtO–C$_6$H$_4$)$_2$	120–122	114a
Brown-HgBr$_2$Te$_2$(*p*-EtO–C$_6$H$_4$)$_2$	109–110	114a
Yellow-HgI$_2$Te$_2$(*p*-EtO–C$_6$H$_4$)$_2$	202–204	114a
Brown-HgI$_2$Te$_2$(*p*-EtO–C$_6$H$_4$)$_2$	125–126	114a

TABLE I (continued)

	M.p. (°C)	Ref.
(f) Hg complexes with tellurol ligands		
$Hg(TePh)_2$		111
$HgTe(p\text{-}EtO\text{-}C_6H_4)_2$	110–112	114a
$[PPh_4]Hg(TePh)_3$	130 (dec.)	113, 187
$[Ph_4P]_5Hg_3(TePh)_{11}$		113
PhTeHgCl	dec. >90	121
$p\text{-}EtO\text{-}C_6H_4TeHgCl$	160–161	114a
Te heterocycles		
	146–147	133

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[a] These complexes are presumably halo-bridged dimers as are the $TeEt_2$ and $Te(n\text{-}Bu)_2$ complexes on the basis of their far-IR spectra. [b] Probable structure is a telluronium salt ($[Me_2TePh]_2[HgI_4]$) analogous to the methyl analog [294].

appropriate mercuric salt in water, ethanol, or acetone. These derivatives were used as a means of characterizing the organotellurium products formed by the photolysis of acetophenone [87] and acetone [86] in the presence of a tellurium mirror (i.e., HgX_2TeMe_2, HgX_2TePh_2, $HgX_2MeTePh$ and $HgI_2Te_2Ph_2$ were isolated in the former case and HgX_2TeMe_2 ($X = Cl, I$) in the latter study). The facile formation of such insoluble mercuric halide complexes has been used as a means of characterizing liquid dialkyl tellurides (i.e., HgX_2TeMe_2 [84–87], $X = Cl, Br, I$; $HgX_2Te(n\text{-}C_5H_{11})_2$ [88]).

Reaction of di-n-amyl telluride with an equimolar amount of $HgCl_2$ in acetone gave a precipitate containing two components, which could not be separated [88]. Mercuric iodide gave, on concentration of the reaction solution, a viscous residue which could not be crystallized but from which the telluride was regenerated by thermolysis [88]. Mercuric bromide, however, gave a precipitate of the 1:1 adduct, which was recrystallized from acetone [88].

The adducts $HgX_2 \cdot TeMe_2$ ($X = Cl, Br, I$) were prepared by reacting cold acetone solutions of the two components, the adducts rapidly precipitating in quantitative yields [85]. They can be recrystallized from acetone but slowly liberate $TeMe_2$ in air [85].

The formation of $HgCl_2 \cdot TeMe_2$ by trapping the volatile product resulting from the action of various molds on potassium tellurite with a solution of mercuric chloride in concentrated HCl (Biginelli's solution) has also been described [84].

The related derivatives $HgCl_2TeR_2$ ($R = Et$, n-Bu), prepared by reacting ethanol solutions of mercuric chloride with the appropriate dialkyl telluride, have been formulated as chloro bridged dimers on the basis of their far-IR spectra [186]. Presumably the other $HgX_2 \cdot TeR_2$ derivatives are also dimeric (or polymeric, as proposed for HgX_2TeAr_2 derivatives on the basis of their Mössbauer spectra [114a]).

Dance and Jones [114a] have reported the synthesis and characterization of a variety of organotellurium–mercury(II) complexes. Reaction of α-Me_2TeI_2[*] with $HgBr_2$ in ethanol gave a 1 : 1 adduct as yellow needles. This adduct was shown to be a weak molecular complex between the products of an anion exchange reaction, $Me_2TeBr_2 \cdot HgI_2$, on the basis of ^{125}Te Mössbauer spectroscopy (the adduct had parameters similar to those of Me_2TeBr_2) and Raman spectroscopy ($\nu_{Te-Br} = 168, 147$ cm^{-1}). The complex decomposed on standing to give HgI_2 and α-Me_2TeBr_2. The ν_{Te-Br} values, which are about 20 cm^{-1} lower in the complex vs. α-Me_2TeBr_2, were interpreted in terms of appreciable $Hg \cdots Br$ interactions in the adduct rather than $Hg \cdots Te$ interaction. The same adduct was formed by the reaction of α-Me_2TeBr_2 and HgI_2 in ethanol. The complex completely dissociated in benzene, precluding a molecular weight determination.

The above observations suggested the use of mercuric halides to effect anion exchange in dialkyl tellurium diiodides. Indeed, refluxing α-Me_2TeI_2 with $HgBr_2$ in a solvent in which α-Me_2TeBr_2 is soluble but HgI_2 is insoluble (e.g., $CHCl_3$) allowed essentially quantitative conversion to α-Me_2TeBr_2 after filtration of the insoluble red HgI_2 and evaporation of the filtrate [114a].

An analogous adduct between α-Me_2TeI_2 and $HgCl_2$ could not be isolated, but reaction of the two compounds in refluxing chloroform did result in quantitative anion exchange [114a]. Diphenyl mercury forms adducts with α-R_2TeI_2 (R = Me, Et) [114a] with the composition $HgPh_2 \cdot 2R_2TeI_2$, the complexes readily precipitating from chloroform solutions. Dance and Jones [114a] have studied the methyl derivative by a variety of physical techniques and formulated it as a telluronium salt (i.e., $[PhMe_2Te]_2HgI_4$ or $[PhMe_2Te^+ I^-]_2 \cdot HgI_2$): ^{125}Te Mössbauer parameters indicate tellurium atoms in essentially a trigonal environment; conductivity shows a 2/1 electrolyte in DMF; the mass spectrum indicates phenyl transfer to tellurium has occurred; ^{13}C NMR confirms a Te–Ph group by the observation of a doublet ($J_{^{125}Te-^{13}C} = 171.6$ Hz) for the aromatic carbon bonded to the tellurium; the Raman spectrum shows $\nu_{Te-Me} = 533$ cm^{-1}, $\nu_{Te-Ph} = 248, 262$ cm^{-1}, $\nu_{Te-I} = 125$ cm^{-1}.

The mercuric chloride adduct of cyclotellurobutane was isolated as white

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[*] Two forms of Me_2TeI_2 have been established by single-crystal X-ray diffraction studies, the true dialkyl tellurium diiodide (α-form) [293] and the telluronium salt $[Me_3Te]^+[MeTeI_4]^-$ (β-form) [294].

crystals when alcohol solutions of the components were mixed [133]. The telluride was released on warming the complex in aqueous NaOH [133].

Diaryl telluride complexes. Lederer [89–101] prepared a number of crystalline complexes of mercuric halides with diaryl tellurides (HgX_2TeAr_2; X = Cl, Br, I) as a routine method of characterizing the diaryl tellurides he prepared by reaction of Grignard reagents with "TeX_2" [11] (see Table I). The chloride complexes were generally prepared by simply shaking an aqueous solution of $HgCl_2$ with an ethereal solution of the telluride. Ethanol or acetone was generally used for the formation of the bromo and iodo complexes. No structural characterization of derivatives of this type was reported until the recent work of Dance and Jones [114a]. The complexes HgX_2TeAr_2 (Ar = Ph, p-EtO–C_6H_4; X = Cl, Br, I) have been formulated on the basis of Mössbauer spectroscopy (parameters characteristic of telluronium salts such as $Ph_3Te^+Cl^-$; $\sigma = 0.35$ mm s^{-1}; $\Delta = 5.83$ mm s^{-1}), IR spectroscopy, and Raman spectroscopy as polymeric species containing $[Ar_2Te^+–HgX]X^-$ units linked through bridging halide groups to give infinite chains [114a]. The Raman spectra of these complexes (e.g., $\nu_{Hg-Te} = 100-140$ cm^{-1}) suggest that the strength of the Hg–Te interaction increases with increasing electronegativity of the halogen (Ph_2TeHgX_2: X = Cl, 133 cm^{-1}; X = Br, 124 cm^{-1}; X = I, 118 cm^{-1}).

Diaryl ditelluride complexes. The first report [87] of a diaryl ditelluride complex involved the use of mercuric iodide to complex the products resulting from the photolysis of acetophenone in the presence of a tellurium mirror (the products were $TePh_2$, $TeMe_2$, PhTeMe and Ph_2Te_2). The complex with diphenylditelluride was reported to be a yellow solid which became orange at 86°C, began to sinter and darken at 92°C, was almost black at 96°C, and melted to a russet-colored liquid at 101–102°C. This melting behavior was reported to be the same as that of an authentic sample of the diphenylditelluride mercuric iodide complex, although no synthetic details or other physical data for the complex were reported [87]. Dance and Jones [114a] have prepared three general types of mercuric halide complexes with diarylditellurides by reaction of the components in ethanol, characterization being by ^{125}Te Mössbauer and far-IR spectroscopy. The type of complex isolated depends on the stoichiometry of the reaction and the mercuric halide used. Reaction of Ar_2Te_2 (Ar = p-MeO–C_6H_4, p-EtO–C_6H_4) and $HgCl_2$ (1:2 molar ratio) in hot ethanol followed by cooling gave yellow products formulated on the basis of elemental analysis as $ArTeHgCl_2$. The ^{125}Te Mössbauer spectra of these complexes indicate that there is only one type of Te present and that it is trigonally coordinated. These complexes were formulated as $Ar_2Te_2(HgCl_2)_2$, analogous organosulfide complexes having been reported [114a].

Yellow complexes of the type $(p\text{-EtO–}C_6H_4)_2Te_2 \cdot HgX_2$ ($X = Br, I$) were isolated by the reaction of the ditelluride with the mercuric halide (1 : 2 molar ratio) in warm ethanol [114a]. The Mössbauer spectra of these yellow complexes indicate a similar Te environment as in the above $HgCl_2$ complexes. With a 1 : 1 molar ratio, complexes were obtained whose ^{125}Te Mössbauer spectra indicated that the Te atoms are two-coordinate and that all Te sites are equivalent, thereby suggesting that the diarylditelluride is weakly complexed in such adducts.

Although cleavage of Te–Te bonds in reactions of diarylditellurides with transition metal substrates to give bridging or terminal $TeAr^-$ ligands is an established reaction for these derivatives (Fig. 5), they can also coordinate to metals with this bond intact.

Indeed, the first crystal structure has recently been reported for a diarylditelluride complex, $(OC)_3Re(\mu\text{-}Br)_2(\mu\text{-}Te_2Ph_2)Re(CO)_3$ [130b], related complexes with bridging S_2Ph_2 [295a], S_2Me_2 [295b], Se_2Ph_2 [296a], and Se_2Me_2 [296b] as well as the parent S_2^{2-} [297] and Se_2^{2-} [298,299] ligands having been described previously. Complexes with $\eta^2\text{-}S_2$ (e.g., $Ru(\eta^2\text{-}S_2)(CO)_2(PPh_3)_2$ [300]) and $\eta^2\text{-}Se_2$ (e.g., $Os(\eta^2\text{-}Se_2)(CO)_2(PPh_3)_2$ [301]) chelating ligands have also been reported recently.

Aryl tellurol complexes. The first derivative incorporating an Hg–TeAr linkage (PhTeHgCl) was reported by Lederer [121], who reacted $HgCl_2$ with a solution of "HTePh" (obtained by cleavage of Te_2Ph_2 with Na in ethanol followed by acidification of the NaTePh solution and ether extraction). The analog, $p\text{-EtO–}C_6H_4TeHgCl$, was prepared by refluxing a solution of equimolar amounts of $Hg(Te(p\text{-EtO–}C_6H_4))_2$ and $HgCl_2$ [114a].

Metallic mercury reacts with Te_2Ar_2 ($Ar = Ph$ [111], $p\text{-EtO–}C_6H_4$ [114a]) in benzene at room temperature to give $Hg(TeAr)_2$ derivatives whose insolubility in organic solvents suggests that they are polymeric materials with bridging $ArTe^-$ ligands. This type of oxidative addition reaction is analogous to that previously described [109] for the reaction of $Pd(PPh_3)_4$ with Te_2Ar_2 ($Ar = 2\text{-thienyl}, p\text{-EtO–}C_6H_4$) to give $[Pd(PPh_3)TeAr(\mu\text{-}TeAr)]_2$ (eqn. 3). Complex mercuric phenyltellurol complexes were prepared by reaction of NaTePh with $Hg(TePh)_2$ [113]

$$\begin{array}{lllll} Ph_2Te_2 & \xrightarrow{Na/liq.\ NH_3} & \{NaTePh\} & \xrightarrow{Hg(TePh)_2/liq.\ NH_3} & [Hg(TePh)_3]^- \\ & & & \uparrow C_6H_6 & \downarrow Ph_4PCl \\ & & & Hg + Te_2Ph_2 & [Ph_4P][Hg(TePh)_3] \end{array} \tag{25}$$

The tetraphenylphosphonium salt is soluble in THF and $CHCl_3$, insoluble in petroleum ether, benzene, ethanol and ether, and air stable in the solid state for several weeks. The tris complex can be readily formed in liquid ammonia

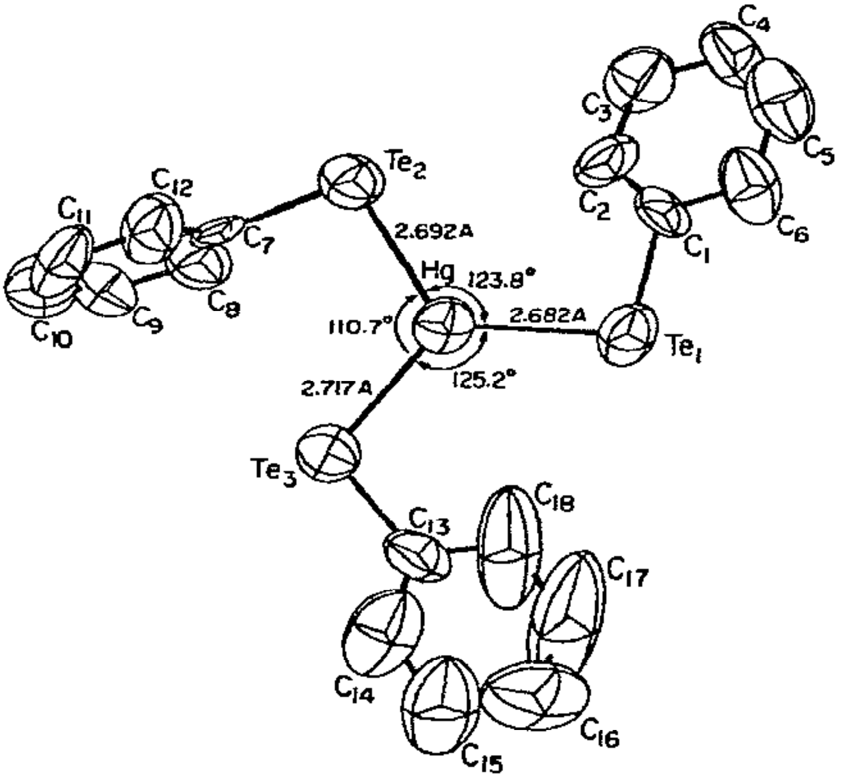


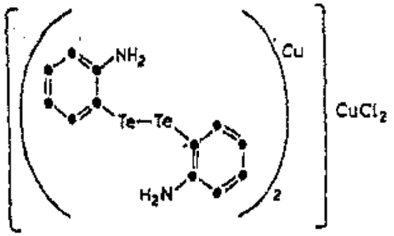
Fig. 6. Molecular structure of [Ph_4P][$Hg(TePh)_3$]. Reproduced with permission from Chem. Ber., 110 (1977) 3672.

by the above reaction, but attempts to react the former complex with another equivalent of Ph_4PTePh in $CHCl_3$ to give $Hg(TePh)_4^{2-}$ gave instead $Hg_3(TePh)_{11}^{5-}$, the Ph_4P^+ salt being isolated as orange-red crystals.

A trigonal planar (D_{3h}) structure for the [$Hg(TePh)_3$]$^-$ anion, proposed on the basis of a detailed study of its far-IR and Raman spectra (Te–Hg vibrations; $\nu_s = 120$ cm^{-1} (Raman); $\nu_{as} = 148$, 137 cm^{-1} (IR) [113]) was subsequently confirmed by a single-crystal X-ray diffraction study of [Ph_4P][$Hg(TePh)_3$] [187] (Fig. 6). The complex has an ionic structure with distances between Te and Hg atoms of adjacent $Hg(TePh)_3^-$ units being generally longer than 10 Å. The three $TePh^-$ ligands in the anion are coordinated in a propeller-like arrangement about the central Hg atom in an approximate planar $HgTe_3$ unit. The analogous thio- and selenophenolate complexes are believed to be trigonal pyramidal, this being one of the few reported three-coordinate trigonal planar Hg(II) complexes. The structure of [Ph_4P]$_5$[$Hg_3(TePh)_{11}$] is unknown.

TABLE 2

Cu, Ag, Au complexes

	Physical data [a]	Ref.
Cu complexes		
(a) Diaryl telluride complexes		
$CuCl(TePh_2)_3$	$\nu_{Cu-Cl}+\nu_{Te-Ph}=260-270$	180
$(TePh_2)_2Cu(\mu\text{-}Br)_2Cu(TePh_2)_2$	$\nu_{Cu-Br}=155, 109$	180
$(TePh_2)_2Cu(\mu\text{-}I)_2Cu(TePh_2)_2$	$\nu_{Cu-I}=161, 111$	180
$(Te(p\text{-tolyl})_2)_2Cu(\mu\text{-}Cl)_2Cu(Te(p\text{-tolyl})_2)_2$	$\nu_{Cu-Cl}=183, 117$	180
$(Te(p\text{-tolyl})_2)_2Cu(\mu\text{-}Br)_2Cu(Te(p\text{-tolyl})_2)_2$	$\nu_{Cu-Br}=164, 92$	180
$CuI(Te(p\text{-tolyl})_2)_2$	$\nu_{Cu-I}=163$	180
$(Te(p\text{-EtO}-C_6H_4)_2)_2Cu(\mu\text{-}Cl)_2Cu(Te(p\text{-EtO}-C_6H_4)_2)_2$	$\nu_{Cu-Cl}=185, 128$ $\delta=0.09;\ \Delta=9.0$	171 180
$Te(p\text{-EtO}-C_6H_4)_2Cu(\mu\text{-}Br)_2CuTe(p\text{-EtO}-C_6H_4)_2$	$\nu_{Cu-Br}=163, 100$ $\delta=0.18;\ \Delta=8.8$	171 180
$Te(p\text{-EtO}-C_6H_4)_2Cu(\mu\text{-}I)_2CuTe(p\text{-EtO}-C_6H_4)_2$	$\delta=0.15$ $\Delta=9.2$	171 180
(b) Diaryl ditelluride complexes		
$CuClPh_2Te_2$	$\delta=0.32;\ \Delta=9.5$ $\nu_{Cu-Cl-Cu}=222$ $\nu_{Te-Te}=170$	 116 117
$CuCl(p\text{-EtO}-C_6H_4)_2Te_2$	$\delta=0.43;\ \Delta=9.2$	116, 117
$CuBrPh_2Te_2$	$\delta=0.38;\ \Delta=8.9$	116, 117
$CuBr(p\text{-EtO}-C_6H_4)_2Te_2$	$\delta=0.24;\ \Delta=9.2$	116, 117
	$\nu_{NH}=3350, 3270, 3205, 3120$ $\Lambda_M(MeCN)=136$	63, 129

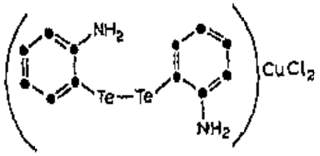
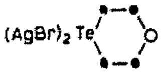
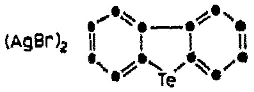
	$\nu_{NH} = 3240$ v. br. Λ_M (MeCN) = 65	63, 129
(c) Dialkyl ditelluride complexes		
$CuClEt_2Te_2$	$\delta = 0.27$; $\Delta = 9.7$	116, 117
$CuBrEt_2Te_2$	$\delta = 0.36$; $\Delta = 9.3$	116, 117
$CuCl(n\text{-}Bu)_2Te_2$	$\delta = 0.40$; $\Delta = 9.4$	116, 117
$CuBr(n\text{-}Bu)_2Te_2$	$\delta = 0.37$; $\Delta = 9.4$	116, 117
$CuCl(n\text{-}C_5H_{11})_2Te_2$	$\delta = 0.32$; $\Delta = 9.3$	116, 117
$CuBr(n\text{-}C_5H_{11})_2Te_2$	$\delta = 0.36$; $\Delta = 9.2$	116, 117
(d) Aryl tellurol complexes		
PhTeCu	$\delta = 0.20$; $\Delta = 9.4$	116, 117, 119
$p\text{-}EtO\text{-}C_6H_4TeCu$	$\delta = 0.31$; $\Delta = 9.5$	116, 117
(e) Alkyl tellurol complexes		
EtTeCu	$\delta = 0.15$; $\Delta = 9.7$	116, 117
n-BuTeCu	$\delta = 0.27$; $\Delta = 9.6$	116, 117
$n\text{-}C_5H_{11}TeCu$	$\delta = 0.18$; $\Delta = 9.6$	116, 117
Ag' complexes		
(a) Dialkyl and alkyl aryl telluride complexes		
$AgITeMe_2$	M.p. 73–74°C	182
$(AgI)_2TeMe_2$	M.p. 137–138°C	182
$(AgBr)_2Te(n\text{-}Bu)_2$	$n_D^{20} = 1.6137$ B.p. 195°C (dec.)	135
$(AgBr)_2TePhEt$	B.p. 200°C (dec.)	135
$(AgBr)_2Te(CH_2CH_2CN)_2$	Pale-brown liquid	135
$(AgBr)_2TePhCOEt$	Pale-yellow viscous liquid	135
$(AgBr)_2TePhCOPh$	Pale-yellow viscous liquid	135

TABLE 2 (continued)

	Physical data [a]	Ref.
(b) Diaryl telluride complexes		
$(AgBr)_2Te(2\text{-naphthyl})Ph$	Pale-yellow crystals	135
$(AgBr)_2Te(p\text{-}MeO{-}C_6H_4)_2$	M.p. 168°C (sealed tube)	134
	Te binding energy = 585.4 eV (vs. 584.7 eV for $Te(p\text{-}MeO{-}C_6H_4)_2$)	135
$(AgI)_2TePh_2$	B.p. 180°C (dec.)	135
$(AgCl)_2TePh_2$		135
$(AgBr)_2Te(o\text{-tolyl})_2$	Pale-yellow viscous liquid	135
$(AgBr)_2Te(2\text{-naphthyl})_2$	Pale-yellow viscous liquid	135
$(AgBr)_2Te(p\text{-}NMe_2{-}C_6H_4)_2$	Pale-yellow crystals	135
$(AgBr)_2TePh(p\text{-tolyl})$	Pale-yellow viscous liquid	135
$(AgBr)_2TePh(p\text{-}Br{-}C_6H_4)$	Pale-yellow viscous liquid	135
(c) Tellurium heterocycles		
	Pale-yellow solid	135
	Pale-yellow solid	135

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[a] Wavelengths, ν, in cm^{-1}; equivalent conductance, Λ, in $ohm^{-1}\ cm^2\ mol^{-1}$; Mössbauer data: δ values are given ± 0.08 mm sec^{-1} vs. $^{125}Sb/Cu$ and Δ values are given ± 0.1 mm sec^{-1}.

(ii) Cu, Ag, Au

Cu

Diaryl telluride complexes. Several complexes of cuprous halides with $TeAr_2$ (Ar = Ph, *p*-tolyl, *p*-$CH_3O-C_6H_4$, and *p*-$EtO-C_6H_4$) have been reported by McWhinnie and Rattanaphani [180]. The complexes, prepared by addition of alcohol solutions of the telluride to aqueous solutions of the halide dissolved in 1 M hydrohalic acid (HCl, HBr) or saturated KI solutions, were obtained with the indicated stoichiometries (Table 2) regardless of the metal : ligand ratio used in the reaction. This is in marked contrast to analogous phosphine systems, which give a wide range of stoichiometries, depending on reaction conditions (e.g., $CuX(PR_3)_n$: $n = 1$ [302], 2 [303], 3 [304,305]; $Cu_2Cl_2(PPh_3)_3$ [304–306]). The moderately high conductivities of these complexes in acetonitrile (61–77 ohm^{-1} cm^2 mol^{-1} vs. values of 120–160 for 1 : 1 electrolytes) was attributed to solvolysis reactions involving molecular complexes rather than the presence of double salts (i.e., $[CuL_n][CuX_2]$; $n = 2$, 4) on the basis of the ν_{Cu-X} bands in their far-IR spectra. This conclusion is supported by measurements of molar conductivities of these solutions as a function of the square root of concentration, which show behavior typical of weak rather than strong electrolytes. Indeed, acetonitrile is known to function as a stabilizing ligand for Cu(I) [307,308]. The most common structure found for these complexes involves dimers with two bridging halide ligands (i.e., $(TeAr_2)_2Cu(\mu\text{-}X)_2Cu(TeAr_2)_2$; X = Cl, Br; Ar = Ph, *p*-tolyl, X = I, Ar = Ph), the Cu(I) assuming its characteristic tetrahedral geometry [309]. A wide variety of Cu(I) halide [304–306] and thiocyanate [310] complexes have been shown to have such dimeric structures. This formulation is supported by their far-IR spectra, two bridge Cu–X–Cu stretching vibrations typically occurring at lower energies than expected for singlet terminal Cu–X vibrations [311–314]. The 2 : 1 complex of CuI with Te(*p*-tolyl)$_2$ exhibited an anomalous X-ray powder pattern, and its far-IR spectrum had a ν_{CuI} at 163 cm^{-1}, a value typical of a terminal Cu–I bond [311–314]. This complex, therefore, has been tentatively assigned a monomeric structure with trigonal planar Cu(I), a stereochemistry which has been well established by several single-crystal X-ray diffraction studies (e.g., $[CuCl(SPMe_3)]_3$, $[Cu(SPMe_3)_3]ClO_4$, $[Cutu_2Cl]$ [315]).

Cuprous iodide was also anomalous in its reactions with $TePh_2$ and Te(*p*-$EtO-C_6H_4$)$_2$, 1 : 1 complexes being obtained. Of the three possible structures for such complexes [linear two-coordinate (e.g., $[Cu(CN)_2]^-$ [316]); tetrameric cubane structure (e.g., $[CuI(AsEt_3)]_4$ [317]); or dimeric trigonal planar with two halo bridges (e.g., $[CuCl(P(C_6H_{11})_3)]_2$ [302]), the last formulation was favored on the basis of the occurrence of strong ν_{CuI} bands at 161 and 111 cm^{-1} for the $TePh_2$ complex. The IR data for CuI(Te(*p*-EtO

$-C_6H_4)_2$) did not allow a structural formulation of this complex.

A Mössbauer study [171] of a series of complexes of several metals with Te(p-EtO$-C_6H_4)_2$ indicated that this ligand functions primarily as a σ donor, using its lone p electron pair with the following order of Lewis acidity established from the measured quadrupole splittings: Hg(II) > Pt(II) > Pd(II) > Cu(I).

Diaryl- and dialkylditelluride complexes. Complexes of cuprous halides with diarylditellurides ($CuXAr_2Te_2$; X = Cl, Br; Ar = Ph, p-EtO$-C_6H_4$) have been prepared by addition of an equimolar amount of Ar_2Te_2 in ether solution to an acetonitrile solution of the cuprous halide (in a nitrogen atmosphere), orange to red precipitates of the complexes being obtained on cooling the reaction solutions [116,117]. The formulation of these complexes as ditelluride complexes with the Te–Te bond intact is based on their color (characteristic of the free ditellurides, polymeric $TeAr^-$ bridged species resulting from Te–Te cleavage generally giving dark brown materials) and the assignment of a ν_{Te-Te} absorption for $CuCl(Te_2Ph_2)$ at 170 cm^{-1} in its far-IR spectrum. This latter absorption is apparently enhanced by coordination, the corresponding band for the free ditelluride occurring at 167 cm^{-1} in its Raman spectrum. The occurrence of a ν_{Cu-Cl} at 230 cm^{-1} in the far-IR [116,117] indicates the presence of bridging rather than terminal chloro ligands. Coordination of both Te atoms of the ditelluride ligands in these complexes is supported by their ^{125}Te Mössbauer spectra, which both give good computer fits for one quadrupole doublet [116,117]. The chemical isomer shifts (δ) are all the same within experimental error and are similar to the values for the free ditellurides, indicating that no significant change in hybridization at Te has occurred on coordination. The quadrupole splitting values were also all very similar but lowered vs. the free ditellurides,

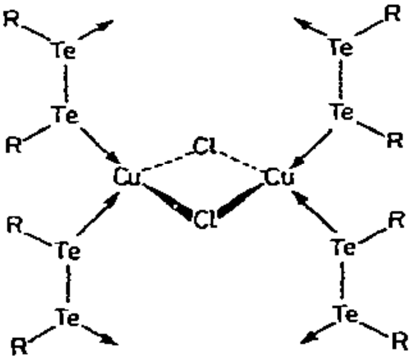
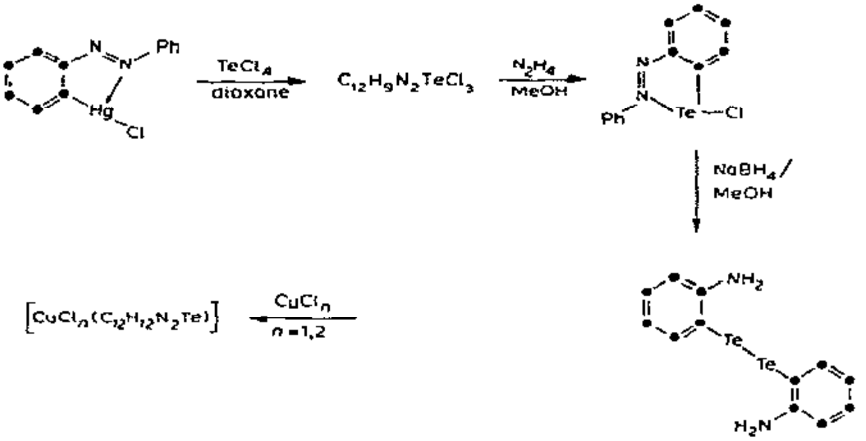


Fig. 7. Proposed structure for diorganoditelluride complexes with cuprous halides.

indicating coordination of the *p*-lone pair, resulting in a lowering of the *p* orbital imbalance. Comparison of these quadrupole splittings with those of Hg(II) complexes ($(EtO-C_6H_4)_2Te_2HgX_2$; X = Cl, Br; $\Delta = 8.9-9.5$ mm sec^{-1} for the Cu(I) complexes vs. 5.1 mm sec^{-1} for the Hg(II) complexes) indicates that Hg(II) has greater Lewis acidity than Cu(I) with respect to this ditelluride ligand. On the basis of the above spectroscopic data, polymeric structures have been proposed for these complexes (Fig. 7). Attempts to obtain single crystals of these complexes for a definitive X-ray diffraction study resulted in decomposition.

Complexes of di(*o*-aminophenyl)ditelluride with CuCl and $CuCl_2$ have also been reported [63,129]. This new ditelluride was prepared by borohydride reduction of the novel *o*-metallated derivative, (2-phenylazophenyl-C,N′)-tellurium(II) chloride



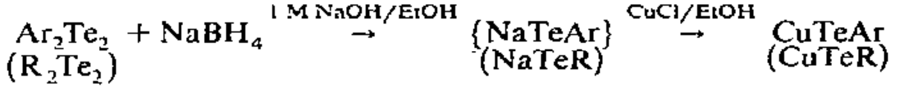
(26)

Reaction of an ethereal solution of di-2-aminophenyl ditelluride with an acetonitrile solution of CuCl under nitrogen gave a brown 1 : 1 complex [63,129]. Unlike the other reported complexes of cuprous halides with ditellurides [116,117], this product could be recrystallized from acetonitrile. The molar conductivity of the complex in acetonitrile indicated a 1 : 1 electrolyte, and its IR spectrum in the ν_{NH} region (Table 2) supports coordination of one of the amino functions of the ditelluride. The complex was formulated as $[Cu((o\text{-}NH_2-C_6H_4)_2Te_2)_2][CuCl_2]$, the cation containing two bidentate ditelluride ligands and tetrahedral Cu(I).

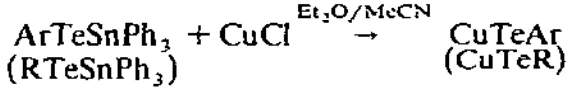
An analogous reaction with anhydrous $CuCl_2$ also gave a 1 : 1 complex [63,129]. This complex, however, has not been well characterized (it gives a molar conductivity of 65 ohm^{-1} cm^2 mol^{-1} in acetonitrile and has a very broad absorption peaking at 3240 cm^{-1} in the ν_{NH} region). The 1 : 1 stoichiometry of the complex was confirmed by quantitative recovery of the ditelluride after treatment with EDTA solution.

Several analogous derivatives with dialkylditellurides have also been prepared $[Te_2R_2]CuX$ (R = Et, n-Bu, n-C_5H_{11}; X = Cl, Br) [116,117] and have been assigned structures similar to the aryl derivatives on the basis of their Mössbauer spectra (Table 2) and color.

Aryl- and alkyltellurol complexes. Highly insoluble and presumably polymeric tellurol complexes, CuTeR (R = Et, n-Bu, n-C_5H_{11}) and CuTeAr (Ar = Ph, *p*-EtO–C_6H_4), have been prepared by the following two routes [116,117]



$$\underset{(R_2Te_2)}{Ar_2Te_2} + NaBH_4 \xrightarrow{1\ M\ NaOH/EtOH} \underset{(NaTeR)}{\{NaTeAr\}} \xrightarrow{CuCl/EtOH} \underset{(CuTeR)}{CuTeAr} \tag{27}$$



$$\underset{(RTeSnPh_3)}{ArTeSnPh_3} + CuCl \xrightarrow{Et_2O/MeCN} \underset{(CuTeR)}{CuTeAr} \tag{28}$$

The similarity of the Mössbauer isomer shifts for these complexes with those observed for diorganotellurides and $ArTeSnPh_3$ suggests that the Te bridges two copper atoms and has a coordination number of three. In a structure in which the Te bridged three copper atoms and has a coordination number of four, considerable rehybridization at the tellurium would be expected, resulting in significant removal of *s* electron density corresponding to one of the localized nonbonding electron pairs and a resulting large shift in the chemical isomer shift vs. TeR_2 derivatives.

Ag

Dialkyl telluride complexes. The Ag(I) complexes $AgI(TeMe_2)_2$ and $(AgI)_2$ $TeMe_2$ have been reported by Coates [182]. Addition of $TeMe_2$ in acetone to a solution of AgI in concentrated aqueous KI (2/1 molar ratio) gave a white precipitate of $AgI \cdot 2\,TeMe_2$ which was recrystallized from acetone with some decomposition (m.p. 73–74°C; white solid). The complex smells strongly of $TeMe_2$, and the ligand can be quantitatively removed by heating at 180°C under vacuum. Addition of a solution of $AgNO_3$ to an acetone solution of the complex gives a heavy yellow precipitate of AgI, leading to the suggestion of the formulation $[Ag(TeMe_2)_2]^+I^-$. However, a far-IR study or a single-crystal X-ray diffraction analysis of this compound is necessary to establish its actual structure. A related compound, $AgCl \cdot 2PPh_3$ [318], was recently shown by single-crystal X-ray diffraction to be a chloro-bridged dimer, the coordination polyhedron around the silver being a distorted tetrahedron. Phosphine complexes with AgI generally form tetrameric complexes with bridging iodo ligands (e.g., $[AgI \cdot PEt_3]_4$ [319], $[AgI \cdot PPh_3]_4$ [320,321]).

The complex $(AgI)_2 \cdot TeMe_2$ (m.p. 137–138°C, dec. to black liquid) precipitates on addition of an acetone solution of $TeMe_2$ to a solution of AgI in concentrated aqueous KI (1:2 molar ratio) [182]. It is insoluble in water, alcohol, acetone and benzene and loses $TeMe_2$ quantitatively on heating at 180°C under vacuum.

The formation constants of Ag(I) complexes with the water-soluble ligands $X(CH_2CH_2CO_2H)_2$ (X = O, S, Se, Te) have been measured potentiometrically, a stability order $Te > Se > S \gg O$ being found [181].

Complexes of AgBr with $Te(n\text{-}Bu)_2$, $Te(CH_2CH_2CN)_2$, PhTeEt, PhTeCOEt, PhTeCOPh and (2-naphthyl)Te(CH_2Ph), having the general formula $(AgBr)_2TeR_2$, were reported in a recent patent [135] which describes their use as light-sensitive compositions in photothermographic elements.

These complexes were prepared by adding a solution of AgBr dissolved in aqueous KBr to an acetone solution of the ligand (a 1:2 molar ratio of ligand to AgBr was used). No spectroscopic data relating to the structure of these complexes were reported. Their photoelectron spectra, however, were recorded and showed that the tellurium binding energy increased by ca. 0.7–0.9 eV in the Ag(I) complexes vs. the free ligands [135]. Presumably the complexes are dimeric with bridging telluride ligands, a bridging bonding mode for $TeMe_2$ having been previously proposed on the basis of NMR data for the complexes $(Bu_4N)_2[X_3Pt(\mu\text{-}TeMe_2)PtX_3]$ (X = Cl, Br) [176].

Diaryl telluride complexes. The first examples of diaryl telluride complexes of Ag(I) were recently reported in patents [134,135] which describe their synthesis and use in photothermographic imaging elements. Complexes of the type $(AgX)_2TeAr_2$ (X = Br; Ar = p-MeO–C_6H_4 [134,135]; o-Me–C_6H_4 [135]; 2-naphthyl [135]; p-Me_2N–C_6H_4 [135]; (Ph)(p-tolyl) [135]; (Ph)(p-Br–C_6H_4) [135] and X = Cl, I; Ar = Ph [135]) have been reported. These complexes presumably have the same structures as the alkyl analogs [135]. As observed for the dialkyl telluride derivatives the ESCA spectra of these complexes showed an increase of ca. 0.7–0.8 eV in the tellurium binding energy upon coordination to Ag(I) [135].

Tellurium heterocycles. Complexes of the formula $(AgX)_2L$ (L = 1-oxa-4-telluracyclohexane, X = NO_3 [134], Br [134]; L = dibenzotellurophene, X = Br [135]) were prepared by the method used for the above alkyl and aryl telluride complexes (i.e., addition of an aqueous solution of $AgNO_3$ or $AgBr_2^-$ to an acetone solution of the ligand). The ESCA data for these complexes showed the typical increase in Te binding energy of 0.6–0.9 eV vs. the free ligand [135]. No other data, other than elemental analysis, were reported for these complexes.

Although Ag(I) salts form a wide variety of complexes with phosphines (i.e., AgL_nX; X = anionic ligand, n = 1–3 or noncoordinating counteranion,

Au

The formation constant of $AuBrTeMe_2$ was measured by potentiometric titration of $Au(MeCN)_2^+$ in acetonitrile ($K = 7.6 \times 10^{12}$), although the product was not isolated [183]. The following stability order was found from a series of titrations: $Me_2S < Me_2Se < Ph_3Sb < PhNC \sim Ph_3As < Me_2Te < MeCN \sim Ph_3P < Ph_2MeP < PhMe_2P$.

The reaction of an ethanol solution of $TePh_2$ with aqueous $AuCl_3$ was reported to cause precipitation of a grey chloroaurate complex (m.p. 154–156°C), but no other details were reported [184]. Indeed, the proposed oxidation state of the gold, Au(III), is questionable, since phosphines are known to reduce Au(III) readily to Au(I) with stabilization of the lower oxidation state by complexation with excess of the ligand (e.g., $AuPPh_3Cl$ [322], $AuP(OPh)_3Cl$ [323]). Analogous chemistry is reasonable for diorganotellurides, facile oxidation to TeR_2X_2 ($X = Cl$, Br, I) by oxidants such as halogens and transition metal chlorides being characteristic reactions of such derivatives [11]. The synthesis of transition metal complexes of diorganotellurides by such ligand reduction processes, well established for Au(I) [184,323], Rh(I) [120] and Cu(I) [310] chemistry using phosphorus and sulfur ligands, is an area that remains to be explored.

(iii) Ni, Pd, Pt

Ni

Only one paper [122] has described the synthesis of well-characterized Ni compounds with organotellurium ligands. The compounds $\pi CpNi(P(n\text{-}Bu)_3)(Te\text{–}X\text{–}C_6H_4)$ ($X = p\text{-}OMe$; p-Me, H, p-Cl, $m\text{-}CF_3$) have been prepared by metathetical reactions

$$\left[\pi CpNi(P(n\text{-}Bu)_3)_2\right]^+ Cl^- + NaTe(X\text{–}C_6H_4) \rightarrow$$
$$\pi CpNi(P(n\text{-}Bu)_3)(Te\text{–}X\text{–}C_6H_4) + NaCl + P(n\text{-}Bu)_3 \quad (29)$$

These complexes, which are stable in the solid state under an inert atmosphere and moderately stable in air, are soluble in benzene and hexane but react with CH_2Cl_2 and CCl_4 to give the complex $\pi CpNiP(n\text{-}Bu)_3Cl$. They react with methyl iodide in benzene solution to give $\pi CpNiP(n\text{-}Bu)_3I$ and $MeTeX\text{–}C_6H_4$. The ^1H NMR spectra of the complexes show a signal at τ 8.3–9.5 ppm due to the phosphine ligand and a sharp singlet at ca. 4.9 ppm due to the cyclopentadienyl protons, the position of the latter resonance showing a linear relationship with the value of the Hammett constant of the substituent in the $-X\text{–}C_6H_4$ ligand. Comparison of these NMR results with those of the corresponding S and Se analogs indicates that the order of transmission of polar effects of the X substituent through the Ni–E ($E = S$, Se, Te) bonds to influence the electron density in the πCp ring is $S < Se < Te$ ($\rho = -17.9$, -18.7 and -19.3, respectively).

The reaction of $Ni(CO)_4$ with $TePh_2$ gave only thermal decomposition with deposition of Te(0) and Ni(0) [191]. Bergman and Engman [159] have reported the synthesis of carboxylic acids by the reaction of $Ni(CO)_4$ with aryl tellurium chlorides in DMF

$$ArTeCl_3 + 2\,Ni(CO)_4 \xrightarrow[(2)\ H_2O]{(1)\ DMF\ (70°C)} ArCO_2H + NiCl_2 + NiTe + 7\,CO + HCl \tag{30}$$

$$Ar_2TeCl_2 + Ni(CO)_4 \xrightarrow[(2)\ 2\ H_2O]{(1)\ DMF(70°C)} 2\,ArCO_2H + NiTe + 2\,CO + 2\,HCl \tag{31}$$

A mechanism involving the oxidative addition of the components of ArTeCl followed by CO insertion has been proposed for this transformation. In contrast to the analogous reactions with aryl mercuric chlorides, which give exclusively the diaryl ketones, this procedure gives predominantly the carboxylic acid with only small amounts of the diaryl ketones as side products. The facile synthesis of $ArTeCl_3$ derivatives with a wide range of functional groups suggests that this chemistry may have considerable utility in organic synthesis.

Pd

Dialkyl telluride complexes. The first monomeric Pd(II) complex with a dialkyl telluride (i.e., $PdCl_2(TeEt_2)_2$) was prepared in 1957 by Chatt and Venanzi [19] by reacting an aqueous solution of $(NH_4)_2PdCl_4$ with $TeEt_2$. The chloro-bridged dimeric analog of this complex and the $Te(n\text{-}Pr)_2$ derivative were also prepared in this work by the reaction of Na_2PdCl_4 with one equivalent of the telluride in ethanol. Alternatively, the dimers can be prepared by reaction of equivalent amounts of Na_2PdCl_4 and $PdCl_2(TeR_2)_2$ in ethanol.

Subsequent studies reported the far-IR [164,166], Raman [164], ^1H NMR [162,163,166,172,173], UV-visible [166] spectra and dipole moments in benzene [164] of the complexes $Pd(TeEt_2)_2X_2$ ($X = Cl$, Br, I).

The chloro and bromo monomeric complexes were prepared by shaking an ethanol solution of the telluride with an aqueous solution of K_2PdX_4 ($X = Cl$, Br), and the iodo complex was prepared by a metathetical reaction between the chloro complex and KI in acetone or ethanol.

The range for the ν_{Pd-Te} vibrations was reported as 135–157 cm^{-1} [166], a range somewhat lower than that reported for the $TeMe_2$ analogs [160]. The complex $PdCl_2(TeEt_2)_2$ has two ν_{Pd-Cl} bands in its solid-state IR spectrum indicative of *cis* geometry, but the bromo and iodo complexes both give one

TABLE 3

Ni, Pd, Pt complexes

	Misc. data	Ref.
Ni complexes		
π CpNi(P(n-Bu)$_3$)TePh	M.p. 49–50°C	122
π CpNiP(n-Bu)$_3$Te-*p*-MeO-C$_6$H$_4$	M.p. 53–54°C	122
π CpNiP(n-Bu)$_3$Te-*p*-tolyl	M.p. 38–39°C	122
π CpNiP(n-Bu)$_3$Te-*p*-Cl-C$_6$H$_4$	M.p. 47–48°C	122
π CpNiP(n-Bu)$_3$Te-*m*-CF$_3$-C$_6$H$_4$	M.p. 43–44°C	122
Pd complexes		
(a) Dialkyl telluride complexes		
TeMe$_2$ClPd(μ-Cl)$_2$PdClTeMe$_2$	ν_{Pd-Cl} [a] (mull) = 348 (t), 270 (b), 289 (b) cm^{-1} Red-brown	160, 161
TeMe$_2$BrPd(μ-Br)$_2$PdBrTeMe$_2$	ν_{Pd-Br} [a] (mull) = 270 (t), 228 (b), 158 (b) cm^{-1} Dark-brown	160, 161
Trans-PdI$_2$(TeMe$_2$)$_2$	ν_{Pd-I} (mull) = 130 cm^{-1} Brown	160, 161
Cis-PdCl$_2$(TeEt$_2$)$_2$	M.p. 97–99°C Maroon	19, 164, 167
	ν_{Pd-Cl}(solid) = 298, 275 cm^{-1}	164
	μ(benzene) = 1.8 D	164
	^{1}H NMR	166
Trans-PdBr$_2$(TeEt$_2$)$_2$	M.p. 110–112°C Maroon	164
	ν_{Pd-Br}(solid) = 259 cm^{-1} 190 cm^{-1} (Raman)	164
	μ(benzene) = 1.8 D	164
	^{1}H NMR	163, 166

Trans-$PdI_2(TeEt_2)_2$	M.p. 87–89°C	164
	Black	
	^1H NMR	163, 166
	μ(benzene) = 1.9 D	164
	ν_{Pd-I} (PhCl soln) = 160 cm^{-1} (Raman)	164
$Pd(SCN)_2(TeEt_2)_2$	M.p. 35–38°C	167
$TeEt_2ClPd(\mu\text{-}Cl)_2PdClTeEt_2$	M.p. 110–125°C (dec.)	19
	Dark red-brown	
$Te(n\text{-}Pr)_2ClPd(\mu\text{-}Cl)_2PdClTe(n\text{-}Pr)_2$	M.p. 131.5–132°C (dec.)	19
	Dark red-brown	
$PdTeEt_2(piperidine)Cl_2$ [b]	ν_{NH} = 3249 cm^{-1}	18, 20
	λ_{max}(hexane) = 340 nm (ϵ 350)	21
$PdTe(n\text{-}Pr)_2H_2N(n\text{-}C_8H_{17})Cl_2$ [b]	ν_{NH} = 3345, 3280 cm^{-1}	20
$PdTe(n\text{-}Pr)_2$(*p*-toluidine)Cl_2	ν_{NH} = 3359, 3286 cm^{-1}	20
Trans-$PdCl_2(Te(CH_2SiMe_3)_2)_2$	M.p. 99°C	13
	ν_{Pd-Cl} (solid) = 348 cm^{-1}	
Trans-$Pd(SCN)_2(Te(CH_2SiMe_3)_2)_2$	M.p. 143°C	13
	ν_{CN} (mull) = 2107 (sp), ($CHCl_3$) 2122 (sp), 2095 (sh) cm^{-1}	
	$A = 2.8 \times 10^4\ M^{-1}\ cm^{-2}$	
Trans-$PdCl_2(Te(CH_2CH_2CH_2SiMe_3)_2)_2$	M.p. 70°C	13
	ν_{Pd-Cl} (solid) = 352 cm^{-1}	
Trans-$Pd(SCN)_2(Te(CH_2CH_2CH_2SiMe_3)_2)_2$	M.p. 64°C	13
	ν_{CN} (mull) = 2106 (sp), ($CHCl_3$) 2113 cm^{-1}	
	$A = 3.2 \times 10^4\ M^{-1}\ cm^{-2}$	
Cis-$PdCl_2(Te(CH_2CH_2Ph)_2)_2$	M.p. 101°C	168
	ν_{Pd-Cl} (mull) = 285, 305, (CH_2Cl_2) 348 cm^{-1}	
Trans-$Pd(TeEt_2)_2PhBr$	M.p. 88–92°C	165
	MW (benzene) = 608 (634 calc.)	
Trans-$Pd(TeEt_2)_2PhCl$	M.p. 32–33°C; ν_{Pd-Cl} (mull) = 281 cm^{-1}	165
Trans-$Pd(TeEt_2)_2PhI$	M.p. 87–90°C	165
Trans-$Pd(TeEt_2)_2$(*o*-tolyl)Br	M.p. 97–102°C	165
Trans-$Pd(TeEt_2)_2$(*p*-tolyl)I	M.p. 87°C	165
	MW (benzene) = 682 (696 calc.)	

TABLE 3 (continued)

	Misc. data	Ref.
Trans-Pd$(TeEt_2)_2$(mesityl)Br	M.p. 97–100°C MW (benzene)=657 (627 calc.) ν_{Pd-Br} (mull)= 165 cm^{-1}	165
Trans-Pd$(TeEt_2)_2$(*o*-Cl-C_6H_4)Br	M.p. 69–71°C MW (benzene)=689 (712 calc.) ν_{Pd-Br} (mull)= 160 cm^{-1}	165
Trans-Pd$(TeEt_2)_2$(*p*-Cl–C_6H_4)Cl	M.p. 99–106°C MW (benzene)=619 (625 calc.) ν_{Pd-Cl} (mull)=281 cm^{-1}	165
Trans-Pd$(TeEt_2)_2$(*p*-Cl–C_6H_4)Br	M.p. 112–124°C (dec.) MW (benzene)=641 (669 calc.)	165
Trans-Pd$(TeEt_2)_2$(*p*-F–C_6H_4)Br	M.p. 110–115°C MW (benzene)=648 (652 calc.)	165
Trans-Pd$(TeEt_2)_2$Ph(SCN)		165
(b) Diaryl telluride complexes		
Trans-Pd$Cl_2(TePh_2)_2$	M.p. 164°C	109, 167
	ν_{Pd-Cl} (mull)=350 (s) cm^{-1}, $\Lambda_M(10^{-3}$ M, DMF)=3.5 ohm^{-1} cm^{-2} mol^{-1} $\lambda_{max}(C_6H_6)=24.81$ cm^{-1} ($\epsilon=58{,}000$)	109
$PdBr_2(TePh_2)_2$	M.p. 180°C Λ_M $(10^{-3}$ M, DMF)=81 ohm^{-1} cm^2 mol^{-1}	109
$Pd(SCN)_2(TePh_2)_2$	M.p. 225–227°C	167
$PdCl_2(Te(C_6F_5)_2)_2$	M.p. 230–232°C	167
$Pd(SCN)_2(Te(C_6F_5)_2)_2$	M.p. 240–245°C	167
$PdCl_2$(Te(*p*-tolyl)$_2)_2$	M.p. 168–169°C	167
$PdCl_2$(Te(*p*-MeO–$C_6H_4)_2)_2$	M.p. 160–162°C	167
$Pd(SCN)_2$(Te(*p*-MeO–$C_6H_4)_2$	M.p. 55°C (dec.) Red melt at 90°C	167

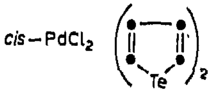
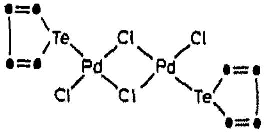
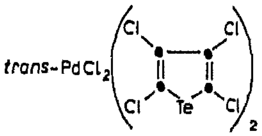
Trans-$PdCl_2(Te(p\text{-}EtO\text{-}C_6H_4)_2)_2$	M.p. 125°C	109
	Λ_M (10^{-3} M, DMF)=3.2 ohm^{-1} cm^2 mol^{-1}	
	$\nu_{Pd\text{-}Cl}$ (mull)=351 cm^{-1}	
	δ=0.31 mm sec^{-1}; Δ=7.61 mm sec^{-1}	171
Trans-$PdBr_2(Te(p\text{-}EtO\text{-}C_6H_4)_2)_2$	M.p. 105°C	109
	Λ_M (10^{-3} M, DMF)=89 ohm^{-1} cm^2 mol^{-1}	
	$\nu_{Pd\text{-}Br}$ (mull)=275 cm^{-1}	
	δ=0.29 mm sec^{-1}; Δ=6.78 mm sec^{-1}	171
(c) Complexes with aryl tellurol ligands		
$(Pd(TePh)_2)_n$		115, 119
$[Pd(PPh_3)(Te\text{-}p\text{-}EtO\text{-}C_6H_4)(\mu\text{-}Te\text{-}p\text{-}EtO\text{-}C_6H_4)]_2$ [c]	M.p. 117°C	109
	Λ_M (10^{-3} M, DMF)=3.3 ohm^{-1} cm^2 mol^{-1}	
	Dark brown	
$[Pd(PPh_3)(Te\text{-}2\text{-}thienyl)(\mu\text{-}Te\text{-}2\text{-}thienyl)]_2$ [c]	M.p. 145°C	109
	Λ_M (10^{-3} M, DMF)=2.3 ohm^{-1} cm^2 mol^{-1}	
	Dark brown	
(d) Heterocyclic ligands		
	M.p. 130°C (dec.)	132
	$\nu_{Pd\text{-}Cl}$=303, 287 cm^{-1}	
	Red-brown	
	M.p. 130°C (dec.)	132
	$\nu_{Pd\text{-}Cl}$=359, 298, 270 cm^{-1}	
	Red-brown	
	Red-brown	132
	$\nu_{Pd\text{-}Cl}$=354 cm^{-1}	

TABLE 3 (continued)

	Misc. data	Ref.
Pt complexes		
(a) Dialkyl telluride complexes		
Cis-$PtCl_2(TeMe_2)_2$	Pale-yellow solid	160
	ν_{Pt-Cl} (solid) = 303, 283 cm^{-1}	
	ν_{Pt-Te} (solid) = 187, 156 cm^{-1}	
Trans-$PtBr_2(TeMe_2)_2$	Light-brown solid	160
	ν_{Pt-Br} (solid) = 245 (s) cm^{-1}	
Trans-$PtI_2(TeMe_2)_2$	Light-brown solid	160
	ν_{Pt-I} (solid) = 147 cm^{-1} (vs)	
$[(n\text{-}Bu)_4N]PtCl_3TeMe_2$	$J_{^{195}Pt-^{125}Te} = -1553$ Hz	176
$[(n\text{-}Bu)_4N]PtBr_3TeMe_2$	$J_{^{195}Pt-^{125}Te} = -1092$ Hz	176
$[(n\text{-}Bu)_4N]PtI_3TeMe_2$	$J_{^{195}Pt-^{125}Te} = -400$ Hz	176
$[(n\text{-}Bu)_4N]_2Cl_3Pt(\mu\text{-}TeMe_2)PtCl_3$	$J_{^{195}Pt-^{125}Te} = 5923$ Hz	176
$[(n\text{-}Bu)_4N]_2Br_3Pt(\mu\text{-}TeMe_2)PtBr_3$	$J_{^{195}Pt-^{125}Te} = 5088$ Hz	176
$Pt(CNS)_2(TeMe_2)_2$ [d]		177
$[(n\text{-}Bu)_4N]Pt(CNS)_3TeMe_2$ [e]	^1H NMR (see Section E(iii))	177
Cis-$PtCl_2(TeEt_2)_2$	M.p. 126–127°C	
	ν_{Pt-Cl} (solid) = 302, 282 cm^{-1}	23
	(310, 304, 282 cm^{-1})	164
	M.p. 126–129°C	164
	μ-2.3 D	164
	(6.0 D)	174
	Variable-temp. ^1H NMR	162, 163, 172, 173
Cis-$PtBr_2(TeEt_2)_2$	M.p. 125–127°C	23
	(127–128°C)	164
	Brown-yellow solid	
	ν_{Pt-Br} (solid) = 217, 208 cm^{-1}	23
	218, 210 cm^{-1}	164
	(PhCl soln.) 203 cm^{-1} (Raman)	164
	μ(benzene) = 1.9 D	164
	Variable-temp. ^1H NMR	162, 163, 172, 173

Trans-$PtI_2(TeEt_2)_2$	M.p. 87–89°C	164
	Maroon solid	
	$\nu_{Pt\text{-}I}$ (solid) = 200 cm^{-1}	
	(PhCl) 153 cm^{-1} (Raman)	
	μ(benzene) = 1.8 D	
	Variable-temp. ^1H NMR	162, 163, 172, 173
$TeEt_2ClPt(\mu\text{-}Cl)_2PtClTeEt_2$	M.p. 142°C (dec.)	14
	Brown-orange solid	
$TeEt_2IPt(\mu\text{-}I)_2PtITeEt_2$	M.p. 160–163°C	173
	Brown solid	
$PtCl_2$(piperidine)$TeEt_2$	M.p. 60.5–61.5°C	15
	Orange solid	
	$\nu_{N\text{-}H} = 3230\ cm^{-1}$	17
	λ_{max}(hexane) = 340 nm ($\epsilon = 350$)	21
Trans-$PtCl_2$(pyridine)$TeEt_2$ [f]	M.p. 78°C (dec.)	22
	^1H NMR spectrum	
Trans-$Pt(TeEt_2)_2PhCl$	M.p. 60–64°C	175
	$\nu_{Pt\text{-}Cl}$ (solid) = 271 cm^{-1}	
Trans-$Pt(TeEt_2)_2$(mesityl)Cl	M.p. 111–116°C	175
	$\nu_{Pt\text{-}Cl}$ (solid) = 269 cm^{-1}	
Trans-$Pt(TeEt_2)_2$(*o*-tolyl)$_2$	M.p. 86–92°C	175
	Colorless solid	
	μ(benzene) = 2.48 D	
Trans-$Pt(TeEt_2)_2PhBr$	M.p. 83°C	175
	Colorless solid	
Trans-$Pt(TeEt_2)_2$(mesityl)Br	M.p. 111–114°C	175
	Ivory solid	
Trans-$Pt(TeEt_2)_2(PhSO_2)Cl$	ν_{SO_2}(asym) = 1185 cm^{-1}, vs	175 [b]
	ν_{SO_2}(sym) = 1095 cm^{-1}, s	
	$\nu_{Pt\text{-}Cl} = 301\ cm^{-1}$, s	
	τ(Ph) = 1.9–2.65 (5)	
	$\tau(CH_2)$ = 7.08 m (8);	
	$\tau(CH_3)$ = 8.46, t (12); J = 7.8 Hz	
Cis-$Pt(TeEt_2)_2$(*p*-tolyl)$_2$	M.p. 114–116°C	173
	Yellow solid	
	^1H NMR	

TABLE 3 (continued)

	Misc. data	Ref.
Trans-Pt(TeEt$_2$)$_2$(*p*-tolyl)$_2$	M.p. 64–65°C ^{1}H NMR	173
Cis-PtCl$_2$(Te(n-Pr)$_2$)$_2$	ν_{Pt-Cl} (solid)$=306, 291$ cm^{-1}	23
ClTe(n-Pr)$_2$Pt(μ-Cl)$_2$PtTe(n-Pr)$_2$Cl	M.p. 120–131°C (dec.) Brown-orange solid	14
Trans-PtTe(n-Pr)$_2$Cl$_2$(piperidine)	$\nu_{N-H\ asym}=3337$ cm^{-1} $\nu_{N-H\ sym}=3270$ cm^{-1}	17
PtCl$_2$(Te(CH$_2$Ph)$_2$)$_2$	M.p. 115°C (dec.)	178
	Green-orange crystals Sol. in CHCl$_3$	179
Cis-PtCl$_2$(Te(CH$_2$CH$_2$Ph)$_2$)$_2$	Orange solid ν_{Pt-Cl} (solid)$=305, 290$ cm^{-1} (*cis*) (CH$_2$Cl$_2$ soln.) 305, 290 cm^{-1} (*cis*) 336 cm^{-1} (*trans*) (toluene soln.) 335 cm^{-1} (*trans*) (Raman: 325 cm^{-1}) ^{125}Te NMR CH$_2$Cl$_2$ soln: $\delta_{cis}=-468.8$ ppm; $J_{^{125}Te-^{195}Pt}=900$ Hz $\delta_{trans}=-423.6$ ppm; $J_{^{125}Te-^{195}Pt}=554$ Hz toluene soln: $\delta_{trans}=-413.6$ ppm; $J_{^{125}Te-^{195}Pt}=601$ Hz	168
(b) Diaryl telluride complexes		
Cis-PtCl$_2$(TePh$_2$)$_2$	M.p. 200°C (dec.)	174
Trans-PtCl$_2$(Te(*p*-EtO–C$_6$H$_4$)$_2$)$_2$ [8]	M.p. 134°C Λ_M(10^{-3} M, DMF)$=5.5$ ohm^{-1} cm^2 mol^{-1} $\lambda_{max}^{MeCN}=26.28$ cm ($\epsilon=60$) $\nu_{Pt-Cl}=296$ cm^{-1} $\delta=0.12$ mm sec^{-1}; $\Delta=6.61$ mm sec^{-1}	109

Cis-$PtCl_2(Te(p\text{-}EtO\text{-}C_6H_4)_2)_2$	$\delta=0.35$ mm sec^{-1}; $\Delta=6.63$ mm sec^{-1}	171
Trans-$PtBr_2(Te(p\text{-}EtO\text{-}C_6H_4)_2)_2$	M.p. 150°C	109

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[a] t=terminal Pd–halogen stretching vibration; b=bridge Pd–halogen–Pd stretching vibration. [b] Complexes not isolated; IR spectra of solutions obtained by dissolving $Pd_2Cl_4(TeR_2)_2$ and the amine in CCl_4 (1:2 molar ratio). [c] See eqn. 3 for the structure of this dimer. [d] Complex was prepared by metathetical reaction between the corresponding bromo complex and KSCN, but no data are reported for the thiocyanate complex. The notation (CNS) for the thiocyanate ligand implies an unknown bonding mode for this ambidentate ligand. [e] A CH_2Cl_2 solution containing $[N(n\text{-}Bu)_4]Pt(CNS)_3TeMe_2$ was obtained by equilibration of $Pt(CNS)_2(TeMe_2)_2$ with $[N(n\text{-}Bu)_4]_2Pt(SCN)_4$. [f] The reaction between $Pt_2Cl_4(TeEt_2)_2$ and pyridine was carried out by adding a CH_2Cl_2 solution of pyridine to a very dilute solution of the dimer to avoid the formation of $PtCl_2(pyridine)_2$ and $PtCl_2(TeEt_2)_2$. [g] This complex, prepared by reacting *t*-$PtCl_2(NCPh)_2$ with 2 equivalents of $Te(p\text{-}EtO\text{-}C_6H_4)_2$, was formulated as the *trans* isomer on the basis of its solubility in benzene and the observation of one $\nu_{Pt\text{-}Cl}$ band [109]. The reported value of the $\nu_{Pt\text{-}Cl}$ band is, however, more characteristic of a *cis* complex [168]. The benzene solubility may be the result of a *cis*→*trans* isomerization upon dissolution, a phenomenon observed for *cis*-$PtCl_2(Te(CH_2CH_2Ph)_2)_2$ [168].

band characteristic of *trans* geometry [164] (see Table 3). All three complexes exist exclusively as the *trans* isomers in benzene solution, on the basis of dipole moment measurements (ca. 1.8 D) [164].

The far-IR spectrum of $PdI_2(TeMe_2)_2$, prepared by addition of $TeMe_2$ to aqueous K_2PdI_4, supports a *trans* configuration for this complex. Similar reactions with PdX_4^{2-} (X = Cl, Br) gave the halo-bridged dimeric complexes [160]. Variable-temperature NMR studies have been reported for the complexes $PdX_2(EEt_2)_2$ (X = Cl, Br, I; E = S, Se, Te) [162,163,172,173]. The complexes all have coalescence temperatures which have been associated with a rapid inversion of configuration at the pyramidal chalcogen [172,173] atom (i.e., *trans*-$PdX_2(TeEt_2)_2$: X = Cl, 30°C; X = Br, 51°C; X = I, 18°C). Since Pd, unlike Pt, has no observable magnetic nuclei (i.e., ^{195}Pt, 33% natural abundance, $I = 1/2$), precluding the observation of a metal–H coupling, the unequivocal assignment of the phenomenon associated with these spectroscopic parameters was not possible for these complexes (e.g., the spectra of the $PtX_2(EEt_2)_2$ complexes showed Pt–H coupling above and below the coalescence temperatures, precluding an intermolecular ligand-exchange process). Indeed, the rather wide variation of coalescence temperatures observed for the Pd complexes as a function of the halide ligand suggests that some process other than chalcogen inversion is operative; i.e., for the series $PtX_2(EEt_2)_2$ (E = S, Se, Te) the variation in the coalescence temperatures for the three halides in a set of complexes with a given chalcogen ligand is < 5°C.

The variable-temperature spectrum of $PdBr_2(TeEt_2)_2$ in the presence of free $TeEt_2$ (< 10 mole % of $TeEt_2$ relative to complex) also gave one coalescence temperature, lower than that observed in the absence of free ligand (< -10°C vs. $+51$°C for the complex alone) [163]. The failure to observe two distinct coalescence temperatures in the spectra of the $PdBr_2(TeEt_2)_2/TeEt_2$ system (as observed in the spectra of *trans*-$PdX_2(SEt_2)_2$, X = Cl, Br, and *trans*-$PtCl_2(SeEt_2)_2$, X = Cl, Br, in the presence of the respective free ligand) precluded the assignment of the coalescence phenomenon for the pure complex to an inversion process. It was suggested that the variable-temperature spectral data may be compatible with both inversion and exchange processes in the $PdBr_2(TeEt_2)_2$ system, the former simply being slower than the latter [163].

The chloro bridges in the dimeric complexes can be cleaved by amines to give the monomeric $Pd(TeR_2)(amine)Cl_2$ complexes (amine = piperidine, n-octylamine, *p*-toluidine) [20]. Infrared studies have shown that such mixed complexes rearrange in CCl_4 solution to give $PdCl_2(amine)_2$ and $PdCl_2(TeEt_2)_2$ [18].

Infrared studies of the $Pd(TeR_2)(amine)Cl_2$ complexes (i.e., the ν_{NH} of the coordinated amine) were interpreted to suggest that the effects transmitted from the Te ligands (as well as other arsine, stibine, amine, sulfide and selenide ligands) across the Pd atom to the N–H bond are mainly electrostatic [20].

The anomalous properties of the phosphine complexes were explained by π-bonding involving d_{xy} (or dp hybrid) orbitals of the metal with vacant low-energy orbitals of suitable symmetry in the phosphine (in view of recent results [324,325], this behavior can be attributed to more efficient σ overlap in the phosphine complexes compared to the other ligands, the latter showing a linear correlation of ν_{NH} with electronegativity of the donor atom). The observation that the ν_{NH} frequencies in the Pd(II) complexes are generally 15–20 cm^{-1} higher than in the Pt(II) analogs is consistent with weaker acceptor properties of Pd(II) vs. Pt(II).

The complexes $PdX_2(TeR_2)_2$ (X = Cl, SCN; R = CH_2SiMe_3, $CH_2CH_2CH_2SiMe_3$) were recently prepared and characterized by IR and NMR spectroscopy [13]. The presence of only one ν_{Pd-Cl} band in the far-IR spectra of the chloro complexes (i.e., 348 cm^{-1} and 352 cm^{-1}, respectively), supports a *trans* geometry. The thiocyanate complexes were formulated as *trans* S-bonded species on the basis of the position and intensity of their ν_{CN} bands. The appearance of low-energy shoulders for the ν_{CN} bands of these complexes in $CHCl_3$ solution was suggested to result from the presence of a small amount of *cis* isomer rather than the N-bonded linkage isomers. The large shifts (i.e., ca. 0.7 ppm) observed in the ^1H NMR spectra of these thiocyanate complexes in the presence of the shift reagent $Eu(fod)_3$-d^{27} and the chemical shifts of the thiocyanate carbons (118.1 and 117.6 ppm, both shifted upfield vs. ionic thiocyanate in these complexes) support Pd–SCN bonding in $CHCl_3$ solution [13]. The bonding proposed on the basis of spectroscopic evidence has been confirmed for *trans*-$Pd(SCN)_2(Te(CH_2$-$CH_2CH_2SiMe_3)_2)_2$ [13] (Fig. 8) by a single-crystal X-ray diffraction study. The complex $PdCl_2(Te(CH_2CH_2Ph)_2)_2$ has been formulated as the *cis* isomer in the solid state (ν_{Pd-Cl} = 285, 305 cm^{-1}) with complete isomerization occurring on dissolution in $CHCl_3$ or toluene (350 cm^{-1} IR; 305 cm^{-1} Raman) [168].

A series of organopalladium(II) compounds, *trans*-$Pd(TeEt_2)_2ArX$ (X = Cl, Ar = *p*-Cl–C_6H_4; X = Br, Ar = Ph, *o*-tolyl, mesityl, *o*-Cl–C_6H_4, *p*-Cl–C_6H_4; X = I, Ar = Ph, *p*-tolyl) have been prepared from *trans*-$Pd(TeEt_2)_2X_2$ and the appropriate Grignard reagent, the yields being generally low [165]. Aryl lithium reagents in these reactions reduced the complexes to Pd(0) even at −78°C, and the reactions with MeMgX (X = Br, I) gave only recovered starting materials. Complexes of the type $Pd(TeR_2)_2Ar_2$ were not obtained even though excess Grignard reagent was used in the reactions (analogous $Pt(TeR_2)_2Ar_2$ complexes are known) [175]. Molecular weights determined osmometrically confirmed monomeric structures for these compounds. *Trans*

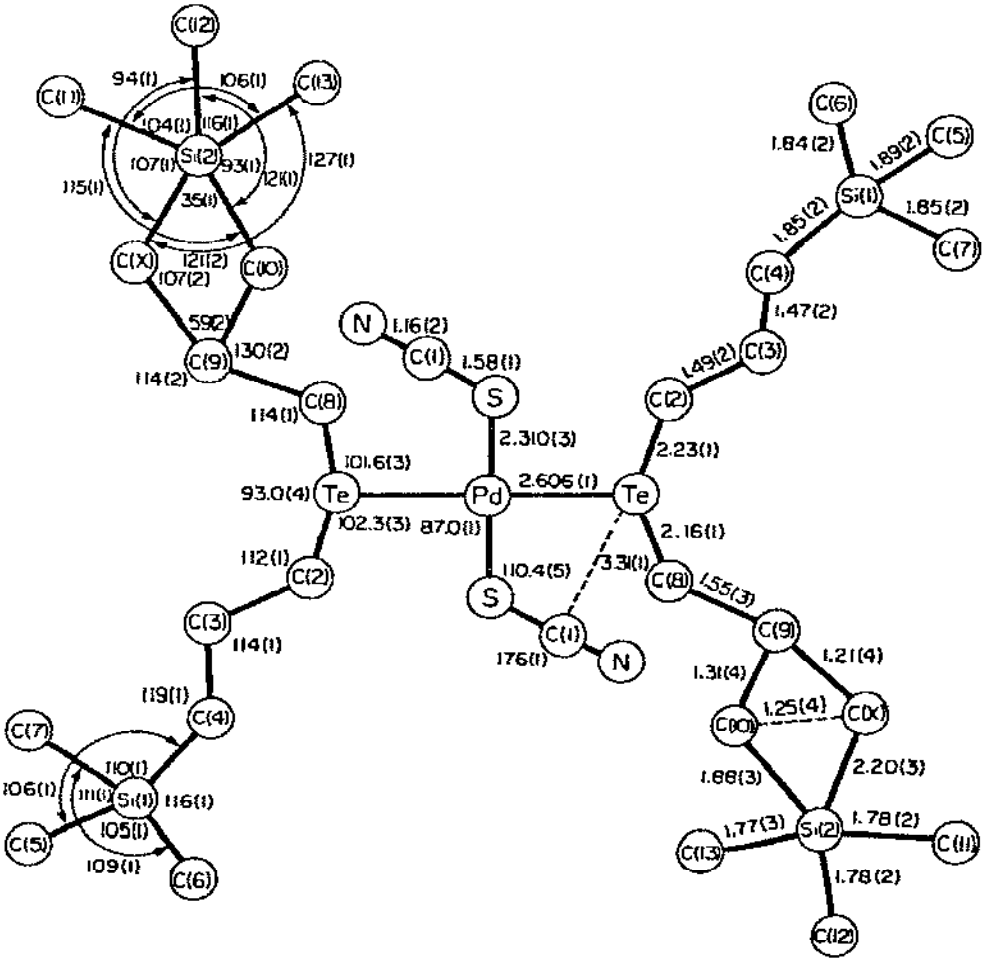


Fig. 8. Molecular structure of *trans*-$Pd(SCN)_2(Te(CH_2CH_2CH_2SiMe_3)_2)_2$. Reproduced with permission from Inorg. Chem., 18 (1979) 2696.

configurations were proposed for the complexes, as expected from the geometry of the starting materials, on the basis of the ν_{Pd-Cl} bands in their far-IR spectra. The rather low values of the ν_{Pd-Cl} vibrations (Table 3) are characteristic of halogen ligands *trans* to an organic ligand. Except for the *p*-Cl and *p*-F–C_6H_4 derivatives, which are relatively stable, the complexes slowly decompose to Pd(0) at room temperature in solution and even in the solid state. The stability of a homologous series increased in the order Cl < Br < I. In general electron-withdrawing substituents in the *para* position of the aromatic ring give complexes of enhanced stability vs. analogs with electron-donating substituents, and the ability of EEt_2 (E = S, Se, Te) ligands to stabilize such organopalladium compounds increases in the order $SEt_2 < SeEt_2 < TeEt_2$. Illustrative of the above considerations, $Pd(SeEt_2)(p\text{-}Y\text{-}C_6H_4)X$ (X = Cl, Br; Y = F, Cl) derivatives were isolated, but attempts to prepare *p*-tolyl derivatives resulted in deposition of Pd(0), and with $TeEt_2$ the very unstable $Pd(TeEt_2)_2I(p\text{-tolyl})$ complex was isolated.

The stability order has been related to the increasing polarizability of the donor atoms going down group VIA and metal → ligand π bonding. Although π bonding between Pd and sulfur (in thioethers) has been reported to be insignificant [326], such π bonding involving the filled 4*d* orbitals of Pd(II) and the empty 4*d* and 5*d* orbitals of Se and Te respectively seems to be important (with Pd–Te > Pd–Se) [327].

Diaryl telluride complexes. Relatively few Pd(II) complexes with diaryl tellurides have been reported (Table 3) [109,167,169,170,171], the most detailed study having been reported by Chia and McWhinnie [109]. The complexes $PdX_2(TeAr_2)_2$ (X = Cl, Br; Ar = Ph, $p\text{-EtO–}C_6H_4$) were prepared by reaction of $PdCl_2(NCPh)_2$ with the telluride (1 : 2 molar ratio) in benzene, the bromo complexes being obtained by a subsequent metathetical reaction with KBr [109]. The high solubility of the complexes in benzene together with the observation of only one $\nu_{\text{Pd–halogen}}$ band in the solid-state far-IR spectra of the complexes was cited as evidence for *trans* geometries in these complexes. The solution structures of these complexes have not been studied. Conductivity measurements in DMF indicate considerable dissociation of the halo ligand in the bromo complexes (Table 3). These authors also reported that $PdCl_2(NCPh)_2$ did not react with Te_2Ar_2 (Ar = $p\text{-EtO–}C_6H_4$, 2-thienyl). A ^{125}Te Mössbauer study [171] of some metal complexes with $Te(p\text{-EtO–}C_6H_4)_2$ indicated the following order of Lewis acidity towards this base: Hg(II) > Pt(II) > Pd(II) > Cu(I).

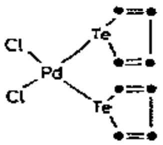
The complexes $PdX_2(TeAr_2)_2$ (X = Cl, Ar = Ph, *p*-tolyl, $p\text{-MeO–}C_6H_4$, C_6F_5; X = SCN^-, Ar = Ph, $p\text{-MeO–}C_6H_4$, $p\text{-}C_6F_5$) have also been reported [167], *cis* geometries for the chloro complexes and *trans* structures for the thiocyanates being suggested by IR evidence. The only other description of diaryl telluride complexes of Pd(II) involved the use of $TePh_2$ in an analytical scheme for the determination of palladium based on the formation of $PdCl_2(TePh_2)_2$, which could be readily extracted into a benzene phase and determined spectrophotometrically at 400 nm [169,170]. The proposed Pd(II) complex, however, was not actually isolated and characterized.

Aryl tellurol complexes. Interesting complexes containing both bridging and terminal $TeAr^-$ (Ar = $EtO\text{–}C_6H_4$, 2-thienyl) ligands have been prepared by oxidative addition reactions between $Pd(PPh_3)_4$ and the corresponding ditelluride [109] (eqn. 3).

Molecular weight determinations have confirmed dimeric structures for these brown complexes [109]*, and their conductivities in DMF are typical of nonelectrolytes.

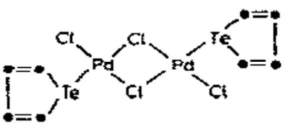
Polymeric species of the composition $(Pd(TePh)_2)_n$ have been prepared by the reaction of $PdCl_2(NCPh)_2$ with PhTeCOPh [115] (eqn. 4) or $PhTeGePh_3$ [119] (eqn. 6).

Te heterocycles. Monomeric (A) and dimeric (B) complexes were obtained from the reaction of Na_2PdCl_4 and tellurophene in methanol at 40–50°C [132].



A

(70% yield)



B

(27% yield)

The formulation of the complexes was based on elemental analysis and their far-IR spectra (Table 3). The two products were separated by their solubility differences in acetone and $CHCl_3$. Reaction of a suspension of the dimeric complex in $CHCl_3$ with excess tellurophene gave the monomer (A). Although it was claimed that the assignments of the ν_{Pd-Cl} bands for these two complexes were made by comparison with the spectra of the corresponding bromo complexes, no data on these latter two complexes were given. Reaction of Na_2PdCl_4 in methanol with tetrachlorotellurophene gave a monomeric complex formulated as *trans*-$PdCl_2(TeC_4Cl_4)_2$ on the basis of elemental analysis and the occurrence of only one ν_{Pd-Cl} band in the far-IR spectrum (Table 3). The larger *trans* effect of tetrachlorotellurophene vs. tellurophene, reflected in the formation of the *trans* complex in the former case and the *cis* complex in the latter case, has been rationalized on the basis of increased π-acceptor property of the chloro-substituted ligand.

Pt

Dialkyl tellurides. The first reported coordination complex with an organotellurium ligand was described by Fritzmann [178] in 1915 (i.e., *cis*-$PtCl_2(Te(CH_2Ph)_2)_2$). This compound, which was prepared by the reaction of an aqueous solution of K_2PtCl_4 with an alcohol solution of the ligand or

---

* The authors report that molecular weight determinations in benzene were obtained by vapor pressure osmometry, but no specific data are given.

by addition of the ligand to an alcohol solution of $[N(n\text{-}Pr)_4]_2PtCl_4$, was assigned a *cis* configuration on the basis of its physical properties (e.g., low solubility in organic solvents). The next report of a dialkyl telluride complex also involved Pt(II). In 1937 Jensen [174] prepared the complexes *cis*-$PtCl_2(TeR_2)_2$ (R = Et, Ph) by reaction of aqueous solutions of K_2PtCl_4 with alcoholic solutions of the ligands. The dipole moment of the ethyl derivative was measured in benzene, the value (6.0 D) supporting a *cis* configuration.

The low solubility of the phenyl derivative precluded a dipole moment measurement, but its properties suggested a similar *cis* configuration. In the 1950s Chatt and co-workers [14–23a], as part of their classic studies of the structures of coordination complexes, prepared several monomeric and halo-bridged dimeric Pd(II) and Pt(II) complexes with $TeEt_2$ and $Te(n\text{-}Pr)_2$ (Table 3). The monomeric complexes were prepared by Jensen's [174] method (i.e., react two equivalents of the dialkyl telluride with an aqueous solution of K_2PtCl_4) [14]. Alternative procedures, which provide for a faster reaction time, involve the use of Na_2PtCl_4 in ethanol at room temperature or K_2PtCl_4 in dilute acetic acid at reflux [14].

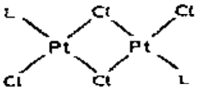
Several papers have described detailed far-IR [23a,164], Raman [164], ^1H NMR [162,163,172,173], and dipole moment [164] studies of the $PtX_2(TeEt_2)_2$ complexes. These systems exhibit rather complex behavior, *cis* → *trans* isomerization occurring on going from solid to solution in some cases as well as rapid telluride ligand exchange and inversion of configuration at the pyramidal tellurium atom in solution. On the basis of far-IR spectroscopy (Table 3), the complexes $PtX_2(TeEt_2)_2$ (X = Cl, Br [23a,164]) were formulated as *cis* isomers in the solid state, and the iodide has been assigned the *trans* geometry [164]. For a series of complexes of the type PtL_2X_2 (X = Cl, Br; L = neutral class b ligand), the position of the ν_{Pt-X} band was considerably dependent on L for the *cis* complexes (i.e., X is *trans* to L), but for the *trans* complexes ν_{Pt-Cl} was almost insensitive to L [23a]. The order of ν_{Pt-Cl} for the complexes with group VIA ligands (i.e., $PtCl_2(ER_2)_2$: $E = S \sim Se \gg Te$) corresponds to the order of the relative *trans* effects of these ligands, the strongest *trans* effect of $TeEt_2$ being reflected in the weakest *trans* Pt–X bond (e.g., ν_{Pt-Cl}: E = S, 337, 318 cm^{-1}; Se, 333, 317 cm^{-1}; Te, 306, 290 cm^{-1}). Dipole moment measurements of benzene solution of $PtX_2(TeEt_2)_2$ support *trans* configurations for all three complexes [164]. Jensen [174] had measured a higher value (6 D) for the dipole moment of the $PtCl_2(TeEt_2)_2$ than the value obtained in this later work (2.3 D). The latter value is somewhat higher than the values for the bromo and iodo complexes (ca. 1.8 D) and this, together with the observation of three ν_{Pt-Cl} bands [164] (the lower two of which correspond to the solid-state values), suggests that there may be an equilibrium mixture of the two isomers present. Infrared, Raman and ^{1}H NMR data support *trans* configurations in solution for the bromo and iodo complexes [164]. For a series of $MX_2(ER_2)_2$ complexes, the tendency towards forming the *trans* isomers in solution follows the orders Pd > Pt, Te > Se > S, and I > Br > Cl. The complete characterization of such complexes, therefore, requires careful measurement of their far-IR spectra in both solid and solution states, Raman [164] and NMR spectroscopy (^{1}H [164], ^{125}Te [168]) and dipole moment measurements [164,174] being useful supplementary structural probes.

Cross and co-workers [162,163,172,173] have used variable-temperature ^{1}H NMR spectroscopy to study inversion of configuration at S, Se and Te in the complexes $M(EEt_2)_2X_2$ (M = Pd, Pt; X = Cl, Br, I; E = S, Se, Te) as well as exchange processes in solutions of these complexes containing excess EEt_2. In studies of the complexes in the absence of excess ligand below the coalescence temperature (i.e., $PtX_2(TeEt_2)_2$: X = Cl, 107°C; X = Br, 110°C; X = I, 105°C), the methylene protons are diastereotopic, forming part of an ABM_3Y ($Y = {}^{195}Pt$, 33% abundant, $I = 1/2$) spectrum with ^{195}Pt satellites, whereas above the coalescence temperatures the methylene protons appear equivalent (A_2M_3Y) [162,163,172,173].

For the SEt_2 and $SeEt_2$ complexes, the retention of the $J_{^{195}Pt-^1H}$ in the spectra above the coalescence temperatures precludes a dissociative mechanism, a fast inversion of configuration at the pyramidal chalcogen atom on the NMR time-scale being unequivocally proposed for the spectral changes [172,173]. The coalescence temperatures indicate that the ease of inversion is S > Se > Te and Pt > Pd. The increasing barrier to inversion for the complexes as one goes down the chalcogen elements [172,173] resembles the situation for the pyramidal group VA compounds [328,329]. For the $TeEt_2$ complexes, however, a ligand dissociation-recombination process could not be unequivocally ruled out, since no Pt–H coupling could be observed in the spectra above the coalescence temperature [172,173]. However, the solvent and concentration independence of the coalescence temperatures, the reversibility of the temperature variation of the NMR spectra, and the similarity of the coalescence temperatures for the different halides of the $Pt(TeEt_2)_2X_2$ series are all consistent with lone pair inversion at the tellurium atom rather than a fast ligand-exchange process being responsible for the observed spectroscopic changes. Variable-temperature NMR studies of the complex $Pt(TeEt_2)_2(p\text{-tolyl})_2$ were, however, unequivocally consistent with a facile inversion of configuration at the pyramidal tellurium atom, since the spectra over the temperature range studied (ambient to −57°C) retained Pt–H coupling (an A_2M_2Y system; $J_{^{195}Pt-^1H} = 29$ Hz) [173]. No line broadening of the methylene resonance was observed down to −57°C, setting this temperature as an upper limit for the inversion process. On the basis of the ability of strongly *trans* activating aryl groups to similarly markedly increase the rate of inversion at sulfur [330], the complex $Pt(TeEt_2)_2(p\text{-tolyl})_2$ was assigned a *cis* configuration.

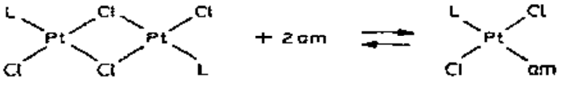
The variable-temperature ^1H NMR spectrum of $PtI_2(TeEt_2)_2$* in the presence of free $TeEt_2$ indicated that very rapid exchange occurs between free and coordinated telluride [162.163]. In the analogous system $PtX_2(SeEt_2)_2$ ($X = Cl$, Br), two distinct coalescence temperatures were observed, a lower-temperature coalescence unaffected by the presence of free $SeEt_2$ and a higher-temperature coalescence involving both free and coordinated ligand, but the $PtI_2(TeEt_2)_2$–$TeEt_2$ system showed only one coalescence, involving both free and coordinated telluride [162,163]. The temperature of this coalescence was considerably lower than that observed in the absence of free telluride, the introduction of even the smallest measurable amount of $TeEt_2$ lowering the coalescence temperature so much that it could not be observed [163]. The addition of only a trace amount of $TeEt_2$ allowed observation of a coalescence at ca. $-10°C$ (vs. $+119°C$ in the absence of added $TeEt_2$) [163]. No ^{195}Pt–^1H coupling was observed above the coalescence temperature. It was not possible, therefore, to rule out unequivocally an associative–dissociative process being responsible for the coalescence in the absence of free ligand [172,173] as in the cases of some of the SEt_2 and $SeEt_2$ complexes, where two distinct coalescence temperatures were observed in the presence of free ligand [163]. Comparison of the various chalcogen ligand systems indicates that the ease of exchange between free and coordinated ligand has the order $TeEt_2 \gg SeEt_2 > SEt_2$ and $Pd > Pt$ [163].

The dimeric complexes $Pt_2Cl_4(TeR_2)_2$ ($R = Et$, n-Pr) [14] were prepared by reacting equivalent amounts of Na_2PtCl_4 and *cis*-$PtCl_2(TeR_2)_2$ in absolute ethanol at room temperature. Since the simple dialkyl telluride complexes isomerize spontaneously, the bridged complexes can be prepared directly by reacting equivalent amounts of TeR_2 and Na_2PdCl_4 in ethanol. The following order of stabilities was established for dimeric complexes of formula A [14]: $PR_3 \sim R_2S > AsR_3 >$ amines $> R_2Te > SbR_3 > R_2Se$.



(A)

The reaction of the chloro-bridged dimers in acetone with amines was also studied by Chatt and Venanzi [15].



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* Infrared and Raman measurements support a *trans* configuration for this complex in the solid state, and dipole moment determinations in benzene support a *trans* geometry in this solvent [164]. The variable-temperature study, however, was done in $CH_2Cl_2/CHCl_3$ [163].

Although only the chloro-bridged complex was investigated for the $TeEt_2$ dimer, the above equilibrium was increasingly in favor of the bridged species in the order $Cl < Br < I$ (i.e., with $(P(n\text{-}Pr)_3)_2Pt_2X_4$ as the substrate). As generally observed for these halo-bridged dimers, the monomer obtained from the reaction with the amine has the *trans* configuration for the $TeEt_2$ derivative. The complexes with dialkyl tellurides tend to disproportionate

$$t\text{-}(TeEt_2)(p\text{-}Me\text{-}C_6H_4\text{-}NH_2)PtCl_2 \rightarrow (TeEt_2)_2PtCl_2 + (p\text{-}Me\text{-}C_6H_4\text{-}NH_2)_2PtCl_2 \quad (32)$$

The monomeric complexes with amines can be recrystallized from light petroleum and are nonelectrolytes in nitrobenzene. Their solubility in carbon tetrachloride and ether suggests a *trans* configuration. In a subsequent study [17], the position and intensity of the N–H stretching frequencies in a series of these amine complexes were measured, and a stability order for the ligands was proposed (e.g., 4-alkylpyridines, piperidine, R_2S, R_2Se, R_2Te, AsR_3, PR_3, SbR_3, $P(OR)_3$, C_2H_4). The ligands to the left of trialkylphosphines were proposed to function solely as σ donors, whereas the phosphines and those ligands to the right were proposed to act as both σ donors and π acceptors of Pt *d* electron density (see refs. 324, 325 for recent discussions of the bonding of organophosphines in transition metal complexes). The assignment of dialkyl tellurides as solely σ donors (with a *trans* effect order: $SEt_2 < SeEt_2 < TeEt_2$) is consistent with the available data, but no detailed studies have been reported addressing the bonding properties of these donors.

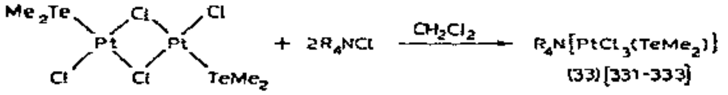
A related study aimed at distinguishing inductive from mesomeric effects was also reported by Chatt and Westland [22] using ^1H NMR spectroscopy to study the monomeric *trans* complexes obtained by cleavage of the halo-bridged complexes $Pt_2Cl_4L_2$ (L = alkyl-phosphines, -arsines, -stibines, -sulfides, -selenides, and -tellurides) with pyridine. The pyridine ligand was chosen as a detector because the π-electron system of the ring can interact with the *d* orbitals on the metal atom, which may be engaged in the π bonding to the ligand in the *trans* position. For the *trans*-$PtCl_2$(pyridine)L complexes, the constancy of the β-proton shifts relative to free pyridine was interpreted as indicating that inductive and mesomeric effects are probably balanced and small at this position. The small shifts observed for the coordinated pyridine ligand in these complexes, however, precluded any meaningful conclusions about the bonding. A study of the electronic spectra of a series of *trans*-$PtCl_2$(piperidine)L complexes [21] gave the following order of ligand field splittings: $P(OMe)_3 > P(n\text{-}Pr)_3 > \text{piperidine} > As(n\text{-}Pr)_3 > SEt_2 > SeEt_2 > TeEt_2$.

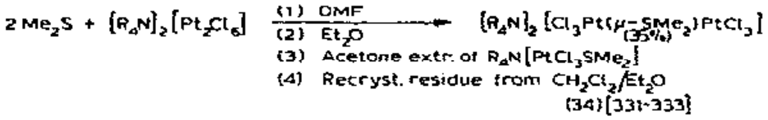
A series of aryl platinum complexes containing diethyl telluride were prepared by reaction of the aryl Grignard reagent and *cis*-$PtCl_2(TeEt_2)_2$ [175a], the aryl bromo derivatives $PtAr(TeEt_2)_2Br$ (Ar = Ph, mesityl) being obtained when 1:4 and 1:2 molar ratios, respectively, of Pt complex to Grignard reagent were used. A similar reaction with *o*-tolyl magnesium chloride (1:2 molar ratio of Pt complex to Grignard) gave $Pt(TeEt_2)_2$(*o*-tolyl)$_2$, which was assigned a *trans* geometry on the basis of its dipole moment (2.48 D) in benzene solution. The bromo ligands in these complexes can be replaced metathetically by chloride (LiCl/MeOH). A *trans* configuration was assigned to the $Pt(TeEt_2)_2ClAr$ complexes on the basis of their low ν_{Pt-Cl} values, characteristic of halo ligands *trans* to a strong activating group. The derivative $Pt(TeEt_2)_2$(*p*-tolyl)$_2$, prepared from $PtI_2(TeEt_2)_2$ and *p*-tolyl lithium in ether, was assigned a *cis* configuration, and the complex obtained by recrystallization of this initial product from water/methanol was assigned a *trans* configuration [173]. The S-sulfinato complex, *trans*-$Pt(TeEt_2)_2(PhSO_2)Cl$, was prepared by SO_2 insertion into the Pt–C bond of the phenyl derivative [175b].

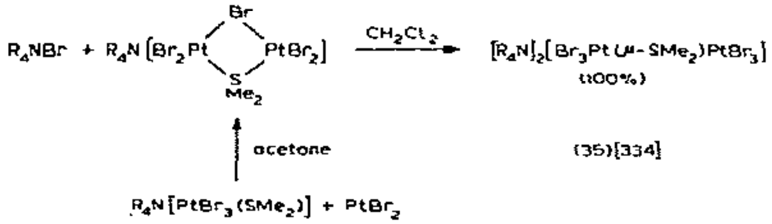
The series of complexes $PtX_2(TeMe_2)_2$ (X = Cl, Br, I) were prepared and their IR and Raman spectra recorded [160,161]. The chloro complex was assigned a *cis* configuration on the basis of its solubility properties and the observation of two ν_{Pt-Cl} stretching frequencies (Table 3) [160], characteristic of C_{2v} symmetry. The bromo and iodo complexes, however, were assigned *trans* configurations [160]. The increasing tendency for the stability of the *trans* isomer in complexes PtX_2L_2 in going from X = Cl to Br to I is well established. For the bromo complex, however, the correspondence of the far-IR and Raman bands suggests that the complex has no center of symmetry (i.e., has *cis* configuration), but the solubility properties and the observation of only one ν_{Pt-Cl} vibration (i.e., D_{2h} symmetry) are both consistent with a *trans* structure [160]. Calculations of the platinum–chalcogen force constants (i.e., $k_{Pt-S} = 2.2$, $k_{Pt-Se} = 1.4$, $k_{Pt-Te} = 2.1$ mdyne Å^{-1}) indicate a bond-strength order Pt–S > Pt–Se < Pt–Te [160]. Since the bond strength would be expected to decrease with decreasing difference in the electronegativity between Pt and the donor atom, going down group VI, it was suggested that considerable π bonding must be involved in the Pt–Te bond (e.g., calculations of the Pt–halogen force constants give the expected trend; $k_{Pt-Cl} = 2.3$, $k_{Pt-Br} = 2.0$, and $k_{Pt-I} = 1.7$ mdyne Å^{-1}). Evidence for the π-bonding ability of dialkyl tellurides was further suggested by the following observations: (1) only the *cis* isomer of $PtCl_2(TeMe_2)_2$ could be prepared and (2) studies of the relative bond moments of the Pt–chalcogen bonds suggest an order S < Se < Te.

A detailed study of the IR spectra in the 4000–400 cm^{-1} region of $TeMe_2$ and $MX_2(TeMe_2)_2$ (M = Pd, Pt; X = Cl, Br, I) complexes showed only slight changes in the internal modes of the telluride ligand on complexation, although careful analysis of the spectra in the CH_3 rocking region allowed differentiation of *cis* and *trans* isomers of these square planar complexes [161]. The values of $^1J_{^{195}Pt-^{125}Te}$ for n-$Bu_4N[PtX_3TeMe_2]$ (X = Cl, Br, I) and $[n\text{-}Bu_4N]_2[X_3Pt(\mu\text{-}TeMe_2)PtX_3]$ (X = Cl, Br) have been obtained by heteronuclear INDOR spectroscopy and direct Fourier-transform ^{125}Te NMR spectroscopy, respectively [176]. The coupling constants (Table 3) decrease markedly in the order Cl > Br > I, with the values for the former monomeric complexes being much less than those for the latter dimeric complexes. The observed J values are much smaller than those observed in the phosphine analogs, and the percent decrease from Cl through Br to I is much greater than in any previously reported series [176]. The unusually small coupling constants in the Pt–Te monomeric complexes compared to the phosphine analogs have been attributed to the presence of nonbonding electrons on the tellurium. Indeed, the coupling constants for the dimeric complexes in which both lone pairs of the bridging tellurium ligand are involved in bonding are much larger and similar to those in $PtCl_3PMe_3$ [176].

The monomeric [331–333] (eqn. 33) and dimeric [334] dimethyl telluride complexes were prepared by the routes previously described for the dimethyl sulfide analogs (eqn. 34,35):

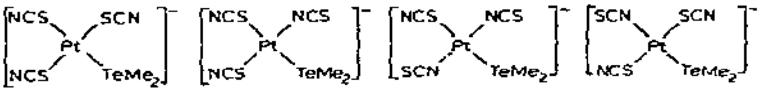






Although attempted metathetical replacement of the chloride ligands in $[N(n\text{-}Bu)_4][PtCl_3TeMe_2]$ with KSCN in acetone resulted in displacement of the telluride ligand, solutions of $[N(n\text{-}Bu)_4][Pt(CNS)_3TeMe_2]$ were obtained by equilibration of $[N(n\text{-}Bu)_4]_2[Pt(SCN)_4]$ with $[Pt(CNS)_2(TeMe_2)_2]$ in CH_2Cl_2 [177]. The neutral complex, $Pt(CNS)_2(TeMe_2)_2$ [177], was prepared by a metathetical reaction between the corresponding chloride [160] and KSCN in acetone, but no data have been reported for this complex. The thiocyanate isomers present in this CH_2Cl_2 solution were identified by

^1H-{^{195}Pt} INDOR spectroscopy [177]. The following isomers were found (along with their relative proportions):



	(1.0)	(0.3)	(0.04)	(0.006)
τ(Me) =	7.75	7.76	7.80	7.86
$^3J_{^{195}Pt-^1H}$ =	33.6 Hz	35.7 Hz	ca. 35 Hz	——
$^1J_{^{195}Pt-^{14}N}$ =	——	367 ± 5 Hz	ca. 450 Hz	——

The number of N-bonded thiocyanate ligands in a given isomer was deduced from the multiplicity of the ^{14}N coupling pattern in the ^1H-{^{195}Pt} INDOR spectrum, and the specific assignments of the mixed complexes were made, assuming a regular upfield shift of the methyl resonances when S- is replaced by N-bonded thiocyanate in the position *cis* to the telluride ligand and a rather larger shift for the *trans* position [177]. These results were compared with similar measurements with complexes containing other neutral ligands having N, P, As, Sb, S and Se donor atoms, the general conclusions being that N-bonding is favored when the neutral ligand contains a light donor atom, when the *trans* ligand has a high *trans* influence, or when a *cis* ligand is bulky [177].

The complex $PtCl_2(Te(CH_2CH_2Ph)_2)_2$, prepared by reaction of the telluride ligand with aqueous K_2PtCl_4, was shown by IR and Raman spectroscopy to have the *cis* configuration in the solid state (ν_{Pt-Cl} = 305, 290 cm^{-1})

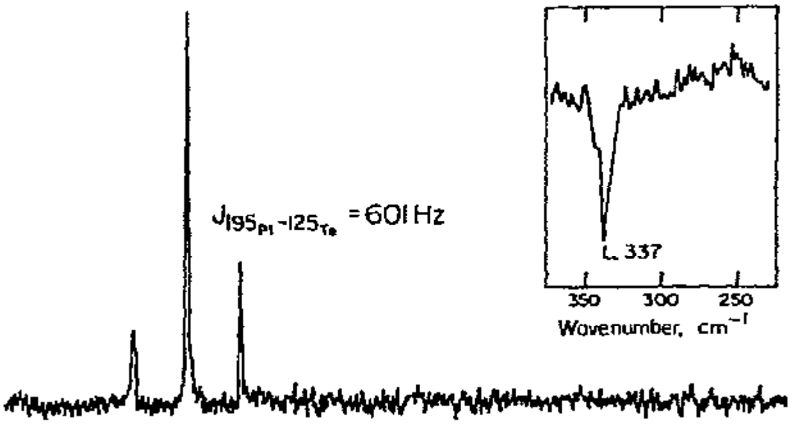


Fig. 9. ^{125}Te NMR and far-IR spectra of $PtCl_2(Te(CH_2CH_2Ph)_2)_2$ in CH_2Cl_2. Reproduced with permission from J. Organomet. Chem., 209 (1981) C41.

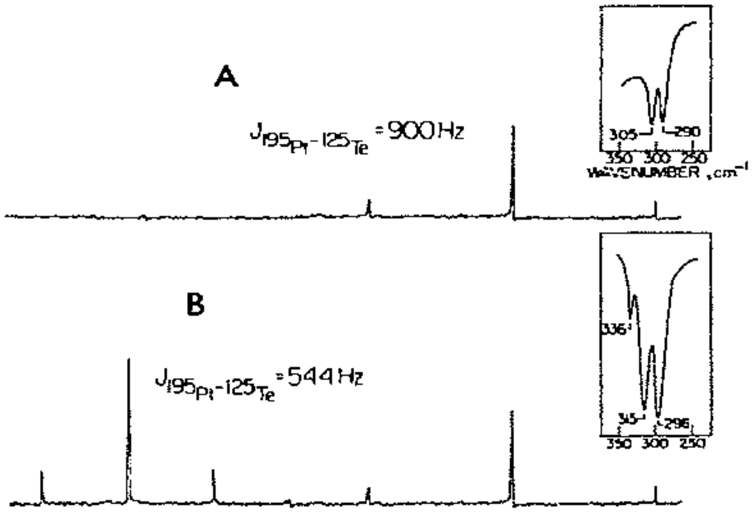


Fig. 10. ^{125}Te NMR and far-IR spectra of $PtCl_2(Te(CH_2CH_2Ph)_2)_2$ in toluene. Reproduced with permission from J. Organomet. Chem., 209 (1981) C41.

[168]. Although the *cis* isomer can be recovered isomerically pure by recrystallization from hot toluene, such solutions have been shown to contain exclusively the *trans* isomer by IR ($\nu_{Pt-Cl} = 337$ cm^{-1}), Raman ($\nu_{Pt-Cl} = 325$ cm^{-1}) and ^{125}Te NMR spectroscopy ($\delta = -413.6$ ppm vs. $Te(S_2CNEt_2)_2$; $J_{^{125}Te-^{195}Pt} = 601$ Hz) (Fig. 9). Solutions of the complex in CH_2Cl_2, however, have been shown by such spectroscopic measurements to contain an equilibrium mixture of *cis* and *trans* isomers, the *cis* isomer exhibiting a triplet ($J_{^{125}Te-^{195}Pt} = 900$ Hz) at higher field ($\delta - 468.8$ ppm) than the *trans* isomer ($\delta - 423.6$ ppm) (Fig. 10). The central signals of these triplets are due to ^{125}Te nuclei bonded to Pt atoms without a nuclear spin, and the two satellites result from ^{125}Te coupled to ^{195}Pt.

Diaryl telluride complexes. Jensen [174] prepared the diphenyl telluride complex of platinum chloride, which he formulated as *cis*-$PtCl_2(TePh_2)_2$ on the basis of its solubility properties (its low solubility precluded a dipole moment measurement, and no far-IR data have been reported for this complex). The only other report of diaryl telluride complexes of Pt is the work of Chia and McWhinnie, who prepared the complexes $PtX_2(Te(p\text{-EtO}-C_6H_4)_2)_2$ (X = Cl, Br) [109]. On the basis of the solubility of these complexes in benzene, they were assigned *trans* configurations. The only far-IR data reported in this work, however, was a ν_{Pt-Cl} band for $PtCl_2(Te(p\text{-EtO}-C_6H_4)_2)_2$ (296 cm^{-1}), which is in the range typical of a *cis* isomer rather than *trans*. It was suggested [109] that kinetic factors determine the initial product in the case of Pt(II) complexes with organotellurium ligands

$$K_2PtCl_4 + 2\ TePh_2 \rightarrow cis\text{-}PtCl_2(TePh_2)_2 \qquad (36)[174]$$

$$trans\text{-}PtCl_2(NCPh)_2 + 2\ Te(p\text{-}EtO\text{–}C_6H_4)_2 \rightarrow trans\text{-}PtCl_2(Te(p\text{-}EtO\text{–}C_6H_4)_2)_2 \qquad (37)[109]$$

(iv) Co, Rh, Ir

Co

The only report in the literature of an organotellurium complex with Co describes the synthesis of $\pi Cp_2Nb(\mu\text{-}TePh)_2Co(CO)_2$ [126] by the reaction of $\pi Cp_2Nb(TePh)_2$ [124] with $Hg(Co(CO)_4)_2$). An analogous derivative could not be obtained using $\pi Cp_2Ti(TePh)_2$ [126]. The complex is stable under nitrogen, but DMSO solutions immediately decompose in air. Its diamagnetism suggests the presence of a Nb–Co bond. A preliminary note [154b] reported ESR evidence for coordination of tellurophene to a square planar Co(II) complex with a Schiff base, *N*,*N'*-*o*-phenylenebis(salicylideneaminato)cobalt(II), but no product was isolated.

The reaction of $TePh_2$ with $Co_2(CO)_8$ in benzene at room temperature gave the paramagnetic, highly insoluble black crystalline complex $[Co_2Te(CO)_5]_n$ [102]. This complex has high aerial and thermal stability.

The mixed cluster compound $FeCo_2(CO)_9Te$ has been prepared in 30% yield by the reaction, in stoichiometric amounts, of $Co_2(CO)_8$ and $Fe_3(CO)_{12}$ with $TeEt_2$ [141]. The structure of this brown, air-stable compound has been shown by single-crystal X-ray diffraction to involve a tetrahedral $FeCo_2Te$ cluster system formed by the symmetrical coordination of an apical Te atom to a basal $FeCo_2(CO)_9$ fragment containing three $M(CO)_3$ groups at the corners of an equilateral triangle and linked to one another by metal–metal bonds [141]. Although the cluster compounds $Co_3(CO)_9X$ (X = S, Se) [141,335] have been prepared by the reaction of $Co_2(CO)_8$ with a variety of sulfur substrates and H_2Se respectively, attempts to prepare the Te analog were unsuccessful [141].

Rh

The complex $[RhCO(TeEt_2)_2Cl]$ has been prepared by the reaction of $[Rh(CO)_2Cl]_2$ with $TeEt_2$ in pentane at room temperature [156]. This brown-yellow complex has a $\nu_{Rh\text{–}Cl}$ band at 299 cm^{-1} [156], a value characteristic of a chlorine *trans* to a CO ligand in a Rh(I) complex [336]. The complex readily undergoes oxidative addition reactions with a variety of substrates (Cl_2, Br_2, I_2, HCl, MeI, $PhSO_2Cl$; Table 4) to give *trans* octahedral Rh(III) complexes [156]. The complex $RhMeCO(TeEt_2)_2ClI$ readily undergoes CO

TABLE 4

Co, Rh, Ir complexes

	M.p. (°C)	Physical data	Ref.
Co complexes			
$\pi Cp_2Nb(\mu\text{-}TePh)_2Co(CO)_2$	157–160	$\nu_{CO} = 1859, 1911\ cm^{-1}$ $\tau(Cp) = 4.73$ (s), 4.99 (s), 5.31 (s) $\tau(Ph) = 2.45–2.85$ (m)	126
$[Co_2Te(CO)_5]_n$		$\nu_{CO} = 2068$ (s), 2027, 1994, 1859, 1841, 1810 cm^{-1}	102
$FeCo_2(CO)_9Te$		Brown, air-stable solid Single-crystal X-ray diffraction	141
Rh complexes			
Trans-$RhCO(TeEt_2)_2Cl$	30	$\nu_{CO} = 1955$ (vs) cm^{-1} $\nu_{Rh\text{-}Cl} = 299$ (s) cm^{-1}	156
$RhCO(TeEt_2)_2Cl_3$	64–75 (dec.)	$\nu_{CO} = 2060$ (s) cm^{-1} $\nu_{Rh\text{-}Cl} = 332$ (s) cm^{-1}	156
$RhCO(TeEt_2)_2ClBr_2$	>30 (dec.)	$\nu_{CO} = 2056$ (vs) cm^{-1} $\nu_{Rh\text{-}Cl} = 314$ (s) cm^{-1}	156
$RhCO(TeEt_2)_2ClI_2$	62–65	$\nu_{CO} = 2043$ (s) cm^{-1} $\nu_{Rh\text{-}Cl} = 328$ (s) cm^{-1}	156
$RhCO(TeEt_2)_2MeClI$	71–78 (dec.)	$\nu_{CO} = 2030$ (m) cm^{-1} $\nu_{Rh\text{-}Cl} = 321$ (m) cm^{-1}	156
$RhCO(TeEt_2)_2MeCOClI$		$\nu_{CO} = 2060$ (vs) cm^{-1} $\nu_{CO(acetyl)} = 1713$ (vs) cm^{-1}	156
$RhCO(TeEt_2)_2PhSO_2Cl_2$		$\nu_{CO} = 2064$ (vs) cm^{-1} $\nu_{Rh\text{-}Cl} = 320$ (s), 292 (vs) cm^{-1}	156
$RhCO(TeEt_2)_2Cl(TCNE)$	120–123 (dec.)	$\nu_{CN} = 2220$ (s) cm^{-1} $\nu_{CO} = 2059$ (s) cm^{-1}	157
$RhCO(TeEt_2)_2Cl(FMN)$	>89 (dec.)	$\nu_{CN} = 2210$ (m) cm^{-1} $\nu_{CO} = 2022$ (s) cm^{-1}	157

mer-$RhCl_3(TeMe_2)_3$		$\delta(^{103}Rh)=3179$ ppm [a] $J_{^{125}Te-^{103}Rh}$: $TeMe_2$ *trans* to $TeMe_2$ +71 Hz; $TeMe_2$ *trans* to Cl +94 Hz	155
mer-$RhBr_3(TeMe_2)_3$		$\delta(^{103}Rh)=2567$ ppm [a] $J_{^{125}Te-^{103}Rh}$: $TeMe_2$ *trans* to $TeMe_2$ +70 Hz; $TeMe_2$ *trans* to Br +93Hz	155
mer-$RhI_3(TeMe_2)_3$		$\delta(^{103}Rh)=1352$ ppm [a] $J_{^{125}Te-^{103}Rh}$: $TeMe_2$ *trans* to $TeMe_2$ +66Hz; $TeMe_2$ *trans* to I +69 Hz	155
$RhCl_3(TePh_2)_3$	197–199	MW(DCE) = 920 (calc. 1055)	120
$RhCl_3CO(TePh_2)_2$	163–165	MW(DCE) = 780 (calc. 801) $\nu_{CO}=2080$ cm^{-1}	120
$Rh(TePh)_3$		Dark-brown solid	120
$RhCl(CO)(TePh_2)_2$	158–159	Chocolate-brown solid $\nu_{CO}=2040$ cm^{-1}; MW(DCE) = 710 (calc. 730)	120
$COTePh_2Rh(\mu\text{-}SCN)_2RhCOTePh_2$	> 50 (dec.)	Brown solid $\nu_{CO}=2060$ cm^{-1} $\nu_{CN}=2135$ cm^{-1} MW(DCE) = 705 (calc. 736)	120
$RhCl(TePh_2)_3$	> 85 (dec.)	Red solid MW(DCE) = 614 (calc. 989)	120
$(Ph_2Te)_2Rh(\mu\text{-}Cl)_2Rh(TePh_2)_2$	> 125 (dec.)	Red solid MW(DCE) = 684 (calc. 702)	120
$RhCOClBr_2(TePh_2)_2$	136–138	Red solid $\nu_{CO}=2060$ cm^{-1} MW(DCE) = 850 (calc. 890)	120
$RhCOClI_2(TePh_2)_2$	> 115 (dec.)	Red solid $\nu_{CO}=2070$ cm^{-1} MW(DCE) = 940 (calc. 984)	120
$RhCOCl(SCN)_2(TePh_2)_2$		Red-brown solid $\nu_{CO}=2080$ cm^{-1} $\nu_{CN}=2140$ cm^{-1} MW(DCE) = 800 (calc. 846)	120
$RhCl_2TePh(TePh_2)_2$		Dark-red solid MW(DCE) = 905 (calc. 942)	120

TABLE 4 (continued)

	M.p. (°C)	Physical data	Ref.
$RhCOCl_2TePh(TePh_2)_2$		Red solid $\nu_{CO}=2050\ cm^{-1}$	120
Ir complexes			
$[Ir(CO)_2TeEt_2Cl]_n$	184–198 (dec.)	$\nu_{CO}=2018$ (vs), 1969 (m) cm^{-1}	158

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[a] In ppm to the high frequency of the resonance frequency corrected to a polarizing magnetic field such that $SiMe_4$ gives a proton resonance of exactly 100 MHz.

insertion into the Rh–Me bond in CH_2Cl_2 to give $RhCO(TeEt_2)_2COMeClI$. A subsequent study [157] extended the substrates which can add to $RhCO(TeEt_2)_2Cl$ to include tetracyanoethylene (TCNE) and fumaronitrile (FMN) (Table 4).

Reaction of rhodium trichloride hydrate with excess $TePh_2$ in ethanol under reflux gave $(Ph_2Te)_3RhCl_3$ [120]. In contrast, although the analogous reaction under mild conditions with a stoichiometric amount of PPh_3 allowed the isolation of $(PPh_3)_3RhCl_3$ [337], the use of excess phosphine reduced the metal to Rh(I) and $(PPh_3)_3RhCl$ was isolated [338]. The latter complex (Wilkinson's catalyst) is an active catalyst for the hydroformylation and hydrogenation of olefins under mild conditions [339]. One of the diphenyl telluride ligands of this complex can be displaced by CO under mild conditions

$$(Ph_2Te)_3RhCl_3 \xrightarrow[CHCl_3,\ 24\ h]{CO} (Ph_2Te)_2CORhCl_3 \qquad (38)$$

Rh(III) complexes with terminal and bridging $TePh^-$ ligands have also been prepared by the following routes [120]

$$\begin{aligned} RhCl_3 \cdot 3\ H_2O + TePh_2 \xrightarrow[\substack{reflux\ 24\ h \\ EtOH}]{37\%\ aq.\ CH_2O}\ & RhCl_2TePh(TePh_2)_2 \\ & \downarrow CO/benzene \\ & RhCl_2COTePh(TePh_2)_2 \end{aligned} \qquad (39)$$

$$RhCl_3 \cdot 3\ H_2O + TePh_2 \xrightarrow[EtOH/reflux\ 30\ min]{40\%\ aq.\ CH_2O/KOH} Rh(TePh)_3 \qquad (40)$$

Analogous reactions with PPh_3 give $Rh(PPh_3)_2Cl(CO)$ [340] and $Rh(PPh_3)_3(CO)H$ [341], respectively. The complex $(TePh_2)_3RhCl$ was, however, prepared by a substitution reaction with a labile Rh(I) ethylene complex [120]

$$[(CH_2{=}CH_2)_2RhCl]_2 + excess\ TePh_2 \xrightarrow[reflux]{MeOH} (TePh_2)_3RhCl \qquad (41)$$

The reactivity of this complex is significantly different from that of the PPh_3 analog [120]

	$Rh(TePh_2)_3Cl$	$Rh(PPh_3)_3Cl$	
$+ CO \rightarrow$	Mixture of carbonylated products $\nu_{CO} = 1950–2040\ cm^{-1}$	$(PPh_3)_2(CO)RhCl$ [338,341]	(42)
$+ CS_2 \rightarrow$	$[(Ph_2Te)_2RhCl]_2$	$(PPh_3)_2(CS)RhCl$ [342]	(43)
$+ F_3CC{\equiv}CCF_3 \rightarrow$	$[(Ph_2Te)_2RhCl]_2$	$(Ph_3P)_2(F_3CC{\equiv}CCF_3)RhCl$ [343]	(44)
$+ C_6H_{13}CHO \rightarrow$	$[(Ph_2Te)_2RhCl]_2$	$(PPh_3)_2(CO)RhCl$ [341]	(45)

Carbonylation of $(Ph_2Te)_3RhCl$ gave a mixture of products [120], and the PPh_3 analog gave the monosubstituted product, which is inert to further CO substitution [338,341]. A variety of other substrates which readily replace PPh_3 gave the chloro-bridged dimer, $[(Ph_2Te)_2RhCl]_2$, in reactions with the diphenyl telluride analog (eqns. 42–45). Methyl iodide oxidatively added to the $(Ph_2Te)_3RhCl$ to give $(Ph_2Te)_2RhClMeI$. $(PPh_3)_3RhCl$ reacted similarly but gave a methyl iodide adduct $(PPh_3)_2RhCl(Me)I \cdot MeI$ [343]. The dimer $[(Ph_2Te)_2RhCl]_2$ was also obtained by simple recrystallization of $(Ph_2Te)_3RhCl$.

Diphenyl telluride [120] (like triphenyl phosphine [344] and $TeEt_2$[156]) reacts with $[Rh(CO)_2Cl]_2$ to give the monomeric substituted product

$$\left[Rh(CO)_2Cl\right]_2 + 4\,TePh_2 \xrightarrow{\text{hexane}} (Ph_2Te)_2Rh(CO)Cl \tag{46}$$

This derivative undergoes oxidative addition reactions with halogens and thiocyanogen (Table 4) but not with methyl iodide. In contrast, the PPh_3 analog does not oxidatively add bromine. A further difference in reactivity between the $TePh_2$ and $TeEt_2$ complexes was noted in the inactivity of $(Ph_2Te)_2Rh(CO)Cl(Me)I$ to CO insertion into the $Rh–CH_3$ bond [120], a facile reaction for the $TeEt_2$ analog [156]. The chloro ligand in $RhCl(CO)(TePh_2)_2$ cannot be simply replaced metathetically by thiocyanate as in the PPh_3 analog; instead, a thiocyanate-bridged dimer is formed, $(OC)TePh_2Rh(\mu\text{-}SCN)_2RhTePh_2(CO)$ [120].

The ^{103}Rh chemical shifts of the complexes *mer*-$RhX_3(TeMe_2)_3$ (X = Cl, Br, I) have been obtained by $^{1}H\text{-}\{^{103}Rh\}$ INDOR measurements [155]. The values of $^{1}J_{^{125}Te-^{103}Rh}$ were relatively insensitive to changes in the halide ligand, in contrast to the unusually large changes observed in $^{1}J_{^{125}Te-^{195}Pt}$ in analogous platinum complexes [345]. The complexes $RhX_3(TeMe_2)_3$ (X = Cl, Br) can readily be prepared by shaking an ethanol solution of $RhCl_3 \cdot 3\,H_2O$ with $TeMe_2$ for several hours, the iodo complex being prepared by metathetical reaction of the chloro complex with KI in acetone [346].

Ir

The only reported Ir complex with an organotellurium ligand is $Ir(CO)_2TeEt_2Cl$, prepared by reacting $[IrCOCl]_n$ with the telluride [158] (Table 4).

(v) Fe, Ru, Os

Fe

Several iron carbonyl complexes with bridging (and in one case, terminal) aryl tellurol ligands have been prepared by reaction of $Fe(CO)_5$, $Fe_3(CO)_{12}$

or $[\pi CpFe(CO)_2]_2$ with diaryl ditellurides. Reaction of $Fe_3(CO)_{12}$ with Te_2Ar_2 (Ar = Ph [110,112], C_6F_5 [110], p-EtO–C_6H_4 [102]) in refluxing petroleum ether (80–100°C) [110] or benzene [102,112] gave the dimeric complexes $(OC)_3Fe(\mu\text{-}TeAr)_2Fe(CO)_3$. Comparison of the ν_{CO} bands of these complexes (Table 5) suggests an increased π-acceptor capacity of the TeC_6F_5-bridged complex, as one would expect [110]. A similar comparison of the ν_{CO} bands of the dimeric complexes $(OC)_3Fe(\mu\text{-}E\text{–}C_6X_5)_2Fe(CO)_3$ (E = S, Se, Te; X = H, F) suggests the following order of increased σ-donor ability (and/or decreased π-acceptor capacity) of the bridging chalcogenide ligand: Te > Se > S [110].

The similarity of the IR spectrum of $(OC)_3Fe(\mu\text{-}TePh)_2Fe(CO)_3$ to those of the μ-EPh (E = S, Se) analogs suggests that all three derivatives have similar structures [112]. The crystal structure determination of $(OC)_3Fe(\mu\text{-}SEt)_2Fe(CO)_3$ [347] has shown it to have a folded Fe_2S_2 ring with an *anti* conformation of the alkyl groups and a "bent" Fe–Fe band. The *syn* isomer of this dimer has also been reported [348,349]. The complex $(OC)_3Fe(\mu\text{-}TePh)_2Fe(CO)_3$ appears to be isomerically pure, but TLC evidence suggests that two isomers may exist for the Se analog, although only one isomer was isolated and characterized [112]. The mass spectrum of $(OC)_3Fe(\mu\text{-}TePh)_2Fe(CO)_3$ shows weak peaks due to the molecular ion and ions corresponding to the loss of 2–5 CO ligands, the strongest peaks being due to the $Fe_2Te_2Ph_2^+$ and $Fe_2Te_2^+$ fragments [112]. The relative abundance of the $Fe_2E_2^+$ ions (i.e., S < Se, Te) as well as the appearance of weak peaks due to FeE_2^+ only for the Se and Te derivatives has been suggested to indicate the following order of iron–chalcogen bond strengths: Te ~ Se > S [112].

The reaction of $Fe(CO)_5$ with $TePh_2$ gave no characterizable product [102] (analogous reactions with PPh_3 gave $Fe(CO)_{5-n}(PPh_3)_n$ ($n = 1, 2$) [350]). The reaction of $Fe_3(CO)_{12}$ with $TePh_2$ (1:3 molar ratio; refluxing cyclohexane), however, gave ca. 25% yield of $Fe(CO)_4TePh_2$ [102]. Diphenyl telluride also substitutes for CO in dihalotetracarbonyliron(II) [102]

$$Fe(CO)_4X_2 + TePh_2 \rightarrow Fe(CO)_3TePh_2X_2 + CO \qquad (47)$$
$$X = Br, I$$

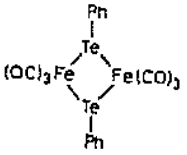
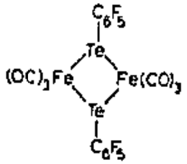
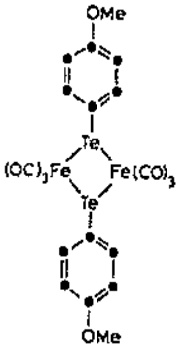
Although IR spectroscopy did not allow an assignment of the structure of these complexes, presumably, on the basis of the more strongly *trans*-directing effect of CO vs. the halide ligands, the $TePh_2$ ligand is *cis* to both halides (a *cis* configuration for $Fe(CO)_4I_2$ has been established by a dipole moment measurement [351]). These substituted derivatives show considerably enhanced stability towards air and moisture vs. the parent dihalides.

Substitution by organotellurium ligands of CO in $Fe(CO)_2(NO)_2$ has also been reported to give monomeric and dimeric complexes

$$Fe(NO)_2(CO)_2 + TePh_2 \xrightarrow[\text{r.t.}]{\text{ether}} Fe(NO)_2COTePh_2 + CO \qquad (48)[102]$$

TABLE 5

Fe, Ru, Os complexes

	M.p. (°C)	Physical data [a]	Ref.
Fe complexes			
	104–106 (dec.) [112]	Air stable $\nu_{CO}(CS_2) = 2056, 2019, 1978, 1969\ cm^{-1}$	110
		Dark-red crystals $MW(CHCl_3) = 675$ (calc. 689) (mass spectrum: 689) $\nu_{CO}(C_6H_{12}) = 2058, 2021, 1990, 1983\ cm^{-1}$	112
		Air stable $\nu_{CO}(CS_2) = 2070, 2041, 2007, 1997\ cm^{-1}$	110
		Red-brown solid μ (benzene) = 4.06 ± 0.07 D	102
$Fe(CO)_4TePh_2$		Red-brown solid $\nu_{CO}(THF) = 2096, 2030, 2000, 1968\ cm^{-1}$	102

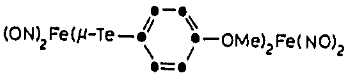
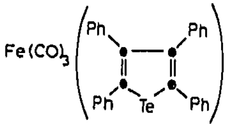
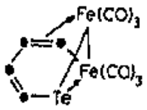
$Fe(NO)_2(CO)(TePh_2)$		Red solid $\nu_{CO}(C_6H_{12}) = 2012\ cm^{-1}$ $\nu_{NO}(C_6H_{12}) = 1764, 1727\ cm^{-1}$	102
$Fe(CO)_3TePh_2Br_2$		Red-brown crystals ν_{CO} (KBr) $= 2016, 1957, 1920\ cm^{-1}$	102
$Fe(CO)_3TePh_2I_2$		Black-brown crystals ν_{CO} (KBr) $= 2088, 2042, 2027\ cm^{-1}$	102
$\pi CpFe(CO)_2TePh$	66	Green crystals MW $(CHCl_3) = 434$ (382 calc.) $\nu_{CO}\ (C_6H_{12}) = 2018, 1976\ cm^{-1}$ ^1H NMR (CS_2): 4.77 ppm	107
$\pi CpCOFe(\mu\text{-}TePh)_2Fe(\pi Cp)CO$		Dark-brown solid MW $(CHCl_3) = 680$ (707 calc.) $\nu_{CO} = 1965, 1937, 1921\ cm^{-1}$ ^1H NMR: (CS_2) 4.48, 4.11 ppm	107
Cis-$\pi CpCOFe(\mu\text{-}Te(p\text{-}EtO\text{-}C_6H_4))_2Fe(\pi Cp)CO$	102–103	Single-crystal X-ray diffraction Dark-brown crystals $\nu_{CO}\ (CS_2) = 1943$ (s) cm^{-1} $\delta(^{57}Fe) = +0.66\ (01)\ mm\ s^{-1}$ $\Delta = 1.64\ (01)\ mm\ s^{-1}$ $\delta(^{125}Te) = +0.06\ (08)\ mm\ s^{-1}$ $\Delta = 6.2\ (1)\ mm\ s^{-1}$	114b
Trans-$(\pi Cp)COFe(\mu\text{-}Te(p\text{-}EtO\text{-}C_6H_4))_2Fe(\pi Cp)CO$	99–101	Dark-brown solid $\nu_{CO}\ (CS_2) = 1934$ (m), 1920 (s) cm^{-1} $\delta(^{57}Fe) = +0.64\ (01)\ mm\ s^{-1}$ $\Delta = 1.68\ (01)\ mm\ s^{-1}$ $\delta(^{125}Te) = +0.01\ (08)\ mm\ s^{-1}$ $\Delta = 6.1\ (1)\ mm\ s^{-1}$	114b
		Green crystals $\mu = 3.00$ D	106
	200–225 (darkens above 150)	Red crystals $\nu_{CO} = 2041, 1965, 1938$ (sh) cm^{-1}	131

TABLE 5 (continued)

	M.p. (°C)	Physical data[a]	Ref.
	50	Red crystals	132
		ν_{CO} (C_6H_{12}) = 2064, 2033, 1995 cm^{-1}	
		^{1}H NMR (acetone-d_6):	
		0.69 (d, J = 9.2 Hz)	
		2.81 (d, d, J = 5.6, 7.5 Hz)	
		4.27 (d, J = 7.5 Hz)	
		4.77 (d, d, J = 5.6, 9.7 Hz)	
		MS: $M^+ - n$CO (n = 0–6)	
$(OC)_3Fe(\mu_2\text{-}Te_2)Fe(CO)_3$		ν_{CO} (C_6H_{14}) = 2067 (m), 2028 (s), 1995 (s) cm^{-1}	139b
$FeCo_2(CO)_9Te$		Brown crystalline solid	141
		Air stable	
		Single-crystal X-ray diffraction	
$Fe_3(CO)_9Te_2$		Grey-black crystals	139a
		ν_{CO} (KBr) = 2044 (m), 2021 (vs), 1999 (vs), 1977 (m), 1962 (s) cm^{-1}	
		(CCl_4) 2081 (w), 2050 (vs), 2030 (vs), 2008 (vs) cm^{-1}	
		(C_6H_{14}) 2045 (s), 2025 (s), 2004 (s) cm^{-1}	139b
		Mass spectrum	142
		TGA	142
		Variable-temp. ^{13}C NMR	143
$Fe_3(CO)_{10}Te_2$	> 100 (dec.)	Black crystals	140
		ν_{CO} (CCl_4) = 2104 (m), 2053 (s), 2046 (s), 2036 (m), 2016 (s), 1991 (s), 1979 (m), 1965 (m) cm^{-1}	
$Fe_3(CO)_9TeS$	124 (dec.)	Black crystals	144, 145
		Air-stable in solid state	
		Sol. in ether, CCl_4, $CHCl_3$, and CS_2	
		ν_{CO} (CCl_4) = 2088 (w), 2055 (vs), 2037 (s), 2015 (s) cm^{-1}	

$Fe_3(CO)_9TeSe$	142 (dec.)	Black crystals	131
		Air-stable in solid state	
		Sol. in ether, CCl_4, $CHCl_3$ and CS_2 ν_{CO} (CCl_4) = 2086 (w), 2052 (vs), 2032 (s), 2012 (s) cm^{-1}	144, 145
$Fe_3(CO)_7(P(n\text{-}Bu)_3)_2Te_2$		Brown liquid ν_{CO} (CCl_4) = 2025 (s), 1983 (vs, br), 1973 (s, sh), 1959 (m, sh), 1931 (m, br), 1920 (m, br) cm^{-1}	140
$Fe_3(CO)_8P(n\text{-}Bu)_3Te_2$		Dark-brown liquid MW = 830 (849 calc.) ν_{CO} (CCl_4) = 2056 (s), 2029 (m), 2016 (vs), 1995 (vs), ~1980 (m, sh), 1950 (m) cm^{-1}	140
$Fe_3(CO)_9P(n\text{-}Bu)_3Te_2$	109	Brown amorphous solid MW = 910 (877 calc.) ν_{CO} (CCl_4) = 2064 (m), 2038 (vs), 2014 (vs), 1955, (m, br), 1982 (s), 1962 (m), 1954 (w, br) cm^{-1}	140
		Variable-temp. ^{13}C NMR	143
$Fe_3(CO)_7(P(OPh)_3)_2Te_2$	130–131	Red amorphous solid ν_{CO} (CCl_4) = 2055 (m), 2034 (s), 2010 (vs), 1976 (s), 1963 (m, br) cm^{-1}	140
$Fe_3(CO)_8P(OPh)_3Te_2$	99	Black crystals MW = 944 (957 calc.) ν_{CO} (CCl_4) = 2060 (s), 2037 (m, sh), 2025 (vs), 2007 (m), 1998 (s), 1981 (m, br) cm^{-1}	140
$Fe_3(CO)_9P(OPh)_3Te_2$	128	Deep-red crystals MW = 962 (985 calc.) ν_{CO} (CCl_4) = 2078 (w), 2046 (vs), 2026 (vs), 2006 (m), 1984 (s), 1972 (m), 1957 (w) cm^{-1}	140
$Fe_3(CO)_7(AsPh_3)_2Te_2$	> 180 (dec.)	Green-brown crystals ν_{CO} (CCl_4) = 2048 (m), 2043 (m), 2029 (s), 2017 (s), 1986 (vs, br), 1937 (m, br) cm^{-1}	140

TABLE 5 (continued)

	M.p. (°C)	Physical data[a]	Ref.
$Fe_3(CO)_8AsPh_3Te_2$	>160 (dec.)	Black crystals MW = 940 (953 calc.) ν_{CO} (CCl_4) = 2068 (w), 2057 (s), 2027 (m), 2018 (vs), 1995 (vs, br), 1944 (m, br) cm^{-1}	140
$Fe_3(CO)_9AsPh_3Te_2$	>115 (dec.)	Brown crystals ν_{CO} (CCl_4) = 2067 (m), 2042 (vs), 2017 (vs), 1982 (s), 1969 (m), 1956 (w) cm^{-1}	140
$Fe_3(CO)_8AsPh_3TeSe$		Black crystals MW (benzene) = 889 (904.4 calc.) ν_{CO} (CCl_4) = 2077 (w), 2067 (s), 2038 (m), 2027 (s), 2005 (s, br), ~1977 (m, sh), ~1955 (w, sh) cm^{-1}	145
$Fe_3(CO)_8AsPh_3TeS$	140	Brown microcrystals MW (benzene) = 840 (857.5 calc.) ν_{CO} (CCl_4) = 2065 (s), 2027 (s), 2005 (s, br), 1975 (m, sh), 1950 (w, sh) cm^{-1}	145
$Fe_3(CO)_7(AsPh_3)_2TeS$	160 (dec.)	Brown microcrystals MW (benzene) = 1050 (1135.7 calc.) ν_{CO} (CCl_4) = 2049 (w), 2037 (m), 2031 (m), 1998 (s), 1990 (s), 1974 (m), 1943 (m) cm^{-1}	145
$Fe_3(CO)_8P(OPh)_3TeS$		Red-brown liquid MW (benzene) = 822 (861.6 calc.) ν_{CO} (CCl_4) = 2069 (s), 2044 (m), 2032 (vs), 2017 (m), 2003 (s), ~1989 (m, sh) cm^{-1}	145
$Fe_3(CO)_7(P(OPh)_3)_2TeS$		Red-brown liquid ν_{CO} (CCl_4) = 2052 (m, sh), 2047 (s), 2010 (vs), ~1996 (s, br), ~1985 (s, br) cm^{-1}	145

$Fe_3(CO)_8P(OPh)_3TeSe$		Red-brown liquid MW (benzene) = 875 (908.5 calc.) ν_{CO} (CCl_4) = 2065 (s), 2041 (m), 2027 (vs), 2013 (m), 2001 (s), ~1985 (m, sh) cm^{-1}	145
$Fe_3(CO)_7(P(OPh)_3)_2TeSe$	45	Amorphous brown solid ν_{CO} (CCl_4) = 2048 (m, sh), 2043 (s), 2008 (vs), ~1998 (s, br), ~1982 (s, br) cm^{-1}	145
Ru complexes			
$RuCl_2(CO)_2(TePh_2)_2$	168	Yellow needles	104
$RuCl_2CO(TePh_2)_3$	177	Orange-golden platelets	104
$RuI_2(CO)_2(Te(n\text{-}Bu)_2)_2$	68		104
$RuI_2(CO)_2(TePh_2)_2$	238		104
$RuI_2CO(TePh_2)_3$		ν_{CO} (CH_2Cl_2) = 1946 cm^{-1} (KBr) = 1943 cm^{-1}	104
$RuI_2CO(Te(n\text{-}Bu)_2)_3$		ν_{CO} (CH_2Cl_2) = 1931 cm^{-1}	104
$RuBr_2(CO)_2(TePh_2)_2 \cdot CH_2Cl_2$	215		104
$RuBr_2CO(TePh_2)_3$		ν_{CO} (KBr) = 1946 cm^{-1} Compound not isolated	104
$(CO)_3Ru(\mu\text{-}TePh)_2Ru(CO)_3$	105–107 (dec.)	Yellow solid MW($CHCl_3$) = 734 (calc. 778) ν_{CO}($CHCl_3$) = 2073, 2044, 2002 (br) cm^{-1}	112
$[Ru(CO)_2(TePh)_2]_{6-7}$	> 200 (dec.)	Dark-orange plates MW($CHCl_3$) = 3700 (n = 6–7) ν_{CO} = 1974, 2030, 2080 cm^{-1}	112
$[Ru(CO)_2(TePh)_2]_{12-14}$	200–220 (dec.)	Orange-brown powder MW($CHCl_3$) = 7800–8200 (n = 12–14)	112
$[(NH_3)_5RuTeMe_2](PF_6)_2$		Yellow solid λ_{max} (0.1 M HCl) = 318 nm (1.41×10^3) 243 nm (4.75×10^3)	154a
$[(NH_3)_5RuTeMe_2]^{3+}$		λ_{max} (0.2 M HCl) = 600 nm (ϵ = 60) Compound not isolated, generated in solution by oxidation of Ru(II) complex	154a

TABLE 5 (continued)

	M.p. (°C)	Physical data [a]	Ref.
$H_2Ru_3(CO)_9Te$	135 (dec.)	Yellow solid ν_{CO} = 2112 (s), 2079 (vs), 2061 (s, sh), 2058 (vs), 2047 (s, sh), 2014 (vs), 2011 (s, sh) cm^{-1} MW (mass spec.) = 690 (calc. 686.8) τ(bridge H^-) = 29.70 ppm (singlet) mass spectrum: M^+, $M^+ - n CO$ ($n = 1, 2$), $[M^+ - 2\ CO] - m[H + CO]$ ($m = 1, 2$) $[Ru_2(CO)_nTe]^+$ $n = 0–4$, Ru_3^+	147
		ν_{CO} = 2111 (m), 2078 (s), 2054 (vs), 2043 (s), 2012 (s), 2006 (s), 1993 (m), 1987 (w) cm^{-1} m/e = 696 (for ^{103}Ru, ^{130}Te)	148
$Ru_3(CO)_9Te_2$ [b]			148
Os complexes			
$OsCl_2(CO)CTe(PPh_3)_2$	221–223	Orange, air-stable crystals ν_{CO}(Nujol) = 2040 cm^{-1} ν_{CTe} = 1046 cm^{-1}	149
$Os_3(CO)_9Te_2$ [c]		ν_{CO} = 2067 (s), 2046 (s), 2006 (s), 2002 (sh) cm^{-1} m/e = 1088 (for ^{192}Os, ^{130}Te)	148

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[a] Infrared data: s, strong; vs, very strong; m, medium; w, weak. NMR data: d, doublet; dd, doublet of doublets. [b] No data were reported for this compound, but infrared (ν_{CO}) and mass spectral data are given in ref. 148 for the S and Se analogs. [c] Although the clusters $Os_3(CO)_9H_2Te$ and $Os_4(CO)_{12}H_2Te$ were also reported in ref. 148 as products of the reaction of $Os_3(CO)_{12}$ with elemental Te, no data are reported for these compounds.

$$2\,\mathrm{Fe(NO)_2(CO)_2} + (p\text{-}\mathrm{MeO{-}C_6H_4Te})_2 \xrightarrow[\text{r.t.}]{\mathrm{C_6H_6}}$$

$$\mathrm{(ON)_2Fe(\mu\text{-}Te\text{-}}p\text{-}\mathrm{MeO{-}C_6H_4)_2Fe(NO)_2} + 4\,\mathrm{CO} \qquad (49)[106]$$

The air- and light-stable derivative $\mathrm{Fe(NO)_2COTePh_2}$ is formed under much less vigorous conditions than required for the substitution reaction with $\mathrm{PPh_3}$ [352]. The diamagnetic complex $[\mathrm{Fe(NO)_2Te\text{-}}p\text{-}\mathrm{MeO{-}C_6H_4}]_2$ has been formulated, on the basis of its IR spectrum, as isostructural with red Roussin's salt, $[\mathrm{Fe(NO)_2SEt}]_2$, the crystal structure determination [353a] of which has shown that each Fe atom is tetrahedrally surrounded by two bridging sulfur atoms and two nitrosyl ligands with an Fe–Fe distance of 2.72 Å.

Reaction of $\mathrm{Te_2Ph_2}$ with $[\pi\mathrm{CpFe(CO)_2}]_2$ gave initially a monomeric complex with a terminal $\mathrm{PhTe^-}$ ligand and, under more forcing conditions, a dimeric complex with $\mathrm{PhTe^-}$ bridging ligands [107,153]

$$\begin{tikzcd} {[\pi\mathrm{CpFe(CO)_2}]_2 + \mathrm{Ph_2Te_2}} \arrow[r, "\text{benzene}", "\text{reflux}"'] & \pi\mathrm{CpFe(CO)_2TePh} \arrow[d, "\begin{array}{l}\text{benzene}\\ \text{reflux}\\ \text{IR lamp}\end{array}"] \\ & \pi\mathrm{CpCOFe(\mu TePh)_2FeCO}\pi\mathrm{Cp} \end{tikzcd} \qquad (50)$$

The dimeric complex was obtained as a mixture of two isomers (TLC and ^{1}H NMR (2 cyclopentadienyl signals) evidence), but the pure isomers could not be isolated. The S and Se analogs were, however, separated into two isomers by column chromatography [107]. Five stereoisomers of such a dimer are possible and for a nonplanar $\mathrm{Fe_2S_2}$ ring each of these can exist in two conformational forms [353b]. The formulations of the two isomers obtained in this work (Fig. 11) were based on spectroscopic evidence. The stabilities of the dimeric Se and Te compounds are considerably greater than that of the S analog. The relative stabilities of the two isomers (Fig. 11) of these dimers also differ significantly for the three chalcogens, the amount of isomer B obtained in the reactions increasing in the order Te (major product) > Se(~ 25%) > S(~ 1%):

	A		B	
E	ν_{CO}($\mathrm{C_6H_{12}}$ soln.) (cm^{-1})	δ_{Cp}($\mathrm{CS_2}$ soln.) (ppm)	ν_{CO} (cm^{-1})	δ_{Cp} (ppm)
S[a]	1982, s	4.43	1953, s 1937, s	4.03
Se	1975, s	4.46	1947, s 1931, s	4.02
Te	1965, m	4.48	1937, 1921	4.11

[a] The crystal structure of this isomer has been reported, the $\mathrm{Fe_2S_2}$ ring being slightly puckered (i.e., the ring is folded about a line through the Fe atoms through ca. 16°) [354].

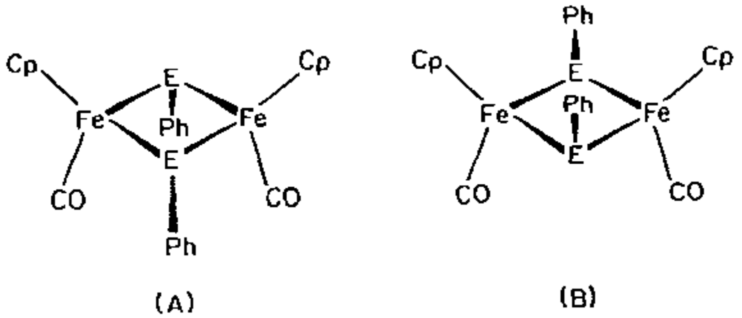

Fig. 11. Proposed structures of $[\pi Cp(CO)FeEPh]_2$ (E = S, Se, Te) dimers.

A similar reaction with $Te_2(p\text{-}EtO{-}C_6H_4)_2$ [114b] gave a dark brown product from which two isomers were separated mechanically after recrystallization of the reaction residue from dichloromethane/hexane. Crystals of the isomer obtained in lower yield (ca. 5%) were shown by single-crystal X-ray diffraction to have the structure in which the cyclopentadienyl rings are *cis* with respect to the puckered Fe_2Te_2 ring and both aromatic groups on the tellurium bridge atoms lie on the same side of the Fe_2Te_2 ring (i.e., Fig. 11B) [114b]. The four-membered Fe_2Te_2 ring is folded by 17° about a line joining the Fe atoms and is similar to the puckering of the ring in $\pi CpCOFe(\mu\text{-}SPh)_2FeCO\pi Cp$, where angles of 16° and 19° for the two independent molecules of the asymmetric unit were reported [354]. Infrared and Mössbauer (^{57}Fe and ^{125}Te) data for both isomers have been reported (Table 5) [114b].

Two brief reports [131,132] of iron carbonyl complexes with tellurophene derivatives have appeared. The reaction of tellurophene with $Fe_3(CO)_{12}$ in boiling benzene gave, besides black $Te_2Fe_3(CO)_9$ and the yellow ferracyclopentadiene complex, $C_4H_4Fe_2(CO)_6$, a red crystalline, sublimable, light-sensitive complex in 18% yield [132]. This complex, which has the empirical formula $C_{10}H_4Fe_2O_6Te$, is monomeric in benzene and gives, on thermolysis, $C_4H_4Fe(CO)_6$. Its IR spectrum is quite different from that of free tellurophene and has three terminal and no bridge ν_{CO} bands (Table 5). Its mass spectrum shows a parent ion at 459 and additional peaks at $459 - n \cdot 28$ ($n = 1$–6), which are generated by successive cleavage of the CO ligands. On the basis of this evidence and its NMR spectrum (Table 5), a metallocycle structure was proposed for the complex (Table 5). Analogous structures have been proposed for thianaphthalene [355], 2,2′-thienyl [356] and arsole [357] iron carbonyl complexes.

The reaction of tetraphenyltellurophene with $Fe_3(CO)_{12}$ in refluxing toluene-benzene (2:1) gave a red crystalline product formulated as (tetraphenyltellurophene)$Fe(CO)_3$ on the basis of its IR spectrum [131].

The cluster compound $FeCo_2(CO)_9Te$ [141] has been discussed in the section on Co complexes. Several other cluster compounds incorporating Te in the framework have been reported [139–146]. The first such cluster compound, reported by Hieber and Gruber [139a] in 1958, was prepared in aqueous solution by telluric acid oxidation of the tetracarbonylferrate anion (the S and Se derivatives were prepared by analogous reactions)

$$\begin{tikzcd}[column sep=small] 3\,[Fe(CO)_4]^{2-} + 2\,TeO_3^{2-} + 10\,H^+ \rightarrow Fe_3Te_2(CO)_9 + 2\,CO + 5\,H_2O \\ Fe(CO)_5 \arrow[u, "NaOH/MeOH"'] \end{tikzcd} \qquad (51)$$

The cluster is obtained as a grey-black, air-stable solid, which is stable even to dilute acids at high temperatures [139a]. The mass spectrum of this cluster shows a molecular peak followed by nine signals of equal intensity, corresponding to the successive loss of the nine carbonyl ligands, the $Fe_3Te_2^+$ peak being the most intense [142]. Loss of Fe atoms from the decarbonylated cluster core is also observed, the following degradation scheme being proposed on the basis of the mass spectral data

$$\begin{tikzcd} Fe_3Te_2(CO)_9 \arrow[r] & Fe_3Te_2(CO)_9^+ \arrow[r] & Fe_3Te_2(CO)_n^+ + 9-n\,CO^+ \arrow[d] & & \\ & & Fe_3Te_2^+ \arrow[r] & Fe_2Te_2^+ \arrow[r] & Fe_2Te^+ \arrow[d] \\ & & & & Fe_2^+ \end{tikzcd} \qquad (52)$$

An analysis of the intensity relations in the mass spectra of the $Fe_3E_2(CO)_9$ ($E = S$, Se, Te) clusters gave the following order of Fe–C bond strengths: $S < Se < Te$. This order corresponds to the decrease in electronegativity going from S to Te, the increased basicity of the Te being reflected in increased covalence of the Fe–C bond [142]. Attempts to identify the residue obtained in the thermogravimetric analysis of $Fe_3Te_2(CO)_9$ by X-ray diffraction were unsuccessful [142].

The structure of this cluster has not been reported, but Dahl et al. showed that the S [358] and Se [359] analogs contain an approximate square pyramidal Fe_3E_2 framework with an iron atom set at the apex and alternate E and Fe atoms at the corners of the basal plane, each Fe having three terminal CO ligands.

Fractional sublimation (0.1 mm Hg, 45°C, 36 h) of the crude product obtained by the method of Hieber and Gruber [139a] (i.e., primarily $Fe_3(\mu_3\text{-}Te)_2(CO)_9$) has been reported [139b] to give a small amount ($< 1\%$ of total) of a black solid formulated on the basis of IR spectroscopy (Table 5) and chemical reactivity as a mixture of $Fe_3(\mu_3\text{-}Te)_2(CO)_9$ and $Fe_2(\mu_2\text{-}Te_2)(CO)_6$.

Although the dimer could not be purified by adsorption chromatography, its oxidative addition product with $Pt(PPh_3)_2(C_2H_4)$ was isolated and purified chromatographically. The cluster $Fe_3(\mu_3\text{-}Te)_2(CO)_9$ is unreactive towards the Pt(0) complex. The formation of the oxidative addition product, $(CO)_6Fe_2(\mu_3\text{-}Te)_2Pt(PPh_3)_2$ [139b], which was characterized by IR, ^{31}P NMR, and field desorption mass spectroscopy, was cited as evidence for the presence of $Fe_2(\mu_2\text{-}Te_2)(CO)_6$ in the sublimate.

The variable-temperature ^{13}C NMR spectrum of $Fe_3Te_2(CO)_9$ ($CDCl_3$ solution) has been interpreted in terms of two discrete carbonyl exchange processes [143]. In the first step, the carbonyls on the apical iron atom become equivalent, and in the second step, those at the basal iron atoms. At room temperature only two resonances are observed, corresponding to the equivalent carbonyls on apical Fe(1) and the two basal iron atoms Fe(2) (Fig. 12). When the temperature is lowered to −87°C, the carbonyls on the apical iron Fe(1) remain equivalent (the solid-state structure predicts two types of carbonyls), while two resonances are observed for the carbonyls on the basal iron atoms (three types of carbonyls on the basal iron atoms are expected for the solid-state structure). Delocalized exchange between CO groups of apical and basal iron atoms does not occur.

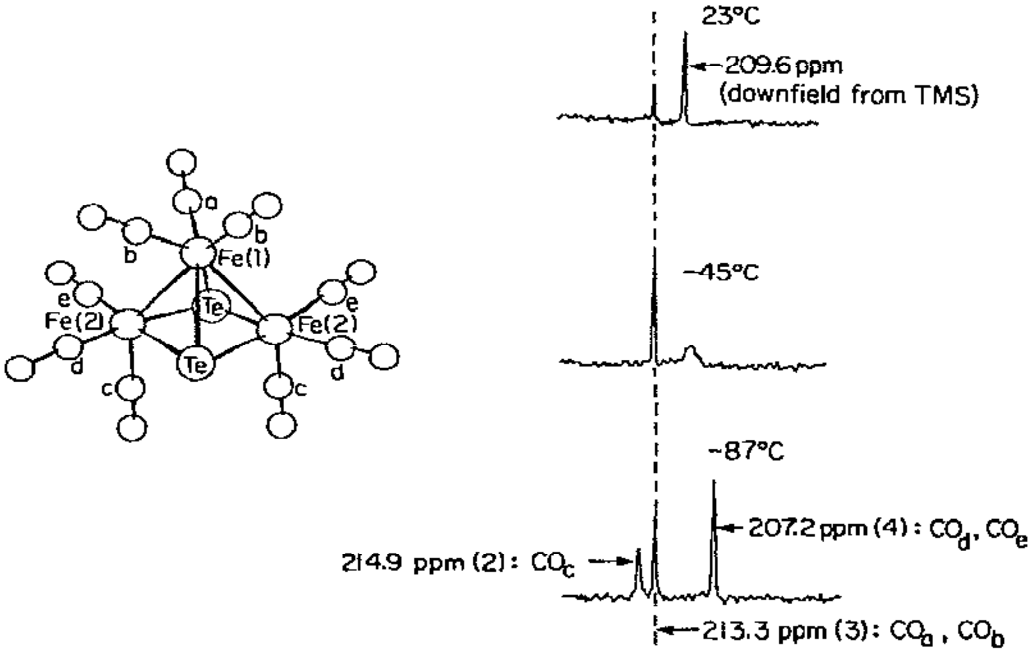

Fig. 12. The structure and variable-temperature ^{13}C NMR spectrum of $Fe_3Te_2(CO)_9$. Reproduced with permission from J. Chem. Soc., Dalton Trans., (1980) 46.

Reaction of $Fe_3Te_2(CO)_9$ under mild conditions with CO, $P(n\text{-}Bu)_3$, $P(OPh)_3$, and $AsPh_3$ gave, initially, ligand addition products, $Fe_3Te_2(CO)_9L$ [140], but under more forcing reaction conditions mono- and disubstituted complexes were obtained for the P and As bases, $Fe_3Te(CO)_{9-n}L_n$ ($n = 1, 2$) [140]. In contrast, the S and Se analogs gave only the latter two types of substitution products [140]. The ligand addition reaction with CO required high CO pressures (70–80 atm) to give the black, rather insoluble, and air-sensitive $Fe_3Te_2(CO)_{10}$. In contrast, the P and As ligands readily undergo this reaction in essentially quantitative yields by reaction of the cluster with ca. 6 equivalents of the ligand in heptane at room temperature for about 1 day. These air-sensitive adducts readily revert to $Fe_3Te_2(CO)_9$ in solution. Similar reactions run at 40–50°C gave mixtures of mono- and disubstituted products, the ratio depending on reaction time, which were separated by TLC. The solid substituted derivatives, as solids or in solution, are stable in an inert atmosphere and decompose only slowly in air, but the liquid derivatives are more unstable [140].

The kinetics of CO isotopic exchange and substitution reactions with the above ligands in the clusters $Fe_3(CO)_9X_2$ ($X = S$, Se, Te) follow an S_N1 and/or S_N2 mechanism, depending on the electronegativity of X and the nucleophilicity of the ligand [146]. The tendency of these clusters to react via S_N2 vs. S_N1 kinetics increases in the direction $CO < AsPh_3 < P(OPh)_3 < P(n\text{-}Bu)_3$, whereas, for the same ligand, the pattern is $S < Se < Te$. Increased chalcogen electronegativity (ca. Te 2.1; Se 2.4; S 2.5) [360] is reflected in increased positive charge on Fe and reduced $Fe \rightarrow CO$ π back donation and an increased ν_{CO} ($Fe_3X_2(CO)_9$: $X = Te$, 2048, 2027, 2007; Se, 2057, 2037, 2017; S, 2063, 2045, 2025 cm^{-1}) [140]. The requirement of Fe–CO bond cleavage for the S_N1 mechanism is consistent with the observed increased tendency for S_N1 substitution in the $Fe_3E_2(CO)_9$ clusters with increasing electronegativity of the chalcogen atom [146].

The variable-temperature ^{13}C NMR spectrum of $Fe_3Te_2(CO)_9P(n\text{-}Bu)_3$ has been reported [143]. Four resonances were observed at −90°C (two doublets corresponding to the three carbonyls on the apical iron ($CO_a(1)$ and $CO_b(2)$, Fig. 13) and two singlets (corresponding to the two distinguishable types of carbonyls on the basal iron atoms (CO_c and $CO_{d,e}$). Raising the temperature merges the two singlets, corresponding to a rapid exchange of the carbonyls on the basal irons, while the two doublets corresponding to the apical carbonyls remain unchanged (Fig. 13). The latter behavior is in contrast to that of the parent $Fe_3Te_2(CO)_9$, which gives a single resonance for all three carbonyls on the axial iron atom over the complete temperature range studied [143].

These spectral results support the presence of two symmetry-equivalent $Fe(CO)_3$ groups and show that only the CO ligands bound to the unique

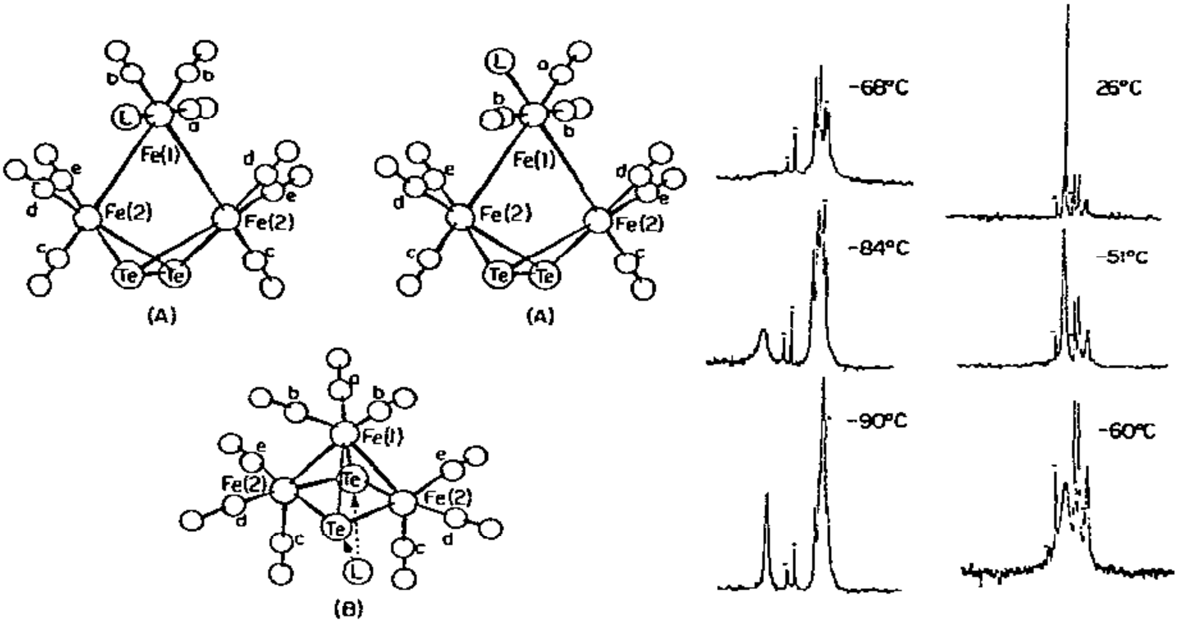

Fig. 13. Variable-temperature ^{13}C NMR spectra and proposed structures for $Fe_3Te_2(CO)_9\text{-}P(n\text{-}Bu)_3$. Reproduced with permission from J. Chem. Soc., Dalton Trans., (1980) 46.

apical iron atom exhibit sizable P–C coupling constants. Two structures have been proposed [143] on the basis of these spectral data (Fig. 13): (1) two isomers of structure A in which the phosphine is coordinated to the apical iron and (2) structure B in which the phosphine bridges the two basal tellurium atoms, its interaction with the cluster being via an empty molecular orbital which has predominantly chalcogen character. The latter structure, B, is more consistent with the chemical properties of the phosphine adduct [140] (e.g., (1) with group VA ligands, the substitution of one CO occurs at only one of the basal iron atoms and (2) the stability of the adducts increases with decreasing electronegativity of the chalcogen).

The clusters $Fe_3(CO)_9ETe$ ($E = S$, Se) have been prepared by reaction of $Fe(CO)_5$ in alkaline methanol solution with an equimolar mixture of sodium selenite and tellurite, respectively, at 0°C [144,145] (e.g., eqn. 51). The mixed clusters were separated from the other products ($Fe_3(CO)_9Te_2$ and $Fe_3(CO)_9E_2$) by thin-layer chromatography [144]. The similarity of their IR spectra (Table 5) to those of the $Fe_3(CO)_9E_2$ ($E = S$ [358], Se [359], Te [139a]) as well as the analogies in elemental formula, preparative methods and properties, suggests that these mixed clusters are isostructural with the former clusters. Substituted derivatives of these mixed chalcogen clusters ($Fe_3(CO)_{9-n}L_nETe$; $E = S$, Se; $n = 1, 2$; $L = AsPh_3$, $P(OPh)_3$) have been prepared by reaction of the parent clusters with a large excess of the ligands (ca. 10:1 molar ratio) in heptane or petroleum ether at 40–100°C, the mono- and disubstituted products being isolated analytically pure by TLC followed by recrystallization [145]. The substituted derivatives, which are generally air stable in the solid state, were obtained in 50% (monosubstituted) and 20% (disubstituted) yields. The disubstituted derivatives give lower ν_{CO} bands compared to the monosubstituted analogs, as expected from the relative π-acceptor ability of the phosphite and arsine ligands vs. CO. Similarly, a decrease in ν_{CO} is observed in a homologous series of Te, E clusters as the electronegativity of the chalcogen decreases (S > Se > Te). Both of these effects produce increased electron density on the iron atoms, which is then delocalized by π back bonding into the carbonyl ligands. The substitution reactions and the CO exchange reactions follow a two-term rate law: rate $= k_1$ [complex] $+ k_2$ [complex][ligand] in which the relative values of k_1 and k_2 depend on the nature of the chalcogen atoms and the ligands [146].

Ru

Hieber and John [104] have reported the synthesis of several ruthenium carbonyl complexes. Reaction of an alcoholic CO-saturated solution of ruthenium trichloride hydrate with diphenyl telluride gave a mixture of mono- and disubstituted complexes, which were separated in yields of 40% and 25%, respectively, by fractional crystallization. Analogous reactions with N, P and As bases gave exclusively the disubstituted products, $RuCl_2(CO)_2L_2$ [361–364]. Disubstituted complexes were also prepared by the reaction of the polymeric carbonyl halides with the telluride [104]

$$[Ru(CO)_2X_2]_n + 2n\,L \xrightarrow[\text{ca. }100°C]{C_6H_6} n\,Ru(CO)_2L_2X_2 \tag{53}$$

where X = I and L = Te(n-Bu)$_2$ or TePh$_2$; X = Br and L = TePh$_2$. The trisubstituted derivatives were also reported to have been formed in small amounts in these reactions. However, they were not isolated but were detected by IR spectroscopy (Table 5). No data other than melting points were reported for the isolated ruthenium complexes. These complexes (Table 5) are generally less stable than the analogs with N and P ligands. Unlike the latter complexes, which undergo facile halide exchange when treated with molecular halogens of stronger oxidizing power, the organotellurium ligands are cleaved from their ruthenium complexes by such treatment [104]

$$\underset{R = \text{n-Bu, Ph}}{Ru(CO)_2TeR_2I_2} \xrightarrow[X = Cl,\, Br]{X_2} Ru(CO)_2X_2 + 2\,TeR_2X_2 + I_2 \tag{54}$$

The only other report of a monomeric Ru complex containing a tellurium ligand is that of Stein and Taube [154a], who described the pentaammineruthenium(II) and (III) complexes with $TeMe_2$. The Ru(II) complex (Table 5) was prepared in 85% yield by allowing a fivefold excess of $TeMe_2$ to react with freshly prepared $[(NH_3)_5RuOH_2](PF_6)_2$ in deaerated acetone, the yellow complex being precipitated by addition of ether. The Ru(III) analog, which was generated in solution by electrochemical and chemical (e.g., Ce(IV), 30% H_2O_2 or O_2 in 0.2 M HCl) oxidation of the Ru(II) complex, was not isolated but was characterized by electronic spectroscopy [154a]. The Ru(II) complex showed reversible electrochemical behavior on a Pt button electrode in cyclic voltammetry over the scan rates 100–1000 mV s^{-1}. The Ru(II) complex was stable to hydrolysis in the 0.1 M HCl medium used for the electrochemical oxidation. The slow hydrolysis reaction, studied by using 4-cyanopyridine as a scavenger for any aquo complex formed, involved replacement of NH_3 rather than $TeMe_2$. The decrease in energy of λ-max for the complexes $[Ru(NH_3)_5EMe_2]^{2+}$ (E = S, 453 nm (ε 300); Se, 487 nm (ε 150); Te, 600 nm (ε 60)) follows the increasing ease of oxidation of the chalcogen ligands, and the corresponding decrease in ε has been explained in terms of a decrease in *s–p* hybridization going down the group VI ligands, the lone pair becoming increasingly "*s*" in character [154a]. The low-energy band in $[Ru(NH_3)_5TeMe_2]^{2+}$ (318 nm) has been assigned as a ligand field transition, and the higher-energy band (243 nm) was assigned as a metal-to-ligand charge transfer [154a].

The reaction of $Ru_3(CO)_{12}$ with diphenyl telluride in 60°C benzene in a 2:3 molar ratio gave a small amount of $(OC)_3Ru(\mu\text{-}TePh)_2Ru(CO)_3$ (ca. 10% of isolated product), the major product being polymeric $[Ru(CO)_2(TePh)_2]_n$ [112]; the latter material was isolated by column chromatography in two fractions, a lower-molecular-weight fraction ($n = 6–7$) and a higher-molecular-weight fraction ($n = 12–14$). The latter fraction constituted about 90% of the isolated reaction products. If the molar ratio of $Ru_3(CO)_{12}$:Te_2Ph_2 was decreased below 2:3, the dimeric product was eliminated, the only reaction products being the two polymers. The behavior of $Ru_3(CO)_{12}$ thus differs from that of $Fe_3(CO)_{12}$, which gave only dimeric product in its reaction with Te_2Ph_2 [112], a reflection of the greater tendency towards substitution of CO by tellurium with $(OC)_3Ru(\mu\text{-}TePh)_2Ru(CO)_3$ than with the iron analog. Although the crystal structure of the Ru dimer has not been reported, the similarity of its IR spectrum to that of $(OC)_3Fe(\mu\text{-}SEt)_2Fe(CO)_3$, the structure of which has been shown to have a folded Fe_2S_2 ring with an *anti* conformation of the alkyl groups [347], suggests the compounds are isostructural. Although the *syn* isomer has also been isolated for the $[Fe(CO)_3SEt]_2$ system [349], no chromatographic evidence for the second isomer of $[Ru(CO)_2TePh]_2$ was found. A cluster rather than a chain structure (e.g., as in $[Ru(CO)_2I_2]_n$ [365]) has been tentatively proposed for

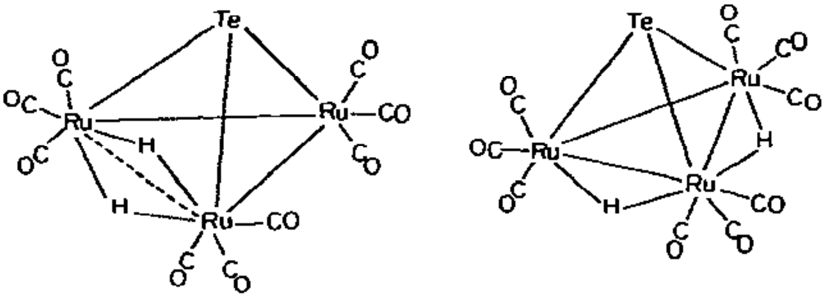

Fig. 14. Proposed structures of $H_2Ru_3Te(CO)_9$.

the polymeric products, on the basis of their IR spectra and solubility properties [112].

Attempts to prepare $Ru_3Te_2(CO)_9$ by reacting $Ru_3(CO)_{12}$ in alkaline solution with tellurite ion (i.e., TeO_2 + aqueous KOH), reaction conditions used in the synthesis of $Fe_3Te_2(CO)_9$ [139a], gave the hydride cluster $H_2Ru_3Te(CO)_9$ [147]. This product was obtained in only 0.5% yield after acidification of the reaction solution with 2 N H_2SO_4 and CCl_4 extraction of the resulting precipitate. The residue from the extraction was a poorly defined polymeric material containing Ru,Te and terminal CO ligands. On the basis of its spectroscopic properties (Table 5), two alternative structures have been proposed for the cluster product (Fig. 14).

Lewis and co-workers [148] have reported that reaction of $Ru_3(CO)_{12}$ with elemental tellurium in n-octane under a CO/H_2 pressure of 35 atm gave a mixture of $Ru_3(CO)_9Te_2$ and $Ru_3(CO)_9H_2Te$, which was separated by thin-layer chromatography.* These workers also reported that carrying out the reaction under a pure CO pressure gave a significantly decreased yield of the hydrido cluster, but yields for these reactions are not given. Infrared data for only the hydrido cluster have been reported (Table 5).

Os

The only Os complex with an organotellurium ligand is the recently reported tellurocarbonyl $OsCl_2(PPh_3)_2(CO)CTe$ [149a]. A number of thio- and selenocarbonyl complexes are known, these ligands generally being introduced by using CE_2 (E = S, [366,367], Se [368,369]), but this is the first example of a tellurocarbonyl complex. Since CTe_2 is unknown, a novel route involving a dichlorocarbene complex was used [149a]

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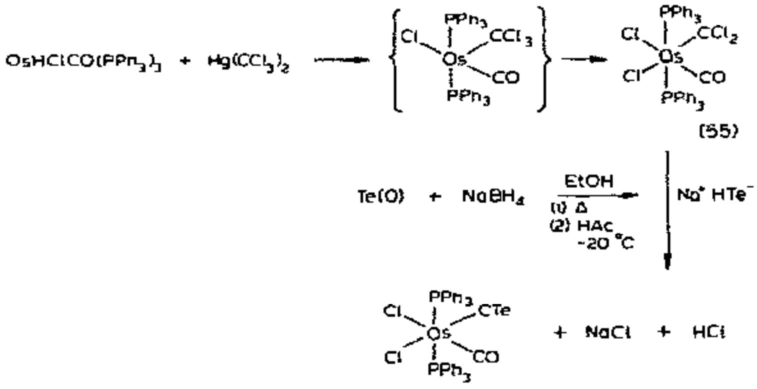
* The S and Se analogs were prepared by similar reactions [148].



(55)

The orange crystalline tellurocarbonyl complex was isolated in 30% yield after column chromatography and characterized by IR spectroscopy (Table 5).

The reaction of $Os_3(CO)_{12}$ with elemental tellurium in refluxing n-octane gave a mixture of $Os_3(CO)_9H_2Te$, $Os_3(CO)_9Te_2$, and $Os_4(CO)_{12}H_2Te_2$ [148], which was separated by thin-layer chromatography. The S and Se analogs were prepared by analogous reactions, and the molecular structure of $Os_4(CO)_{12}H_2Se_2$ was established by single-crystal X-ray diffraction. In the latter structure the four Os and two Se atoms define a distorted trigonal prism with each Se atom capping a triangular arrangement of Os atoms and two Os–Os distances in each Os_3Se unit being nonbonded (ca. 4 Å). Three terminal carbonyl ligands are bonded to each Os atom, and the two hydride ligands presumably edge-bridge the two long Os–Os bonds, since the carbonyl ligands bend away from the edges. Infrared data for $Os_3(CO)_9Te_2$ have been reported (Table 5).

(vi) Mn, Tc, Re

Mn

Dialkyl telluride complexes. Although Hieber and Kruck reported in early work dealing with organotellurium ligands in transition metal carbonyl chemistry that a variety of substitution products could be obtained from reactions with $TePh_2$, similar reactions with $Te(n\text{-}Bu)_2$ did not give analogous substitution products [102]

$$2\,Mn(CO)_5Cl + 2\,Te(n\text{-}Bu)_2 \xrightarrow[35°C]{\text{ether}} [(OC)_4MnCl]_2 + 2\,CO + 2\,Te(n\text{-}Bu)_2 \quad (56)$$

$$\left(+2\,TePh_2 \xrightarrow[35°C]{\text{ether}} Mn(CO)_3(TePh_2)_2Cl\right) \quad (57)$$

Although both aromatic and aliphatic organophosphines readily give substitution products with manganese carbonyls such as $Mn_2(CO)_{10}$ [370,371] and $Mn(CO)_5Cl$ [372–375], only the chloro-bridged dimer was obtained in the reactions with $Te(n\text{-}Bu)_2$. However, in view of the low yield (ca. 40%) of the same dimeric product obtained on heating $Mn(CO)_5Cl$ in petroleum ether (100–102°C) [372], the essentially quantitative yield obtained here was rationalized in terms of a catalytic effect of the dibutyl telluride ligand, an unstable monosubstituted product being invoked as an intermediate [102]

$$2\ Mn(CO)_5Cl + 2\ Te(n\text{-}Bu)_2 \rightarrow 2\ \{Mn(CO)_4(Te(n\text{-}Bu)_2)Cl\} + 2\ CO \tag{58}$$

$$2\{Mn(CO)_4(Te(n\text{-}Bu)_2)Cl\} \rightarrow [Mn(CO)_4Cl]_2 + 2\ Te(n\text{-}Bu)_2 \tag{59}$$

The difference in reaction products obtained with $TePh_2$ and $Te(n\text{-}Bu)_2$ was explained in terms of increased metal → tellurium back bonding in the case of the former ligand.

Diaryl telluride complexes. The first reported work dealing with organotellurium ligands in transition metal carbonyl chemistry was reported by Hieber and Kruck [102] in 1962. Although the reaction of $Mn_2(CO)_{10}$ with diphenyl telluride cleaved a Te–C bond in this ligand to give a dimeric product with $TePh^-$ bridges, substitution products were isolated in reactions with manganese pentacarbonyl halides

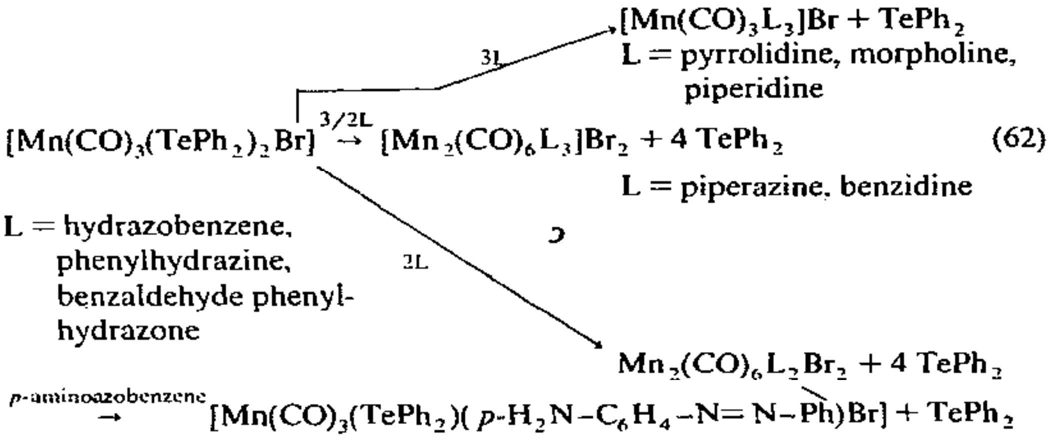
$$Mn(CO)_5X + 2\ TePh_2 \xrightarrow[\text{ether}]{35°C} Mn(CO)_3(TePh_2)_2X \tag{60}$$
$$X = Cl, Br, I$$

These reactions go readily in refluxing ether to give air- and moisture-stable products which are nonelectrolytes.

In contrast to analogous reactions [372–375] with phosphines, arsines, and stibines, no monosubstituted derivatives could be isolated [102], nor could more than two carbon monoxides be substituted in these reactions. Although the IR spectra of the substituted products did not allow an unequivocal assignment of their stereochemistry, it was proposed that the halide and diphenyl telluride ligands are mutually *cis* in these complexes. A dark-green nitrosyl complex was obtained by passing NO through these carbonyl complexes [102]

$$\begin{aligned}&2\ Mn(CO)_3(TePh_2)_2Cl + 6\ NO \rightarrow\\ &\quad 2\ Mn(NO)_3(TePh_2) + 6\ CO + TePh_2 + TePh_2Cl_2\end{aligned} \tag{61}$$

This complex was characterized only by IR spectroscopy, since it could not be isolated in pure form because its solubility was similar to that of $TePh_2$. Substitution reactions of $Mn(CO)_3(TePh_2)_2Br$ with a variety of nitrogen bases were studied by Hieber and Stanner [105], one or both of the tellurium ligands being replaced, depending on the nitrogen ligand used



$$[Mn(CO)_3(TePh_2)_2Br] \xrightarrow{3L} [Mn(CO)_3L_3]Br + TePh_2$$

L = pyrrolidine, morpholine, piperidine

$$[Mn(CO)_3(TePh_2)_2Br] \xrightarrow{3/2L} [Mn_2(CO)_6L_3]Br_2 + 4\,TePh_2 \qquad (62)$$

L = piperazine, benzidine

$$[Mn(CO)_3(TePh_2)_2Br] \xrightarrow{2L} Mn_2(CO)_6L_2Br_2 + 4\,TePh_2$$

L = hydrazobenzene, phenylhydrazine, benzaldehyde phenylhydrazone

$$\xrightarrow{p\text{-aminoazobenzene}} [Mn(CO)_3(TePh_2)(p\text{-}H_2N{-}C_6H_4{-}N{=}N{-}Ph)Br] + TePh_2$$

Aryl tellurol complexes. The reaction of $Mn_2(CO)_{10}$ with $TePh_2$ for 125 h at 125°C in *p*-xylene gave the orange, air-stable dimer $(OC)_4Mn(\mu\text{-}TePh)_2Mn(CO)_4$ [102]. Although bridging $ArTe^-$ ligands are generally introduced with a ditelluride [106,107,109–112,114a,b], a telluroester (ArTeCOAr′) [115], or a $ArTeMAr'_3$ derivative [116,117,119], a similar Te–C bond cleavage with formation of $PhTe^-$ bridging ligands has been reported in the reaction of $RhCl_3$ with $TePh_2$ [120] (eqn. 40). Indeed, dimeric selenium analogs, $(OC)_4Mn(\mu\text{-}SeR)_2Mn(CO)_4$ (R = alkyl, aryl), have been prepared from diselenides (eqn. 63) and R_3SnSeR' (eqn. 64) reagents

$$Mn(CO)_5H + RSeSeR \rightarrow (OC)_4Mn(\mu\text{-}SeR)_2Mn(CO)_4 \qquad (63)[376]$$

$R = CX_3, C_2X_5, C_3X_7$; X = H, F

$$Mn(CO)_5Cl + Me_3SnSeR \rightarrow (OC)_4Mn(\mu\text{-}SeR)_2Mn(CO)_4 \qquad (64)[377]$$

R = Me, Et, Ph

The similarity of the IR spectra of $(OC)_4Mn(\mu\text{-}TePh)_2Mn(CO)_4$ [151] and $(OC)_4Mn(\mu\text{-}Br)_2Mn(CO)_4$ (the crystal structure of which has established a D_{2h} molecular configuration [378]), indicates the compounds are isostructural.

Heterocyclic ligands. Only one Mn complex with a heterocyclic tellurium ligand has been reported, $Mn(CO)_3(phenoxtellurine)_2Cl$, prepared by reacting $Mn(CO)_5Cl$ with two moles of the heterocycle in ethanol at 50°C [102].

Lappert et al. [138b] have recently reported the first metal complexes with a tellurourea-type ligand (e.g., *cis*-$Br(OC)_4Mn\{Te{=}\overline{CN(Et)[CH_2]_2N}Et\}$; see eqn. 73).

Ligands with a Te–group IVA element bond. The reaction of $Mn(CO)_5Br$ with $E(SnMe_3)_2$ ($E = Se$, Te) in benzene gave the air-stable dimeric complexes $(OC)_4Mn(\mu\text{-}ESnMe_3)_2Mn(CO)_4$ (91% and 11% yields, respectively) [127]. Unlike the Se complex the Te analog does not undergo thermolysis to give the tetramer (i.e., $[(OC)_3Mn(SeSnMe_3)]_4$) but rather decomposes only on heating in organic solvents [127]. It does, however, resemble the Se complex in its reaction with ethereal HCl, the air-sensitive dimer $(OC)_4Mn(\mu\text{-}TeH)_2Mn(CO)_4$ being formed. Although the strong ν_{CO} bands of this dimer obscure the ν_{Te-H} band, the ^1H NMR spectrum shows the expected high-field Te–H signal (Table 6). Although the chemistry of the Te dimer was not investigated, the Se dimer reacted with diazomethane as well as CO [127]

$$(OC)_4Mn(\mu\text{-}SeH)_2Mn(CO)_4 + CH_2N_2 \rightarrow (OC)_4Mn(\mu\text{-}SeMe)_2Mn(CO)_4 \quad (65)$$

$$(OC)_4Mn(\mu\text{-}SeH)_2Mn(CO)_4 + CO(250\ \text{atm}) \xrightarrow{CCl_4} Mn(CO)_5SeH \quad (66)$$

Tc

Although no Tc compounds with organotellurium ligands have been reported, substitution reactions of $M(CO)_5X$ ($M = Tc$, Re; $X = Cl$, Br, I) with ER_2 ($E = S$, Se; $R = n\text{-}Bu$, Ph) have been reported to give the complexes $[Tc(CO)_3EPh_2Cl]_2$ ($E = S$, Se), and presumably the tellurium ligands would give analogous substitution products [103].

Re

Relatively few Re complexes with organotellurium ligands have been reported. Reactions of $Re(CO)_5X$ ($X = Cl$, Br, I) with TeR_2 ($R = n\text{-}Bu$, Ph) in refluxing ethanol gave the disubstituted products, $Re(CO)_3(TeR_2)_2X$, in poor yields for $Te(n\text{-}Bu)_2$ but in essentially quantitative yields for $TePh_2$ [103]. This enhanced reactivity of $TePh_2$ vs. $Te(n\text{-}Bu)_2$ was also found in the substitution reactions with $Mn(CO)_5Cl$ [102] (eqns. 58 and 59). On the basis of IR spectroscopy, *cis* configurations were assigned to all the complexes except $Re(CO)_3(Te(n\text{-}Bu)_2)_2X$ ($X = Br$, I). The complex $Re(CO)_3(Te(n\text{-}Bu)_2)_2Cl$ was isolated as two fractions, the pure *cis* isomer and a mixture of *cis* and *trans* isomers [103].

The monosubstituted complex $Re(CO)_4(TeEt_2)Cl$ was prepared by a substitution reaction with $(OC)_4Re(\mu\text{-}Cl)_2Re(CO)_4$, the disubstituted derivative being formed under more forcing conditions [152]

$$(OC)_4Re(\mu\text{-}Cl)_2Re(CO)_4 + 2\ TeEt_2 \xrightarrow[r.t.]{CCl_4} Re(CO)_4(TeEt_2)Cl \quad (67)$$

$$(OC)_4Re(\mu\text{-}Cl)_2Re(CO)_4 + 4\ TeEt_2 \xrightarrow{CCl_4/reflux} Re(CO)_3(TeEt_2)_2Cl + CO \quad (68)$$

TABLE 6

Mn, Tc, Re complexes

	M.p. (°C)	Misc. data	Ref.
Mn complexes			
(a) Dialkyl telluride complexes			
$Mn(CO)_4Te(n\text{-}Bu)_2Cl$		Proposed as intermediate in the reaction: $2\ Mn(CO)_5Cl + 2\ Te(n\text{-}Bu)_2 \xrightarrow{\Delta}$ $(CO)_4Mn(\mu\text{-}Cl)_2Mn(CO)_4 + 2\ CO + 2\ Te(n\text{-}Bu)_2$ Complex not isolated	102
(b) Diaryl telluride complexes			
$Mn(CO)_3(TePh_2)_2Cl$		Orange-yellow needles Air stable Sol. in benzene, $CHCl_3$ and EtOH $\nu_{CO}(KBr) = 2013$ (vs), 1955 (vs), 1919 (vs) cm^{-1}	102
$Mn(CO)_3(TePh_2)_2Br$		Orange crystals Sol. in benzene ν_{CO} (KBr) = 2016 (vs), 1957 (vs), 1920 (vs) cm^{-1}	102
$Mn(CO)_3(TePh_2)_2I$		Orange-red solid Sol. in organic solvents $\nu_{CO}(KBr) = 2024$ (vs), 1963 (vs), 1916 (vs) cm^{-1}	102
$Mn(NO)_3TePh_2$		Cpd. identified by IR; not isolated because solubility similar to that of $TePh_2$ ν_{CO} (THF) = 1794 (m), 1703 (vs) cm^{-1}	102
$Mn(CO)_3TePh_2(p\text{-}H_2N\text{–}C_6H_4N_2Ph)Br$	116	Dark-red solid ν_{CO} (KBr) = 2023 (s), 1959 (s), 1923 (s) cm^{-1}	105
(c) Tellurol complexes			
$(CO)_4Mn(\mu\text{-}TePh)_2Mn(CO)_4$		Orange needles MW (benzene) = 722 (calc. 743.4)	102

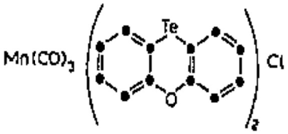
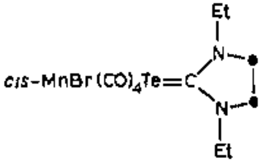
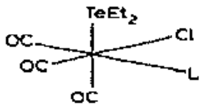
		Sol. in benzene, ether and pet. ether Air stable $\mu = 1.45$ D ν_{CO} (THF) = 2096 (s), 2030 (vs), 2000 (vs), 1968 (m), cm^{-1} ν_{CO} (CCl_4) = 2056 (A_1 (1)), 2006 (B_2), 1996 (A_1 (2)), 1965 (B_1) cm^{-1}	151
$(CO)_4Mn(\mu\text{-}TeH)_2Mn(CO)_4$	70 (dec.)	Light-brown powder ν_{CO} (C_6H_{12}) = 2054, 2000, 1998, 1974, 1964 cm^{-1} δ(Te–H) = −12.8 ppm (CH_2Cl_2)	127
(d) Heterocyclic ligand			
		Yellow needles ν_{CO} (KBr) = 2018 (vs), 1950 (vs), 1911 (vs) cm^{-1}	102
(e) Tellurourea ligand			
	80	Red crystals $\nu_{CN_2} = 1525$ cm^{-1} $\delta(^{13}C) = 154$ ppm (vs. $SiMe_4$)	138b
(f) Ligands with a Te–Group IVA element bond			
$(CO)_4Mn(\mu\text{-}TeSnMe_3)_2Mn(CO)_4$	150 (dec.)	Red, air-stable solid ν_{CO}(C_6H_{12}) = 2048, 1996, 1989, 1968, 1954 cm^{-1}	127
Re complexes			
(a) Dialkyl telluride complexes			
Cis-$Re(CO)_3(Te(n\text{-}Bu)_2)_2Cl$	20	ν_{CO} (CH_2Cl_2) = 2017 (vs), 1925 (vs), 1891 (vs) cm^{-1} Mixture of *cis* and *trans* isomers: ν_{CO}(CH_2Cl_2) = 2020, 1991 (s), 1926 (vs), 1888 (sh), 1870 (vs) cm^{-1}	103

TABLE 6 (continued)

	M.p. (°C)	Misc. data	Ref.
Trans-Re(CO)$_3$(Te(n-Bu)$_2$)$_2$Br		ν_{CO}(CH$_2$Cl$_2$) = 1994 (w), 1870 (m) cm^{-1}	117
Trans-Re(CO)$_3$(Te(n-Bu)$_2$)$_2$I		ν_{CO} = 1995 (m), 1867 (s) cm^{-1}	103
Cis-Re(CO)$_3$(TeEt$_2$)$_2$Cl	42	ν_{CO} (CCl$_4$) = 2022 (s), 1937 (s), 1898 (s) cm^{-1}	152
Cis-Re(CO)$_4$(TeEt$_2$)Cl	48	ν_{CO} (Nujol) = 2100 (m), 2010 (s), 1995 (s), 1918 (s) cm^{-1}	152
(b) Diaryl telluride complexes			
Re(CO)$_3$(TePh$_2$)$_2$Cl	132	ν_{CO}(CH$_2$Cl$_2$) = 2034 (s), 1939 (vs), 1907 (vs) cm^{-1}	103
Re(CO)$_3$(TePh$_2$)$_2$Br	134	ν_{CO} (CH$_2$Cl$_2$) = 2030 (vs), 1943 (vs), 1907 (vs) cm^{-1}	103
Re(CO)$_3$(TePh$_2$)$_2$I	149	ν_{CO} = 2028 (vs) 1944 (vs), 1910 (vs) cm^{-1}	103
Miscellaneous complexes			
(CO)$_3$Re(μ-Br)$_2$(μ-Te$_2$Ph$_2$)Re(CO)$_3$		ν_{CO} (CCl$_4$) = 2054, 2039, 1962, 1957, 1932 Red crystalline solid (C$_6$H$_6$/C$_7$H$_{16}$)	130b
(CO)$_3$Re(μ-I)$_2$(μ-Te$_2$Ph$_2$)Re(CO)$_3$		ν_{CO} (CCl$_4$) = 2049, 2034, 1960, 1933	130b
(CO)$_4$Re(μ-TeSnMe$_3$)$_2$Re(CO)$_4$		δ(SnMe) = 0.66 ppm ν_{CO} (C$_6$H$_{12}$) = 2075 (m), 1999, 1992, 1987, 1974, 1949 cm^{-1}	127

The monosubstituted complex was assigned a *cis* configuration on the basis of IR spectroscopy (C_s symmetry; $3A' + A''$), and a similar analysis of the disubstituted derivative (three strong ν_{CO} bands observed, C_S: $A'_a + A'_b + A''$, and a ν_{Re-Cl} characteristic of a *trans*-OC–Re–Cl linkage) supported the following structure [152]:



Comparison of the ν_{CO} bands for a series of analogous complexes with group VIA donor atoms led to the following order of bond strengths: Re–Se > Re–Te ~ Re–S > Re–O [152].

The reaction of $M(CO)_5Cl$ (M = Mn, Re) with $Te(SnMe_3)_2$ in benzene or 1,2-dimethoxyethane gave the dimeric complexes $(OC)_4M(\mu\text{-}TeSnMe_3)_2\text{-}M(CO)_4$. The Mn derivative was isolated and fully characterized, but the Re complex was rather unstable and was characterized only spectroscopically (Table 6) [127].

Dimeric complexes with bridging diphenyl ditelluride ligands have been

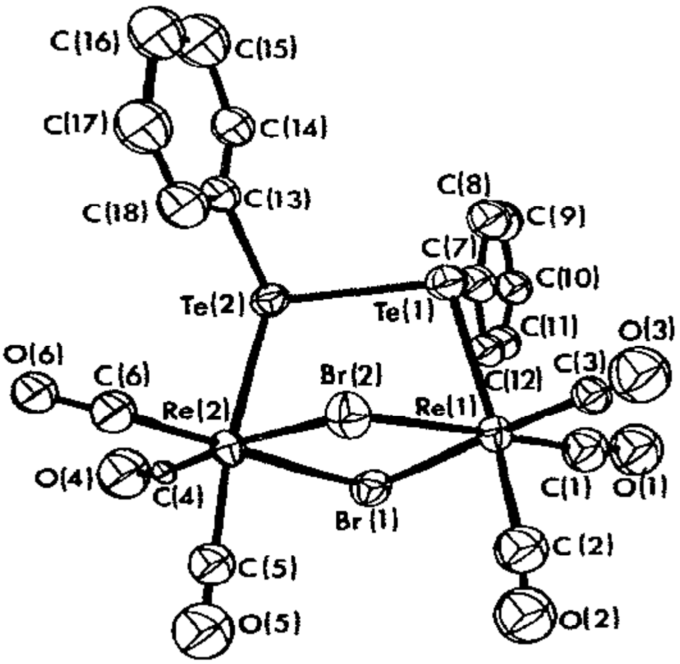


Fig. 15. Molecular structure of $(OC)_3Re(\mu\text{-}Br)_2(\mu\text{-}Ph_2Te_2)Re(CO)_3$. Reproduced with permission from J. Chem. Soc., Dalton Trans., (1981) 1004.

prepared by the following reactions [130b]:

$$[\mathrm{Re_2Br_2(CO)_6(THF)_2}] + \mathrm{Te_2Ph_2} \xrightarrow[\text{r.t.}]{\text{PhMe}} [\mathrm{Re_2Br_2(CO)_6(Te_2Ph_2)}] + \mathrm{THF} \quad (69)$$

$$2[\mathrm{Re(CO)_3I}] + \mathrm{Te_2Ph_2} \xrightarrow[120^\circ\mathrm{C}]{\text{PhMe}} [\mathrm{Re_2I_2(CO)_6(Te_2Ph_2)}] + 4\,\mathrm{CO} \quad (70)$$

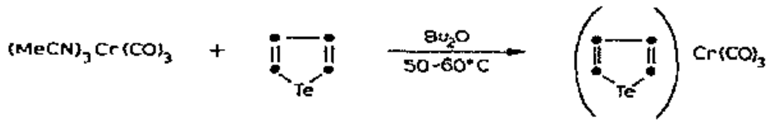
A dimeric structure with bridging bromo and diphenyl ditelluride ligands, $(OC)_3Re(\mu\text{-}Br)_2(\mu\text{-}Te_2Ph_2)Re(CO)_3$ (Fig. 15) was established for the former complex by a single-crystal X-ray diffraction study [130b]. The presence of the Te_2Ph_2 ligand is shown by the Te–Te separation of 2.794(5) Å, the corresponding values for the sum of the covalent radii and the experimental value for Te_2Ph_2 being 2.74 Å and 2.712 Å, respectively. The Re···Re non-bonding distance is 3.945(2) Å. The angle of fold about the Br···Br vector in the Re_2Br_2 fragment is significantly smaller here (13.2°) than for the sulfur (33°) and selenium (31°) analogs [130b]. These values can be rationalized by decreased strain of the bridge unit afforded by the larger E–E bond length.

The similarity of the IR spectra of the iodo and bromo analogs suggests they have the same structure.

(vii) Cr, Mo, W

Cr

Attempts to substitute $TePh_2$ in $Cr(CO)_6$ failed even after 24 h of heating the compounds at 125°C [191], but the π complex, tellurophene chromium tricarbonyl, was prepared in 80% yield by the following reaction [132]



(71)

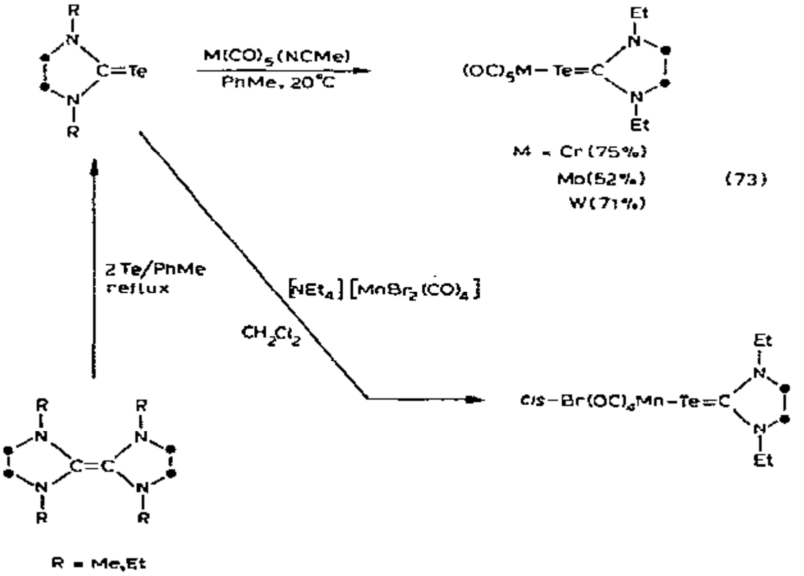
The purple-red crystalline compound was soluble in benzene as a monomer and was vacuum sublimed at ca. 65°C without decomposition. The higher dipole moment of this complex vs. the thiophene analog has been attributed to the larger atomic distance of Te (1.37 Å) vs. sulfur (1.04 Å), which would give a lengthening of the metal–ring distance. The ^1H NMR spectrum of the complex consists of two multiplets at 3.5 and 4.0 ppm (acetone-d_6), which correspond to the AA′BB′ pattern of the free heterocycle (τ 1.1 and 2.1). A comparison of this spectrum with those of the free heterocycle and 2,5-dideuterotellurophene showed that in both cases the low-field signal is assigned to the α protons, which are, therefore, shifted in the π complex to higher field than the β protons [132]. The relation and direction of the shifts of these two signals, therefore, correspond to those found with the thiophene system [379], but the absolute magnitude is larger.

The complexes $Cr(CO)_5Te(EMe_3)_2$ (E = Ge [136], Sn [136,137], Pb [136]) have been prepared by substitution reactions with the photochemically generated $Cr(CO)_5$ THF complex

$$Cr(CO)_6 \xrightarrow[THF]{h\nu} \{Cr(CO)_5THF\} \xrightarrow[0°C]{Te(EMe_3)_2} Cr(CO)_5Te(EMe_3)_2 \qquad (72)$$

The high light sensitivity of the telluride ligands necessitated this two-step reaction rather than direct irradiation of the two substrates, as with the analogous selenides [136,137]. The complexes are quite sensitive to air and moisture and slowly decompose in the solid state even at 0°C. The IR and Raman spectra of the complexes [136] (Table 7) are very similar to those of the S [380] and Se [381] analogs, a result interpreted to indicate that the three organometallic chalcogens have similar σ-donor and π-acceptor properties. The ^1H NMR spectra of the complexes in benzene all had a singlet main signal with $J_{^1HC-^{119,117}Sn}$ or $J_{^1HC-^{207}Pb}$ satellites, and in the $(OC)_5CrTe(GeMe_3)_2$ complex, a three-bond $J_{^1HCGe-^{125}Te}$ was also observed (Table 7). The increase in the latter coupling constant from that observed in the free ligand (3.5 Hz vs. 5.5 Hz) was attributed to an increase in s character of the Ge–Te bond from chiefly p^2-hybridized Te in the free ligand to sp^3-hybridized tellurium in the complex [136].

The pentacarbonyls $Cr(CO)_5(CF_3)_2ETeMe$, (E = P, As) have also been prepared by the above indirect photochemical substitution method [138a]. The complexes were isolated as red-brown oils in 23% and 14% yields,

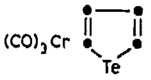


(73)

Scheme 1

TABLE 7

Cr, Mo, W complexes

	M.p (°C)	Physical data	Ref.
Cr complexes			
	>145 (dec.) (→Cr(CO)$_6$)	Purple-red, air-stable crystals, sublimable (65°, high vacuum) Soluble in benzene as a monomer ν_{CO} (benzene) = 1967 (A_1), 1895 and 1872 (E) cm^{-1} μ (benzene) = 6.10 ± 0.1 D λ_{max}(C$_6$H$_{12}$) 415 (ϵ 5890), 212 (ϵ 31,630), 580 (sh), 320 (sh), 260 (sh) nm τ (acetone-d_6) = 3.5 (m), 4.0 (m) ppm	132
(CO)$_5$CrTe(SnMe$_3$)$_2$	73 (dec.) [137] 85 (dec.) [136]	Yellow, air-sensitive crystals ν_{CO}(C$_5$H$_{12}$) = 2059 (w), (R: 2061); 1967 (m) (R: 1970), 1943 (s) (R: 1944), 1940 (s) (R: 1938), 1925 (m) (R: 1922), 1898 (w) (R: 1890) cm^{-1} δ (benzene) = +407.2 Hz (benzene as internal standard) $J_{{}^1HC^{117}Sn}$ = 52.5 Hz $J_{{}^1HC^{119}Sn}$ = 54.5 Hz	136, 137
(CO)$_5$CrTe(GeMe$_3$)$_2$	91 (dec.)	Yellow, air-sensitive crystals ν_{CO}(C$_5$H$_{12}$) = 2064 (w) (R: 2051), 1974 (m) (R: 1971), 1940 (vs) (R: 1943), 1934 (vs) (R: 1928), 1927 (m) (R: 1916), 1900 (w) (R: 1901) cm^{-1} δ(benzene) = +401.6 Hz (benzene as internal standard) $J_{{}^1HCGe^{125}Te}$ = 8.5 Hz	136
(CO)$_5$CrTe(PbMe$_3$)$_2$	101	Yellow, air-sensitive crystals ν_{CO}(C$_5$H$_{12}$) = 2058 (w) (R: 2053), 1976 (w) (R: 1971), 1938 (vs) (R: 1930), 1935 (sh) (R: 1928), 1930 (sh) (R: 1924), 1900 (w) (R: 1888) cm^{-1}	136

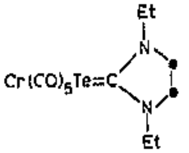
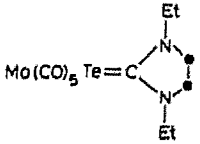
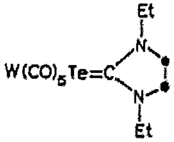
		δ (benzene) = +370.2 Hz (benzene as internal standard) $J_{^{13}C-^{207}Pb}$ = 57.8 Hz	
$Cr(CO)_5(CF_3)_2PTeMe$		Red-brown oil $\nu_{CO}(C_6H_{12})$ = 2087 (m), 2016 (vw), 1987 (s), 1977 (vs) cm^{-1}	138a
$Cr(CO)_5(CF_3)_2AsTeMe$		Red-brown oil $\nu_{CO}(C_6H_{12})$ = 2076 (w), 1986 (s), 1976 (vs) cm^{-1}	138a
	85	Orange solid ν_{CN_2} (mull) = 1535 cm^{-1} $\delta(^{13}C)$ = 150 ppm (vs. TMS)	138b
$[PPN][Cr(CO)_5TeH]$	66 (dec.)	Brown solid ν_{CO}(THF) = 2023, 1910, 1858	149b
$Cr(CO)_5(TeEt_2)$	29–32	Dark red solid	149b
$[PPN][(OC)_5Cr(\mu\text{-}TeH)Cr(CO)_5]$	62 (dec.)	Red solid ν_{CO}(THF) = 2050, 2025, 1919, 1900, 1862	149b
Mo complexes			
$\pi CpMo(CO)_3TePh$	80–82	Dark-violet, air-stable crystals sol. in benzene, CS_2 and $CHCl_3$ ν_{CO} = 2016 (vs), 1948 (sh), 1937 (vs) cm^{-1} ^1H NMR: τ 4.72 (s), Cp complex multiplet for phenyl hydrogen resonances	108
$[\pi CpMo(CO)_2TePh]_2$	175–176	Dark-brown, air-stable crystals sol. in aromatic hydrocarbons, CS_2, and $CHCl_3$ $\nu_{CO}(CS_2)$ = 1960 (s), 1935 (vs), 1876 (vs), 1860 (s) cm^{-1} ^1H NMR: τ 4.88 (s), Cp resonance	108
$[\pi CpMo(TePh)_2]_n$	> 190 (dec.)	Dark-brown solid, insoluble in water and organic solvents, no ν_{CO} (in 1700–2200 cm^{-1} region)	108
$\pi Cp_2Mo(TePh)_2$	198–199	Brown, air-stable crystals ^1H NMR (DMSO-d_6): τ 4.72 (s, Cp), τ 2.50–3.15 (m, Ph)	124
$\pi Cp_2Mo(Te(p\text{-}Me\text{-}C_6H_4))_2$	192–194	Brown, air-stable crystals ^1H NMR ($CDCl_3$) τ 4.68 (s, Cp); τ 2.31 (d) and 3.01 (d), (C_6H_4)	124

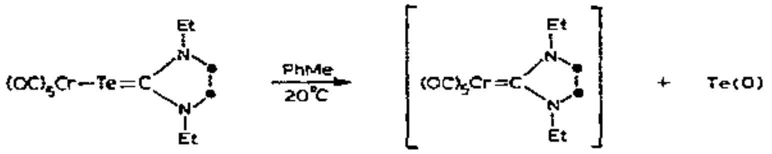
TABLE 7 (continued)

	M.p. (°C)	Physical data	Ref.
$(\eta^7\text{-}C_7H_7)COMo(\mu\text{-}TePh)_2MoCO(\eta^7\text{-}C_7H_7)$	118 (dec.)	Black needles $\nu_{CO}(CH_2Cl_2) = 1985$ (vs), 1935 (s) cm^{-1} $\nu_{CO}(KBr) = 1990$ (vs), 1947 (vs) cm^{-1} $\delta(CDCl_3) = 5.24$ (s, C_7H_7), 7.27 (m) and 7.73 (m) (Ph)	125
	75	Yellow solid ν_{CN}, (mull) $= 1525\ cm^{-1}$ $\delta(^{13}C) = 152$ ppm vs. TMS	138b
$Mo(CO)_5(CF_3)_2PTeMe$		Dark-brown oil $\nu_{CO}(C_6H_{12}) = 2095$ (m), 2019 (vw), 1990 (s, sh), 1985 (vs), 1981 (vs) cm^{-1} $\delta\ (C_6D_6) = 1.68$ ppm ($J_{^{31}P-^{1}H} = 7.0$ Hz) $\delta(^{19}F;\ C_6D_6) = -56.0$ ppm ($J_{^{31}P-^{19}F} =$ 66.9 Hz), vs. internal CCl_3F $\delta\ (^{31}P;\ C_6D_6) = +32.5$ ppm (vs. 85% H_3PO_4)	138c
W complexes			
$\pi Cp_2W(TePh)_2$	212–213	Brown solid ^1H NMR ($CDCl_3$): τ 4.66 (s, Cp), τ 2.10–2.95 (m, Ph)	124
$\pi Cp_2W(Te\text{-}p\text{-}tolyl)_2$	212–214	Brown solid ^1H NMR ($CDCl_3$): τ 4.69 (s, Cp) τ 2.31 (d) and 3.02 (d) (C_6H_4)	124
	86	Yellow solid ν_{CN}, (mull) $= 1538\ cm^{-1}$ $\delta(^{13}C) = 150$ ppm vs. TMS	138b

$[AsPh_4][W(CO)_5TeH]$	107 (dec.)	Brown solid ν_{CO}(THF) = 2040, 1908, 1859 ^{1}H NMR (d_6-DMSO; values in ppm relative to external TMS): $AsPh_4^+$: 8.18 m TeH^-: −8.28 s	149b
$[AsPh_4][(OC)_5W(\mu\text{-}TeH)W(CO)_5]$	115 (dec.)	Olive-green solid ν_{CO}(THF) = 2060, 2045, 1924, 1900, 1863	149b

respectively. The $(CF_3)_2PTeMe$ complex has good thermal and light stability in the solid state and solution in the absence of oxygen, but the complex with the weaker donor $(CF_3)_2AsTeMe$ decomposes in solution over a few days, even with the exclusion of air and light. The spectroscopic results (Table 7) support the coordination of both the As and Te atoms in the $(CF_3)_2AsTeMe$ complex, whereas the $(CF_3)_2PTeMe$ is isomerically pure and bonded through the P atom [138a].

Lappert et al. [138b] recently reported the first metal complex with a ligand incorporating a tellurourea function (see Scheme 1, page 217). These metal complexes are moderately air stable in the solid state and stable indefinitely under an inert atmosphere in the dark. They are thermally and photochemically sensitive to tellurium extrusion. The Cr complex undergoes Te extrusion at 20°C in toluene to give the corresponding carbene complex



(74)

This reaction was accelerated by heat, light, or reaction with mercury. The crystal structure of the Cr complex has been reported [138b] (Fig. 16).

The first examples of complexes with the TeH$^-$ ligand have recently been prepared by photochemical (eqn. 75) and thermal (eqn. 76) substitution reactions [149b].

$$\begin{tikzcd} M(CO)_6 \arrow[r, "THF", "h\nu"'] & M(CO)_5\ (THF) + CO \arrow[d, "-40^\circ C\ M=Cr,\ W"', "Na_2Te\ EtOH/-60^\circ C"] & \\ & Na^+[M(CO)_5TeH]^- \arrow[r, "C^+Cl^-"] & C^+[M(CO)_5TeH] \end{tikzcd} \qquad (75)$$

$$C^+ = PPN^+,\ M = Cr$$
$$C^+ = AsPh_4^+,\ M = W$$

$$[PPN][Cr(CO)_5Cl] + Na_2Te \xrightarrow[r.t.]{EtOH} [PPN][Cr(CO)_5TeH] \qquad (76)$$

These very air-sensitive complexes, which are soluble in polar solvents, were characterized by IR and ^1H NMR spectroscopy (Table 7). The chromium complex was alkylated to give the neutral diethyl telluride complex [149b]

$$[PPN][Cr(CO)_5TeH] + [Et_3O][BF_4] \xrightarrow{EtOH} (OC)_5Cr(TeEt_2) \qquad (77)$$

The TeH$^-$ ligand can also function as a bridging group, as evidenced by the

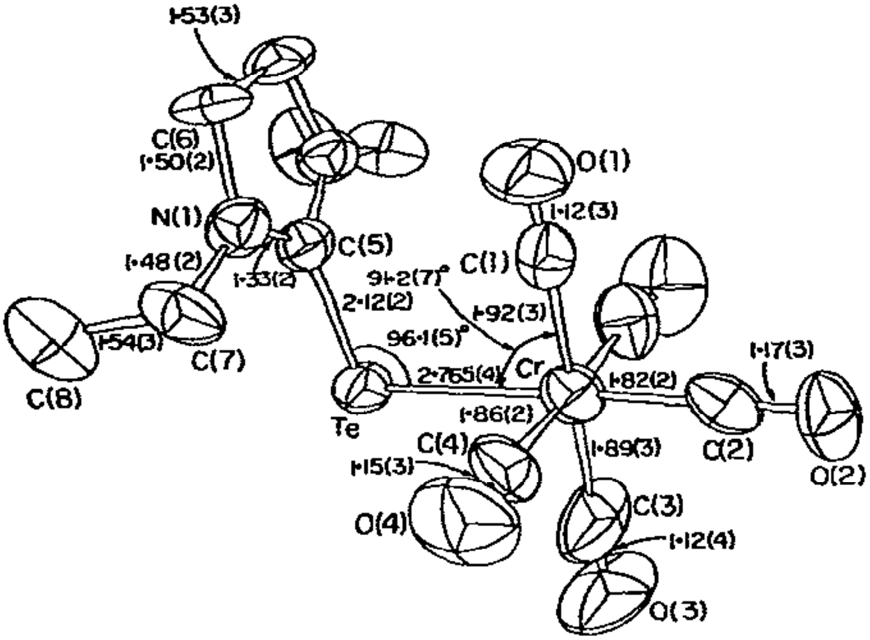
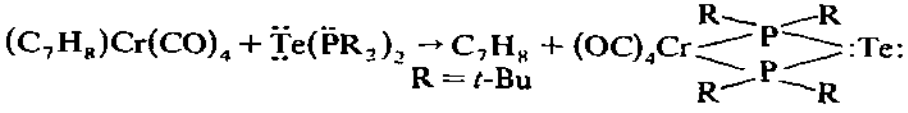


Fig. 16. Molecular structure of $Cr(CO)_5\{Te{=}\overline{CNEtCH_2CH_2NEt}\}$. Reproduced with permission from Chem. Commun., (1980) 635.

isolation of dinuclear complexes from the reaction of the monomeric complexes with the photochemically generated labile $M(CO)_5(THF)$ complexes

$$C^+[M(CO)_5(TeH)]^- + \underset{\substack{\uparrow \text{THF} \\ | \; h\nu/-40°C \\ M(CO)_6}}{M(CO)_5(THF)} \rightarrow C^+[(OC)_5M(\mu\text{-TeH})M(CO)_5]^- \qquad \begin{array}{l} M = Cr,\ C^+ = PPN^+ \\ \quad\ W,\ C^+ = AsPh_4^+ \end{array} \tag{78}$$

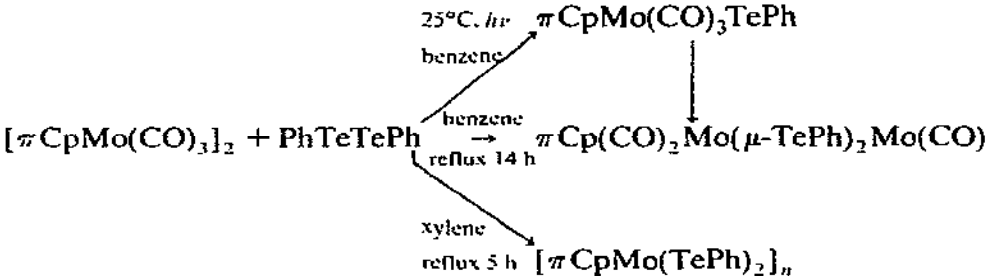
Tetracarbonyl(norbornadiene)chromium(0) reacts with tellurobis(di-*t*-butylphosphane) in toluene at room temperature to give the red crystalline complex $[Cr(CO)_4P_2\text{-}t\text{-}Bu_4Te]$ which has been assigned a CrP_2Te chelate structure on the basis of spectroscopic evidence (i.e., IR, NMR (^1H, ^{31}P, ^{125}Te), and mass spectroscopy) [382,383].



$$(C_7H_8)Cr(CO)_4 + \ddot{\underset{..}{T}}e(\ddot{P}R_2)_2 \xrightarrow[R\,=\,t\text{-}Bu]{} C_7H_8 + (OC)_4Cr\begin{array}{c} R_2P \\ R_2P \end{array}\!\!>\!:\!Te: \tag{79}$$

Mo

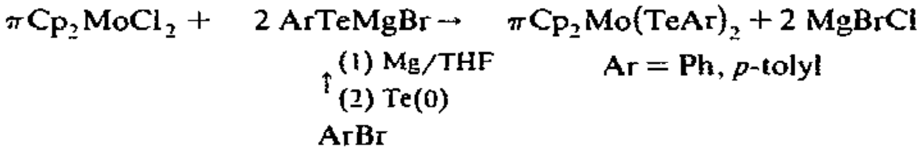
The reaction of Te_2Ph_2 with $[\pi CpMo(CO)_3]_2$ in ca. equimolar amounts gave a variety of products involving different coordination modes of the $PhTe^-$ ligand, depending on the severity of the reaction conditions [108]



$$\begin{tikzcd} & \pi CpMo(CO)_3TePh \arrow[d] \\ {[\pi CpMo(CO)_3]_2} + PhTeTePh \arrow[ur, "25°C, h\nu", "benzene"'] \arrow[r, "benzene", "reflux\ 14\ h"'] \arrow[dr, "xylene", "reflux\ 5\ h"'] & \pi Cp(CO)_2Mo(\mu\text{-}TePh)_2Mo(CO)_2\pi Cp \\ & {[\pi CpMo(TePh)_2]_n} \end{tikzcd} \qquad (80)$$

A third carbonyl-containing product was also detected by IR spectroscopy when the monomer was refluxed for 12 h in toluene, but the main product of the thermolysis was the decarbonylated polymeric $[\pi CpMo(TePh)_2]_n$ [108]. The highest-energy carbonyl stretching frequencies in the complex $\pi CpMo(CO)_3EPh$ are: S, 2033 cm^{-1}; Se, 2026 cm^{-1}; Te, 2016 cm^{-1}; the order of "softness" of the chalcogens ($Te > Se > S$) being reflected in the increased bonding between Mo and CO in this order. Conversely, the ease of thermolysis of the monomeric to dimeric complexes follows the order $S > Se > Te$. Although geometrical isomers are possible for the dimeric complex, the ^1H NMR spectrum of $[\pi CpMo(CO)_2TePh]_2$ showed only one kind of Cp proton [108].

Complexes of the type $(\pi Cp)_2Mo(TeAr)_2$ have been prepared by metathetical reactions from the corresponding chloride [124]



$$\begin{tikzcd} \pi Cp_2MoCl_2 + & 2\,ArTeMgBr \arrow[r] & \pi Cp_2Mo(TeAr)_2 + 2\,MgBrCl \\ & ArBr \arrow[u, "(1)\ Mg/THF", "(2)\ Te(0)"'] & Ar = Ph,\ p\text{-tolyl} \end{tikzcd} \qquad (81)$$

These complexes react with concentrated HCl to give the starting dichloride and with MeI to give πCp_2MoI_2 (and presumably ArTeMe) [124]. Although the complexes are quite stable in the solid state, CH_2Cl_2 solutions decompose on standing ca. 1 day, the Se analogs being somewhat more stable [124]. This enhanced stability of the Se analogs is similar to that found for $\pi CpNi(P(n\text{-}Bu)_3)EAr$ ($E = Se$, Te) [122] and $\pi Cp_2M(EAr)_2$ ($M = Ti$, Zr) [123] but is opposite that found for $\pi CpFe(CO)_2EPh$ [107] and $\pi CpMo(CO)_3EPh$ [108].

Reaction of PhTeLi (PhLi + Te(0) in ether) with $(\eta^7\text{-}C_7H_7)Mo(CO)_2Br$ gave the symmetrically double-bridged species $(\eta^7\text{-}C_7H_7)COMo(\mu\text{-}$

$TePh)_2MoCO(\eta^7\text{-}C_7H_7)$ as black needles in 54% yield [125].

The complex $Mo(CO)_5(CF_3)_2PTeMe$ was prepared in 27% yield by reacting the tellurium ligand with the photochemically generated complex $Mo(CO)_5THF$ [138c], analogous Cr complexes having been prepared by this route [138a]. The complex, obtained as a dark-brown oil, was characterized by IR (ν_{CO}), NMR (^1H, ^{19}F, and ^{31}P), and mass spectroscopy (Table 7).

The tellurourea complex $[(OC)_5Mo\{Te{=}\overline{CN(Et)CH_2CH_2N}Et\}]$ has been prepared by a substitution reaction starting from $Mo(CO)_5(NCMe)$ (see eqn. 73) [138*b*].

W

The tungsten complexes $\pi Cp_2W(TeAr)_2$ (Ar = Ph, *p*-tolyl), were prepared by metathetical reactions from the corresponding chlorides [124]

$$\pi Cp_2WCl_2 + 2\,ArTeMgBr \xrightarrow[r.t.]{THF} \pi Cp_2W(TeAr)_2 \tag{82}$$

These complexes, which are moderately soluble in $CHCl_3$, CH_2Cl_2, THF, acetone, DMSO, and CS_2 but insoluble in other organic solvents, readily react with concentrated HCl to regenerate the starting dichloride. They also react with MeI to give πCp_2WI_2 [124].

The tellurourea complex $[(OC)_5W\{Te{=}\overline{CN(Et)CH_2CH_2N}Et\}]$ was prepared as described in eqn. 73 [138b]. The complexes $AsPh_4[W(CO)_5TeH]$ (eqn. 75) and $AsPh_4[(OC)_5W(\mu\text{-}TeH)W(CO)_5]$ (eqn. 78) were prepared by the routes used for the Cr analogs.

(viii) V, Nb, Ta

No vanadium complexes with tellurium ligands have been reported, although the metathetical reaction used to prepare $\pi Cp_2V(SeAr)_2$ (Ar = Ph, *p*-tolyl: πCp_2VCl_2 + ArTeLi) could presumably be extended to the tellurium analogs [124].

The Nb complex, $\pi Cp_2Nb(TePh)_2$, has been prepared in 80% yield by such a route [124]. Like the Mo and W analogs, this complex reacts with concentrated HCl to regenerate the dichloride and with MeI to give the diiodide [124]. Unlike the latter derivatives, however, $\pi Cp_2Nb(TePh)_2$ is very air sensitive in both the solid state and solution. Organotellurium-bridged heteronuclear complexes have been prepared by the following routes [126]

$$\begin{tikzcd} & \pi Cp_2Nb(\mu\text{-}TePh)_2Fe(NO)CO \\ & (80\%) \\ \pi Cp_2Nb(TePh)_2 \arrow[uur, "+1/2\ Hg[Fe(CO)_3(NO)]_2", "acetone/r.t."'] \arrow[dr, "+1/2\ Hg[Co(CO)_4]_2"', "acetone/r.t."] & \\ & \pi Cp_2Nb(\mu\text{-}TePh)_2Co(CO)_2 \\ & (90\%) \end{tikzcd} \tag{83}$$

TABLE 8

V, Nb, Ta complexes

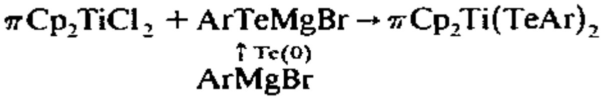
Complex	M.p. (°C)	Misc. data	Ref.
$\pi Cp_2Nb(TePh)_2$	137–142	Moss-green crystals, air-sensitive in solid state and solution	124
$TaCl_5TeMe_2$		Dark-brown solid ^{1}H NMR (CH_2Cl_2, −60°C) $\delta = 2.54$ ppm $\Delta\delta = \delta\,(TaCl_5TeMe_2) - \delta(TeMe_2) = 0.62$ ppm	150
$TaBr_5TeMe_2$		Black solid ^{1}H NMR (CH_2Cl_2, −60°C) $\delta = 2.58$ ppm $\Delta\delta = \delta(TaBr_5TeMe_2) - \delta(TeMe_2) = 0.67$ ppm	150
$\pi Cp_2Nb(\mu\text{-}TePh)_2Fe(NO)CO$	170–171	Brown crystals $\nu_{NO} = 1623$ (s) cm^{-1} $\nu_{CO} = 1845$ (s) cm^{-1} τ_{Cp} (ppm) = 4.64 (s), 4.83 (s), 4.90 (s), 5.07 (s), 5.25 (s), 5.31 (s)	126
$\pi Cp_2Nb(\mu\text{-}TePh)_2Co(CO)_2$	157–160	Brown crystals $\nu_{NO} = 1859$ (s) cm^{-1} $\nu_{CO} = 1911$ (s) cm^{-1} τ_{Cp}(ppm) = 4.73 (s), 4.99 (s), 5.31 (s)	126

The complexes, which are stable under N_2, have enhanced air stability in both solution and the solid state compared to the parent $\pi Cp_2Nb(TePh)_2$. Their IR spectra support their formulation as μ-TePh complexes with terminal CO ligands, and their ^{1}H NMR spectra indicate the presence of *cis* and *trans* isomers (3 and 6 Cp resonances for the Nb, Fe and Nb, Co dimers, respectively) [126].

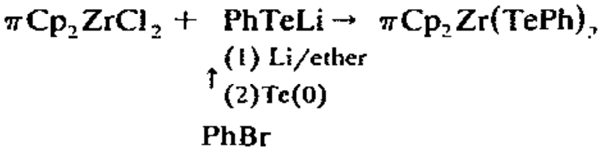
The only other reported complexes of a group VB metal with a tellurium ligand are the TaX_5TeMe_2 ($X = Cl$, Br) derivatives, prepared by reacting the pentahalides with excess dimethyl telluride in CH_2Cl_2 [150]. The relative stability of a series of such adducts (TaX_5EMe_2; $X = Cl$, Br; $E = O$, S, Se, Te) has been determined by ^{1}H NMR in CH_2Cl_2 at −60°C. At room temperature, in the presence of excess ligand, the adducts showed only one signal in their ^{1}H NMR spectra as the result of a rapid exchange process [150], but at lower temperature two distinct signals are observed, that corresponding to coordinated ligand appearing at lower field than free ligand. Competitive equilibria between different bases for the pentahalides were also studied by NMR spectroscopy, the stability of the adduct, with EMe_2 ($E = O$, S, Se, Te) increasing with the atomic number of the donor atom.

(ix) Ti, Zr, Hf

The monomeric complexes $\pi Cp_2M(TeAr)_2$ ($M = Ti$, $Ar = Ph$, *p*-tolyl; $M = Zr$, $Ar = Ph$) have been prepared by metathetical reactions [123]



$$\pi Cp_2TiCl_2 + \underset{\substack{\uparrow Te(0) \\ ArMgBr}}{ArTeMgBr} \rightarrow \pi Cp_2Ti(TeAr)_2 \qquad (84)$$



$$\pi Cp_2ZrCl_2 + \underset{\substack{\uparrow (1)\ Li/ether \\ (2) Te(0) \\ PhBr}}{PhTeLi} \rightarrow \pi Cp_2Zr(TePh)_2 \qquad (85)$$

Selenium analogs, $\pi Cp_2Ti(SePh)_2$, have also been prepared from the reaction of πCp_2TiCl_2 with HSePh [384] in the presence of NEt_3 (a route not feasible for the tellurium complex owing to the instability of tellurols) as well as by oxidative addition ($\pi Cp_2Ti + Ph_2Se_2$) [385]. The latter route is feasible for the tellurium analog; several such examples of the use of diaryl ditel-

TABLE 9

Ti, Zr, Hf complexes

Complex	M.p. (°C)	Misc. data	Ref.
$\pi Cp_2Ti(TePh)_2$	123–126	Red-brown solid ^1H NMR (CS_2) τ 4.15 (s, Cp) τ 2.26–2.50 and 2.72–2.98 (Ph)	123
$\pi Cp_2Ti(Te\text{-}p\text{-}tolyl)_2$	165–167	Red-brown solid ^1H NMR (CS_2) τ 4.18 (s, Cp) τ 2.48 (d) and 2.98 (d) (Ph) τ 7.59 (s, Me)	123
$\pi Cp_2Ti(\mu\text{-}TePh)_2Fe(NO)_2$	156–157	Green solid MW (benzene) = 681 (calc. 703) $\nu_{NO} = 1623$ (s) cm^{-1} $\nu_{CO} = 1845$ (s) cm^{-1} ^1H NMR (acetone-d_6) τ 4.68 (s), 4.71 (s), 4.83 (s), Cp τ 2.60–2.84 (m, Ph)	126

lurides as substrates in oxidative addition reactions have been reported [106,107,109–112,114].

These complexes are very air sensitive, especially in solution. Interestingly, $\pi Cp_2Nb(TePh)_2$ cannot be prepared by using PhTeMgBr, the Li reagent being necessary to effect the metathesis [123]. The organotellurium-bridged heteronuclear complex $\pi Cp_2Ti(\mu\text{-}TePh)_2Fe(NO)_2$ has also been prepared by a route analogous to that described above for Nb, Fe and Nb, Co dimers [126]

$$\pi Cp_2Ti(TePh)_2 + 1/2\ Hg[Fe(CO)_3NO]_2 \rightarrow \pi Cp_2Ti(\mu\text{-}TePh)_2FeCONO \quad (86)$$

(x) Lanthanides and actinides

The only complex of the *f* elements containing a tellurium ligand is the violet-black diphenyl ditelluride adduct $UCl_5(Ph_2Te_2)$, prepared by reacting the pentachloride with Te_2Ph_2 in a 1:1 molar ratio in benzene [130a]. The complex, which is soluble in $CHCl_3$, CH_2Cl_2, $MeNO_2$ and MeCN and decomposes above 151°C, has not been characterized with respect to the bonding of the tellurium ligand.

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NOTE ADDED IN PROOF

Several new complexes with tellurium ligands as well as additional data for some previously reported compounds have been published recently (Table 10).

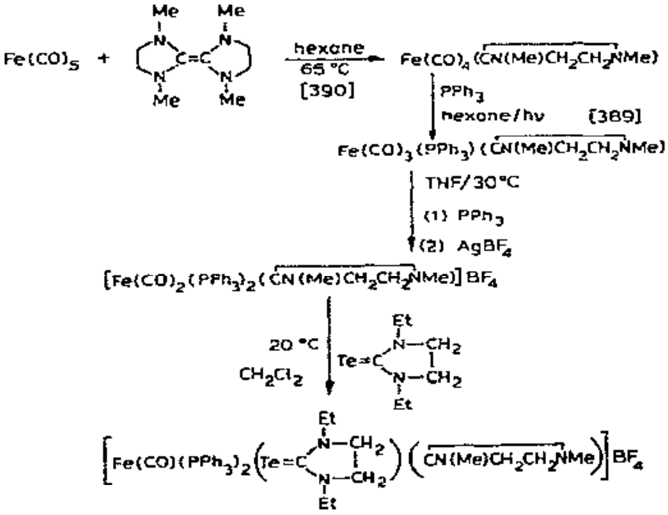
Pt

The complex $PtCl_4(TeCl_4)_2$ has been characterized in the solid state by IR and Raman spectroscopy in the 60–700 cm^{-1} region [386]. These data (Table 10) support a *trans* structure, $TeCl_4$ being coordinated through the chloride (e.g., $PtCl_6(TeCl_3)_2$) [386].

Diphenylditelluride was reported to be unreactive towards $Pt(PPh_3)_2(C_2H_4)$ [387]. Related oxidative addition reactions of $Pd(PPh_3)_4$ with Te_2Ar_2 (Ar = *p*-EtO–C_6H_4, 2-thienyl [109]) as well as $Pt(PPh_3)_4$ with Te_2(*p*-tolyl)$_2$ and *p*-MeO–C_6H_4TeCN [388] have, however, been reported.

Fe

Another example of a complex with the tellurourea ligand, $Te{=}\overline{CN(Et)CH_2CH_2N}Et$ (see eqn. 73), has been reported by Lappert et al. [389]



(87)

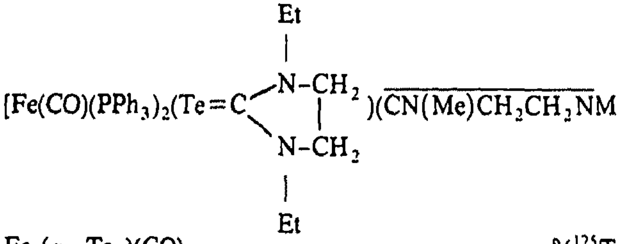
This paramagnetic Fe(I) carbene complex was not isolated, but its infrared spectrum was recorded in solution (Table 10).

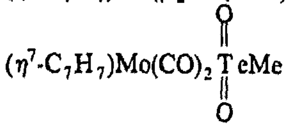
The chemistry of $Fe_2(\mu_2\text{-}Te_2)(CO)_6$ and $Fe_3(\mu_3\text{-}Te)_2(CO)_9$ has been further explored by Rauchfuss and co-workers [387,391,392].

The dimer $Fe_2(\mu_2\text{-}Te_2)(CO)_6$, a side product in the synthesis of $Fe_3(\mu_3\text{-}Te)_2(CO)_9$ [139b], has been isolated in solution in 4.3% yield by nonaqueous

TABLE 10

Recently reported complexes with tellurium ligands

Pt complexes $PtCl_4(TeCl_4)_2$	ν_{as}(Pt–Cl) = 355 (vs) cm^{-1} (IR); ν_s(Pt–Cl) = 352 (s) cm^{-1} (R) ν_{as}(Pt–$TeCl_4$) = 324 (m) cm^{-1} (IR); ν_s(Pt–$TeCl_4$) = 324 (s) (R) δ(Cl–Pt–Cl) = 178 (w) cm^{-1} (IR) δ($TeCl_4$–Pt–Cl_4Te) = 162 (w) cm^{-1} (IR) ν_{as}(Te–Cl) = 374 cm^{-1} (IR), 383 cm^{-1} (R); ν_s(Te–Cl) = 170 cm^{-1} (IR); δ_{as}(Cl–Te–Cl) = 175 (w) cm^{-1} (R); δ_s(Cl–Te–Cl) = 144 (m) (IR)	[386]
Fe complexes		
 $[Fe(CO)(PPh_3)_2(Te{=}C(N(Et)CH_2CH_2N(Et)))(\overline{CN(Me)CH_2CH_2NMe})]BF_4$	$\nu_{CO}(CH_2Cl_2)$ = 1861 cm^{-1}	[389]
$Fe_2(\mu_2\text{-}Te_2)(CO)_6$	$\delta(^{125}Te)$ = −733 ppm (upfield from neat $TeMe_2$) $\nu_{CO}(C_6H_{12})$ = 2067, 2028, 1995 cm^{-1} electron-impact mass spectrum: $Fe_2Te_2(CO)_x$ x = 2–6 ($Fe_2Te_2^{+}$ = 100% peak) Mol. wt. ($C_6{}^{56}Fe_2O_6{}^{128}Te^{130}Te$) = 537.6499; found 537.6500	[391]
$Fe_3(\mu_3\text{-}Te)_2(CO)_9$	$\nu_{CO}(C_6H_{12})$ = 2045, 2025, 2004 cm^{-1} $\delta(^{125}Te)$ = +1123 ppm (downfield from $TeMe_2$)	[391]

$Fe_3(\mu_3\text{-}Te)_2(CO)_{10}$	$\nu_{CO}(C_6H_{12})=2104, 2054, 2049, 2038, 2019, 1994, 1984, 1972\ cm^{-1}$ red needles	[391]
$(OC)_6Fe_2(\mu_3\text{-}Te)_2Pt(PPh_3)_2$	$\nu_{CO}(C_6H_{12})=2034\ s, 1995\ vs, 1960\ s\ cm^{-1}$ field-desorption mass spectrum → molecular ion $\delta(^{125}Te)=-861$ ppm (upfield from neat $TeMe_2$) $J(^{125}Te\text{-}^{195}Pt)=561$ Hz $\delta(^{31}P)=+19.3$ ppm (upfield from 85% H_3PO_4) $J(^{31}P\text{-}^{195}Pt)=2846.4$ Hz	[387]
$Fe_3(\mu_3\text{-}Te)_2(CO)_9PPh_3$	crystal structure [392] variable-temperature ^{31}P NMR [392]	
$Fe_2(\mu_2\text{-}TePh)_2(NO)_4$	$\nu_{NO}(CH_2Cl_2)=1770, 1750\ cm^{-1}$ ^1H NMR: $\delta=7.2$ s electron-impact mass spectrum: $M^+=646$	[393]
$Fe_2(\mu_2\text{-}TeCH_2Ph)_2(NO)_4$	$\nu_{NO}(CH_2Cl_2)=1765, 1745\ cm^{-1}$ electron-impact mass spectrum $M^+=674$	[393]
Mo complexes		
$(\eta^7\text{-}C_7H_7)Mo(CO)_2TePh$	crystal structure (Fig. 17)	[395]
$(\eta^7\text{-}C_7H_7)Mo(\mu_2\text{-}Te(n\text{-}Bu))_3Mo(\eta^7\text{-}C_7H_7)$	no data reported	[395]
 $(\eta^7\text{-}C_7H_7)Mo(CO)_2\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{Te}}Me$	red-brown thermally unstable crystals $\nu_{CO}=1990, 1930\ cm^{-1}$ $\nu_{Te\text{-}C}=470\ cm^{-1}$ $\nu_{Te=O}=960, 785, 750, 695\ cm^{-1}$ τ 2.33 (s)	[396]

gel permeation chromatography of the product of the reaction of K_2TeO_3 and $KHFe(CO)_4$ [391]. The complex was previously isolated, contaminated with $Fe_3(\mu_3\text{-}Te)_2(CO)_9$, by vacuum sublimation of the above reaction product and characterized by a selective oxidative addition reaction with $Pt(C_2H_4)(PPh_3)_2$ [139b]. The product of the latter reaction is $(OC)_6Fe_2(\mu_3\text{-}Te)_2Pt(PPh_3)_2$, the trimer being inert towards the Pt complex. The dimer has now been characterized by IR, mass spectrometry, and ^{125}Te NMR (Table 10) [391]. The solid decomposed when the chromatographic solution was evaporated under N_2 or CO, impure $Fe_4(\mu_3\text{-}Te)_4(CO)_{12}$ being proposed as the product. The ^{125}Te chemical shifts of the dimer and $Fe_3(\mu_3\text{-}Te)_2(CO)_9$, surprisingly, differ by 1856 ppm (Table 10).

The instability of $Fe_2(\mu_2\text{-}Te_2)(CO)_6$ was rationalized in terms of the steric strain associated with the small closed cluster incorporating the large Te atoms. Indeed, this thermally unstable dimer has been proposed as an intermediate in the synthesis of $Fe_3(\mu_3\text{-}Te)_2(CO)_9$ via an oxidative addition reaction of $HFe(CO)_4^-$ across the Te–Te bond of the dimer.

$$\begin{tikzcd}
Fe_2(\mu_2\text{-}Te_2)(CO)_6 + K^+[HFe(CO)_4]^- \arrow[r, "H^+"] & Fe_3(\mu_3\text{-}Te)_2(CO)_{10} \arrow[d] \\
TeO_3^{2-} + K^+[HFe(CO)_4]^- \arrow[u, "\text{several steps}"] & Fe_3(\mu_3\text{-}Te)_2(CO)_9
\end{tikzcd} \tag{88}$$

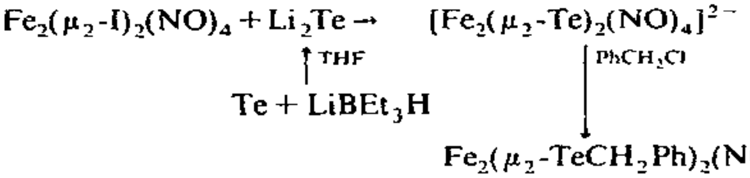
The proposed oxidative addition reaction of $HFe(CO)_4^-$ is analogous to the previously reported reaction with $Pt(PPh_3)_2(C_2H_4)$ [139b].

The initial decacarbonyl product is readily decarbonylated thermally or chemically (with Me_3NO) to give the stable nonacarbonyl. The decacarbonyl was obtained in 70% yield by a modification of Hieber and Gruber's [139] original method in which the reaction was carried out at 0°C and the thermally labile product was extracted into CH_2Cl_2 after acidification [391] (rather than Soxhlet extraction with hot petroleum ether as in the original reference [139]).

Further details of the synthesis and properties of $(CO)_6Fe_2(\mu_3\text{-}Te)_2Pt(PPh_3)_2$ have appeared [387]. This mixed-metal cluster and the S and Se analogs were prepared in 70% yield by the previously described oxidative addition reaction [139b]. The cluster was purified by preparative TLC and characterized by NMR (^{31}P and ^{125}Te) and IR [387] (see Table 10).

A single-crystal X-ray structural determination of $(CO)_6Fe_2(\mu_3\text{-}Se)_2Pt(PPh_3)_2$ [387] has confirmed the structure proposed for these mixed-metal clusters [139b]. A single-crystal X-ray diffraction study of $Fe_3(\mu_3\text{-}Te)_2(CO)_9PPh_3$ [387,392] has shown that a nido-arachno cluster rearrangment has accompanied adduct formation (see ref. 140 and Fig. 13 for the previously proposed structures for this adduct of $Fe_3(\mu_3\text{-}Te)_2(CO)_9$ and PPh_3).

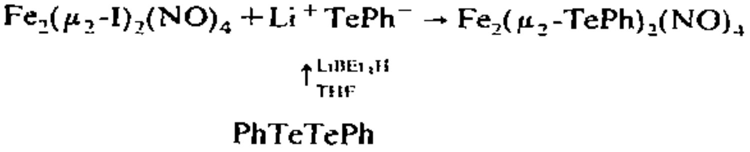
The Te analog of Roussin's red salt, $[Fe_2(\mu_2\text{-}Te)_2(NO)_4]^{2-}$, has been prepared in solution and used as a reagent for the synthesis of a neutral alkylated derivative [393]



$$\begin{tikzcd} Fe_2(\mu_2\text{-}I)_2(NO)_4 + Li_2Te \arrow[r] & {[Fe_2(\mu_2\text{-}Te)_2(NO)_4]^{2-}} \arrow[d, "PhCH_2Cl"] \\ Te + LiBEt_3H \arrow[u, "THF"] & Fe_2(\mu_2\text{-}TeCH_2Ph)_2(NO)_4 \end{tikzcd}$$

(89)

The neutral phenyl analog was prepared by a metathetical reaction [393]



$$\begin{tikzcd} Fe_2(\mu_2\text{-}I)_2(NO)_4 + Li^+TePh^- \arrow[r] & Fe_2(\mu_2\text{-}TePh)_2(NO)_4 \\ PhTeTePh \arrow[u, "LiBEt_3H"', "THF"] & \end{tikzcd}$$

(90)

The cleavage of the P–Te bond induced by Me_3SnH in the previously reported $Cr(CO)_5(CF_3)_2PTeMe$ [138a] has been studied [394]. No reaction products were isolated, but the products were characterized in toluene solution by ^1H and ^{19}F NMR

$$Cr(CO)_5(CF_3)_2PTeMe \xrightarrow[Me_3SnH]{-20°C} Cr(CO)_5(CF_3)_2PH + Me_3SnTeMe \tag{91}$$

$$\xrightarrow{0°C} Cr(CO)_5(CF_3)_2PSnMe_3 + Cr(CO)_5(CF_3)_2PH \tag{92}$$

The cleavage reactions of a number of complexes with coordinated $R_2EE'R'$ (R, R' = Me, CF_3; E = P, As; E' = S, Se, Te) derivatives were investigated in this study. The same primary products are obtained in such reactions as for the free ligands although the reaction rate is significantly decreased upon coordination.

The crystal structure of the complex $\eta^7\text{-}C_7H_7Mo(CO)_2TePh$ has been reported (Fig. 17) [395]. This monomeric complex and the dimer $[\eta^7\text{-}C_7H_7Mo(CO)TePh]_2$ were formed in the reaction of $\eta^7\text{-}C_7H_7Mo(CO)_2Br$ with $TePh^-$. The Mo–Te bond distance (279.7 pm) is 15 pm shorter than the sum of the covalent radii, indicating a considerable double-bond character.

An analogous reaction of $\eta^7\text{-}C_7H_7Mo(CO)_2Br$ and $Te(n\text{-}Bu)^-$ was reported to give the triply telluro-bridged species $(\eta^7\text{-}C_7H_7)Mo(\mu\text{-}Te(n\text{-}Bu))_3Mo(\eta^7\text{-}C_7H_7)$ [395].

The first example of TeO_2 insertion into a metal–carbon bond has been

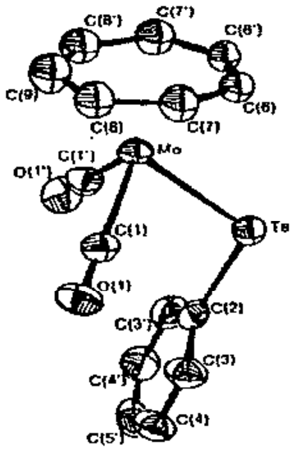
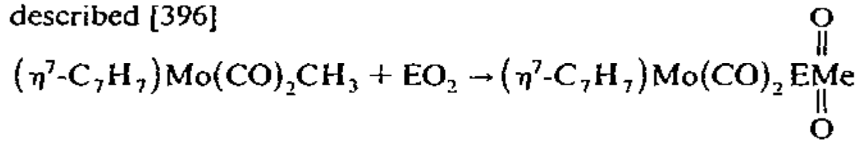


Fig. 17. Molecular structure of (η^7-C_7H_7)Mo(CO)$_2$TePh. Reproduced with the permission of A. Rettenmeier, K. Weidenhammer and M. Ziegler, Z. Anorg. Allg. Chem., 473 (1981) 91.

described [396]



$$(\eta^7\text{-}C_7H_7)Mo(CO)_2CH_3 + EO_2 \rightarrow (\eta^7\text{-}C_7H_7)Mo(CO)_2\,\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{E}}Me \qquad (93)$$

E = S, Se, Te

The TeO_2 was generated in a metal-atom reactor (ether matrix; −196°C) and subsequently reacted with the methyl compound at −78°C. The complex was too thermally unstable, decomposing in a few minutes at room temperature, to allow an X-ray structural investigation. A monomeric formulation was supported by the similarity of the spectral properties (Table 10) with those of the S analog, for which the molecular weight was determined by osmometry. The analogous phenyl derivative gave insertion only with SO_2.

W

The compounds πCpW(CO)$_3$TePh and [πCpW(CO)$_2$TePh]$_2$, prepared from πCpW(CO)$_3$H and Te_3Ph_2, have been described in two Ph.D. theses [153,397].

V

A highly insoluble and presumably polymeric compound, [πCpV(TePh)$_2$]$_x$, prepared from πCpV(CO)$_4$ abd Te_2Ph_2, has been reported in a Ph.D. thesis [397] but no detailed publication on this material has appeared.

A review of the coordination chemistry of thioethers, selenoethers, and telluroethers has appeared recently [398].