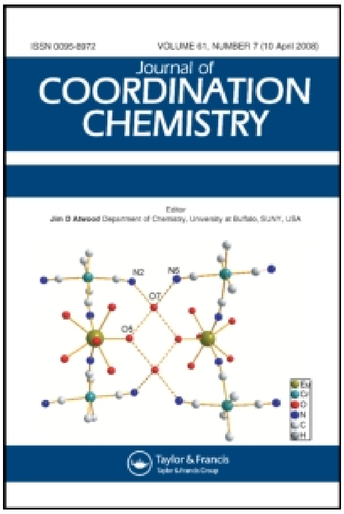

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The Chemistry of Multidentate Organotellurium Ligands

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THE CHEMISTRY OF MULTIDENTATE ORGANOTELLURIUM LIGANDS

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The ligand chemistry of various multidentate tellurium donors has been developed during the last decade. These developments are reviewed and possibilities in this area projected.

Keywords: Tellurium, ligands, multidentates

INTRODUCTION

The ligand chemistry of 'soft'-donors has continued to be among the most attractive research areas of inorganic chemistry. Of the various donors of this type, phosphorus and sulfur ligands have been investigated very extensively as compared with others like arsenic, antimony and selenium. Tellurium ligands have not received much attention, although of course they are expected to be quite interesting due to the very large size of the donor atom. The reasons for this appear to be a general misconception about the extreme toxicity and air sensitivity of organotellurium compounds and the complete non-availability of such ligands commercially until a few years ago. Even now only a few diorganyl tellurides are marketed. Up to the beginning of the eighties, mainly monodentate Te-ligands[2] were investigated. These developments have been reviewed by Gysling[1,2] and Berry.[3] In the last decade, particularly in the later half, several research groups including ours have focussed their attention on bi- and polydentate tellurium ligands. The main aim of the present paper is to review developments and to promote interest in this area. Since the scope of the review is restricted to multidentate Te ligands, reports which have appeared after the publication of the above mentioned reviews on monodentate Te donors have not been included.

Bidentate ligands

The chemistry of several neutral and anionic Te ligands of the types (Te,Te), (Te,O), (Te,N) and (Te,P) has been explored during the last few years. The synthesis of potential bidentate ligands of the (Te,As), (Te,Sb) and (Te,Se) type has also been reported, but their ligation has yet to be investigated. The developments are summarized below.

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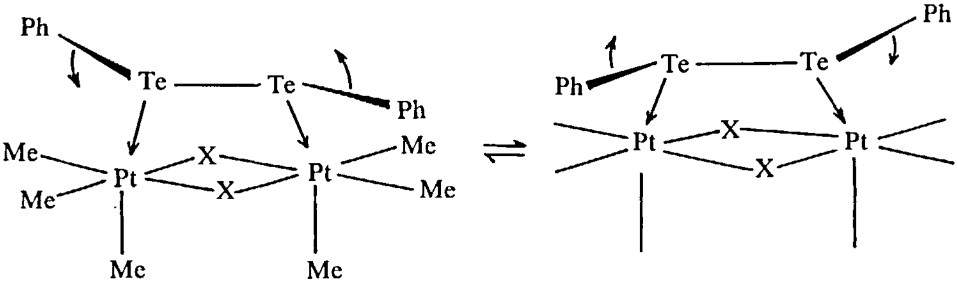
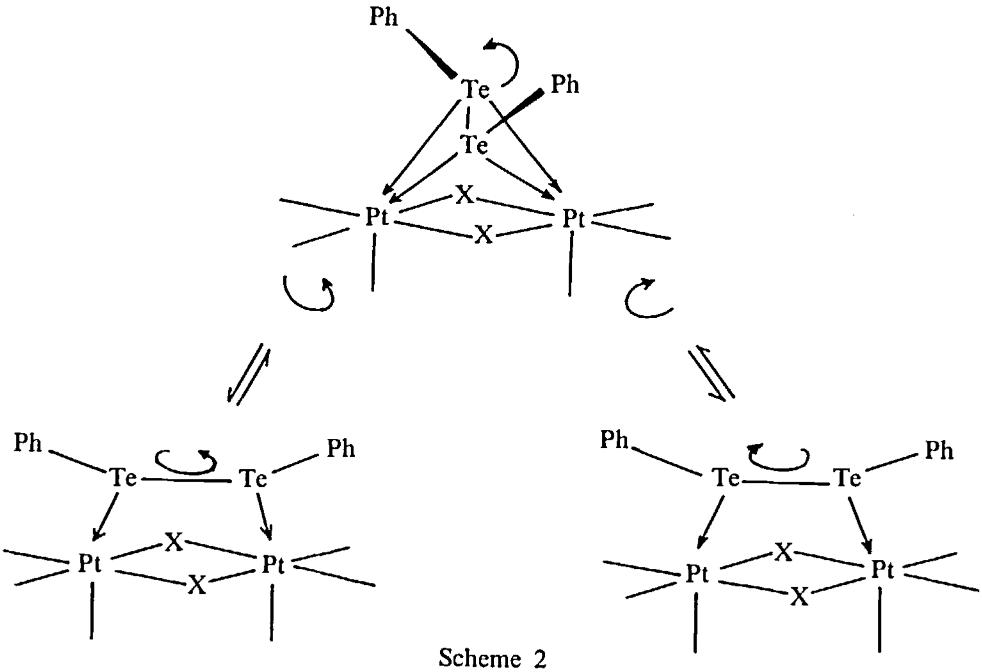
(Te,Te) Ligands

Some new examples in which RTeTeR (R = alkyl or aryl group) behaves as a bridging (Te,Te) ligand[1,2] have been added during the last few years. In CH_2Cl_2 the reaction of $[C_5H_5Fe(CO)_2(THF)]BF_4$ with RTeTeR (R = CH_3, $n\,C_4H_9$, t-C_4H_9, C_6H_5) has been reported to result in $[(C_6H_5Fe(CO)_2)_2(\mu\text{-RTeTeR})](BF_4)_2$,[4] if the two reactants are in a 1 : 1.5 molar ratio, but neither its solid state nor solution structure has been examined in detail. The reaction of $[PtX(CH_3)_3]_4$ with Te_2Ph_2 yields $[\{PtX(CH_3)_3\}_2\{Te_2Ph_2\}]$ (**1**),[5] when X is Br and I. If X is Cl, the ditelluride fails to bring about fission of the tetranuclear platinum complex. In **1** the Te_2Ph_2 fragment bridges the two platinum atoms ($^1J(^{195}Pt\text{–}^{125}Te)$ = 880–950 Hz) and the complex exhibits in solution two different modes of fluxionality over the temperature range −20 to +65°C. The lower energy process for which only the equatorial $PtCH_3$ signals in the ^1H NMR spectrum are averaged, has been attributed to the double chalcogen inversion (Scheme 1) in which the tellurium ligand atoms are inverted either synchronously or in a correlated manner. The $\Delta G^{\neq}$, $\Delta S^{\neq}$ and $\log(A/S^{-1})$ values for this transformation (59.7 ± 0.1 kJ mol^{-1}, 16 ± 7 J K^{-1} mol^{-1} and 13.3 ± 0.4, respectively) indicate it to be strictly intramolecular. The $\Delta G^{\neq}$ value is higher than that with comparable sulfur and selenium analogues. All three $PtCH_3$ signals in the ^1H NMR coalesce at around +50°C. This high energy process has been ascribed to a ligand commutation process as in Scheme 2; the transition state involves a seven-coordinate Pt(IV) species. In this transition state the rotational scrambling of all $PtCH_3$ groups would be a facile process. The $\Delta G^{\neq}$, $\Delta S^{\neq}$ and $\log(A/S^{-1})$ values for this intermetallic ligand commutation/methyl scrambling process have been reported as being 64.5 kJ mol^{-1}, 32 ± 2 J K^{-1} mol^{-1} and 15.2 ± 0.1, respectively. Khandelwal *et al.*[6] have reported that Ar_2Te_2 (Ar = C_6H_5, 4-$MeOC_6H_4$ and 4-$EtOC_6H_4$), on reaction with Na_2PdCl_4 in ethanol at temperatures <40°C, forms $[(PdCl_2)_2(\mu\text{-ArTeTeAr})_2(PdCl_2)]$ (**2**) in which each ArTeTeAr fragment has been proposed to bridge two Pd atoms. Similar reaction[7] does not occur between ArTeTeAr and K_4PtCl_4. The reaction at temperatures >40°C, even in the case of Pd, yields $[PdCl(TeAr)]_n$. The larger size of the Pt ion appears to be responsible for the different behaviour. However, the structure of **2** is only supported by IR, Raman (ν(Te–Te): 170, 175 cm^{-1} and ν(Pd–Cl): 295, 283 cm^{-1}) and ^1H NMR spectra.



Scheme 1

Several ditelluroether ligands, $RTe(CH_2)_nTeR$ (R = aryl or alkyl group; Table I), have been synthesized[8–17] during the last five years by nucleophilic reaction of



Scheme 2

TABLE I
Known $RTe(CH_2)_n$ TeR ligands.

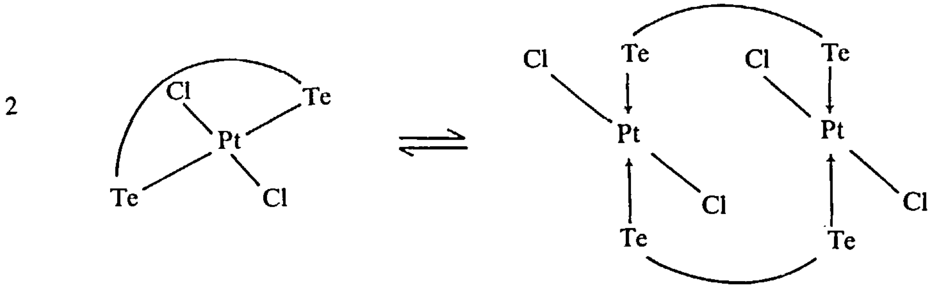
$RTe(CH_2)_nTeR$ species	Ref.
$RTeCH_2TeR$	
R = Me, Et, *n*-Pr, *i*-Pr	
n-Bu, *i*-Bu, *t*-Bu, *s*-Bu	10, 13
C_6H_5, $C_6H_5CH_2$	8, 10
4-MeC_6H_4, 4-$MeOC_6H_4$,	12, 13
4-$EtOC_6H_4$	14
4-$(Me)_2NC_6H_4$, 4-$C_6H_5OC_6H_4$	14
2-thienyl, 2-furyl, 1- and 2-naphthyl	16
benzo[b]thien-2-yl, *N*-tosyl-2-indolyl, ferrocenyl	17
$RTe(CH_2)_3TeR$	9, 10
R = Me; Ph	
$RTe(CH_2)_5TeR$	8
R = 4-$EtOC_6H_4$	
$RTe(CH_2)_6TeR$	8
R = 4-$EtOC_6H_4$	
$RTe(CH_2)_7TeR$	8
R = 4-$EtOC_6H_4$	
$RTe(CH_2)_8TeR$	11
R = 4-$EtOC_6H_4$	
$RTe(CH_2)_9TeR$	8
R = 4-$EtOC_6H_4$	
$RTe(CH_2)_{10}TeR$	8
R = 4-$EtOC_6H_4$	

RTeLi or RTeNa with the dihalides, $X(CH_2)_nX$. Of course the first member of this series, $RTeCH_2TeAr$, has been known for some time. It was first synthesized in 1970 by the reaction[12] of CH_2N_2 with R_2Te_2 (*1*). New examples[13,14] of $RTeCH_2TeR$ ligands were added later by using a similar route. By reacting PhTeLi with CH_2I_2, bis(phenyltelluro)methane has been synthesized.[5] However, derivatives corresponding to $n = 2$ and 4 have not been synthesized so far. The nucleophilic attack of PhTeLi/Na at XCH_2CH_2X ($X = \text{halogen}$) results in ethene + R_2Te_2, and at $X(CH_2)_4X$ in a cyclic product, $R\overline{Te(CH_2)_3C}H_2X$, because, after replacement of one X by RTe, the internal quaternization is always faster than nucleophilic attack by RTe^- on the other C–X bond of the dihalide.

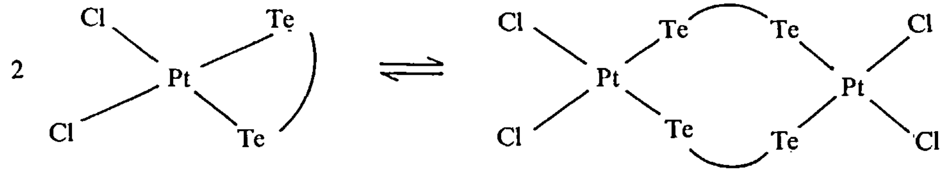
$$RTeTeR + CH_2N_2 \longrightarrow RTeCH_2TeR + N_2 \qquad (1)$$

^1H, $^{13}C\{^1H\}$ and $^{125}Te\{^1H\}$ NMR data for $RTe(CH_2)_nTeR$ derivatives have been analyzed[10,13,14] in detail. The signal in the $^{125}Te\{^1H\}$ NMR spectrum undergoes shielding when n increases. For example, for $MeTeCH_2TeMe$, the tellurium signal appears around δ 212 ppm (with respect to neat Me_2Te), and for $MeTe(CH_2)_6TeMe$ and $MeTe(CH_2)_{10}TeMe$ at 106 and 104.5 ppm, respectively. A large deshielding of the Te signal occurs when R is changed from alkyl to aryl as the Te signal of $PhTeCH_2TePh$ appears around δ 584 ppm. The contribution of various groups to the $^{125}Te\{^1H\}$ NMR chemical shifts of $RTe(CH_2)_nTeR$ has been estimated[10,13] empirically. ^1J(Te–C), ^2J(Te–C) and ^2J(Te–H) have also been reported for these compounds[10,13] and found to be generally 3 to 5 times greater than those of selenium analogues. The telluromethanes $(PhTe)_2CH_2$ and $(MeTe)_2CH_2$ exhibit a large quadrupole splitting[13] (11.0 and 10.5 $mm\,s^{-1}$, respectively) in their Mössbauer spectra, as is the case with Ph_2Te and Me_2Te, indicating that the presence of a second tellurium in the $TeCH_2Te$ linkage has no significant effect on the electronic environment at tellurium.

Nearly two dozen derivatives of the type $RTeCH_2TeR$ have been known for many years but surprisingly nothing has been published on their ligation behaviour so far. The ligand chemistry of their phosphorus analogues has however become quite diverse and is expanding further. Attempts[18] to investigate the ligation of $(4\text{-}EtOC_6H_4Te)_2CH_2$ have been frustrated by poor solubility of its Pd(II), Pt(II) and Hg(II) complexes which do not yield suitable crystals for X-ray. The coordination chemistry[11] of $(4\text{-}EtOC_6H_4Te)(CH_2)_n(TeC_6H_4\text{-}4\text{-}OEt)$ (3) where $n = 6, 7, 8, 9, 10$ with Hg(II), Pd(II) and Pt(II) has been investigated by McWhinnie and coworkers. Insoluble complexes of the ligand with $n = 6$ are presumed to be polymeric. The $^{13}C\{^1H\}$ NMR signal of the alkyl carbon atom linked directly to Te undergoes significant deshielding (≈ 20 ppm) on complexation, and this may be a good diagnostic tool, particularly for ligands in which Te is linked to at least one alkyl group. The $^{125}Te\{^1H\}$ NMR spectra of the platinum(II) complex of 3 ($n = 8$) at -10 to 40°C exhibit four signals, A, B, C and D, which become sharp at 40°C (δ 573, 545.5, 543.5 and 527 ppm, respectively). The four signals have been interpreted in terms of the equilibria shown in Scheme 3. At 70°C, resonance C resolves into two lines (δ, 548.7 and 549.1 ppm). This has been assigned to either inversion at coordinated tellurium (that is, each invertomer giving one resonance) or to the process in equation (*2*), where the difference between the *cis, cis*; *cis, trans*; and *trans, trans* dimers are resolved for C but not for B. ^{125}Te NMR spectra of the palladium(II) and platinum(II) complexes of the ligands for which $n = 7$, 9 or 10 have not been investigated in detail, but the room temperature spectra at least

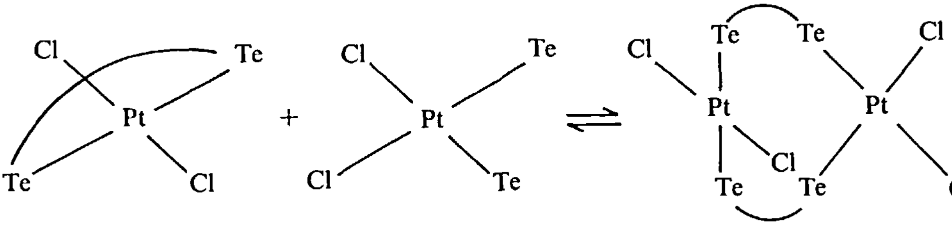


(resonance D) (resonance C)



(resonance A) (resonance B)

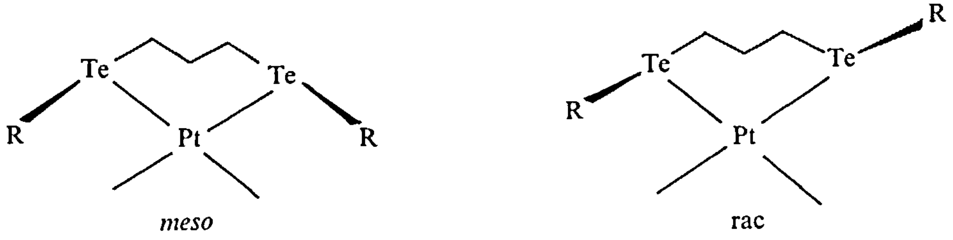
Scheme 3



(2)

(resonance B and C)

suggest the coexistence of *cis* and *trans* isomers. In the absence of any single crystal structure determination of these complexes, nothing unambiguous can be said about their structures except that the ligands $RTe(CH_2)_nTeR$ coordinate through both Te atoms with Pd(II), Pt(II) and Hg(II). Palladium(II) and platinum(II) complexes of the composition $[M(L\text{-}L)X_2]$ (M=Pd or Pt, X = Cl, Br or I and L–L = $PhTe(CH_2)_3TePh$ or $MeTe(CH_2)_3TeMe$) have been isolated.[19] The structure of $[Pd(PhTe(CH_2)_3TePh)Br_2]$ has been studied by X-ray diffraction. The geometry at Pd is square planar and the Ph groups of the ligand are in a *syn* (*meso*) conformation. ^1H, $^{125}Te\{^1H\}$ and $^{195}Pt\{^1H\}$ NMR spectral studies have shown that two diastereoisomers of the ligand are present in solution for each complex (*meso* and *rac*



Scheme 4

invertomers; Scheme 4), with the former having higher abundance. The ${}^{1}J({}^{195}Pt-{}^{125}Te)$ coupling constants (257–1000 Hz for the *meso* form; 113–1200 Hz for the *rac* form) follow the orders Cl > Br > I and Ph > Me. These Pd/Pt(II) complexes cannot be oxidized by halogens to species of the type $[M(L-L)\ X_4]$, as is the case with Pt(II) complexes of dithioethers[20] and diselenoethers.[21]

Bidentate (Te,Te) ligands o-$C_6H_4(TeR)_2$[22] (4), where R = Me or Ph, have been synthesized recently by treating frozen solution of LiTeMe or LiTePh in THF (−196°C) with *o*-dibromobenzene. Their ${}^{1}H$, ${}^{13}C\{{}^{1}H\}$ and ${}^{125}Te\{{}^{1}H\}$ NMR spectral data have been reported. Complexes[23] of 4 having compositions $[n\text{-}Bu_4N][Ir\{o\text{-}C_6H_4(TeMe)_2\}X_4]$ and $[M\{o\text{-}C_6H_4(TeMe)_2\}X_2]$, where M = Pd, Pt and X = Cl, Br, have been synthesized and characterized by electronic, IR, ${}^{1}H$, ${}^{195}Pt\{{}^{1}H\}$ and ${}^{125}Te\{{}^{1}H\}$ NMR spectroscopy. In solution, *meso* and *rac*, invertomers have been identified for each complex and the former is probably more abundant. The ${}^{1}J({}^{195}Pt-{}^{125}Te)$ coupling constant is 280–1190 Hz for the *meso* form and 414–1206 for the *rac* form. The coordination shift in the ${}^{125}Te\{{}^{1}H\}$ NMR of these complexes follows the order Pt < Ir < Pd and its magnitude is large (δ, 370–510 ppm) as well as in a high frequency region in comparison to $[M\{PhTe(CH_2)_3TePh\}X_2]$ and *cis*-$[M(TeMePh)_2X_2]$ (M = Pd, Pt; X = Cl, Br, I). The 'chelate ring contribution' ($\Delta_R = \Delta_{\text{chelate complex}} - \Delta_{\text{equivalent } cis \text{ monodentate complex}}$; $\Delta = \delta({}^{125}Te)_{\text{complex}} - \delta({}^{125}Te)_{\text{free ligand}}$) in the complexes of 4 has been found to be in the range 129–446, much higher than that for $RTe(CH_2)_3TeR$, which forms a six membered chelate ring. When $[Pd\{o\text{-}C_6H_4(TeMe)_2\}I_2]$ is heated for short periods in DMSO or the solution allowed to stand for several days at room temperature, monodemethylation occurs with the formation of $[\{Pd(o\text{-}C_6H_4(TeMe)Te)I\}_4]$[24] (5) whose structure (depicted in Fig. 1) has been deduced on the basis of single crystal X-ray diffraction studies.[24] The signal for the bridging tellurium in the ${}^{125}Te\{{}^{1}H\}$ NMR spectrum of 5 has been reported around δ, 427 ppm. Realkylation of 5 does not occur on treatment with MeI. The complex $[Co\{o\text{-}C_6H_4(TeMe)_2\}X_2]BPh_4$[25] (X = Br or I) has been prepared by air oxidation of mixtures of anhydrous CoX_2, ligand and $NaBPh_4$ in nitromethane, and characterized by electronic and ${}^{59}Co$ NMR spectra. The iodo complex has been found to be a *trans* isomer but both *cis* and *trans* forms are present with other halides. All these cobalt(III) complexes have been reported to be highly moisture-sensitive. Since their chloro analogues cannot be synthesized, it is probably the presence of Br or I which makes the otherwise 'hard' metal ion Co(III) softer. An interesting observation made with respect to the ${}^{59}Co$ NMR data is that the resonances of dithio, diseleno and ditelluro ether complexes occur at similar frequencies. This contrasts with the case of group 15 donor ligands, where replacement of phosphorus by arsenic and then antimony produces significant high frequency shifts.[26,27]

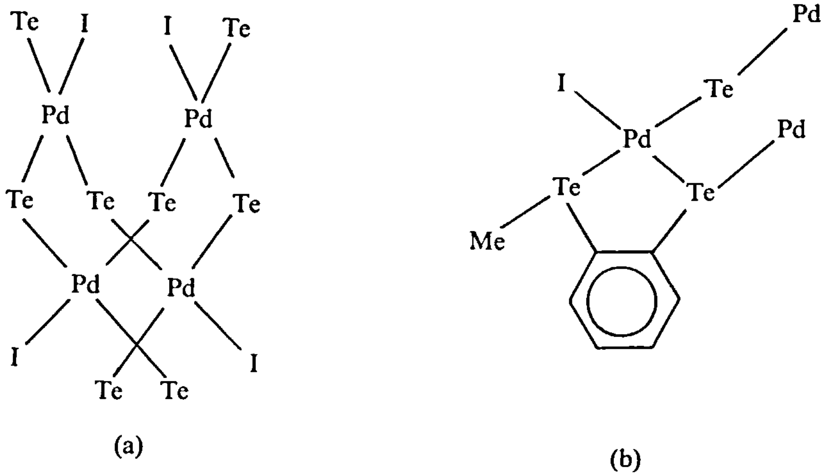
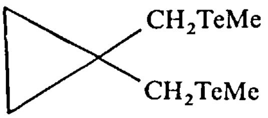


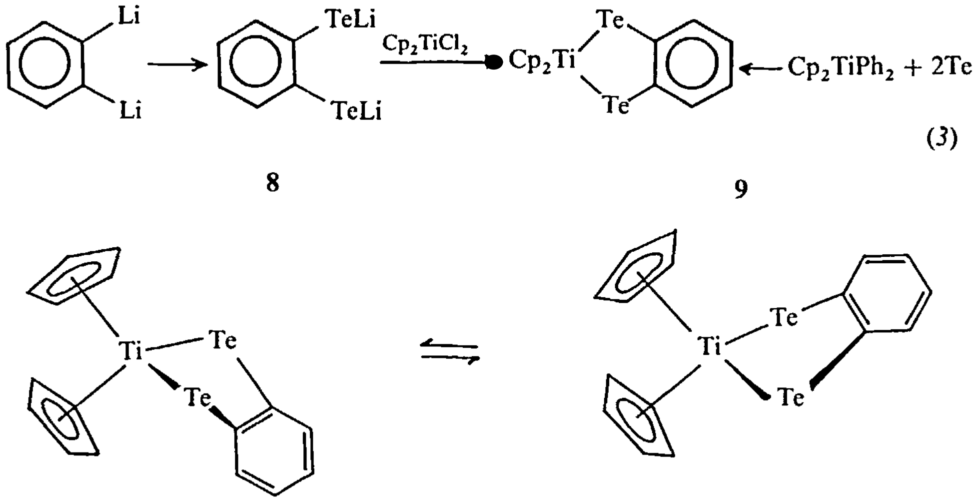
FIGURE 1 (a): Heavy atom framework of **5**, showing Pd, Te and I involved in the tetrameric unit; (b): ligand environment around Pd.

The synthesis of a neutral bidentate (Te,Te) ligand, 1,2-bis(*p*-ethoxyphenyltelluromethyl)benzene (**6**), and preliminary investigations on its coordination behaviour have been reported by McWhinnie's research group.[28] Nucleophilic attack of *p*-$EtOC_6H_4Te^-$ on 1,2-bis(bromomethyl)benzene resulted in **6**, which forms intractable complexes of stoichiometry [PdCl.**6**], [PtCl.**6**] and [HgCl.**6**]. Based on ν(M–Cl) values alone (NMR not possible due to poor solubility), these complexes have been suggested to be dimeric or polymeric. However, the ^{125}Te Mössbauer spectrum of the platinum complex indicated the +2 oxidation state of the platinum ion and not +1, as suggested by the stoichiometry. The synthesis of a (Te,Te) ligand, **7**, has been accidentally achieved in the reaction,[7] of $C(CH_2Br)_4$ with MeTeLi, but its complexation has yet not been evaluated.



7

The anionic (Te,Te) ligand benzene-1,2-ditellurolate (**8**) has been generated[29] *in situ* in THF at −78°C by the reaction given in (*3*), and in turn reacted with Cp_2TiCl_2 to give **9**[30] which may also be synthesized by insertion of Te in the appropriate Ti–C bond. Derivatives of Zr analogues to **9** have also been reported.[31] In the ^1H NMR spectra of **9** and its Zr analogue the Cp singlet (δ, 5.76 ppm) splits into two signals of equal intensity at temperatures below −40°C. This happens due to 'freezing' of chelate ring inversion as shown in Scheme 5. The value for ΔG_c^* (≈ 50 kJ mol^{-1}) for the ring inversion of **9** does not differ significantly from that of its S/Se analogue.



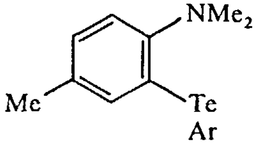
(3)

8 **9**

Scheme 5

(Te,N) Ligands

There have been no reports on the coordination chemistry of potentially bidentate (Te,N) ligands until recently, when Singh *et al.*[32,33] reported the synthesis of **10** and **11**, and their ligand chemistry. **10** has been obtained by reactions given in Scheme 6,



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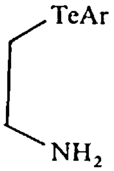
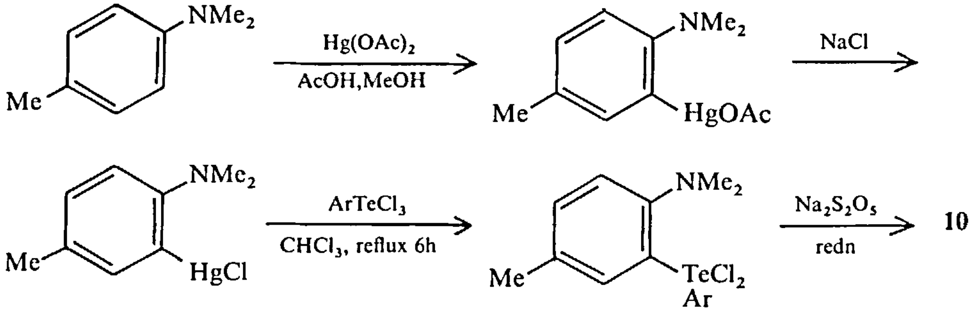


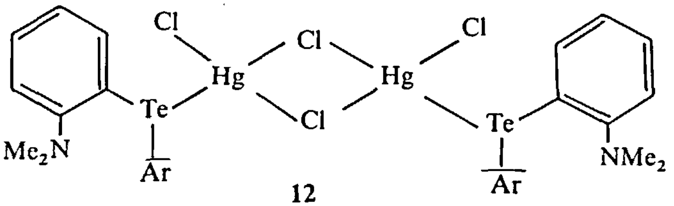
11

(Ar = C_6H_5, 4-$MeOC_6H_4$, 4-$EtOC_6H_4$)

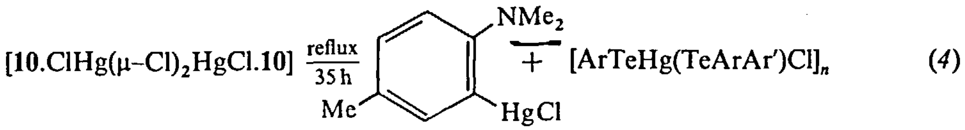


Scheme 6

and **11** by nucleophilic reaction of $ArTe^-$ with $NH_2CH_2CH_2Cl$. The ligand **10** forms complexes with Hg(II), Pt(II) and Pd(II) of stoichiometry $[MX_2.\mathbf{10}]$ (X = Cl or Br). For the mercury(II) complexes, the IR, Far-IR (upto $50\,cm^{-1}$), ^1H and ^{13}C NMR spectra ($\nu(Hg\text{–}Br_b$, $156\,cm^{-1}$, unaffected NMe_2 in NMR) suggest that **10** does not coordinate through NMe_2 and therefore the tetrahedral geometry around Hg(II) is completed through dimer formation as shown in **12**. This has been supported by X-ray diffraction studies on single crystals of $[HgBr_2.\mathbf{10}]$,[34] which demonstrate it to be $[\mathbf{10}.BrHg(\mu\text{-}Br)_2HgBr.\mathbf{10}]$. The bromine bridges are somewhat asymmetrical as Hg–Br (bridging) bond lengths are 2.755(1) and 2.710(1) Å. In palladium(II) and platinum(II) complexes, **10** behaves as a bidentate ligand[32] because the signal for the NMe_2 protons in the ^1H NMR spectrum is deshielded (0.7–0.8 ppm) and split into two signals of almost equal intensity. $[\mathbf{10}.ClHg(\mu\text{-}Cl)_2HgCl.\mathbf{10}]$ on refluxing in toluene for 35 h undergoes the reaction given in equation (4).

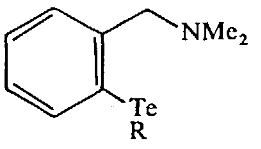


12

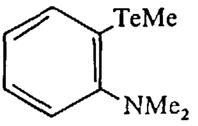


$$[\mathbf{10}.ClHg(\mu\text{-}Cl)_2HgCl.\mathbf{10}] \xrightarrow[35\,h]{reflux} \text{(Me, }NMe_2\text{, HgCl aryl)} + [ArTeHg(TeArAr')Cl]_n \qquad (4)$$

The ligand **11** forms a complex of stoichiometry $[HgCl_2.\mathbf{11}]$ at room temperature and which dimerize[33] on heating. It has been suggested that in the dimer two Hg atoms are bridged by two molecules of **11**. The NH_2 protons of **11** in the ^1H NMR spectrum are deshielded (≈2 ppm) on complexation with Hg(II). Similarly, the Te/NCH_2 groups of **11** in the ^{13}C NMR exhibit deshielding of 11–19 ppm on complexation. On the basis of these deshielding effects, bidentate behaviour of **11** with Hg(II) has been concluded. The CH_2 rocking vibrations in the IR spectra of $[HgCl_2.\mathbf{11}]$ appear in the range 925–890 and 825–815 cm^{-1}, and this fact has been used to conclude that the CH_2 groups of **11** adopt a *gauche* conformation in its Hg-complexes. The synthesis of tellurides **13a**[35] and **13b**,[22] which may act as bidentate



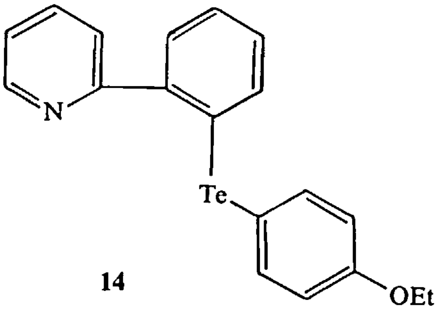
13a



13b

(R = Me, Et, *n*-Bu)

(Te,N) donors has been reported, but coordination behaviour is yet to be explored. Recently, McWhinnie *et al.*[52] have synthesized **14** by carrying out mercuration of 2-phenylpyridine, followed by transmetallation with $ArTeCl_3$ and reduction of the resulting $ArAr'TeCl_2$ compound with N_2H_4. Cu_2Cl_2 forms complexes[56] with **14** of



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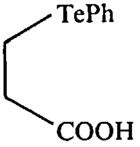
stoichiometries $[Cu_3Cl_3.\mathbf{14}].0.5CH_3CN$ in the cold, and $[Cu_2Cl.\mathbf{14}].0.5EtOH$ on refluxing. CuX_2 (X = Cl or Br) reacts with **14** in the cold to form $[CuCl.\mathbf{14}]/[CuBr.\mathbf{14}].H_2O$, whereas on refluxing, the two react to give $[Cu_3Cl_3.\mathbf{14}].H_2O$ and $[Cu_2Cl_2.\mathbf{14}].0.5EtOH$, depending on the experimental conditions. However, a definite solution or solid state structure has not yet been reported for either of these copper complexes.

(Te,O) Ligands

Synthetic routes[10,22,36–39,50] to a variety of (Te,O) ligands **15–21** are available, and for **15–18** from the early seventies. Almost no attention has been paid to their ligand chemistry except one report in which formation constants for silver(I) and some bivalent first row transition metal ions with **15** have been measured.[40] Recently, the ligand chemistry of the (Te,O) donors **22** and **23** has been investigated. ^1H NMR spectra of **22**, synthesized[41] by reacting $ArTe^-$ with chloroacetic acid, have revealed



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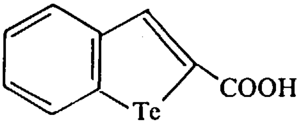

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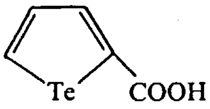

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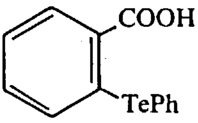

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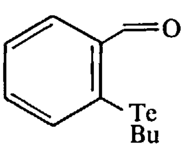

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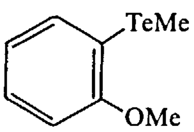

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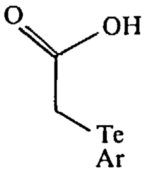

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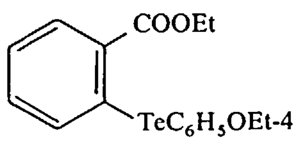
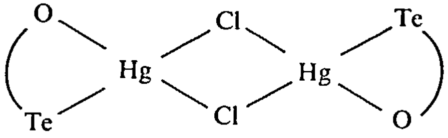


23

(Ar = C_6H_5, 4-$MeOC_6H_4$, 4-$EtOC_6H_4$)

that hydrogen bonding in $PhTeCH_2COOH$ is stronger than in acetic acid, but decreases when Me/EtO is substituted at a position *para* to Te. A Hg-complex of **22** has been synthesized and is presumed to have structure **24** on the basis of its IR, ^1H

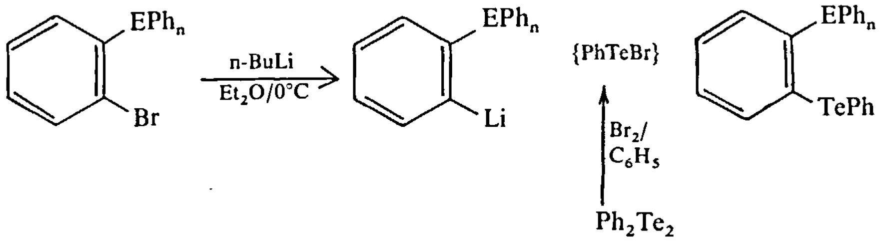


24

and ^{13}C NMR spectra (Δ[ν(C═O) − ν(C—O)], 320 cm^{-1}; deshielding of $TeCH_2$ in ^{13}C NMR by 11 ppm,). Complexes of **23** with Tl(I), Ag(I), Co(II), Ni(II), Cu(II), Cr(III) and Fe(III) have been synthesized.[42] By examining their IR, electronic and Mössbauer spectra (in the case of iron), in conjunction with magnetic properties, it has been concluded that ligation through tellurium may be invoked only in the case of Tl, Ag and Ni. Other complexes are simple carboxylates. However, structures of none of these complexes has been sorted out, presumably due to their poor solubility and crystal quality.

Other (Te,Y) Type Ligands

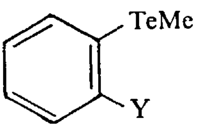
Gysling and Luss[43] have suggested that by using (5), a variety of hybrid organotellurium ligands may be synthesized. However, only the ligation of the (Te,P)



(5)

(E = S, Se, Te, N, P)

ligand has been investigated. $K_2Pt(SCN)_4$ reacts with this ligand, resulting in $[Pt(SCN)_2(Te\text{–}P)]$, which on recrystallization from DMF gives $[Pt(Te\text{–}P)_2]$ $[Pt(SCN)_4]$.2DMF, in which coordination through phosphorus and tellurium has been confirmed by X-ray diffraction. Levason and coworkers[22] have reported the synthesis of several hybrid organotellurium ligands (**25**) which may act as bidentate ligands. The reaction depicted in (*6*) has been used to synthesize **25**. However, no attempt has been made to study their ligation. Recently, a (Te,S) ligand, 2-(aryltelluro)ethylmethyl sulphide (**26**),[44] has been synthesized by reaction of $ArTe^-$ with $ClCH_2CH_2SMe$. The Pd(II) and Pt(II) complexes of **26** having stoichiometry $[MCl_2.$**26**$]$ have been isolated.[44] Coordination of **26** through both S and Te has been concluded on the basis of IR, ^1H and ^{13}C NMR spectra ($^2J(^{13}C–^{195}Pt)$ 22–27 Hz, ν(Pd–Cl): 350, 390 cm^{-1}; ν(Pt–Cl): 300, 320 cm^{-1}) for square planar Pd(II) and Pt(II) complexes. Signals due to SMe, SCH_2 and $TeCH_2$ in the ^{13}C NMR spectra undergo deshielding of 4–11 ppm on complexation with Pd(II)/Pt(II).



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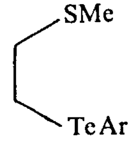
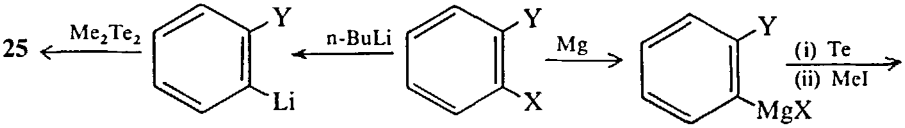


26

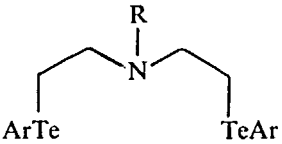
Y = SMe, SeMe, PMe_2, $AsMe_2$, $SbMe_2$ Ar = $4\text{-}MeOC_6H_4$, $4\text{-}EtOC_6H_4$



(*6*)

Terdentate Ligands

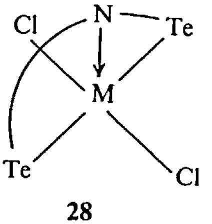
The number of known organotellurium compounds which may be considered as potential terdentate ligands is very small.[45,46] There has been no report of their ligand chemistry until recently, when Singh *et al.*[47] reported the synthesis of bis[(2-aryltelluro)ethyl]amine and bis[(2-aryltelluro)ethyl]methyl amine (**27**), and their coordination behaviour. The synthesis of **27** has been effected by reacting $ArTe^-$ with $Me/HN(CH_2CH_2Cl)_2$. With Hg(II), Pd(II) and Pt(II), **27** forms complexes of stoichiometry $[MCl_2.$**27**$]$. The NH and NMe proton signals in the ^1H NMR spectra of the Hg complexes do not show any deshielding with respect to those of the ligands and therefore ligation of **27** with Hg has been concluded to be through only its two



27

(R = H, CH_3; Ar = C_6H_5, $4\text{-}MeOC_6H_4$, $4\text{-}EtOC_6H_4$)

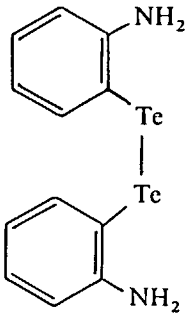
Te atoms (as Ar protons in the ^1H NMR and CH_2Te in the ^{13}C NMR exhibit deshielding when **27** ligates with Hg(II)). For palladium and platinum complexes, structure **28** is proposed on the basis of their IR (ν(PdCl) 320 cm^{-1}; ν(Pt–Cl) 330 cm^{-1}), ^1H and ^{13}C NMR spectra (NH protons ≈ 5 ppm downfield relative to **27**; carbons of CH_2Te and CH_2N 5.6–9.5 ppm downfield relative to those of the ligand). An interesting potentially terdentate Te ligand, $MeC(CH_2TeMe)_3$,[10] has been synthesized by reacting MeTeLi with $MeC(CH_2Cl)_3$ but no complex has been isolated so far. Similarly, the synthesis of a potentially terdentate Te ligand, bis[2-(2-pyridyl)phenyl]-telluride,[52] has been reported, but not its ligand chemistry.



28

Tetradentate and Higher Polydentate Ligands

The first potentially tetradentate ligand di-2-aminophenylditelluride (**29**), synthesized by McWhinnie *et al.*,[48] forms complexes with Cu(I) and Cu(II) of composition $[CuCl_n.\mathbf{29}]_n$, with $n = 1$, 2, but low solubilities, presumably due to polymeric structures, precluded definitive characterization. The synthesis (7) of a potentially tetradentate ligand, 1,6-bis-2-butyltellurophenyl-2,5-diazahexa-1,5-diene (**30**),[49,50] has been reported. It forms a thirteen-membered chelate ring with Hg by coordinating through two Te atoms, as revealed by X-ray diffraction studies of the mercury complex. McWhinnie and coworkers[50–52] have also reported the synthesis of **31** to **35**, which may act as a tetra- or higher polydentate ligands, but their coordination behaviour has not been explored. However, the complexation of **30** and **36** with Pd(II), Pt(II), Rh(I) and Rh(III) has been investigated recently.[53] Compounds of stoichiometries [Pd/PtCl(**30**)(H_2O)]Cl, [$PdCl_2$.**36**], [$PtCl_2$.**36**].H_2O, [$RhCl_3$.**36**].$2H_2O$, [$RhCl_3$.**36**].H_2O and [RhCl.**30**/**36**] have been isolated but none of them has been assigned any definite structure. However, by using electronic, IR, ^1H, ^{125}Te and ^{195}Pt



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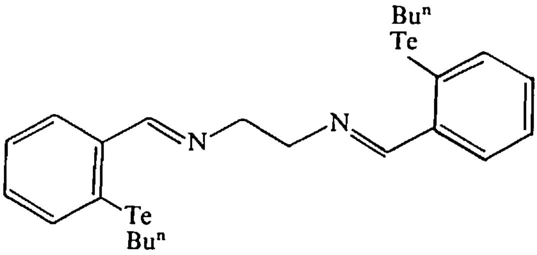

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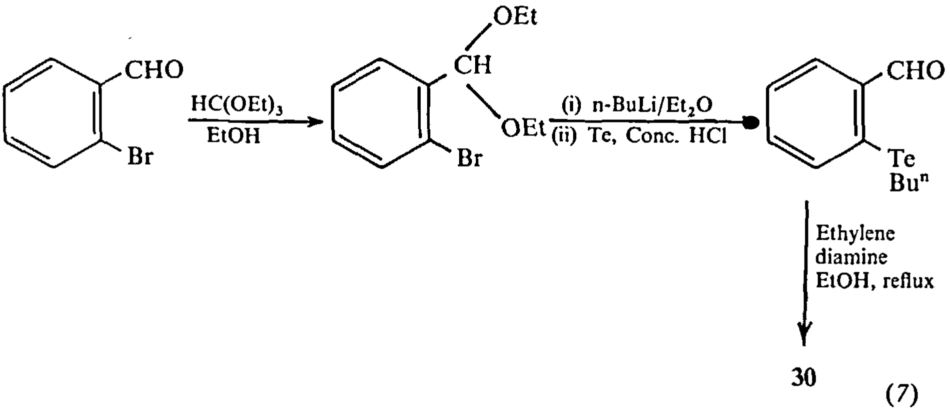

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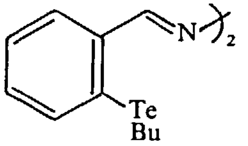

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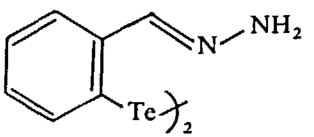

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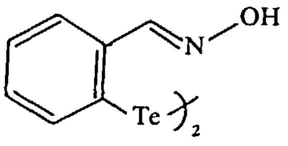

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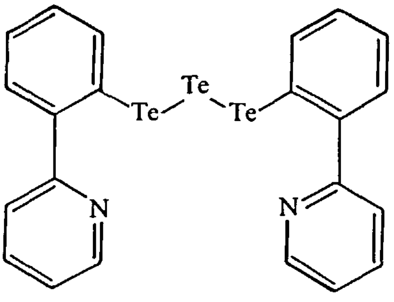

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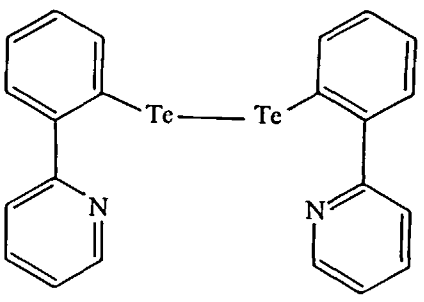
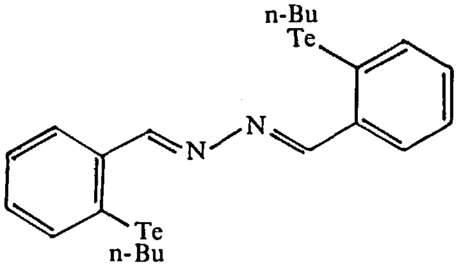


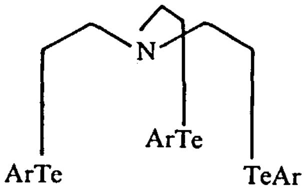
35

NMR spectra in conjunction with conductance measurements, it has been concluded that **30** and **36** both ligate with Rh(I), Pt(II) and Pd(II) through two Te atoms only. In the case of Rh(III), coordination through the azomethine nitrogen atom has to be invoked. For [$PdCl_2$.**36**], some evidence for both *cis* and *trans* isomers (ν(Pd–Cl): 345, 332 and 288 cm^{-1}) has been obtained. [PtCl(**30**)(H_2O)]Cl decomposes in polar solvents to give a Pt(IV) complex, [$PtCl_2$(**30**)$^{2-}$], where (**30**)$^{2-}$ denotes the ligand **30**



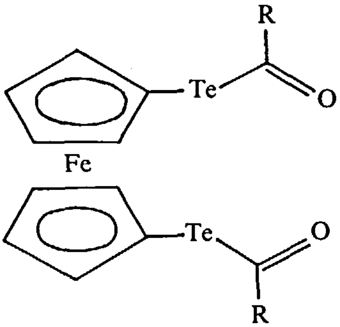
36

which has lost two butyl groups. However, *cis*-[$PtCl_2$.**36**] does not undergo dealkylation. Recently a potentially tetradentate tripod ligand **37** has been synthesized by



37

Singh and Srivastava[54] by reacting $ArTe^-$ with $N(CH_2CH_2Cl)_3$. Its Hg(II) complex, having stoichiometry [$HgCl_2$.**37**], has been synthesized and characterized by IR, ^1H and ^{13}C NMR spectra in conjunction with conductance and molecular weight measurements. The ligand **37** coordinates with Hg(II) only through two Te atoms ($TeCH_2$ is deshielded ≈ 12 ppm in the ^{13}C NMR on complexation) and in solution these coordinated Te atoms undergo a fast exchange with the third free Te, at least on the NMR time scale (as MeO/EtO signals in the ^1H and ^{13}C NMR do not split on complexation). The potentially tetradentate ligands $C(CH_2TeAr)_4$[10,51] (Ar = Ph or 4-$EtOC_6H_4$) have been synthesized by reacting $ArTe^-$ with $C(CH_2Cl)_4$, but there is no report on their ligand chemistry. Synthesis of a potentially tetradentate ligand **38** has been reported by the route shown in (*8*), but again there is no report on its complexation behaviour.



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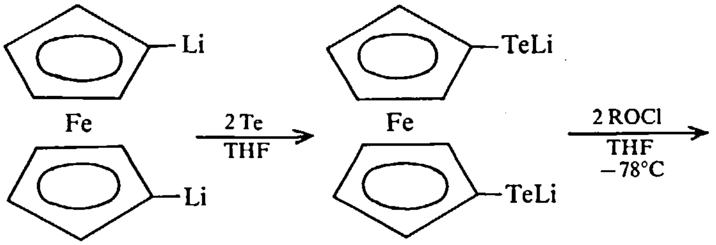

(*8*)

CONCLUSIONS

Over the last 6–7 years there has been a considerable growth in the synthesis of polydentate Te ligands and at the moment a variety of such species are known and which may be synthesized in good yield through fairly simple procedures. Comparatively less work is reported on complexes of these potential polydentate Te ligands. Sometimes the metal complexes of such ligands defy all attempts at characterization because they give neither good crystals nor exhibit adequate solubility for recording NMR spectra. This may be partly responsible for the slow development of associated ligand chemistry. A recent report[25] that 'hard' metal centres like Co(III) may ligate with the Te donor ligands is encouraging, for those interested in multidentate Te ligands. Similarly, interest in hybrid organotellurium ligands may be rewarding and, present trends reveal, future ligand chemistry is expected to grow significantly.

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