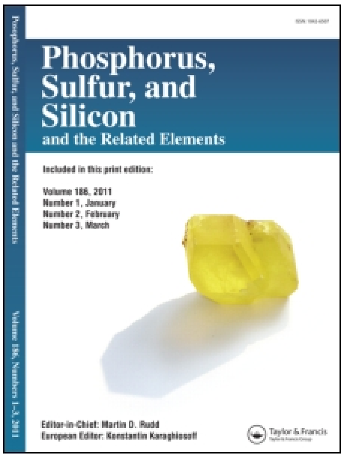

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Intra-Molecular Co-Ordination - A Route to Novel Organo Tellurium Compounds

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INTRA-MOLECULAR CO-ORDINATION - A ROUTE TO NOVEL ORGANO TELLURIUM COMPOUNDS

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Abstract Molecules containing intra-molecular Te←N co-ordinate bonds are now a well established feature of organotellurium chemistry. Methods of synthesis of such compounds are reviewed and discussed. The considerable quantity of X-ray crystallographic data available for the materials is reviewed and the influence of the group bonded trans to the Te←N bond on the length of that bond is discussed for a series of tellurium(II) compounds. Some cross comparisons with related compounds of bismuth and selenium are made.

Recent studies of the Lewis basicity of some organotellurium compounds containing intra-molecular Te←N bonds reveal considerable lability of organic groups from co-ordinated tellurium. In some cases (e.g. Hg(II)) well defined products result, but in other cases (e.g. Pd(II)) ill defined materials of enriched inorganic content are obtained.

INTRODUCTION

This year (1991) the Royal Society of Chemistry (U.K.) celebrates the 150th anniversary of the formation in 1841 of The Chemical Society. It is interesting to note that the preparation of the first organotellurium compound, Et_2Te, by Wohler[1] in 1840 predates that foundation by one year. The past 151 years have seen periods of rapid growth and periods of relative stagnation in the development of the subject. In 1974 Irgolic[2] published a still useful book which summarised very fully progress to that time. It was very striking that the contributions to the subject were dominantly synthetic. Few rigorous physical studies of organotellurium compounds had been reported and the potential of some of the compounds as ligands in co-ordination chemistry had scarcely been realised. The paucity of compounds containing tellurium to nitrogen bonds was another noteworthy feature — indeed the folk-lore then current implied that these compounds should be "unstable". We are now wiser.

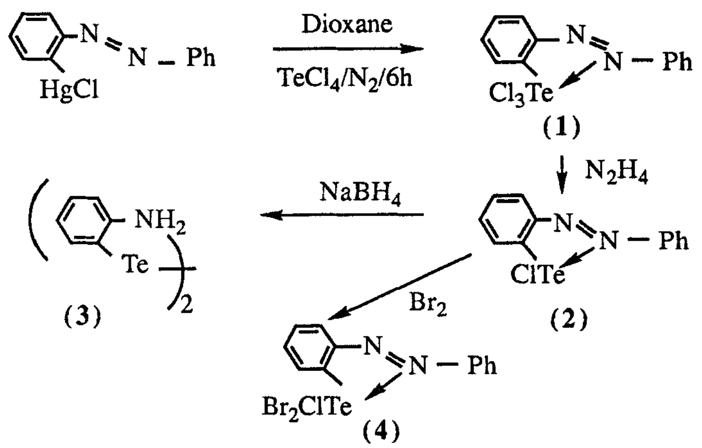
The author's interest in the area of organotellurium chemistry was generated by a review produced by Petragnani and Moura Campos[3]. It seemed that a number of unanswered structural problems might be addressed by detailed spectroscopic examination and our early contributions were dominated by applications of vibrational spectroscopy[4,5,6] and ^{125}Te Mössbauer spectroscopy[7,8,9] to compounds the syntheses of which were often available in the literature. Soon a desire to synthesise new compounds grew too great to resist and it was decided to explore the Te←N co-ordinate bond.

Early efforts to prepare simple co-ordination compounds of, say, pyridine by reaction of $RTeCl_3$ (R = Ph or p-EtO.C_6H_4) with the base in supposedly dry solvents gave, via adventitious ingress of water, pyridinium salts[10] i.e. $(C_5H_5NH)[RTeCl_4]$.

Sadekov et al[11] reported a yellowish-green complex of N-benzylideneaniline and $TeCl_4$ from benzene solution which showed an increase in υ(C=N) compared with the free base. For the same reaction, in our hands,[12] hydrolysis problems were again enhanced by the presence of the basic ligand and a yellow product LH[Te(O)Cl_3], (L = N-benzylideneaniline) with υ(C=N)= 1650 cm^{-1} (cf L, υ(C=N) = 1630 cm^{-1}) was obtained. The classic work[13] in which organopalladium and -platinum compounds were prepared by the direct reaction of $PdCl_2$ or $PtCl_2$ with azobenzene suggested that ortho-telluration of azobenzene may occur directly given the well established electrophilic behaviour of $TeCl_4$[14]. Refluxing $TeCl_4$ and azobenzene in a range of solvents gave no product, however no hydrolysis of the halide was noted.

INTRA-MOLECULAR TELLURIUM-NITROGEN CO-ORDINATE BONDS: SYNTHETIC CONSIDERATIONS

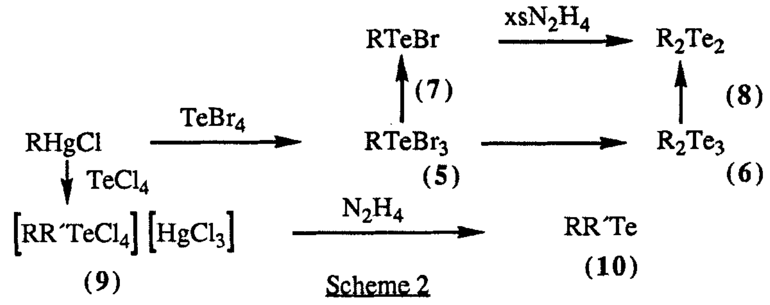
Mercuration of azobenzene followed by a trans-metallation reaction with $TeCl_4$ provided a satisfactory route to tellurated azobenzenes[15] (Scheme 1).



Scheme 1

Compound (2) was the first compound containing a Te←N intra-molecular co-ordinate bond to be structurally characterised[15]. Subsequent attempts to synthesise (1)[16] led to products of variable m.p. despite tolerable C, H, N analytical data, a problem caused by some degree of mercury contamination (N.B. relative molecular masses: $TeCl_3$ = 234.1, HgCl = 236.1). A definitive synthesis is now available[16] and (1) has been crystallographically characterised; it appears that a polymorphous form of (2) also exists (m.p.s. 80°C, 125°C).[16,17] The range of compounds in scheme 1 may be extended by metathesis e.g. the chloro-group in (2) may be replaced by acetato-[18], thiocyanato-[18], or dialkyldithiocarbamato-[19].

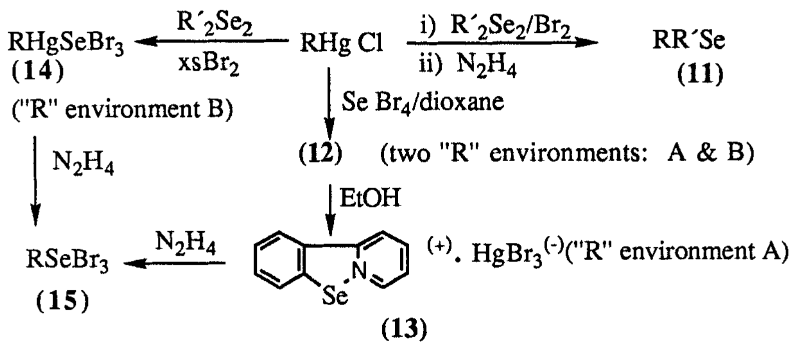
The mechanism of the trans metallation reaction is a matter of some interest, an associative route being one possibility. Phenylazophenyl (C′, N) mercury(II) chloride is in fact dimeric[20] and another reagent, 2-(2-pyridyl)phenylmercury(II) chloride, of importance in our work has been shown by Constable[21] to be tetrameric. Thus the speculation that molecular species involving both mercury and tellurium may be intermediates in the trans-metallation process is not unreasonable. Indeed, Al-Salim[22] in his investigation of the 2-(2-pyridyl)phenyltellurium system did isolate a compound later proved to be $[RR'TeCl][HgCl_3]$[23] (R = 2-(2-pyridyl)phenyl-, R′ = p-ethoxyphenyl) which is denoted (9) in scheme 2.



Scheme 2

(R = 2-(2-pyridyl)phenyl- ; R′ = p-ethoxyphenyl-).

The chemistries of selenium and tellurium are not always identical and there are subtle differences between the reactions of selenium and tellurium compounds with 2-(2-pyridyl)phenylmercury(II) chloride as a comparison between schemes 2 and 3 illustrates. Although selenium(IV) starting materials were employed the final products contain selenium(II) e.g. $[C_{11}H_8NSe]$ $[HgBr_3]$[24] **(13)**. A comparison of **(13)** and **(14)** in scheme 3 is of interest since these are believed to be related as [RSe] $[HgBr_3]$ and [RHg] $[SeBr_3]$ (R= 2-(2-pyridyl)phenyl-).

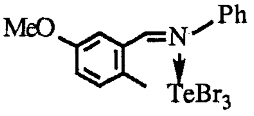


Scheme 3

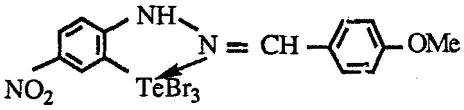
(R = 2-(2-pyridyl)phenyl- ; R′ = p-ethoxyphenyl-).

Compound **(12)**, scheme 3, has the stoicheiometry $RSeHgBr_3.0.5$ dioxane but has two distinct "R" environments (N.M.R.) denoted A and B. These environments correspond to the single environment (A) of **(13)** and (B) of **(14)**. There is then circumstantial evidence in schemes 2 and 3 for an associative mechanism for the trans-metallation reaction.

Trans-metallation using organomercury derivatives has been successful for the synthesis of a range of tellurated azomethines and phenylhydrazones e.g. **(16)** and **(17)**[25]:

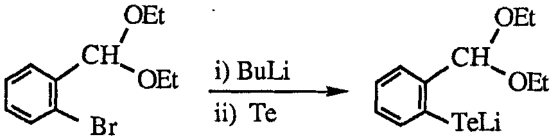


(16)



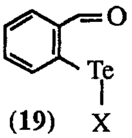
(17)

Piette and Renson[26,27] were among the first to use intra-molecular co-ordination to stabilise organotellurenyl halides via Te←O co-ordinate bonds. They developed organolithium methodology such as:



(18)

Treatment of **(18)** with a variety of reagents, followed by removal of the protecting groups gives a wide range of compounds **(19)**.

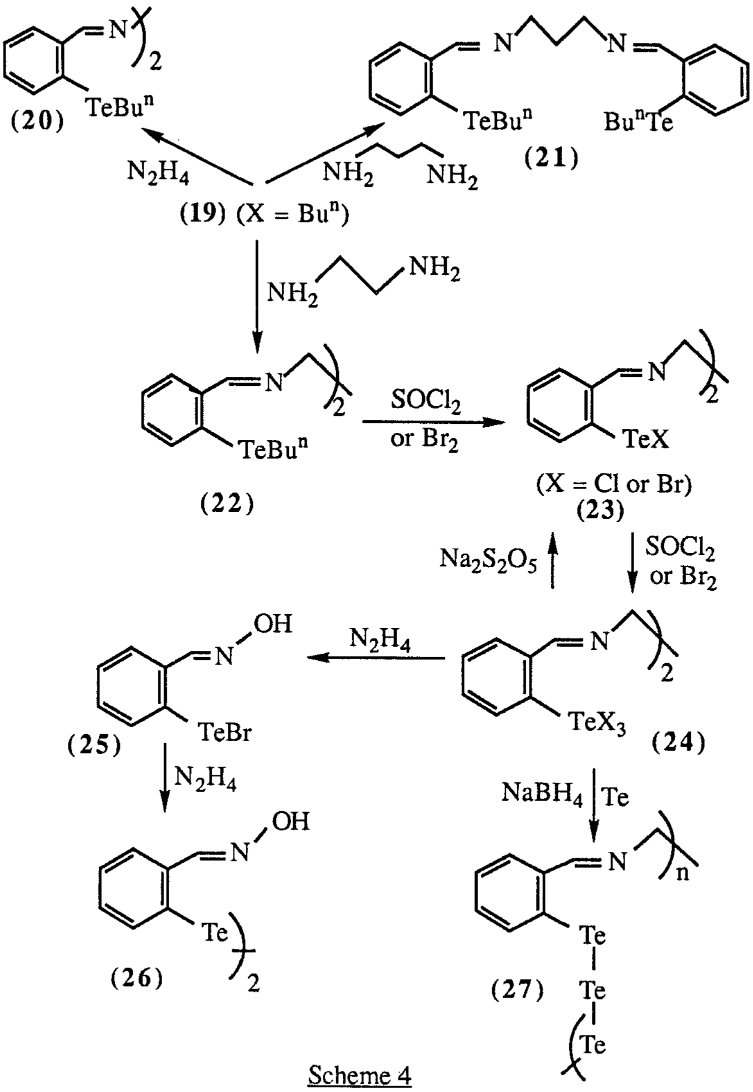


(19)

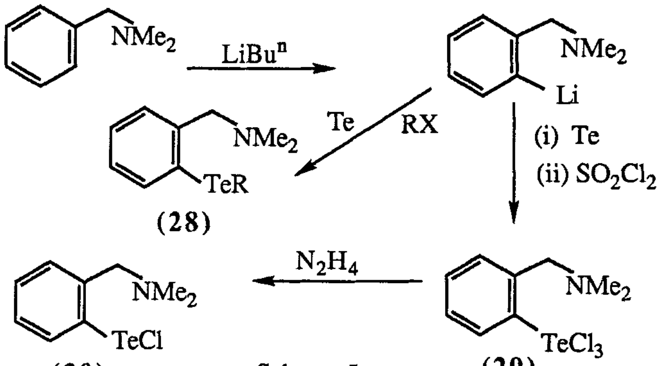
e.g. X = Cl, Br, I, CH_3, Bu^n

The ability of **(19)** to form Schiff bases enabled this methodology to be adapted to the synthesis of compounds with Te←N bonds[28] as illustrated in scheme 4.

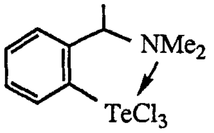
Direct lithiation of aromatic amines can lead to species with Te←N(sp^3) as opposed to Te←N(sp^2) bonds as the work of Singh demonstrates[29] in scheme 5. Similar syntheses have led to the isolation and X-ray characterisation of a chiral tellurium compound **(31)**[30].


(20)
TeBu^n
N
2
(21)
TeBu^n
Bu^nTe
N
N
N2H4
NH2
NH2
(19) (X = Bu^n)
NH2
NH2
(22)
TeBu^n
SOCl2
or Br2
(23)
TeX
(X = Cl or Br)
Na2S2O5
SOCl2
or Br2
(24)
TeX3
N2H4
(25)
TeBr
OH
N2H4
(26)
Te
OH
NaBH4
Te
(27)
Te
Te
Te
n

Scheme 4

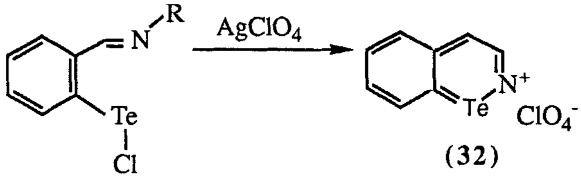


Scheme 5

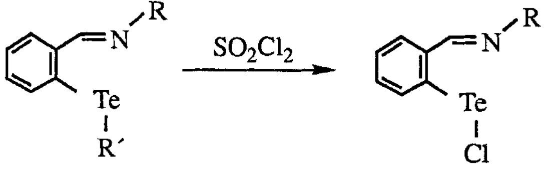


(31)

The school led by Sadekov and Minkin has recently made considerable contributions to the chemistry of tellurated azomethines. The synthetic methodology follows that outlined above and a number of structural determinations are available (see later). The following reaction[31] is of interest, the product being related to (13) in scheme 3:

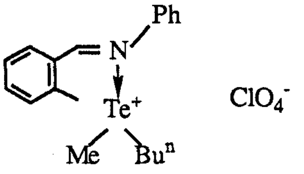


The ready formation of this stable cationic species suggests that it might play some role as an intermediate when Te-R′ bonds are broken by halogenating reagents:[32]

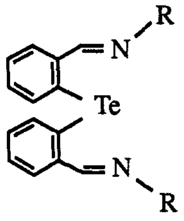


Similar cationic intermediates may be involved for the transformation (22)→(23) in scheme 4.

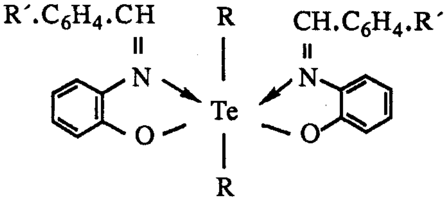
Other variations reported by the Russian workers include a novel telluronium salt (**33**), the telluride (**34**),[34] and the formation of intra-molecular co-ordinate bonds via the anionic group (X) in R_2TeX_2 e.g. (**35**)[35].



(33)



(34)



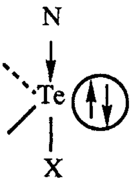
(35)

The cation of (**33**) is a further example of a structually characterised chiral tellurium compound.

STRUCTURAL CONSIDERATIONS

The molecular structures of organotellurium compounds containing intra-molecular Te←N bonds are unremarkable as such. Thus, in general, members of the series $RTeX_3$(X=Cl,Br) are square based pyramidal with the vacant co-ordination position trans to the Te-C bond notionally occupied by a spare pair of electrons conferring pseudo-octahedral geometry. Inter-molecular contacts are rare (see data in table I). The Te←N distances are relatively constant for those of the three compounds in table I (table entries 1, 14, 15 — average Te-N = 2.416 Å), but that for No.16 at 2.244 Å is significantly less. All values are greater than the sum of the Pauling[42] covalent radii (2.11 Å), but very much less than the van der Waals distances[42] (3.70 Å).

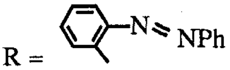
Other Te(IV) compounds (table entries 6 and 17) are novel telluronium salts. The structures of both may be considered pseudo - trigonal bipyramidal (**36**) with X=Me (No. 6) and Cl (No.17).

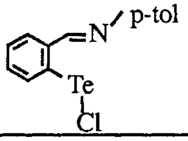
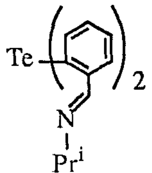
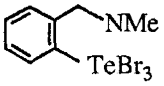
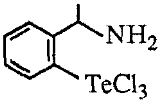


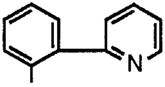
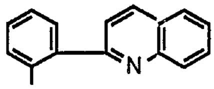
(36)

For No.6 the Te←N interaction is very weak (2.750 Å), within the van der Waals distance but much greater than the sum of the covalent radii. The Te-C distance of the trans methyl-group of 2.137 Å is quite normal and the Me-Te-N angle is 164.9°C. With the more electronegative chlorine in 17 the Te-N distance is 2.31 Å. It has been suggested[43] that tellurium is best regarded as ellipsoidal when in pseudo-trigonal bipyramidal co-ordination and estimates of $r_{\text{equatorial}}$ (1.37 Å) and r_{axial} (1.54 Å) for Te(IV) have been made[43]. Thus the calculated Te-N length is 2.28 Å, quite close to that observed. The observed (2.43 Å) and calculated (2.53 Å) Te-Cl distances differ to a greater extent. It appears that the strength of the Te→N interaction is a function of the electronegativity of the group trans- to N.

TABLE I Bond length data for Te←N compounds

Compounds	Ref.	Bond Lengths (Å)		
		Te←N	Te-C	Other
Azobenzene Series R =  Te(IV) 1) RTeCl$_3$ (1)	16	2.417(4)	2.114(5)	-
Te(II) 2) RTeCl (2)	15	2.23(2) 2.19(2)	2.04(2)	Te---Cl 3.66, 3.67
3) RTeS$_2$ CNMe$_2$	19	2.340(7)	2.101(8)	Te---5 2.568(2), 3,225(3)
4) RTeOOCCH$_3$	18	2.260(4)	2.074(4)	Te---O 2.167(4), 2.953(4)

5) RTeSCN	18	2.243(3)	2.073(4)	Te—S 2.672(1) Te---N (inter-mol) 3.535(3)
Azomethine Series Te(IV) 6) (33)	33	2.750(4)	(Me)2.137(6) (Bu)2.147(5) (Ar)2.120(5)	
7) (35)	36	2.962 2.923	(Me) 2.10	Te—O 2.13, 2.10
Te(II) 8) 	32	2.218(6) 2.239(6)	2.107(7) 2.088(7)	
9) (20)	40	2.773 2.239(6)	(Bu)2.181(10) (Ar)2.111(8)	
10) HgCl$_2$. L	40	2.786 2.752	(Bu)2.161(12) 2.146(12) (Ar)2.101(12) 2.149(11)	
11) (34)	34	2.702(3)	2.128(4) (Chelate) 2.162(4) (free-trans N)	
12) 	38	2.72	2.13 (Chelate) 2.16 (trans N)	
Te(I) 13) (26)	28	2.822(5) 2.876(5)	2.136(8) 2.142(8)	
Benzylamine Series Te(IV) 14) 	29	2.42(1)	2.12(1)	
15) 	30	2.411(7)		

Phenylpyridine Series R= 		R′= 		R'= p-EtO.$C_6H_4^-$
Te(IV) 16) RTeBr_3 (5)	22	2.244(14)	2.110(19)	Te---Br 3.596(3)
17) RR"TeCl,HgCl_3 (9)	23	2.31(2)	(R) 2.11(3)	
Te(II) 18) RTeBr (7)	41	2.236(11)	2.111(6)	Six independent molecules in asymmetric unit.
19) RR"Te (10)	22	2.695(4)	(R) 2.138(6) (R")2.144(6) (trans-N)	
20) RTeS_2CNMe_2	22	2.354(4)	2.111(5)	Te-S (trans N) 2.518 Te---S (non-bonding)
21) R′TeS_2CNMe_2	38	2.365(4) 2.385(4)	2.124(5) 2.135(4)	3.667(1) Te-S (trans N) 2.569(1), 2.543(1)Te---S (intra-mol)
22) R_2Te_3 (6)	37	2.554(7)		3.222(1), 3.230(1) Te-Te
23) RR"Se (11)	39		1.932(4)	2.776(1)

(N.B. where inequivalent molecules are present in the asymmetric unit, data are given for each molecule)

For Te(II) compounds of the type RTeX (X = Cl, Br, dithiocarbamate) there is more evidence of inter- or extra intra-molecular contracts. Thus, the psuedo-trigonal bipyramidal "T" shaped molecules may make a fourth long contact along a vector bisecting the angle between the equatorial lone pairs of electrons. Judgement of how real such interactions are is complicated by the various estimates of the van der Waals radius of tellurium which are available — 2.20 Å (Pauling$^{42)}$), 2.06 Å (Bondi $^{44)}$), 1.9 Å (Briegleb$^{45)}$). It may reasonably be stated that the tendency to weak secondary interactions trans to the Te-C bond is greater for RTeX than for RTeX_3.

The Te←N bond length for organotellurenyl halides in table I is remarkably constant with an average value of 2.223 Å which compares with a predicted value of 2.28 Å (r_{axial}, Te(II) = 1.54 Å$^{43)}$). The change of the trans-ligand from halogen to oxygen (table I, No.4) gives Te←N = 2.260 Å, and to sulphur (SCN, table I, No.5), 2.243 Å. Change of the trans-ligand to dithiocarbamate (table I, Nos. 3, 20,

21) increases the Te←N bond length by approximately 0.14 Å (average of 3, 20, 21 = 2.361 Å). The dithiocarbamates are prone to show a second long Te---S interaction within the van der Waals distance, usually in the molecular plane of the "T" skeleton (Nos., 3, 21); for No.21 however the dithiocarbamate is twisted out of the molecular plane and an essentially non-bonding distance of 3.667 Å between Te and the second sulphur atom results. Given the great chemical similarity of 20 and 21, the structures must be determined as much by crystal forces as by the strength or weakness of any Te---S secondary interaction. $PhTe(S_2CNEt_2)_3$[46] has a seven co-ordinate tellurium atom. An attempt was made to prepare tris-dimethyldithiocarbamato-(phenylazophenyl [C′, N])tellurium(IV)[19] to investigate if Te would opt for 8-co-ordination or, if 7 - co-ordinate, would the nitrogen - or one dithiocarbamate sulphur - atom remain unco-ordinated? In the event, although compounds of the formula $(C_{12}H_9N_2)Te(dmdtc)_3$ were isolated (dmdtc = dimethyldithiocarbamate), ^{125}Te Mössbauer spectroscopic evidence suggested them to be charge transfer complexes : $RTe^{II}(dmdtc)\cdot(dmdtc)_2$.[19] The desired composition was eventually achieved with 2-(2-pyridyl)phenylbismuth compounds which were not susceptible to reductive elimination reactions. Thus Ph Bi $(dedtc)_2$ is dimeric (6 co-ordinate via long secondary Bi---S contacts) but $(C_{11}H_8N)Bi(dedtc)_2$ is a six co-ordinate monomer in which a weak Bi←N interaction is preferred to an inter molecular Bi---S contact[47] (dedtc = diethyldithiocarbamate), thus demonstrating some affinity of "soft" metal centres for the 2-pyridyl-nitrogen atoms.

Four compounds of Te(II) in table I are of the type RR′Te (nos. 9, 11, 12, 19). All show much longer (weaker) Te←N contacts than those in RTeX (e.g. 2.695 - 2.773 Å, cf van der Waals distance of 3.70 Å). Thus a trans-bonded carbon atom exercises a much larger trans-influence on the Te←N bond than halogen, oxygen, or sulphur. However, there is also evidence of reciprocal lengthening of the Te-C bond trans to nitrogen. This is best illustrated by compound No.11 (**34**) (where R = R′ in RR′Te) for which Te-C ("equatorial") = 2.128(14) Å and Te-C ("axial", trans-N) = 2.162(14) Å, For No.9 also the Te-C distances are 2.111(8) Å (aryl) and 2.181(10) Å (butyl) ; although some 0.03 Å may be accounted for by the change from sp^2 C to sp^3 C, the lengthening of the Te-C bond trans to N seems real. A comparison of compound No. 23, table I with No.19 is interesting. In the selenium compound, the plane of the 2-pyridyl-group is twisted away from the C-Se-C plane and no bonding Se---N interaction can be considered. By contrast, in No.19, the weak Te←N interaction maintains the tellurated 2-phenylpyridine moiety in an almost planer configuration.

Compound No.13, table I, a ditelluride has tellurium in a formal oxidation state of (I) and the Te←N distances, although within the sum of the van der Waals radii, are very long (2.822 (5) and 2.876 (5) Å). By contrast, the tritelluride No.22 in table I has the relatively short Te←N distance of 2.554(7) Å. This observation has led to the suggestion that the compound may be regarded as bis[2-(2-pyridyl)phenyltellurenyl] telluride[22]. To the extent that it is valid to use the Te←N bond length as a measure of the Lewis acid strength of tellurium in those compounds, we have in summary:

$$\underset{(\mathrm{Cl,Br=X})}{\mathrm{RTeX}} > \underset{(\mathrm{Cl,Br=X})}{\mathrm{RTeX_3}} > \mathrm{(RTe)_2Te} > \mathrm{RTe(R')} > \mathrm{RTe\text{-}TeR}\ .$$

THE LEWIS BASICITY OF Te←N COMPOUNDS

One reason for the synthesis of many of the compounds of the type RR′Te was to investigate their ligand chemistry with a range of metal ions. Some data obtained from such experiments are reviewed briefly.

Mercury(II) has a good affinity for tellurium ligands. The complex of $HgCl_2$ and compound (**22**) is of 1 : 1 stoicheiometry. The Te←N contacts remain intact in the co-ordinated ligand (compound No.10, table I),[40] thus the ligand is bidentate via the two tellurium atoms and the chelate ring formally consists of 13 atoms. By contrast, compound No.19 in table I (**10** in scheme 2), also of the type RR′Te, undergoes a totally different reaction, albeit via a 1 : 1 complex intermediate:

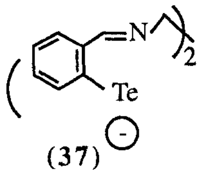
$$\mathrm{2RR'Te + 2HgCl_2} \xrightarrow[\text{temp.}]{\text{room}} \mathrm{2[(RR'Te)\ .\ HgCl_2]}$$

$$\xrightarrow[\text{ethanol}]{\text{reflux}} \mathrm{R'HgCl\ +\ (RTeCl)_2\ .\ R'HgCl} \qquad (36)$$

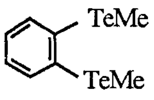
(R = 2-(2-pyridyl)phenyl-; R′=p-ethoxyphenyl-)

The process has been termed *reverse trans-metallation.*[48] The product has a unit cell comprising 4 discrete molecules of RTeCl and discrete molecules of R′HgCl; no significant short inter-molecular contacts occur and the compound may be termed an inclusion compound[41]. Surprisingly, the ligand RR′Te for which R′ = p-methoxyphenyl gives the 1 : 1 complex and fails to react further.

In contrast to the clean reactions of mercury(II) chloride with **10** and **22**, the co-ordination chemistry with ions such as Pd(II), Pt(II), Rh(I) and Cu(I) is more complex. Compound **22** forms stoicheiometric complexes with Pd(II) e.g. $PdCl_2$ (**22**).H_2O, no evidence for Pd←N co-ordinate bonds was found and it is believed that the ligand is bidentate via two tellurium atoms. Spectroscopic evidence suggested that "face to face" dimeric structures with bridging rather than chelating organotellurium ligands must be considered[50]. With Pt(II), more complex behaviour was observed. Thus, whilst it is possible to isolate an initial complex, $PtCl_2$ (**22**).H_2O, more prolonged reaction leads to loss of the n-butyl-groups from (**22**) and the isolation of $PtCl_2$ (**37**).$2H_2O$. Solution N.M.R. studies (^{125}Te, ^{195}Pt) support the view that the butyl-group is labile and also that the final product contains Pt(IV), but no more specific mechanistic information was forthcoming[49]. Rhodium(I) complexes were mainly of interest in that [RhCl (**22**)] provided rare evidence for the involvement of an azomethine nitrogen atom in co-ordination to the metal[50].



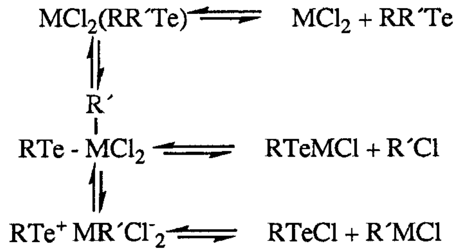
(37)



(38)

The migration of alkyl-(methyl-) groups from tellurium co-ordinated to palladium has recently been observed by others[50] when considering Pd(II) complexes of **38**. Further investigations of ligands such as **10** has established that aryl groups may also become very labile in the presence of ions such as Pd(II), Pt(II) and Cu(I). If **10** is denoted RR′Te where R = 2-(2-pyridyl)phenyl- and R′ = p-ethoxyphenyl- then products such as R′Te PdCl, RPdCl, $R_2R'TePt_2Cl_5$ are identified together with other phases containing progressively more inorganic material e.g. "R'_7 R_4 Cl_9 Pt_9 Te_9". Unfortunately, the great lability of both R and R′ results in materials which are extremely difficult to characterise, but the readiness with which the complexes decompose to give products of high metal/tellurium content is an observation of potential interest[51]. With Cu(I), some better defined materials arise on reaction of halide salts with **10** e.g. CuCl(**10**)[52], but in this case also evidence of organic-group lability is noted. It may be that species analogous to

13 (scheme 3) have a mechanistic role to play e.g. using a metal halide "MCl_2" for illustrative purposes:



$$\begin{tikzcd} MCl_2(RR'Te) \arrow[r, shift left] \arrow[d, shift left] & MCl_2 + RR'Te \arrow[l, shift left] \\ RTe\text{-}MCl_2(R') \arrow[r, shift left] \arrow[u, shift left] \arrow[d, shift left] & RTeMCl + R'Cl \arrow[l, shift left] \\ RTe^+ MR'Cl^-_2 \arrow[r, shift left] \arrow[u, shift left] & RTeCl + R'MCl \arrow[l, shift left] \end{tikzcd}$$

The design of volatile organotellurium ligands with organic groups which labilise on complex formation could have application in the new technologies, such as, MOCVD being developed for the growth of thin films of telluride semi-conductors on a variety of substrates.

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