Aspects of secondary bonding intramolecular interaction in organomercury and organochalcogen derivatives

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Abstract. Recent trends in the area of intramolecularly coordinated organomercury and organochalcogens derivatives are reviewed. Intramolecular coordination in organomercury derivatives facilitates the formation of mercurametallamacrocycle and leads to novel metal–metal interaction with closed shell ions. It also plays a key role in stabilizing telluroxanes as well as in the activation of chalcogen–carbon bonds.

Keywords. M–C bond cleavage; metallophilic; secondary bonding intramolecular interaction; organochalcogen; telluroxane; transmetallation.
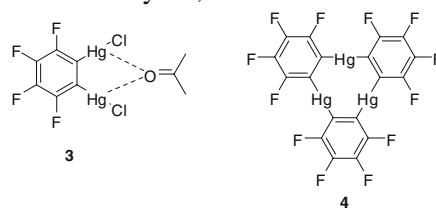
1. Introduction

Secondary bonding interactions E···X (E = Hg, Se, Te; X = N, O) involving mercury/chalcogen and heteroatoms continue to draw considerable attention due to their crucial role in various areas. The well-established applications of these interactions include; (i) template-free synthesis of mercuramacrocycle,[1a] (ii) isolation of hypervalent organochalcogen compounds, (iii) chiral reagents for asymmetric synthesis, (iv) ligands for isolation of MOCVD precursors, and (v) glutathione peroxidase mimics.[1b] Our group has interest in different aspects of the chemistry of organomercury and organochalcogen compounds. In continuation of our work, we report here on some newer aspects of organomercury and organochalcogen chemistry where secondary bonding plays an important role in the template-free synthesis of mercurametallamacrocycles, stabilization of telluroxanes and the activation of E–C bond (E = Se, Te).
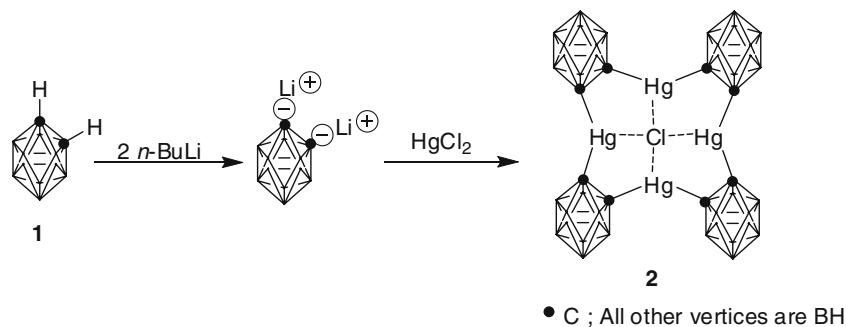
2. Organomercury chemistry

The chemistry of organomercury compounds is one of the well-studied areas in organometallic chemistry. The early development of organomercurial chemistry as compared to other organometallic compounds can be attributed to the high stability of organomercury compounds to air and moisture. Among the various applications of organomercurials, their use as

transmetallating agents[2] for introducing various metals Pd(II), Pt(II), Au(I) and reagents for various functional group transformations in organic synthesis[3] are ubiquitous. Multidentate organomercury compounds having Lewis acidic centers can act as electrophilic hosts[4a] and hence are potential candidates to trap electron-rich species as well as to build novel supramolecular architectures. One of the examples of such Lewis acidic behaviour was reported by Hawthorne and co-workers during the synthesis of a tetranuclear mercuracarborand which was isolated as a chloride complex (scheme 1).[4b]

These mercuracarborands and their derivatives can readily form complexes with halide ions, nitrate ion and tetrahydrofuran.[5] The Lewis acidity of organomercurials can be further improved by attaching suitable electronegative substituents such as fluoro group to the organic substrate. There are numerous examples in literature which document the use of fluoro-organomercurials as electrophilic hosts for anions and electron-rich neutral molecules.[6] Trimeric perfluoro-*ortho*-phenylenemercury has been extensively studied in this respect. It not only binds with electron-rich substrates such as aldehydes, ketones, sulfoxides, sulfides but also with aromatic hydrocarbons, N-heterocycles and alkynes, etc.[6]
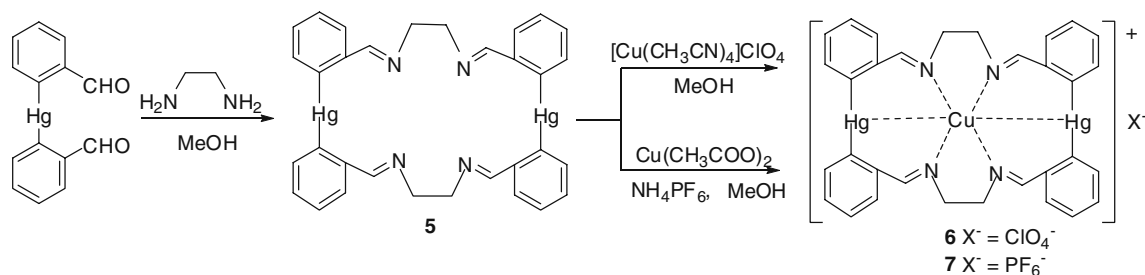
Scheme 1.

Another important feature of organomercury compounds is their ability to display metallophilic interactions. Several organomercurials exhibit short intermolecular Hg$\cdots$Hg metallophilic interactions in the solid state and display unusual luminescent properties.[7] These metallophilic interactions are attractive in nature and are quite common among closed-shell metal ions, such as gold(I), silver(I), copper(I).[8] Hg(II) being closed shell as well as isoelectronic with Au(I), is a potential candidate for displaying metallophilic interactions. Recent theoretical studies on these attractive interactions suggest that such interactions are mainly due to dispersive forces which are further augmented by relativistic effects for heavy elements.[9] Although homometallic closed shell interactions are well-known in literature, heterometallic interactions involving three or more consecutive closed shell ions are relatively scarce. Catalano and co-workers have reported metal ion or atom encapsulation in metallacryptands, which are formed by self-assembly, resulting in different types of closed-shell $d^{10}\cdots d^{10}$ interactions.[10]
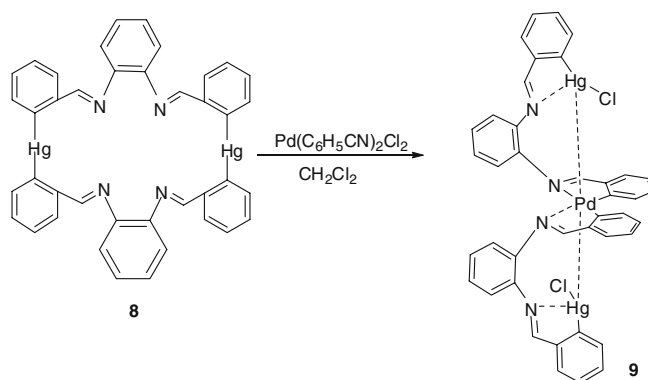
We have employed the secondary bonding E$\cdots$O/N (E = Se, Te) intramolecular interaction to synthesize a number of novel selenium and tellurium based macrocycles.[11] The secondary interaction of chalcogens with nitrogen led to interesting reactivities of the macrocycles with different metal ions. We envisaged that the secondary bonding intramolecular interaction can also be employed for the synthesis of mercury based metallamacrocycles. The resulting metallamacrocycle that may form, will have Lewis acidic mercury as soft acid and imine nitrogen as Lewis base donors. Therefore, the resulting macrocycles will be able to coordinate to both 'hard' and soft 'base' ions. Apart from this, Lewis acidic organomercury could also prove suitable hosts for closed shell d^{10}/d^8 metal ions and may

lead to heterometallic metal$\cdots$metal systems. With this idea, the reaction of *bis*(*o*-formylphenyl)mercury with ethylenediamine was carried out which resulted in the formation of a novel 22-membered metallamacrocycle (**5**) in high yield.[1a] The reaction can be viewed as a [2 + 2] cycloaddition of aldehyde with the diamine. Secondary bonding Hg$\cdots$O intramolecular interaction present in the precursor *bis*(*o*-formylphenyl)mercury plays an important role in macrocyclization of aldehyde with the diamines. It is due to this secondary interaction that the reaction proceeds to completion even without the use of any template which is generally employed for the synthesis of macrocycles. In macrocycle **5**, all the four nitrogens are interacting to mercury, with the distances of 2.750, 2.760, 2.777 and 2.773 Å, thus exhibiting Hg$\cdots$N interaction. Macrocycle **5**, when treated with one equivalent of [Cu(CH$_3$CN)$_4$]ClO$_4$ in methanol, afforded an orange–yellow coloured complex **6**. One of the important features of the Cu(I) complex **6** as evident from X-ray crystallography, was the presence of Hg$\cdots$Cu$\cdots$Hg interaction. The intramolecular Cu$\cdots$Hg interatomic distances of 2.921 Å and 2.919 Å in **6** are much shorter than the sum of the van der Waals radii of the copper and mercury atoms (r_{vwd} = 1.40 and 1.75 Å, respectively). The Cu(I) center is coordinated to all four nitrogen atoms as well as to the two mercury atoms to give a distorted octahedral geometry. Crystal packing of **6** revealed that, the cations of **6** are linked by a Hg$\cdots$Hg intermolecular interaction (Hg$\cdots$Hg 3.20 Å) to give a chain of six d^{10} ions.

Interestingly, the treatment of ligand **5** with Cu(OCOCH$_3$)$_2$, followed by an excess of ammonium hexafluorophosphate gave the Cu(I) complex **7** with PF$_6^-$ as the counter ion (scheme 2) instead of expected Cu(II) complex.[12] The Cu(I) complexes were found to be luminescent at 77K as well as at

Scheme 2.

Scheme 3.

room temperature in acetonitrile solution. The reaction of mercuramacrocycles with other d^{10} ions have also been explored. The reaction of ligand **5** with AgClO$_4$ afforded ([**5**·Ag]ClO$_4$) complex which exhibits distorted octahedral geometry around Ag as well as Hg···Ag···Hg interaction. Similar, attempted coordination of Hg^{II} with **5** leads to facile cleavage of the ring and entrapment of a hydroxide ion.[1a]

On the other hand, the reaction of macrocycle **8** with an equimolar amount of [PdCl$_2$(PhCN)$_2$] leads to transmetallation of the aryl group from mercury to palladium and affords a trimetallic complex **9** containing two mercury and one palladium (scheme 3).[13] The facile transmetallation of the aryl group from mercury to palladium has taken precedence over coordination by nitrogen/mercury, and results in the formation of cyclometallated palladium with *cis* disposition of the aryl groups. The two imino nitrogen coordinated to palladium are also in *cis* geometry with N···Pd···N bond angle being 103.25(7)°. It is observed that the geometry around central palladium atom is deviated from the square planar geometry with the diagonal angles N–Pd–C angles being 165.27(9)° and 164.31(9)°. The strong

interaction of Hg with one of the imino nitrogen as well as with palladium is also responsible for deviation of Cl–Hg–C angles from linearity which in this case is 165.58(7)° and 169.13(7)°. The complex has Hg···Pd distances of 3.1020(3) Å and 3.2337(3) Å, which are significantly less than the sum of the van der Waals radii of Hg and Pd (r_{vwd} = 1.75 and 1.63 Å, respectively) and hence display intramolecular Hg^{II}···Pd^{II}···Hg^{II} interaction. The coordination of nitrogen to mercury atoms makes the groove around mercury non-linear, the Hg-Pd-Hg angle being 162.898(7)°. It is noteworthy that Gabbaï and co-workers have reported intermolecular Pd(II)···Hg(II)···Pd(II) closed-shell interaction, which in fact is reversal of the Hg^{II}···Pd^{II}···Hg^{II} system.[14]

DFT calculations on the crystal geometry confirmed the presence of Hg^{II}···Pd^{II}···Hg^{II} interaction with location of the bond critical points (bcp) between Hg···Pd bonds. The NBO analysis revealed the origin of the Hg···Pd···Hg interaction to (i) donation of electron density from the palladium 4d orbital to the antibonding σ* orbital of the Hg–C bond and (ii) donation from the σ orbital of the Pd–C bond to the antibonding σ* orbital
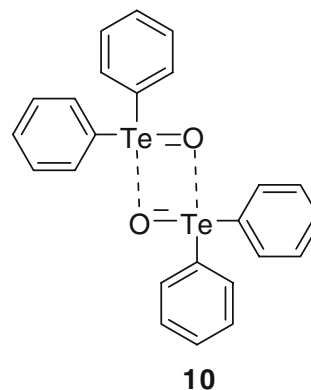
of the Hg–C bond. Complex **9** is weakly luminescent in solid state, and exhibits a macrocycle-**8**-based emission band at 530 nm ($\lambda_{ex} = 477$ nm).
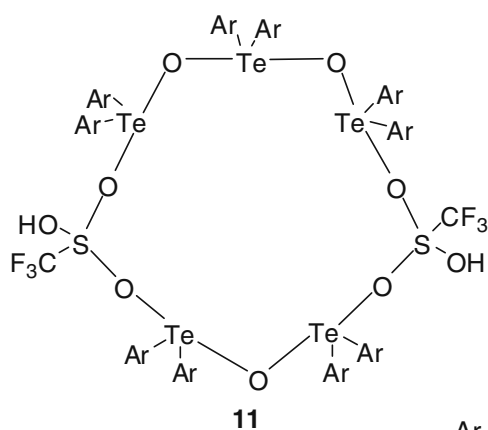
3. Organotellurium chemistry

Organotellurium compounds have been known for their rich chemistry and are widely used in many areas such as electronic conductors, as reagent for organic synthesis, in metallurgy and in biochemistry.[15] Tellurium compounds having oxygen atoms linked to them are known as oxotellurides. These oxotellurides are generally synthesized by hydrolysis reaction of organotellurium halides or by oxidizing organotellurides and ditellurides. Often these oxotelluride such as telluroxides, tellurinic acid, tellurinic anhydride, tellurone and tellurium oxy-bromides are used as catalysts in organic synthesis as well as in organometallic reactions as oxygen carrier.[16]

Diorganotellurium oxides, R_2TeO (R = alkyl, aryl), have been known since early 20th century and are usually prepared by alkaline hydrolysis of diorganotellurium dihalides.[17] Surprisingly, the structure of first well-characterized diphenyltelluroxide (Ph_2TeO) **10** was reported in late 90's by Alcock and Harrison.[18] The solid state structure suggested that the two crystallographically independent units are linked together by short secondary Te–O interaction (2.55(1) Å) giving rise to a dimeric structure. Later on Naumann *et al.*[19] and Klapötke *et al.*[20] independently published the crystal structure of $(C_6F_5)_2TeO$ (as toluene solvate) and (as CH_2Cl_2 and benzene solvates) respectively. The solid state structure for this compound was also found to be similar to the former one with relatively shorter
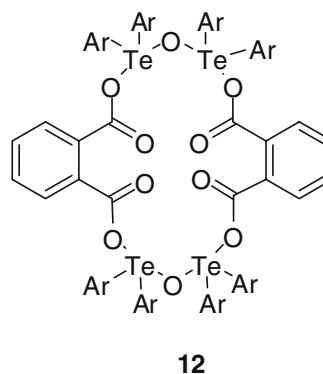
secondary Te···O interaction (2.200(1) Å). Recently Beckmann *et al.* have reported the structure of (p-$MeOC_6H_4)_2TeO$ having polymeric arrangement of Te–O bond in a zig-zag confirmation rather than the usual dimeric form.[21]

10

Though the use of telluroxide as mild oxidizing agent in organic chemistry and as oxygen transfer reagent in organometallic chemistry is well-known,[16] recently there is a considerable interest because of its usage in various fields. For example, Kobayashi *et al.* have isolated oligotelluroxane **11** by the reaction of telluroxide with cationic ditelluroxanes.[22] The ditelluroxides have also been successfully used to isolate macrocyclic multi-telluranes **12** by the reaction of cationic ditelluroxane with sodium phthalate.[23] Beckmann and coworkers have demonstrated that solutions containing di-*tert*-butyltin oxide and di-p-anisyltellurium oxide readily absorb gaseous CO_2 to produce a molecular tellurastannoxane.[24] In a recent study it has been found that telluroxide compounds exhibit hydrolysis capacity and can be used as hydrolase mimic.[25]
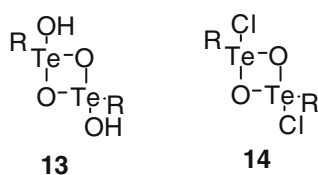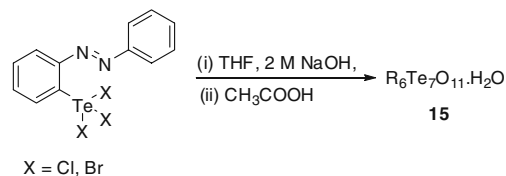

11

12

Ar = MeC_6H_5

In contrast to the hydrolysis products of organotellurium dihalides whose structures and reactivities are now well-understood, the hydrolysis products of aryltellurium trihalides are not well-characterized. Initial studies on hydrolysis reactions revealed that the hydrolysis of phenyl and substituted phenyl trihalides in water results in the formation of partial hydrolysed product such as $RTe(O)X$ (R = C_6H_5, p-$EtOC_6H_4$) (X = Cl and Br). Whereas, hydrolysis under alkaline condition results in the formation of $RTe(OH)_3$, $RTeO(OH)$ and $R_2Te_2O_3$. It was observed that (p-$EtOC_6H_4$)$_2$TeO(OH) upon treatment with dilute acid can also afford completely hydrolysed product (p-$EtOC_6H_4$)$_2$Te$_2$O$_3$. They further concluded that the iodo-derivative is difficult to hydrolyse under normal condition.[26] Later on Comasseto *et al.* found that alkaline hydrolysis when carried out in the presence of phase transfer catalyst also results in the formation of tellurinic anhydride, $R_2Te_2O_3$ (R = C_6H_5, p-$EtOC_6H_4$).[27]

Beckmann and co-workers have demonstrated the synthesis of $RTe(O)OH$ (**13**) and $RTe(O)Cl$ (**14**) by kinetically controlled hydrolysis of 2,6-$Mes_2C_6H_3TeCl_3$ in two layer system of toluene and 0·5M sodium hydroxide solution.[28] The molecular structures of **13** and **14** comprise of asymmetric four-member Te_2O_2 ring with exocyclic OH and Cl group respectively. The geometry around tellurium has been described as distorted trigonal-bipyramidal. Due to the presence of bulky substituent, no further aggregation was observed. Giolando and co-workers obtained an anionic Te–O cluster having general formula of $[Li(THF)_4][\{(Pr^iTe)_{12}O_{16}Br_4\{Li(THF)Br\}_4\}Br]·2THF$.[29] This air sensitive cluster was obtained serendipitously while preparing isopropyl hex-1-ynyl telluride and was formally claimed as the condensation product of organotellurium trihydroxide.

13   **14**

R = 2,6-Mes$_2$C$_6$H$_3$

From the above discussion it is quite clear that most of the studies on the hydrolysis reaction have been performed using bulky ligands or substituted benzene and it was found that the hydrolysed products thus obtained are either dimeric or polymeric (*vide infra*). It is well-known that intramolecular coordination helps in the stabilization and isolation of monomeric and labile

Scheme 4.

chalcogen species. Our group has a long standing interest in exploring the role of intramolecular coordination in stabilizing rather unstable organochalcogen species.[30] Utilizing the concept we and others have been successful in the isolation of several labile organochalocogen derivatives.[31] There have been no studies on the hydrolysis reaction of intramolecularly coordinated organotellurium halides, we thought of investigating it by using ligand which has potential N-donor atom. The remarkable stability of 2-phenylazophenyl under alkaline and acidic condition and its unique donor property inspired us to study the hydrolysis reaction of its halides (RTeCl, R_2TeCl_2, RTeCl$_3$, RTeBr$_3$). Our main target was to isolate intramolecularly stabilized well-defined monomeric or condensed organo-oxotellurides using 2-phenylazophenyl. However, the alkaline hydrolysis of *bis*(2-phenylazophenyl-C,*N'*)tellurium(IV) dichloride gave *bis*(2-phenylazophenyl-C,*N'*)tellurium(IV) oxide which has secondary Te···O interaction giving rise to dimeric structure. The hydrolysis of (2-phenylazophenyl-C,*N'*)tellurium(IV) trichloride under reflux condition resulted in the isolation of co-crystal of monomeric tellurinic acid and its sodium salt. Similarly, when we hydrolysed (2-phenylazophenyl-C,*N'*)tellurium(IV) trihalide a novel heptatellurium covalent cluster **15** having Te–O linkage was obtained (scheme 4).[32] This molecule has several unique features e.g., all the peripheral tellurium and oxygen atoms are linked together in a boat shape conformation, molecule has three types of tellurium viz. 3-coordinated, 4-coordinated and 5-coordinated and all are in the same oxidation state.

4. Cleavage reactions of organochalcogens by transition metals

Activation and cleavage of the Se–Se, Te–Te, C–Se and C–Te bonds by transition metals (viz. Pd, Pt, Hg, Rh, etc.) is an important feature of the coordination chemistry of organoselenium and organotellurium ligands.

A detailed understanding of the coordination chemistry of organoselenium and organotellurium ligands is essential to reveal the mechanistic details of the various catalytic processes in which these are involved. In this context some leading trends observed in the synthetic application of heavier organochalcogens include; (i) use of diorganoselenides and diorganotellurides as substrates in catalytic coupling reactions to form C–C bonds by activating C–Se or C–Te bonds, (ii) use of diorgano diselenides to undergo addition to multiple bonds, especially to –C≡C– catalytically, (iii) synthesizing symmetrical and unsymmetrical diorganoselenides and tellurides catalytically from electrophilic substrates incorporating various functionalities and R_2E_2 (E = Se, Te) as nucleophilic precursor and (iv) use of organoselenium compounds as ligands in various catalytic organic transformations.

Organoselenides were used in Kumada coupling reactions as source of aryl, vinyl and allyl functions in as early as 1980 by Takei and co-workers.[33] However, the use of organoselenides in coupling reactions has not received much attention thereafter. Organotellurides have also been used in catalytic carbon–carbon bond formation as aryl or vinyl synthons. Uemura and co-workers reported palladium-catalysed Fujiwara–Heck cross coupling reactions between organic tellurides and alkenes.[34] Palladium catalysed coupling of vinylic tellurides for the synthesis of conjugated enyne and enediyne has been systematically studied by Zeni and co-workers employing Suzuki, Sonogashira and Negishi coupling methodologies.[35] More recently, Stefani and co-workers have reported Suzuki–Miyaura cross-coupling reactions of aryl tellurides with potassium aryltrifluoroborate salts catalysed by Pd(0) complexes.[36] The key step of the coupling reactions was proposed to be the migration of an organic moiety from Te to Pd in the organotelluride-Pd(II) complex to generate the organopalladium intermediate. The proposed mechanism has been supported by 'fishing' and characterization of intermediates by ESI-MS and ESI-MS/MS experiments.[37]

Vinyl selenides are an important class of compounds which can conveniently prepared by addition of R_2Se_2 or RSeH to alkynes catalysed by transition metals like Pd, Ni or Rh. Beletskaya and co-workers have outlined the achievements and challenges in this area in a recent review.[38]
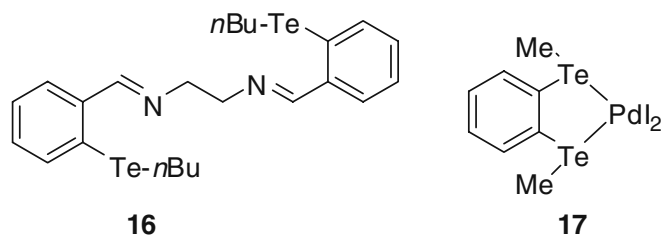
Another important recent trend where activation of E–E bond is relevant is the synthesis of diorganochalcogenides from diorganodichalcogenides employing various catalytic strategies. For example, employing a bimetallic catalyst system consisting of hydrated $CuCl_2$ and $SnCl_2$ a range of unsymmetrical selenides have been prepared by Roy and co-workers.[39a] Other variants include La/I_2,[39b] CuI/Mg-bipy,[39c] $RuCl_3$/Zn,[39d] Pd(PPh$_3$)$_4$,[39e] RhCl(PPh$_3$)$_3$/H$_2$,[39f] InBr$_3$/Zn,[39g] etc.

Use of heavier chalcogens as ligands for catalysts in the coupling reactions has high potential and recently it has been reported by Yao and co-workers that selenium ligated palladium complexes act as highly active and efficient catalysts for the Heck reaction.[40] Szabó and co-workers[41] and Yao and co-workers[42] have demonstrated the utility of SeCSe-Pd(II) pincer complex in the catalytic phenylselenylation of organohalides and allylation of aldehydes respectively.
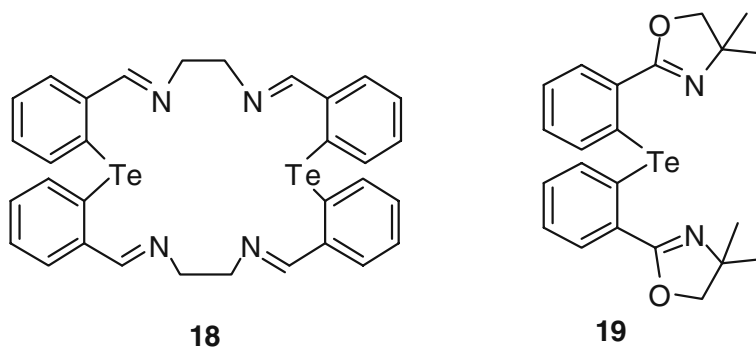
The C–Se bond is inherently stronger than the C–Te bond and activation and cleavage of the former is not very common. The activation of the C–Se bond in a vinyl selenide by a Pt(0) complex has been reported by Kambe and co-workers.[43] In a study involving addition of diaryl dichalcogenides to terminal alkynes under microwave irradiation, Beletskaya and co-workers also identified a process in which C–Se bond was activated and cleaved to generate monoselenide from diselenide by Pd(OAc)$_2$/phosphine catalytic system in the absence of alkyne.[44] Using quantum mechanical calculations they have shown that both mononuclear [Pd(SePh)$_2$(PPh$_3$)$_2$] and dinuclear palladium complexes [Pd$_2$(SePh)$_4$(PPh$_3$)$_2$] can catalyse the C–Se bond cleavage reaction and the reactions involving dinuclear complexes can proceed with smaller energy requirements, which is due to stabilization of the bridging selenium ligands.

The C–Te bond cleavage has received current interest due to its relevance in catalysis. McWhinnie and co-workers and Levason and co-workers observed the lability and cleavage of the C–Te bond by transition metal ions much earlier.[45] The telluroether ligand **16** on reaction with PtCl$_2$ underwent a cleavage of the butyl group and the C–Te cleavage was monitored by NMR studies.[45a] The cleavage of a methyl group from a telluroether complex of palladium, **17** on heating has been reported by Levason and co-workers.[45b]
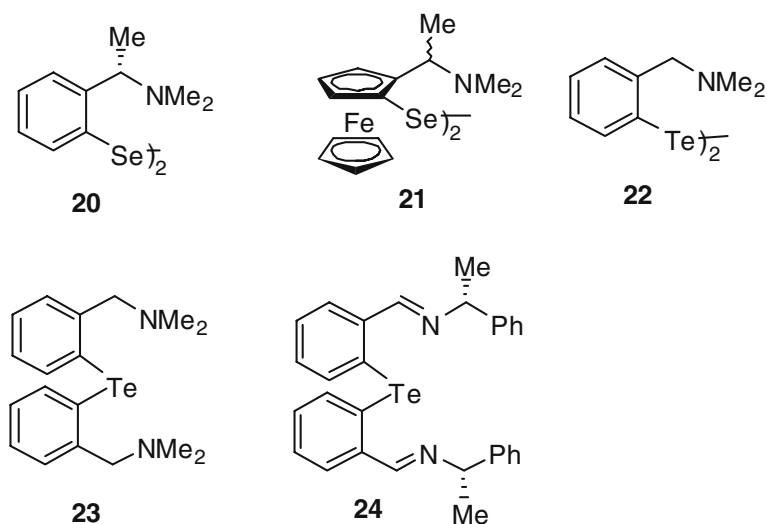

16   **17**

The cleavage of C–Te is facilitated by the strong N→Te intramolecular interaction, which involves donation of a nitrogen lone pair to the σ^* orbital of the *trans* C–Te bond.[46] A facile C–Te bond cleavage and transmetallation in the reaction of the 22-membered azamacrocyclic ligand **18** with $HgCl_2$ and $Pt(COD)Cl_2$ have been reported by our group.[47] We have also reported the facile cleavage of the C–Te bond in *bis*[2-(4,4-dimethyl-2-oxazolinyl)phenyl] telluride **19** on reaction with $HgCl_2$.[48]
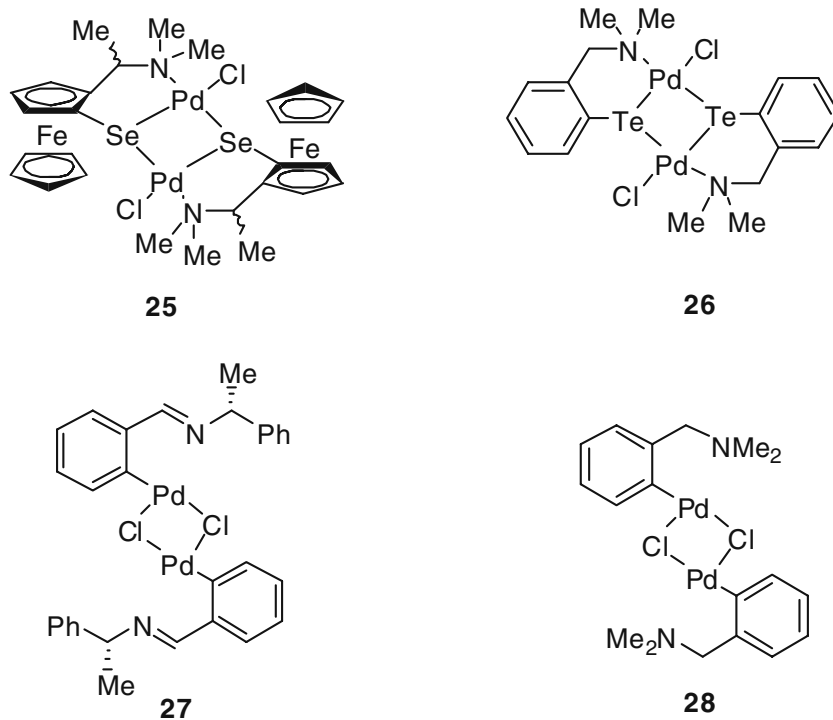

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In contrast to the activation and cleavage reactions of R_2E_2 (E = Se, Te) by Pd(0)/Pt(0) complexes, there are very few examples of cleavage reactions of R_2E_2 by Pd(II).[49] Very recently Singh *et al.* reported on the cleavage reactions of a series of a related chiral and achiral multidentate selenium and tellurium ligands **20–24** with Pd(II) complexes.[49]
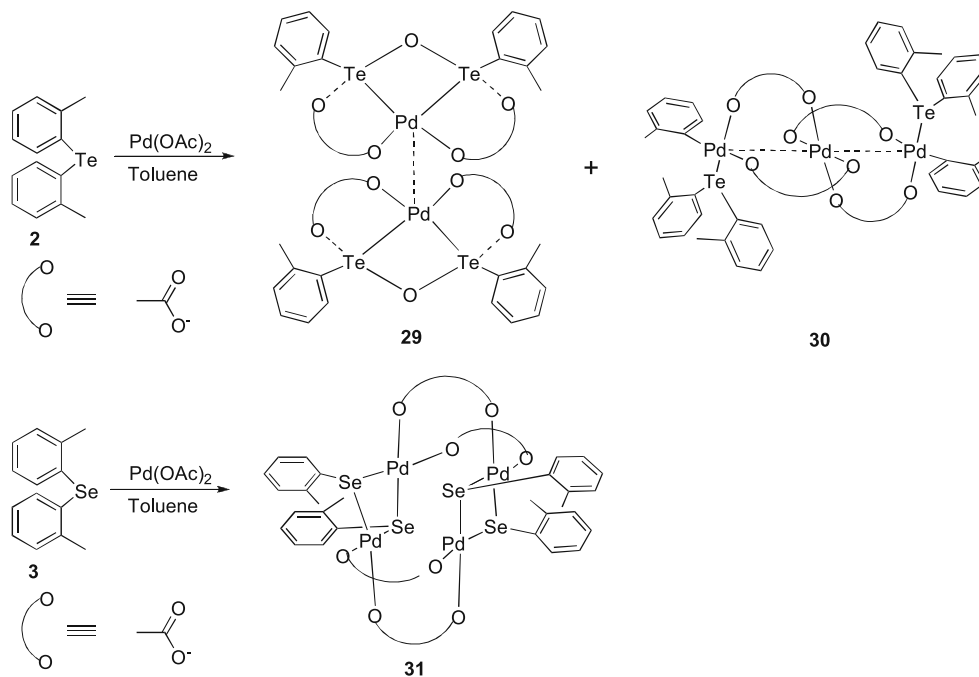

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The excellent palladium complex could not be isolated from the reaction of the diselenide **20** with Pd(COD)Cl$_2$ and the isolated fraction was characterized as RSeCl. Diselenide **21** provided a selenolate bridged dinuclear complex **25** on reaction with Pd(II). Ditelluride **22** underwent cleavage of the Te–Te bond on reaction with Pd(II) and a similar tellurolate bridged dinuclear complex **26** was obtained. In addition to that, a dimeric chloro-bridged telluranyl chloride, $(RTeCl)_2$ was isolated and characterized. It was argued that the R_2E_2 ligands underwent a formal self-redox reaction on treatment with Pd(II) salts. Tellurides **23** and **24** afforded transmetallated dinuclear Pd(II) complexes **27** and **28** along with the dimeric telluranyl chloride, $(RTeCl)_2$.

25

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27

28

Acetato-bridged dinuclear palladacycle obtained from Pd(OAc)$_2$ and P(o-tol)$_3$, the so-called Hermann palladacycle is well-known in homogeneous catalysis as excellent catalyst for the Heck and Suzuki coupling reactions.[50] We wondered whether a similar palladacycle could be synthesized from E(o-tol)$_2$, (E = Se, Te)

2

Pd(OAc)$_2$
Toluene

29

+

30

3

Pd(OAc)$_2$
Toluene

31

Scheme 5.

on reaction with Pd(OAc)$_2$. However, some unexpected interesting results were obtained in the reactions (scheme 5).[51] Reaction between *bis*(*o*-tolyl)telluride and palladium acetate in toluene provided a novel oxygen-bridged hexanuclear (**29**) and a linear trinuclear (**30**) palladium complex. *Bis*(*o*-tolyl)selenide provided another interesting selenolate and acetate bridged tetranuclear palladium complex (**31**).

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