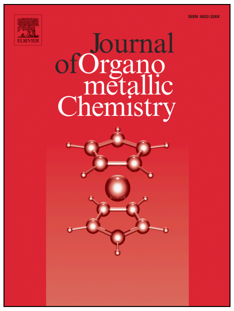

Synthesis, structure and reactivity of *β*-chalcocyclohexenals: Dichalcogenides and chalcogenides

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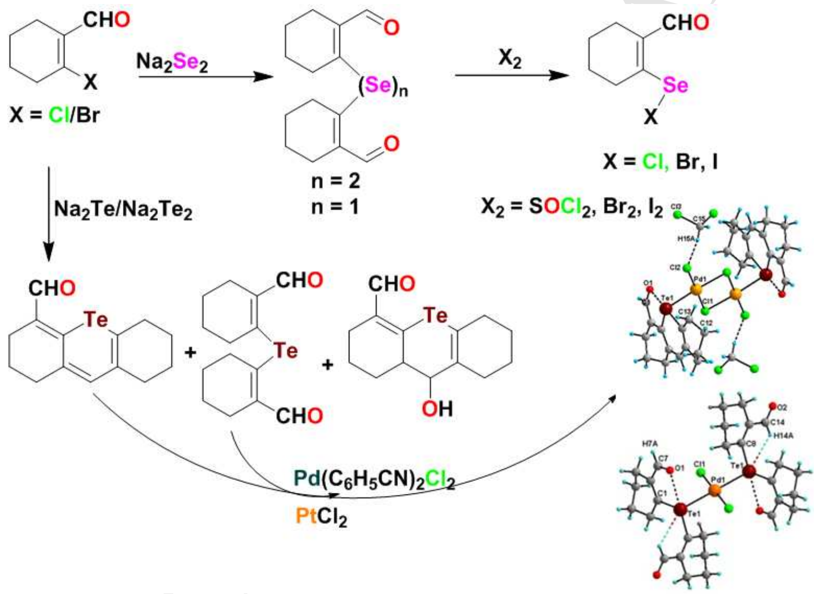
Synopsis

Due to presence of secondary bonding interaction in alicyclic system substrate leads to the isolation of dichalcogenide and monochalcogenides with the reaction of Na_2E_2/Na_2E (E = S, Se, Te). The complexation reaction of monochalcogenides with Pd(II) and Pt(II) afforded the exclusive metal complexes without any cleavage.



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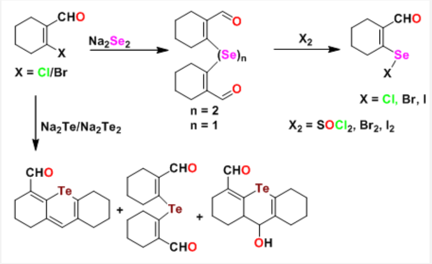
Keywords:

β-Chalcocyclohexenals

Dichalcogenides

Chalcogenides

Intramolecular secondary bonding



The organochalcogen derivatives derived from alicyclic substrates, *β*-bromocyclohexenal/*β*-chlorocyclohexenal, show stronger Se···O/Te···O intramolecular interaction compared with the corresponding aromatic analogues.

Abstract: The present work describes the synthesis and characterization of a series of organochalcogen compounds derived from *β*-chlorocyclohexenal (**27a**)/*β*-bromocyclohexenal (**27b**) which are stabilized by E···O (E = S, Se, Te) intramolecular secondary bonding interaction (IM-SBI). Di-(2-formylcyclohex-1-ene)sulfide (**21**) was prepared by treating **27b** with disodium sulfide. Di-(2-formylcyclohex-1-ene)diselenide (**28**) was obtained by reacting **27a** with disodium diselenide. The reaction always produced a mixture of di-(2-formylcyclohex-1-ene)diselenide (**28**) and di-(2-formylcyclohex-1-ene)selenide (**29**). Attempts to synthesize di-(2-formylcyclohex-1-ene)ditelluride **30** by the reaction of **27b** with disodium ditelluride afforded a mixture of monotellurides; 3,4,5,6,7,8-hexahydro-*2H*-9-telluraanthracene-1-carbaldehyde (**26**), di-(2-formylcyclohex-1-ene)telluride (**22**) and 9-hydroxy-2,3,5,6,7,8,9,9a-octahydro-1H-telluroxanthene-4-carbaldehyde (**31**). Reactions of **28** with halogenating reagents afforded the corresponding organylselenenyl halides; selenenyl chloride **35**, selenenyl bromide **36** and selenenyl iodide **37**. Tellurides **26** and **22** were used as ligands for metal complexation reactions.

Introduction

The chemistry of organochalcogen derivatives having intramolecular E···X secondary bonding interactions (where E = Se Te; X = N, O) has attracted considerable current interest owing to its applications in various fields such as; (a) in the isolation of novel/unstable organochalcogen compounds[1] (b) in organic synthesis[2] (c) ligand chemistry[3] and (d) enzyme mimetic.[4] For example, Wirth and co-workers[5] have reported that due to the presence of intramolecular Se···O interaction, an asymmetric product was formed in the electrophilic selenenylation reaction of alkenes using asymmetric selenium reagent **1**. Goldstein and Burling *et al.*[6] have demonstrated that the molecular structure of biologically active selenazofurin was controlled by intramolecular Se···O interaction. Diorganyl diselenides having weak intramolecular Se···O interactions are considered to be important class of selenoenzyme Glutathione Peroxidase (GPx) mimics.[7] Wirth *et al.*[7a] were first to report the GPx-like activity of a new class of diselenides **1** containing an oxygen atom in close proximity to the selenium. Recently, several other related derivatives such as chalcogenides and their halides having oxygen donating group such as formyl (**2-7**),[8] hydroxyl (**8-10**),[9] nitro (**11-14**),[10] and amide (**15-16**)[11] at *ortho*-position (Chart 1) have been reported and extensively studied. Also the O···Se IM-SBI has been probed by single crystal X-ray,[9, 12] NMR[13] and theoretical studies.[14]

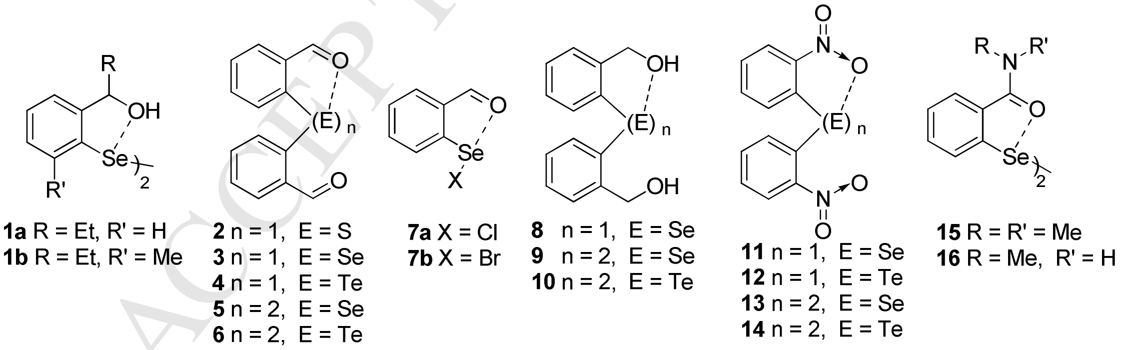
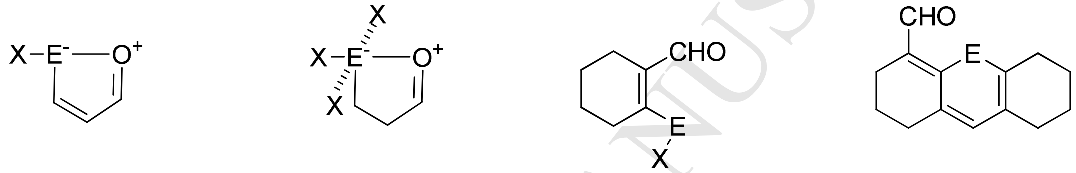


Chart 1. Arylchalcogen derivatives with *ortho*-oxygen donating atom

Compared to the arylchalcogen derivatives stabilized by IM-SBI with oxygen, the alkyl analogues and in particular, the alicyclic analogues have not been systematically investigated.

Some examples of related *β*-aryltellurovinyl aldehydes and ketones have been prepared by nucleophilic addition reaction of aryltellurolate anion ($ArTe^-$) to a triple bond of *α*-acetylenic aldehyde and ketones.[15] Detty and coworkers have made a significant contribution in the area of *β*-chlorotellurenyl ketones **17-20**.[16] Concerning chalcogen derivatives of alicyclic substrates, though the synthesis of di-(2-formylcyclohex-1-ene)sulfide **21**[17] has been reported, there is no report about the intramolecular interaction and structural aspects. Minkin and co-workers have explored the chemistry of di-(2-formylcyclohex-1-ene)tellurides **22-23** and their derivatives.[14, 18] Mollier and coworkers have studied related 3,4,5,6,7,8-hexahydro-*2H*-9-chalcaanthracene-1-carbaldehydes **24-26**.[19]



17 E = Se; X = Cl, Br
18 E = Te; X = Cl, Br

19 E = Se; X = Cl, Br
20 E = Te; X = Cl, Br

21 E = S, X = 2-$CHOC_6H_8$
22 E = Te, X = 2-$CHOC_6H_8$
23 E = Te, X = Me

24 E = S
25 E = Se
26 E = Te

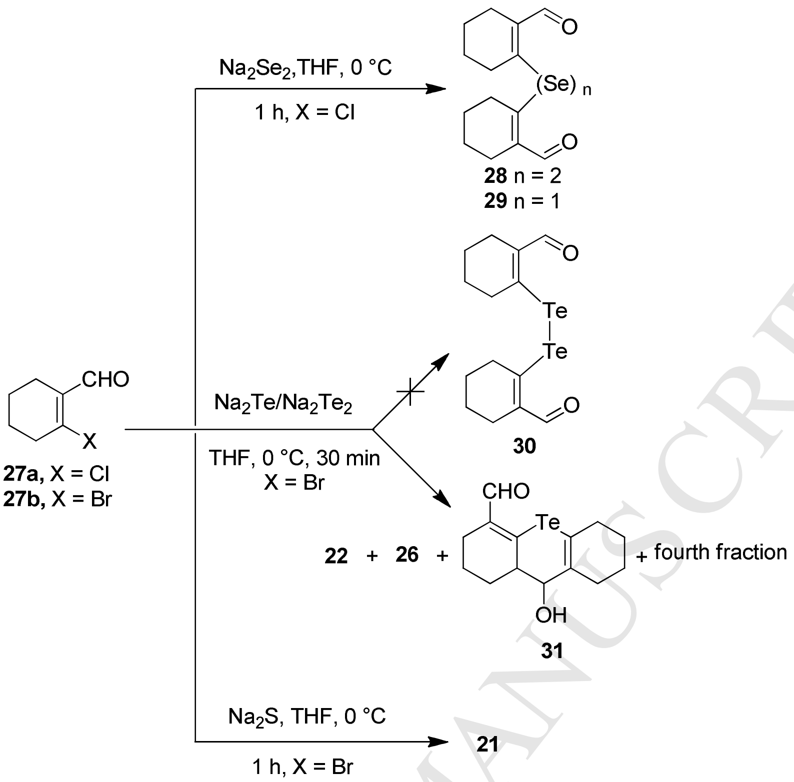
Chart 2. Alkylchalcogen derivatives with heteroatom (e. g. O) donating atom

The coordination chemistry of transition metal ions, in particular platinum group metal ions Pd(II) and Pt(II), with heavier organochalcogen (Se, Te) ligands has attracted considerable current interest.[3b-d, 20] These complexes have been used as catalysts in C-C/C-E (E = S, Se,Te) bond formation. The complexation of Pd(II) and Pt(II) with heavier chalcogen ligands not only leads to; (i) the formation of coordinate complexes but also (ii) to the cleavage of the E-C bond or (iii) even complete decomposition of complexes under metallation. The cleavage of the C-E bond is mostly observed for the Te ligands which are stabilized by IM-SBI. For example, McWhinnie and coworkers[21] have observed dealkylation of 1,6-bis-2-butyltellurophenyl-2,5-diazahexa-1,5-diene upon complexation reaction with $PtCl_2$. A similar result has been also reported by Kemmitt and co-workers.[22] 2-(2-Pyridyl)(*p*-ethoxyphenyl-)tellurium, reacted with $HgCl_2$ at room temperature to afford cleaved C-Te bond,[23] while the reaction with Pd(II)Cl_2 and Pt(II)Cl_2 led to isolation of very complex systems.[24] Singh and coworkers have reported a facile C-Te bond cleavage/transmetalation in the reaction of the 22-membered telluraaza Schiff base macrocycle with $HgCl_2$[25] and $Pt(COD)Cl_2$.[26] They have also observed the facile cleavage of the C-Te bond in bis[2-(4,4-dimethyl-2-oxazolinyl)phenyl]telluride, bis[2-(((*R*)-methylbenzylamino)methinyl)-phenyl]telluride 1,1'-(tellurobis(2,1-phenyllene))bis(N,N-dimethylmethanamine) and 22-membered azamacrocyclic on reaction with $HgCl_2$, $Pd(C_6H_5CN)Cl_2$ / $Pd(COD)Cl_2$ and $PtCl_2$ respectively.[26b, 27] An analogous reaction of bis[2-(4,4-dimethyl-2-oxazolinyl)phenyl]telluride with a Pd(II) chloride afforded a yellow-orange solid, which was insoluble in common organic solvents, presumably due to formation of a polymeric complex and further characterization could not be carried out.[8e] Kaur *et al.* reported the cleavage of C-Te and Te-Te bond in bis[2-((dimethylamino)methyl)phenyl]telluride and ditelluride with Pd^{II} ions.[28] *The cleavage of C-Te bond in these cases 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.* In continuation of our work on intramolecularly coordinated organochalcogens, we extend this work to the alicyclic system, *β*-chloro-/bromocyclohexenal and report the synthesis and isolation of the first structurally characterized alicyclic diselenide and selenides and their derivatives like halides stabilized by intramolecular interactions and compare the structural and reactivity with the much studied aryl analogues. Along with this we also present stable metal complexes of Pd(II) and Pt(II) of di-(2-formylcyclohex-1-ene)telluride (**22**) and 3,4,5,6,7,8-hexahydro-*2H*-9-telluraanthracene-1-carbaldehyde (**26**). The C-Te bond remains intact in these complexes.

Results and discussion

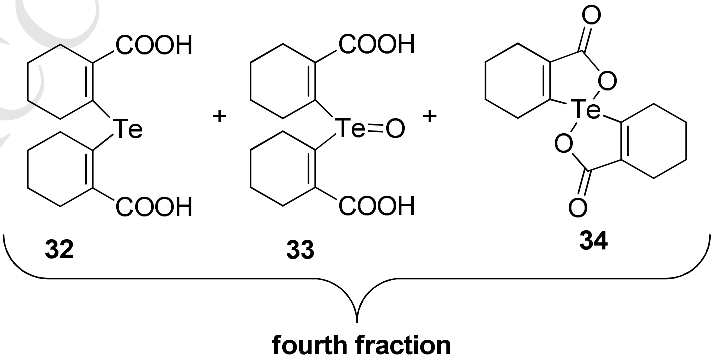
Synthesis

The precursor, *β*-chlorocyclohexenal **27a** was synthesized by treating cyclohexanone with phosphoryl chloride in *N,N*-dimethylformamide by following the literature procedure.[29] *β*-Chlorocyclohexenal **27a** is not indefinitely stable even on storing at low temperature (-13 °C). After long periods of time (in a refrigerator), it suddenly decomposes more or less violently with the evolution of hydrogen chloride and formation of a black tar. Incautious distillation can also lead to a similar result. Therefore, we chose another substitute, *β*-bromocyclohexenal, which is more stable and quite easy to handle.[30] For better yields of organochalcogens, it is best to prepare this compound freshly before use. The key chalcogen derivative, di-(2-formylcyclohex-1-ene)diselenide **28** was obtained by the disodium diselenide route[31] (Scheme 1). The reaction always gave a mixture of **28** and di-(2-formylcyclohex-1-ene)selenide **29** and it was difficult to separate the mixture by fractional crystallization. These could be separated by column chromatography with very slow elution using petroleum ether and ethyl acetate (0-2%) as the mobile phase. The first fraction isolated was **28** as a pale yellow solid and the second fraction was **29** as a yellow solid. Hence the yield of the desired product, di-(2-formylcyclohex-1-ene)diselenide (**28**), was very low. Syper *et al.*[8c] have also obtained a mixture of bis(*o*-formylphenyl)diselenide (**5**) and bis(*o*-formylphenyl)selenide (**3**) along with other side products during the preparation of bis(*o*-formylphenyl)diselenide (**5**) from *o*-bromobenzaldehyde. As expected, *β*-chlorocyclohexenal **27a** is much more reactive than the aromatic analogue, *o*-chlorobenzaldehyde. Due to the higher reactivity of **27a**, the preparation of diselenide **28** required very mild condition (0 °C) and short time (30 min) compared with the formation of bis(*o*-formylphenyl)diselenide which occurred under vigorous reaction condition {12 h room temperature and further reflux for 6 h containing hexamethylphosphoramide (HMPA)}.

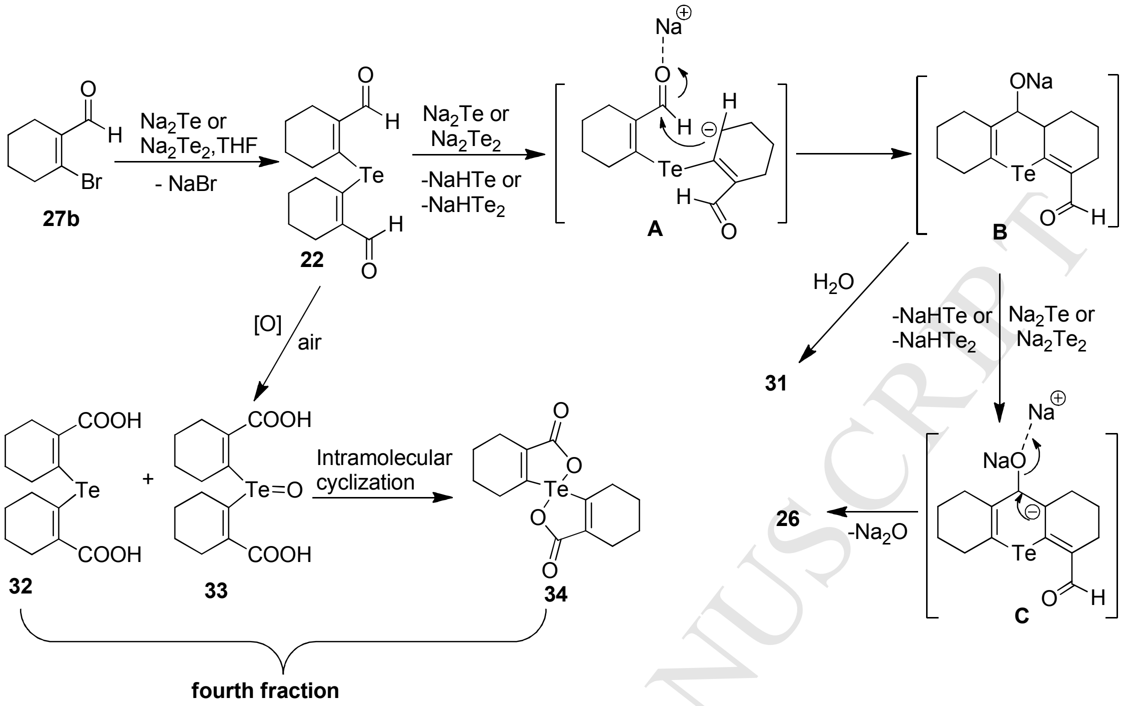


Scheme 1. Synthesis of alicyclic organochalcogens

Attempts to synthesize **30**, the tellurium analogue of **28** by the reaction of disodium ditelluride with **27b** (Scheme 1), yielded a mixture of products; di-(2-formylcyclohex-1-ene)telluride **22**,[18] 3,4,5,6,7,8-hexahydro-*2H*-9-telluraanthracene-1-carbaldehyde (**26**),[19, 32] its precursor 9-hydroxy-2,3,5,6,7,8,9,9a-octahydro-1H-telluroxanthene-4-carbaldehyde (**31**) and the fourth fraction {a mixture of **32**, **33** and **34**[33] (identified by ^{125}Te NMR and mass spectrometry)}, instead of the desired ditelluride.

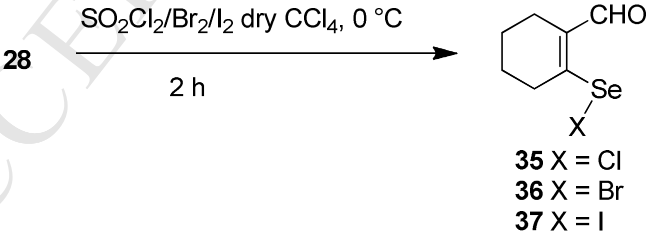


The products were separated by column chromatography using petroleum ether and ethyl acetate (5%) as an eluent. The first fraction isolated was **26** (3.04 g; 29%) as dark red liquid and the second fraction was telluride **22** (2.01g; 12%) as light yellow solid. The third fraction afforded telluride **31** (2.44 g; 22%) as deep yellow solid. The fourth fraction was as a pale white solid (combined yield 3.23 g) as a mixture of **32**, **33** and **34** (*vide infra*). It was only soluble in methanol and DMSO and could not be purified. The products **32**, **33** and **34**, presumably, formed due to the aerial oxidation of reactive telluride **22** (Scheme 2). A similar observation has been reported by Selvakumar *et al.* in the reaction of the n-butyltellurolate and 2-bromo-5-tert-butyl-isophthalic acid dimethyl ester.[34] The preparation of compounds **22**[18] and **26**[19, 32] has been reported in literature using slightly different methods. To improve the yield of telluride **22**, the reaction **27b** was carried out with Na_2Te. The reaction yielded the same mixture of four products; **22** (0.82; 18%), **26**(1.26 g; 14%), **31**(1.11 g; 21%) and the fourth fraction (combined yield 1.40 g) with only the ratio of products formed being different. In both the cases the ratio of the fourth fraction i.e. the oxidized products was highest. The presence of the mixture of oxidized products **32**, **33** and **34** was evident from the ^{125}Te NMR spectrum. The ^{125}Te NMR chemical shifts for the compounds **32**, **33** and **34** were observed at 1214 (**32**), 1184(**33**), 1083(**34**)[33] ppm respectively. It was further confirmed by mass spectrometry. The mass spectrum of the fourth fraction showed three prominent *m/z* peaks at 381, 393 and 377 corresponding to **32**, **33** and **34** respectively. The plausible mechanism for the formation of **22**, **26**, and **31** is given in Scheme 2. The formation of intermediates **A**, **B** and **C** could occur due to Na_2Te/Na_2Te_2 facilitated deprotonation of **22** as indicated in Scheme 2. Alternatively, NaOH, resulting from air exposed Na metal surface while cutting and transferring into the reaction flask, can act as base for the intramolecular cyclization and elimination reaction. The areal oxidation of **22,** presumably, occurs during the workup in open atmosphere. In contrast, the aryl analogue of **22**, i.e., bis(*o*-formylphenyl)telluride (**4**) is quite stable and posed no such problems in workup.[8e] To compare the structural features among monochalcogenides, di-(2-formylcyclohex-1-ene)sulfide[17] (**21**) was also prepared. It was obtained by treating **27b** with disodium sulfide.



Scheme 2. Plausible mechanism for the formation of **26**, **31**, **32**, **33** and **34**

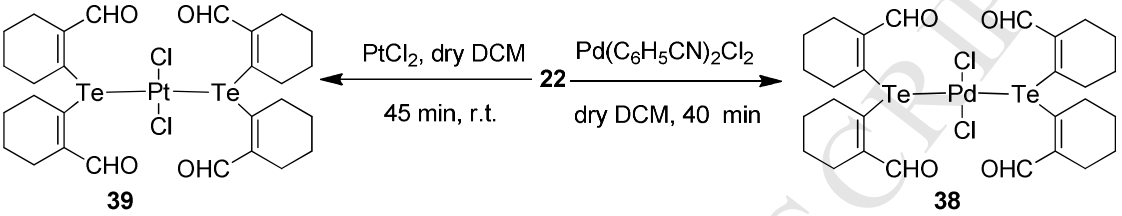
The selenenyl halides **35-37** were obtained by reacting **28** with different halogenating reagents. The selenenyl chloride **35** was obtained as a pale white solid by reacting **28** with a stoichiometric amount of sulfuryl chloride. The bromo- and iodo-derivatives **36-37** were synthesized by a similar method using stoichiometric amounts of bromine and iodine respectively (Scheme 3).



Scheme 3. Synthesis of selenenyl halides

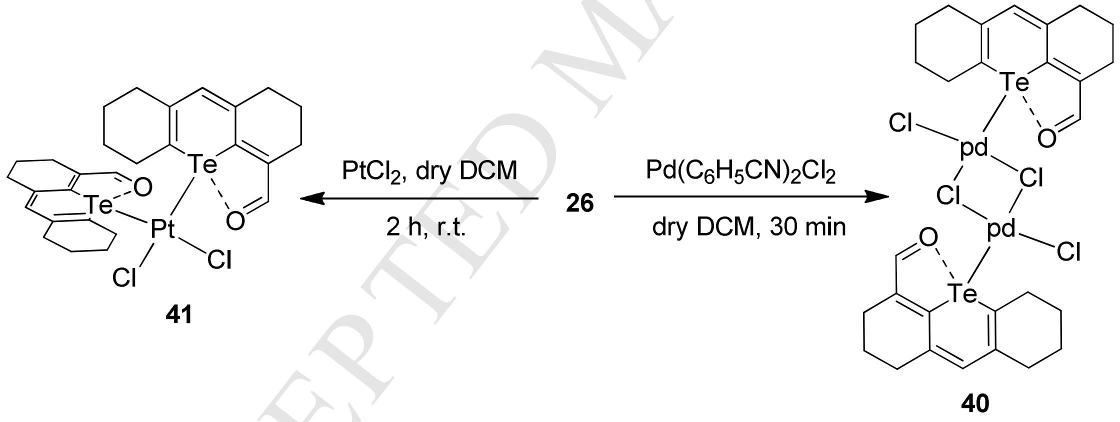
Complexation with Pd(II) and Pt(II)

Tellurides **22** and **26** were used as ligands for the complexation studies. The reactions of **22** with Pd(C_6H_5CN)$_2$Cl$_2$ and PtCl$_2$ afforded the corresponding mononuclear complexes **38** as yellow solid and **39** as a red solid (Scheme 4). These were recrystallized from a mixture of dichloromethane/hexane (4:1).



Scheme 4. Synthesis of **38** and **39**

Interestingly, the reaction of **26** with Pd(C_6H_5CN)$_2$Cl$_2$ in CH$_2$Cl$_2$ afforded Pd(II) complex **40** as a dimer (v*ide infra*) whereas PtCl$_2$ yielded **41** as a monomer (Scheme 5).



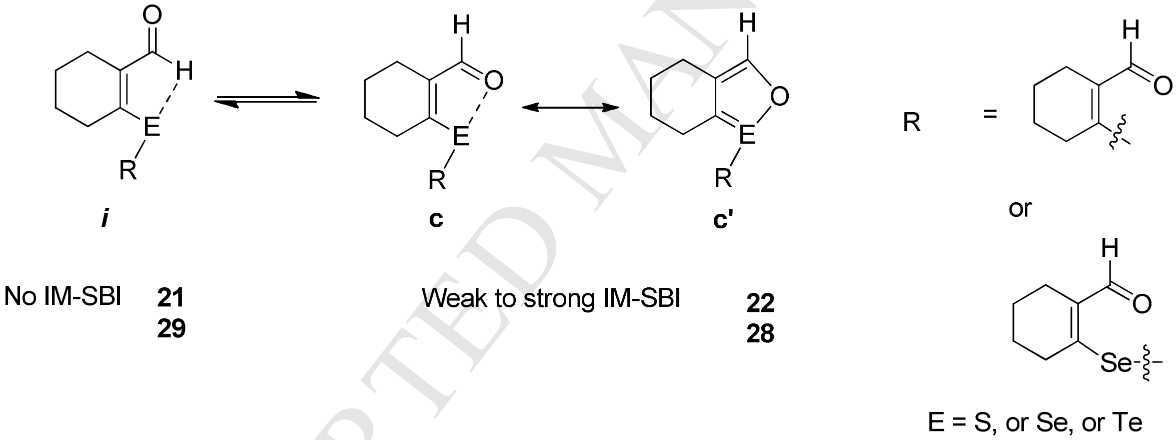
Scheme 5. Synthesis of **40** and **41**

GPx-like activity

Diselenide **28** was evaluated for its GPx-like antioxidant catalytic activity.[33] It is a more efficient catalyst in comparison with ebselen, (2-phenyl-1,2-benzisoselenazol-3(2H)-one) and bis(*o*-formylphenyl)diselenide. However di-(2-formylcyclohexenyl)selenide (**29**) does not show any significant GPx-like activity.

Spectroscopic studies

(i) FT-IR: IR-spectroscopy is a wonderful experimental tool to study the relative strength of E···O interaction in carbonyl group coordinated organochalcogen compounds. Generally, the presence of weak to strong E···O interaction involves the mixed contribution of c and its resonance form c' for the ground state electronic structure of carbonyl substituted aryl/alkyl chalcogen compounds (Scheme 6). As we can see from the scheme, contributing form c' has reduced C=O double bond character. It is in turn reflected in IR stretching frequency. Compounds with strong C=O···E interaction have lower carbonyl stretching frequency ($\nu_{C=O}$) (Table 1).



Scheme 6. Possible structures of cyclohexenal based chalcogen compounds

For example, diselenide **28** has lower $\nu_{C=O}$ (1655 cm^{-1}) than that observed for the monoselenide **29** (1663 cm^{-1}). This indicates either absence or presence of very weak Se···O interaction in compound **29**. In accordance with this prediction, X-ray structural analysis indicated the absence of Se···O interaction in the latter system (*vide infra*). In general, the observation of split or doubled $\nu_{C=O}$ indicates the distinct orientation of the two carbonyl groups in diorganyl dichalcogenides/monochalcogenides (**3-5**). Hence, the observation of doubled $\nu_{C=O}$ (1669 and 1645 cm^{-1}) for telluride **22** could be due to the two distinct orientations of the carbonyl groups with respect to the tellurium center. The stretching frequency at 1645 cm^{-1} corresponds to the intramolecularly coordinated carbonyl, whereas the peak at 1669 cm^{-1} corresponds to the stretching of non-coordinating carbonyl (supported by single crystal X-ray crystallography).[35] The plausible reason for the presence of Te···O interaction in telluride **22** could be the increased polarizability of its valance shell electrons in comparison to lower electron polarizability of its lighter congeners sulfur and selenium. In aryl systems (**2**-**5**), there is a significant reduction of υC=O stretching frequency of the carbonyl group involved in secondary interaction while going from S to Se system. Although the stretching frequency of C=O involved in secondary bonding in Te system **4** is relatively unaffected in comparison to selenium system **3**, the generally observed trend from X-ray analysis and computation is that Te···O interaction is much stronger than the Se···O interaction.[1j, 9] Therefore, good acceptors Te-C (σ*) or Se-Se (σ*) orbitals facilitate adaptation of c-like structures (c or c', e. g. **28** and **22**) and poor acceptors S-C/Se-C (σ*) orbitals facilitate the adaptation of its structural isomer *i*-like structure (e.g **21** and **29**). A single $\nu_{C=O}$ frequency was observed for the metal complex **38** (1675 cm^{-1}). The reason for the observation of the single $\nu_{C=O}$ for the carbonyl groups of **38** is unclear. Two distinct $\nu_{C=O,}$ 1669 and 1678 cm^{-1}, have been observed for the metal complex **39**. It indicates the presence of slightly different carbonyl groups in compound **39**. The observation of two different Te···O distances from X-ray analysis (*vide infra*) further corroborates with IR analysis. It is interesting to note that there is a significant increase of $\nu_{C=O}$ 1675 and 1678 cm^{-1} for **38** and **39** respectively from the ligand $\nu_{C=O}$ (1669 and 1645 cm^{-1}). This could presumably be due to retraction of the flow of electron density to the carbonyl group via *σ,β*-unsaturated carbonyl π-framework. It could occur as a consequence Te-M σ-bonding interaction. In other words, due to the Te-M σ-bonding, the extent of conjugation is slightly reduced in the*σ,β*-unsaturated carbonyl π-framework of the coordinated ligand (**22**) in comparison to its unligated form. The longer O···Te distances (2.688(4) and 2.940(6) Å) (*vide infra*) observed for **38** in comparison to the corresponding distance observed in free ligand **22** (2.662 Å)[35] further supports the IR analysis.

Table 1. ^{1}H, ^{77}Se NMR chemical shifts and IR stretching frequencies

Compound Entry	^{1}H NMR CHO (ppm)	^{77}Se/^{125}Te NMR (ppm)	FT-IR $\upsilon_{C=O}$ (cm^{-1})	Compound Entry	^{1}H NMR CHO (ppm)	^{77}Se/^{125}Te NMR (ppm)	FT-IR $\upsilon_{C=O}$ (cm^{-1})
21	10.41	-	1663	**2**[8a]	10.33	-	1674
29	10.20	370	1663	**3**[8c]	10.28	393	1652, 1681
22	9.99	764	1669, 1645	**4**[8e]	10.27	686	1654,1694
28	9.97	490	1655	**5**[8d]	10.20	468	1665, 1692

(ii) ^{1}H, ^{77}Se and ^{125}Te NMR studies

Interestingly, in ^{1}H NMR spectra of **22** and **28**, the aldehydic peaks are upfield shifted as compared with their aromatic analogues **4**[8e] and **5**[8d] (Table1) respectively. In selenenyl halides also, the formyl protons are shifted to the upfield region (9.56; **35**, 9.43; **36**, 9.08; **37**) as compared with the aromatic analogues **7a** (10.27 ppm) and **7b** (10.12 ppm) (Table 2).[8f] Further the coordination of tellurium with Pd/Pt in complexes **38-41**, leads to an upfield shift of the aldehydic protons compared to the ligands **22** (9.99 ppm) and **26** (9.77 ppm). The ^{1}H NMR spectrum of the mixture of three compounds (**32**, **33** and **34**), did not exhibit any peak in the region of aldehydic proton. Only broad peaks were observed in the region of 2.48-1.55 ppm corresponding to the alicyclic protons.

Table 2. ^{1}H, ^{77}Se NMR chemical shifts of selenenyl halides

Compound Entry	^{1}H NMR CHO (δppm)	^{77}Se NMR (δppm)	Compound Entry	^{1}H NMR CHO (δppm)	^{77}Se NMR (δppm)
35	9.56	1266	**7a**[8f, g]	10.27	1114
36	9.43	1234	**7b**[8f, g]	10.12	1030
37	9.08	1040	-	-	-

For compound **28**, the ^{77}Se NMR chemical shift was observed at 490 ppm, which is significantly downfield shifted with respect to **5** (468 ppm) (Table 1).[8d] The relative downfield shift indicated the presence of stronger intramolecular Se···O interaction in **28** compared to **5**. This was confirmed by X-ray structure (*vide infra*). However, the ^{77}Se NMR spectrum of **29** shows peak at 370 ppm which is significantly upfield as compared with 393 ppm for **3**.[8c] This indicated the absence of Se···O intramolecular interaction in **29** (*vide infra*). In the case of **22**,^{125}Te signal[18] is observed at 764 ppm which is quite downfield shifted with respect to the ^{125}Te peak observed for the **4** (686 ppm)[8e]. This again confirms the presence of stronger intramolecular Te···O interaction in **22**. The ^{77}Se chemical shift of **35** (1266 ppm) is significantly downfield from that reported for 2-formylphenylselenenyl chloride **7a** (1114 ppm).[8f, g] Similarly, the chemical shift of selenenyl bromide **36** (1234 ppm) is much higher than those reported for 2-formylphenylselenenyl bromide **7b** (1030 ppm)[8f, g] and methyl 2-(bromoselanyl)benzoate (1042 ppm).[36]

In the cases of **38** and **39**, the ^{125}Te NMR peaks appeared at 837 and 818 ppm respectively which are expectedly in deshielded region as compared with **22** (764 ppm). In the cases of metal complexes **40** and **41**, ^{125}Te peaks are observed at 685 and 573 ppm respectively and are upfield shifted with respect to the ^{125}Te peak observed for the ligand **26** (834 ppm). This is probably due to the back donation of electrons from metal to the Te centers.[37]

Mass spectrometric studies

The HRMS of compounds showed peaks at 273.0924 [M+Na]$^{+}$(**21**), 378.9735 [M+H]$^{+}$ (**28**), 299.0557 [M+H]$^{+}$ (**29**), which are in good agreement with the corresponding calculated values of 273.0925 [M+Na]$^+$(**21**), 378.9715 (**28**) and 299.0550 (**29**) respectively. The mass spectrum of the mixture of three products showed peaks at *m*/*z* 381 [M+H]$^+$ (**32**), 393 [M]$^+$ (**33**) and 377 [M+H]$^+$ (**34**). The mass spectrum of **39** showed molecular ion peak at *m/z* 958 [M+H]$^+$. In the case of **40**, the molecular ion peak could not be observed. The base peak observed at *m/z* 330 corresponds to the ligand $[C_{14}H_{16}OTe]^+$ and shows very low intensity peak at *m/z* 487 corresponding to the $[C_{14}H_{18}O_2TeClPd]^+$. The Pt(II) complex of **41** shows a very low intensity peak at *m/z* 944 [M+Na]$^+$.

X-ray crystallographic studies

Molecular structure of 21

The molecular structure of compound **21** is depicted in Figure 1 along with significant bond lengths and bond angles. The geometry around the sulfur atom is V-shaped with the bond angle (<C8-S1-C7) being 100.93(6)°. This is close to that observed for related aromatic derivative bis[2-(4,4-dimethyl-2-oxazolinyl)phenyl]sulfide (103.8(2)°).[38] Interestingly, the oxygen atoms of both the formyl groups are positioned away from the sulfur center, whereas in the case of bis[2-(4,4-dimethyl-2-oxazolinyl)phenyl]sulfide, one of the oxazolinyl ring was intramolecularly coordinated through its nitrogen atom to S. The S-C bond distances of 1.776(1) S1-C8 and 1.777(1) Å S1-C7 compare well with the S-C bond distance of 1.774(4) Å reported for bis[2-(4,4-dimethyl-2-oxazolinyl)phenyl]sulfide.[38]

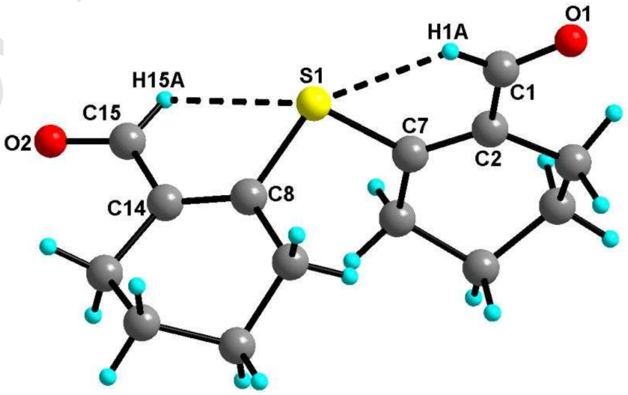


Figure 1. Molecular structure of compound **21**. Selected bond lengths (Å) and bond angles (°): S1-C8 1.776(1), S1-C7 1.777(1), O1-C1 1.209(2), O2-C15 1.213(2), C8-S1-C1 100.93(6).

Interestingly, in molecule **21**, instead of S···O intramolecular interaction, a short C-H···S intramolecular interaction was observed. The short interatomic distances between sulfur and hydrogens (C-H···S) are 2.685(3) and 2.661(4) Å with bond angles 105.3(1)° and 106.6(1)°. These are significantly shorter than the sum of the bond distance of van der Waals radii of sulfur and hydrogen atoms (2.89 Å).[39] The presence of a weak C-H···S intramolecular interaction was further confirmed by NBO (Natural Bond Orbital analysis) and AIM (Atoms in Molecules) analysis (*vide infra*). The packing diagram of **21** shows two weak C-H···O-intermolecular interactions (Figure S64). The bond distances are O2···H11B and O1···H13A 2.4601(1) and 2.588(1) Å respectively which are less than the sum of the van der Waals radii O2+H1B (2.72 Å). The bond angle <C11-H11B-O2 is 168.24°.

Molecular structure of 29

The molecular structure of **29 (**Figure 2**)** is similar to that of the corresponding sulfur compound **21**. The geometry around the selenium atom is V-shaped with <C(1b)-Se-C(1a) bond angle of 98.9(11)° which, as expected, is slightly less than that of **21** (C-S-C 100.93(6)°) but more than that of **22** (C-Te-C 95.8(3)°).[35] The C1A-Se-C1B bond angle in **29** is close to that reported for the structure of **3** (97.8°)[8b]. Similar to compound **21**, both the oxygens of formyl group in **29** are *trans (or anti)* to the selenium center. This is in contrast to the aromatic compound **3**[8b] and alicyclic di-(2-formylcyclohexenyl)telluride **22**[35] where one of the oxygen atoms lies in the plane thereby forming a five-membered heterocyclic ring *via* intramolecular E···O coordination. Theoretically, one can predict three possible (*syn*, *syn*), (*syn, anti*), (*anti, anti*) isomers for di-(2-formylcyclohexenyl) chalcogenides (*vide infra*). However, from the basic principles of organic chemistry one would anticipate that (*anti, anti*) configuration is the most stable configuration due to the higher stability of *trans*-α,β-unsaturated carbonyl systems with respect to *cis*-α,β-unsaturated carbonyl systems. It is indeed found for the sulfur and selenium systems, **21** and **29** respectively. The finding of (*syn*, *anti*) configuration for

compound **22** with a relatively strong Te···O interaction could be due to the highly polarizable nature of the valence shell electrons of tellurium center in its low-valent state. It appears that stabilization energy resulting from Te···O interaction contributes to the reorganization energy required for rearranging from (*anti*, *anti*) to (*syn*, *anti*) orientation.

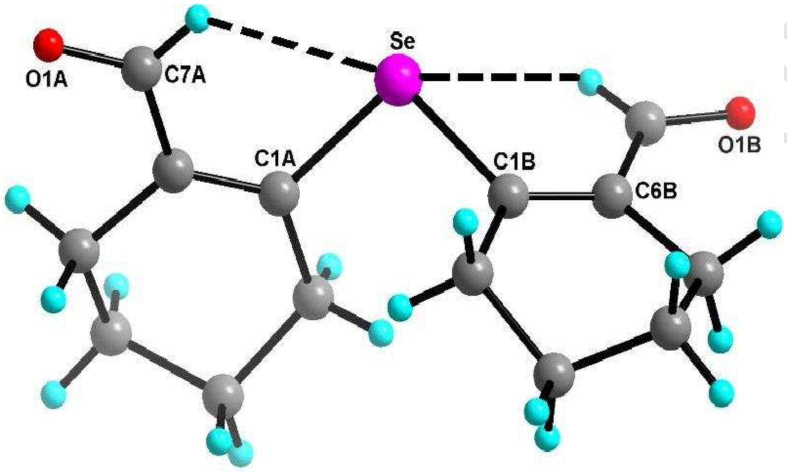


Figure 2. Molecular structure of compound **29**. Selected bond lengths (Å) and bond angles (°): Se-C1A 1.946(1), Se-C1B 1.927(3), C1B- Se-C1A 98.9(1), C7-H9··Se 2.723, C14-H18···Se 2.763.

Similar to the sulfur analogue **21**, in molecule **29**, a short C-H··Se intramolecular interaction was observed. The short interatomic distances between selenium and hydrogens (C-H··Se) are 2.763Å and 2.723 Å which are significantly shorter than the reported for diselenocin[40] (2.92 Å) and are in good agreement with reported alicyclic bis(2-hydroxymethylcyclohex-1-ene)selenide (2.710 and 2.704 Å).[33] The C-H··Se bond angles for **29** are 108.4° and 110.618° which are close to C-H··Se bond angles of bis(2-hydroxymethylcyclohex-1-ene)selenide (110.8° and 112.4°) and diselenocin (101.7° and 107.0°). The presence of C-H···Se intramolecular interaction was further proved by NBO and AIM (*vide infra*).

Computational studies

To gain more information about the intramolecular E···H (E = S, Se) interaction, density functional theory calculations were carried out using Gaussian09 suite of programs.[41] The geometry of **21** (Table S1) and **29** (Figure 3, Table S2) was optimized at B3LYP/6-

31+g(d) basis set. The NBO[8f] and AIM[42] calculations were carried out using 6-311+g** basis set. The optimized bond distances and bond angles are in good agreement with the experimental values. The calculated bond distance for S···H distances (2.651 Å) and Se···H distance (2.705 Å) are close to the experimental values (2.685(3) and 2.661(4) Å; **21** and 2.763 Å and 2.723Å); **29**. Further, the NBO analysis with second-order perturbation method reveals that a stabilizing orbital interaction is operating between one of the E (S, Se) lone pairs with the C-H σ* orbital of the formyl group. The NBO second-order perturbation energies for C-H···S (**21**) and C-H···Se (**29**) are 0.79 kcal mol^{-1} for ($E_{\text{C-H}\cdots\text{S}}$) and 1.22 and 1.24 kcal mol^{-1} ($E_{\text{C-H}\cdots\text{Se}}$) respectively. The latter is in good agreement with those reported for bis(*o*-formylphenyl)diselenide.[43] Apart from this we have studied the relative energies among three conformers of **29**, i.e., (**29a**(*syn*, *anti*), **29b**(*syn*, *syn*) and **29c**(*anti*, *anti*)) in detail. Computed relative energies of the three most important conformers are given in Figure 3. The relative energies of the conformers are in the order of **29b**(-3094.1853760 Hartree) > **29a** (-3094.1945698 Hartree) > **29c** (-3094.1956416 Hartree). Based on these energies we can infer that **29c** (*anti*, *anti*) when hydrogens, instead of oxygen are in *syn* configuration with respect to the selenium is energetically more favorable.

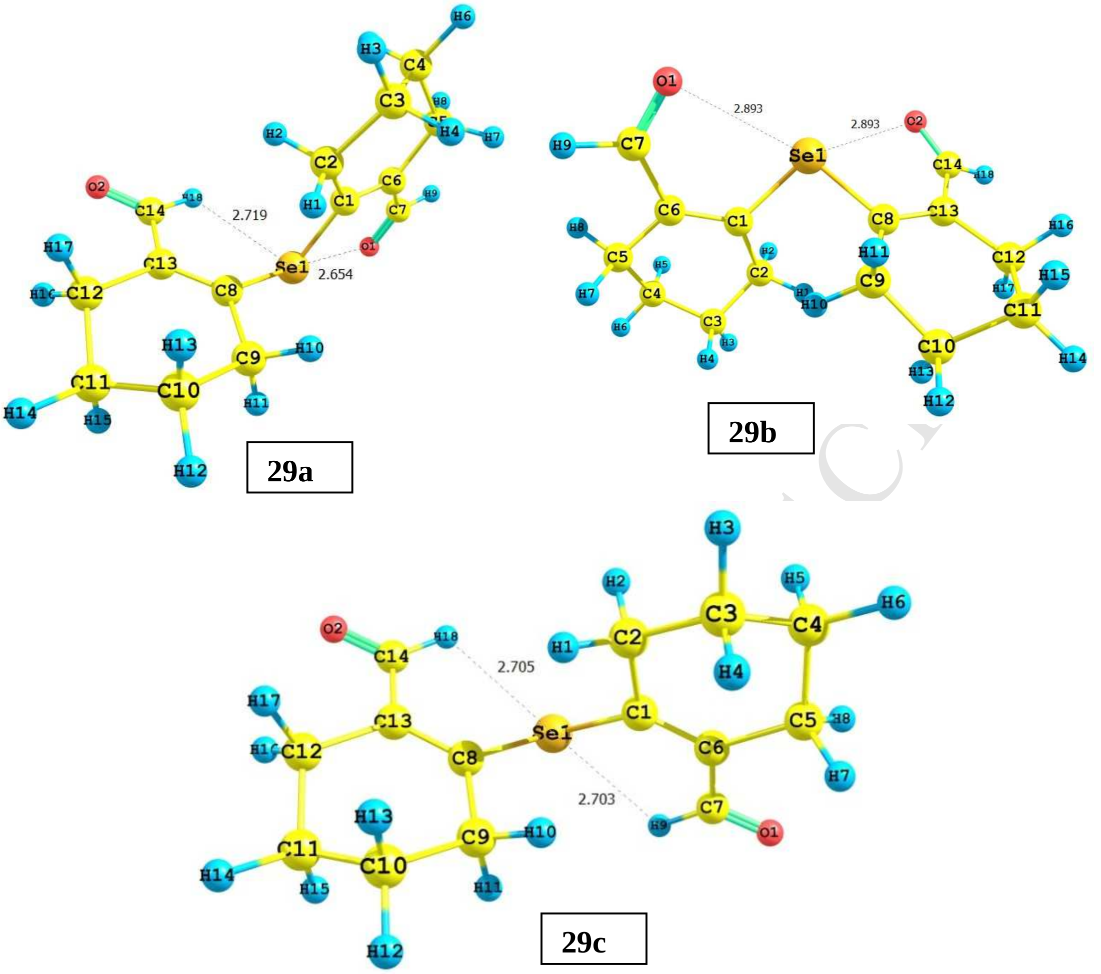


Figure 3. The B3LYP/6-31+g(d) optimized geometries of **29**

The presence of C-H···E interaction was further confirmed by AIM. On carrying out AIM analysis of **21** and **29**, the bond critical points were located in between C-H···E which confirms the presence of C-H···E short interaction (Figure S71). The values of electron density (ρ) at the bond critical point (bcp) for C-H··E (E = S, Se) were 0.0142 (**21**) and 0.0144 and 0.0143 a.u (**29**). The negative values of total energy density H at bcp observed for E···H-C interaction support the contribution of covalent character and in corollary with orbital interaction energy ($E_{\text{C-H}\cdots\text{E}}$) predicted by the NBO analysis (Table 3). Although Se···H-C interaction is predominantly covalent, the observation of positive value of Laplacian ($\nabla^2\rho$) at the bcp (Table 3) implies the fact that the considerable ionic contribution to the C-H···E interaction cannot be ruled out.

Table 3. Summary of quantum chemical calculations on **21** and **29**

Compound	$E_{\text{C-H}\cdots\text{E}}$ kcal mol^{-1}	$\rho_{\text{C-H}\cdots\text{E}}$ a.u.	$\nabla^2\rho_{\text{C-H}\cdots\text{E}}$	*H*
21	0.79	0.0142	0.0474	-0.0016
29	1.22, 1.24	0.0144, 0.0143	0.0435, 0.0435	-.0014, -0.0014

AIM calculations were carried out at the B3LYP/6-311+g** level.

Molecular structure of 28

Compound **28** crystallizes in *P*-1 space group with two molecules in the asymmetric unit Out of the two molecules, one has a transoid geometry (C25-Se4-Se3-C15, 102.84°) and the other has a cisoid geometry (C1-Se2-Se1-C9, -84-02°). Interestingly, in the case of aromatic analogue **5**,[44] both the molecules in the asymmetric unit have cisoid geometry with the torsion angles of -86.28° and -86.32°. The geometry around each selenium atom is approximately T-shaped (cisoid conformer, Figure 4). The Se-Se distance [Se1-Se2 2.357(2) Å] is comparable to the values of Se-Se bond distances reported for related diselenides.[44-45]

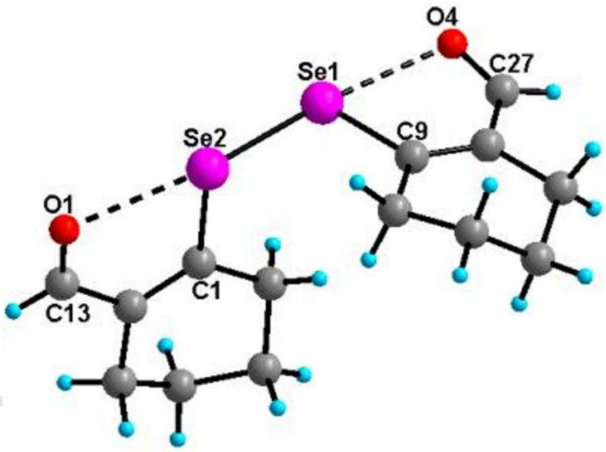


Figure 4. Molecular structure of compound **28**. Selected bond lengths (Å) and bond angles (°): Se1···O4 2.657(1), Se2···O1 2.637(1), Se1-Se 2.357(2), C1-Se2-Se1-C9, -84.02.

The Se···O distances Se1···O4 2.657(1) and Se2···O1 2.637(1) Å), are much longer than the sum of the covalent radii (1.89 Å) of selenium and oxygen,[46] however, these distances are much shorter than the sum of their van der Waals radii (3.42 Å).[39] These Se···O distances are significantly shorter than those observed for **5**[44] (2.720-2.751 Å) and

3[8b] (2.806 Å). The packing diagram shows two types of a weak C-H···O hydrogen bonding (Figure S65). The H···O bond distances of H4B···O1 and H7B···O4 are 2.500(1) Å and 2.544(1) Å respectively with bond angles C7B-H7B···O4 (177.4°) and C4B-H4B···O1 (162.2°) and eventually form the two dimensional network.

Molecular structure of 31

The coordination geometry around the tellurium atom is T-shaped in which the tellurium is directly bonded to two carbon atoms and intramolecularly coordinated to the oxygen atom of formyl group with bond angle of O-Te-C14A 165.7(5)° (Figure 5). The Te···O bond distance { 2.720(6) Å } is comparatively longer than the observed for **26** {2.591(5) Å}[32] and **22** (2.662 Å).[35] This is probably due to high conjugation and pseudo-aromatic character in **26** which is lacking in **31**.

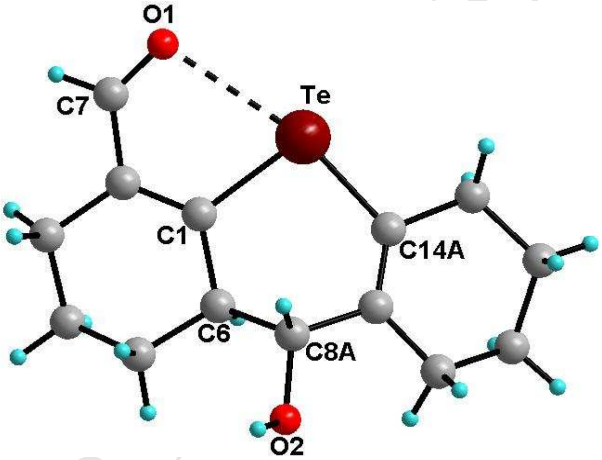
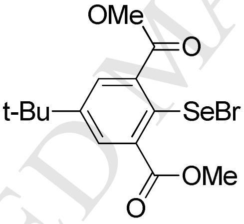


Figure 5. Molecular structure of compound **31.** Selected bond lengths (Å) and bond angles (°): Te-O1 2.720(6), Te-C1 2.099(6), Te-C1 2.049(2), C7-O1 1.196(1), C8A-O2 1.421(2), O-Te-C14A 165.7(5), C1-Te-C14A 94.87(4).

The two-dimensional packing diagram shows O-H···O intermolecular hydrogen bonding with O1···H2 bond distance of 2.052(2) Å which is much shorter than the sum of their van der Waals radii (2.72 Å) (Figure S66).

Molecular structure of 36

Molecules of **36** crystallize in triclinic crystal system with *P*-1 space group with two molecules present in the asymmetric unit (Figure 6). The asymmetric unit contains two crystallographically independent molecules (A and B) with slight differences in bond distances and bond angles. The coordination geometry around selenium (Se1A) or Se1B is T-shaped. The intramolecular Se···O bond distances are 2.111(1) Å (Se1A···O1A) and 2.116(1) Å (Se1B···O1B). These Se···O bond distances are much shorter than the sum of the van der Waals radii (3.42 Å) and are slightly longer than the sum of the covalent radii (1.89 Å) of selenium and oxygen atom.[46] These Se···O distances are much shorter than the Se···O distances of 2.305(2) Å and 2.420(2) Å reported for **7b** and **42**, respectively. The Se-C bond distances are 1.87 Å (Se1A-C1A 1.898(1), Se1B-C1B 1.873(2)), are shorter than those reported for [2-(4,4-dimethyl-2-oxazolinyl)phenyl]selenenyl bromide (1.926(4) Å).[47] The Se-Br bond distances of 2.487(3) and 2.509(3) Å in **36** are slightly elongated as compared to that reported for **7b** (2.403(4) Å),[8h] and **42**[45] (2.371(9) Å). This strong Se···O interaction is also reflected in O1B-Se1B-Br1B bond angle of 178.8(3)° which is close to the linear arrangement as compared with the reported value of O···Se-Br 166.31(7)° for selenenyl bromide **42**.[45]



42

Although the molecule is monomeric, it is further stabilized by a weak intermolecular Se1B···Br1A interaction with another molecule present in the asymmetric unit (Figure 6). The intermolecular Se1B···Br1A bond distance 3.654(3) Å is about 0.1 Å higher than that reported for [2-(4,4-dimethyl-2-oxazolinyl)phefnyl]selenenyl bromide (3.556(9) Å)[47] and of slightly lower (~ 0.08 Å) than the sum of the van der Waals radii of selenium and bromine atom (3.73 Å).[39]

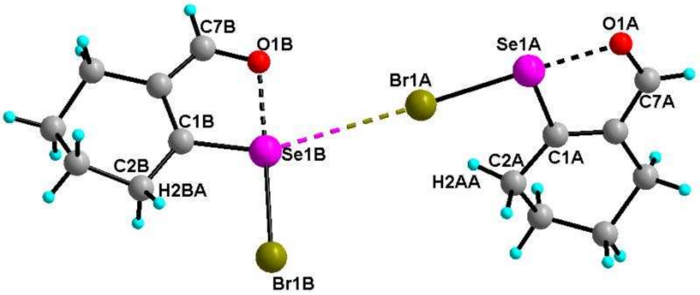


Figure 6. Molecular structure of **36** showing the two molecules of asymmetric unit along with intermolecular Se···Br interaction. Selected bond distances (Å) and bond angles(°): Br1A-Se1A 2.487(3), Se1B-Br1B 2.509(3), Br1A···Se1B 3.654(3), Se1A-C1A 1.898(1), Se1B-C1B 1.873(2), Se1A-O1A 2.111(1), Se1B-O1B 2.116(1), Se1A-Br1A-Se1B 171.69(1).

Iwaoka and coworkes[8f, g] have shown a linear correlation between the relative Se···O distance and the logarithm of the n(O)→σ*Se orbital interaction energy (Figure S69). Using the correlation plot, an interaction energy of 70.25 kcal mol^{-1} is estimated for **36**. This is the highest interaction energy reported for any selenenyl bromide.

Molecular structure of 39

The molecular structure of **39** reveals that Pt is bonded to the two chlorine atoms and two alicyclic units *via* tellurium atoms (Figure 7). Interestingly, both the oxygen atoms of the formyl groups are intramolecularly coordinated to the tellurium atoms with Te···O bond distances of 2.688(4) and 2.940(6) Å.

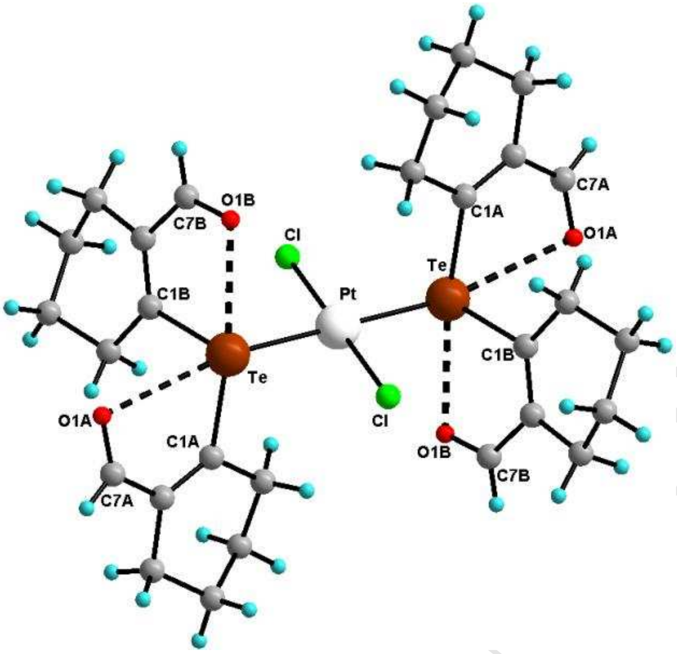


Figure 7. Molecular structure of compound **39.** Selected bond lengths (Å) and bond angles (°): Te-C1B 2.129(6), Te-C1A 2.171(6), Pt-Cl 2.319(1), Pt-Te 2.584(3), Te-Pt-Te 180.0, C1B-Te-C1A 96.0(2).

Thus, the tellurium atoms behave simultaneously as Lewis acid as well as Lewis base. The Pt-Te bond distance observed, 2.584(4) is in fair agreement with reported Pt-Te bond distances of 2.518(6) Å[48] and 2.528(5) Å.[49] The packing diagram of **39** shows intermolecular hydrogen bonding between formyl oxygen of one molecule and formyl hydrogen of the other molecule (Figure S68). The distance between H7BA and O1A is 2.477(4) Å and bond angle <C7B-H7BA-O1A is 149.7(1)°. The molecular structure of compound **38** is similar to the molecular structure of **39**, but good quality of single crystal suitable for X-ray analysis could not be obtained (Please see supporting information, Figure S67).

Molecular structure of 40

Complex **40** (Figure 8) crystallizes as a dimer and is associated with two molecules of dichloromethane. The geometry around palladium is distorted square planar in which Pd is surrounded with three chlorine atoms and one tellurium atom with bond angle of Cl-Pd-Cl 178.75(7)°. The geometry around tellurium is distorted tetrahedral in which tellurium is bonded with two carbon atoms and intramolecularly coordinated with oxygen atom. The Pd-Te and Pd-Cl (terminal) bond lengths in **40** are 2.516(1) Å and 2.291(2) Å) respectively which are slightly shorter than the Pd-Te (2.546(6) Å) and Pd-Cl (2.360(2)) bond distance of related $Pd_2[2\text{-}Me_2NCH_2C_6H_4Te]_2Cl_2$.[28] The Pd-Te, Pd–Cl1(μ-Cl) and Pd–Cl (terminal) bond distances are 2.516(1), 2.405(2) and 2.291(2) Å, respectively which are in good agreement with those reported for analogous complexes of palladium with $Pd_2(\mu\text{-}Cl)_2Cl_2(TeMes_2)_2$[20b] ((Pd-Te (2.506(14) Å), Pd–Cl1(μ-Cl)2.403(4) and Pd-Cl (2.290(4) Å), bis(trimethylsilylmethyl)tellane[50] (Pd-Te (2.591(5) Å) and Pd-Cl (2.30(1) Å) and N-morpholine[51] (Pd–Te 2.505(6) Å, Pd(1)–Cl(1) 2.357(2) Å, Pd(1)–Cl(2) 2.288(2) Å).

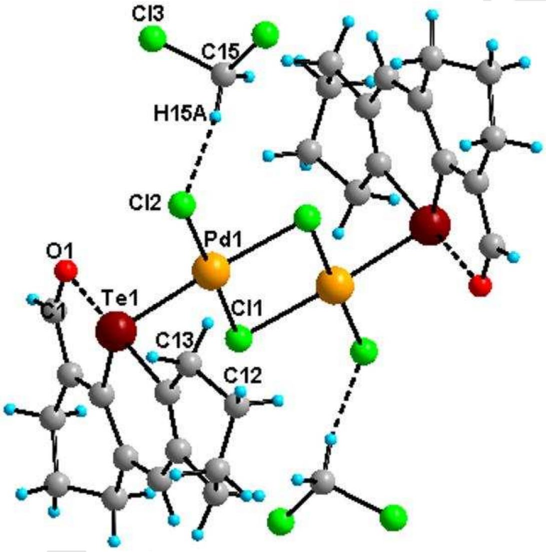
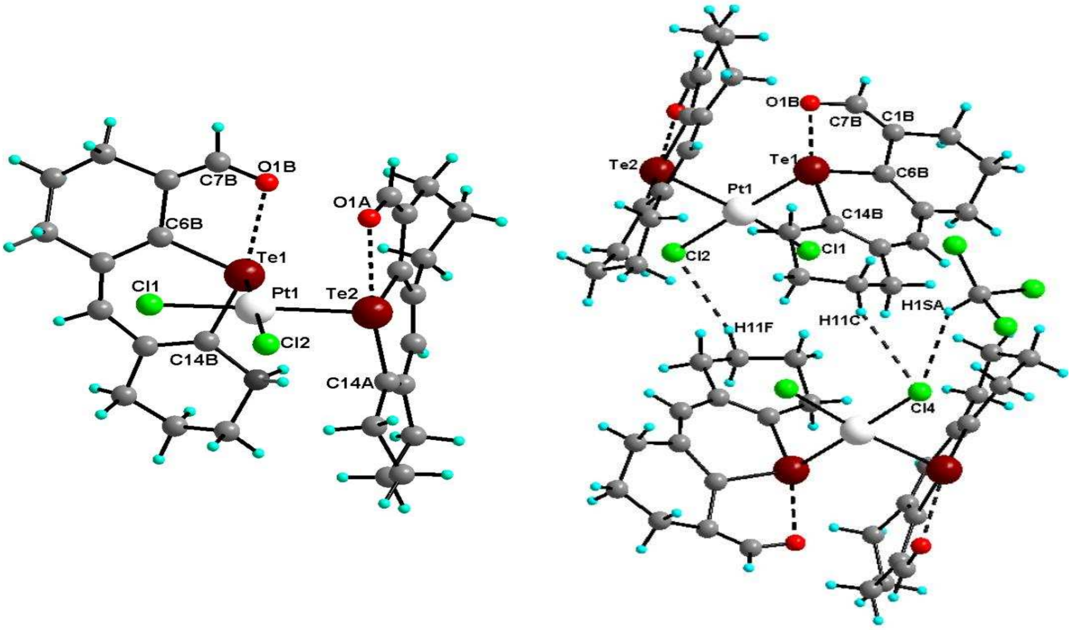


Figure 8. Molecular structure of compound **40.** Selected bond lengths (Å) and bond angles (°): Te1···O1 2.652(7), Te1-C8 2.111(9), Te1-C14 2.119(8), Te1-Pd1 2.516(1), Pd1-Cl2 2.291(2), Pd1-Cl1 2.329(2), C8-Te1-C14 95.6(3), C8-Te1-Pd1 105.5(2), Cl2-Pd1-Cl1 178.75(7).

Molecular structure of 41

The platinum complex, **41**, crystallizes as a monomer with two molecules of $CHCl_3$ solvent (Figure 9). Although the % R factor for crystal data refinement is high (14.5%), the X-ray crystallographically observed elemental composition of the compound **41** indicating coordination of two molecules of **26** to $PtCl_2$, confirms to the elemental composition measured in elemental analysis. The observation of *m/z* corresponding to $[\mathbf{41}+Na]^+$ in mass spectral analysis also indicated the coordination of two molecules of **26** to $PtCl_2$ (*vide supra*). The X-ray structure indicated that the geometry around platinum is square planar in which both of the chlorine atoms are in cis configuration. All the atoms, $PtTe_2Cl_2$, involved in complex formation are in the same plane confirming its square planar geometry. However, due to the bulkiness of the ligand **26,** Te1-Pt-Te2 angle is slightly obtuse (96.43(6)°), which in turn affects the other angles within plane. A similar cis configuration was observed in $[Pt(TeMes)_2(dppp)].3C_6H_6$ complex.[52] The bond distance between Te and oxygen is 2.644(7) Å which is relatively longer than that found in the corresponding ligand **26** (Te···O; 2.591(5) Å). The Pt–Te bond lengths in **41** are 2.542(2) and 2.551(3) Å are slightly longer than the reported for $[Pt(TeMes)_2(dppp)].3C_6H_6$ (2.6394(3)Å).[52]



(41a) **(41b)**

Figure 9. Molecular structure of compound **41.** (**41a**) one unit; (**41b**) two unit with $CHCl_3$ solvent); Selected bond lengths (Å) and bond angles (°): Te1···O1B 2.644(7), Pt2-Te3 2.542(2), Pt2-Te4 2.551(3), Pt1-Cl1 2.311(6), Pt1-Cl2 2.338(7), Pt1-Te1 2.538(19), Pt1-Te2 2.541(19), Cl1-Pt1-Te2 172.75(18), Cl2-Pt1-Te1 175.5(2), Cl2-Pt1-Te2 82.74(18),Te1-Pt1-Te2 96.43(6), Cl1-Pt1-Cl2 90.4(2)

For all the four complexes **38-41** there was no cleavage of C-Te/Te-Pd bond observed even in the presence of strong intramolecular Te···O interaction. This could be due to stronger Te-C bond present in alicyclic systems.

Conclusion

Di-(2-formylcyclohex-1-ene)sulfide, **21** and di-(2-formylcyclohex-1-ene)selenide **29** do not exhibit any intramolecular E···O interaction. In both the chalcogenides, the formyl groups are in anti configuration with respect to the chalcogen (S/Se) atoms. *The structural comparison of monochalcogenides (**21**, **22** and **29**) indicates that, for compounds **21** and **29** the prevalence of (anti, anti) configuration dominates over (syn, anti) configuration with the intramolecular E···O (E = S, Se) interactions. Whereas the* *latter configuration predominates over the former in tellurium system **22** due to propensity of low-valent tellurium to form a relatively stronger Te···O interaction in relation to its lighter congeners (S and Se).* From the current results and their comparison with the aromatic analogues, however, it is observed that the strength of Se···O intramolecular interactions in alicyclic diselenide and their halide derivatives is greater than the aromatic counterparts. This is probably due to the incomplete delocalization of the lone pair of electrons present on the oxygen. Compound **31**, an intermediate in the formation of **26,** has been isolated. The formation of a dimer *via* intermolecular interaction in **36** is unusual. Monotellurides **22** and **26** afforded complexes of Pd(II) and Pt(II) without cleavage or transmetallation occurring during metallation.

Experimental section

All the organochalcogen compounds were synthesized under nitrogen or argon atmosphere using standard Schlenk line techniques. Solvent were purified and dried by standard procedures and were freshly distilled prior to use.[53] All the chemicals used were reagent grade and were used as received. Melting points were recorded in capillary tubes. The NMR spectra were recorded in $CDCl_3$ solvent. The ^1H (400 MHz/500 MHz), ^{13}C (100/125 MHz), ^{77}Se (76.4/95.4 MHz) and ^{125}Te (126.3/157.8 MHz) spectra were recorded on a Varian Mercury plus or Bruker Avance spectrometer. Chemical shifts cited were referenced with respect to TMS for (^1H and ^{13}C) as internal standard and Me_2Se (for ^{77}Se), Me_2Te (for ^{125}Te) as external standards. Elemental analysis was performed on Carlo-Erba model 1106 and Eager 300 EA112 elemental analyzers. The IR spectra were recorded in the range 400-4000 cm^{-1} by using KBr pellets for solid samples on a Thermo Nicolet Avatar 320 FT-IR spectrometer. Mass spectral (MS) studies were completed by using a QTOF Micro mass spectrometer with electrospray ionization (ESI) mode analysis. In the case of isotopic patterns, the value is given for the most intense peak. In column chromatography, silica gel was used as a stationary phase whereas petroleum ether (60-80°C) and ethyl acetate were used as mobile phase.

1. Synthesis of 21:[17b] To a stirred solution of disodium sulfide (0.55 g, 7.1 mmol) in dry THF (50 mL) was added β-bromocyclohexenal **27b** (3.66 g, 14.1 mmol) at 0 ^{o}C. The reaction mixture was stirred for 30 min and monitored by TLC (5% petroleum-ether and ethyl acetate). The resultant mixture was poured into water and extracted with ethyl acetate. The organic layer was dried over Na_2SO_4 and concentrated under vacuum to give a pale yellow liquid. The liquid was triturated with hexane to obtain **21** as an off white solid. Yield: 0.49 g (58%). mp. 140-142 ^{o}C (Lit.138-139 ^{o}C); ^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) 10.41 (s, -CHO, 2H), 2.41-2.34 (m, 8H), 1.70-1.64 (m, 8H); ^{13}C NMR ($CDCl_3$): δ 21.3, 23.3, 24.5, 34.4, 142.4, 151.7, 190.9; ESI-HRMS: *m/z* calcd. for $C_{14}H_{18}SO_2Na$: *m/z* 273.0925; Found: 273.0924 $[M+Na]^+$. FT-IR $\upsilon_{C=O}$ 1663 cm^{-1}. Anal. Calcd for $C_{14}H_{18}SO_2$: C, 67.16; H, 7.25; S, 13.81; found C, 67.36; H, 7.26; S, 15.14.

2. Synthesis of 28: Disodium diselenide was synthesized according to literature procedure using freshly cut sodium (1.59 g, 70.0 mmol), selenium (5.58 g, 70.0 mmol), in the presence of a catalytic amount of naphthalene in dry THF (50 mL) under N_2 atmosphere.[31] To this purple colored reaction mixture, β-chlorocyclohexenal (**27a)**[29] (10.1 g, 70.0 mmol) was added at 0 ^{o}C. After stirring for 1 h at ice cold temperature, the mixture was allowed to come to the room temperature and the stirring was continued for an additional half an hour. Then the reaction mixture was poured into water and filtered through sintered funnel and extracted with ether. The organic layer was dried over Na_2SO_4 and concentrated under vacuum to give a yellow liquid containing the mixture of di-(2-formylcyclohexenyl)diselenide **28** and di-(2-formylcyclohexenyl)selenide **29**. Both the compounds were separated by column chromatography using 2% ethylacetate in petroleum ether. The first fraction obtained was di-(2-formylcyclohexenyl)diselenide **28** as a pale yellow solid and the second fraction was di-(2-formylcyclohexenyl)selenide **29** as a yellow solid. Di-(2-formylcyclohexenyl)diselenide **28** was recrystallized from ethylacetate/ petroleum ether. Yield: 1.21 g (6%); mp 123-125 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) 9.97 (s, -CHO, 2H), 2.70-2.66 (m, 4H), 2.46-2.42 (m, 4H), 1.76-1.68 (m, 8H); ^{13}C NMR ($CDCl_3$): δ 21.7, 24.1, 26.3, 35.6, 136.3, 154.8, 192.2; ^{77}Se NMR ($CDCl_3$): δ 490; ESI-HRMS: *m/z* calcd. for $C_{14}H_{18}Se_2O_2$ $[M]^+$ 378.9715; found 378.9735. FT-IR ($\upsilon_{C=O}$) 1655 cm^{-1}. Anal. Calcd. for $C_{14}H_{18}Se_2O_2$: C, 44.70; H, 4.82; found C, 44.80; H, 4.59.

29 : Yield: 2.081 g (40%); mp. 125-127 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ(ppm) 10.20 (s, -CHO, 2H), 2.51-2.50 (m, 4H), 2.39-2.38 (m, 4H), 1.71-1.68 (m, 8H); ^{13}C NMR (CDCl$_3$): δ 21.4, 23.9, 25.2, 36.5, 141.5, 151.3, 192.8; ^{77}Se NMR (CDCl$_3$): δ 370; ESI-HRMS: *m/z* calcd. for $C_{14}H_{18}SeO_2$: 299.0550; found: 299.0557 $[M]^+$; FT-IR $\upsilon_{C=O}$ 1663 cm^{-1}. Anal. Calcd for $C_{14}H_{18}$ SeO_2: C, 56.57; H, 6.10; found C, 56.08; H, 5.80.

3. Synthesis of compound 30: Disodium ditelluride was prepared by a similar procedure as adopted for **28** using Te powder (4.01 g, 32.1 mmol), freshly cut sodium (0.74 g, 32 mmol), catalytic amount of naphthalene and THF (40 mL).[31] After the addition of *β*-bromocyclohexenal **27b** (5.99 g, 32.1 mmol) at 0 °C, the reaction mixture was allowed to stir for 45 min. After stirring for 45 min the reaction mixture was poured into water and workup was performed following a similar procedure as described for **29** to get an orange oily liquid. Purification by column chromatography (3% ethyl acetate/petroleum ether) gave four products instead of ditelluride **30**. The first fraction isolated was **26** (3.04 g; 29%) as dark red liquid and the second fraction was telluride **22** (2.01g; 12%) as light yellow solid. The third fraction afforded telluride **31** (2.44 g; 22%) as deep yellow. The fourth fraction was as a pale white solid (3.23 g) as an oxidized products (**32-34**) of **22**.

Compound 26:[19, 32] Dark red solid, Yield: 3.04 g (29%); mp. 94-96 °C; ^{1}H NMR (400 MHz CDCl$_3$): δ(ppm)) 9.77 (s, -CHO, 1H), 6.58 (s, 1H) 2.86-2.83(t, *J* = 6.0 Hz, 2H), 2.70-2.68(m, 2H), 2.55-2.54(m, 2H), 1.95-1.90 (m, 2H), 1.84-1.76 (m, 4H), 1.75-1.74 (m, 2H); ^{13}C NMR (CDCl$_3$): δ 23.2, 23.4, 23.5, 30.6, 33.1, 33.6, 35.7, 125.8, 127.9, 128.0, 131.1, 133.5, 133.9, 139.0, 139.5, 147.4, 185.7; ^{125}Te NMR (CDCl$_3$): δ 834 ppm; ESI-HRMS: *m/z* calcd. For $C_{14}H_{16}OTe$: 331.0332, Found: 331.0343 $[M]^+$. Anal. Calcd for $C_{14}H_{20}TeO_2$: C, 48.3; H, 5.79; found C, 48.7; H, 5.17.

Compound 22: Pale yellow crystals, Yield: 2.01g (12%); mp. 138-140 °C (Lit.137-138 °C); ^{1}H NMR (CDCl$_3$): δ(ppm) 9.99 (s, CHO, 2H) 2.64-2.49 (m, 8H), 1.78-1.62 (m, 8H); ^{125}Te NMR (CDCl$_3$): δ 764; Anal. Calcd. for $C_{14}H_{18}TeO_2$: C, 48.61; H, 5.25; found C, 48.72; H, 5.20,

Compound 31: Deep yellow solid, Yield: 2.44 g (22%); mp. 140-142 °C; ^{1}H NMR (CDCl$_3$): δ(ppm) 9.69 (s, CHO, 1H), 3.95 (d, *J* = 10.04 Hz,1H), 2.66-2.44 (m, 4H), 2.34-

2.05 (m, 4H), 1.82-1.34 (m, 6H); ^{13}C NMR ($CDCl_3$): δ 21.8, 23.1, 23.7, 25.9, 27.0, 29.8, 33.6, 48.4, 78.9, 113.0, 132.2, 141.7, 148.9, 192.3; ^{125}Te NMR ($CDCl_3$): δ 616; Calcd. for $C_{14}H_{18}TeO_2$: C, 48.61; H, 5.25; found C, 48.95; H, 4.79.

Mixture of compounds 32, **33** and **34**[33]**:** Pale white solid, Yield: 3.23 g ; mp. 155 °C (decomposed), 164-166 °C; ^{125}Te NMR ($CDCl_3$): δ(ppm) 1214, 1184, 1083; ESI-MS: *m/z* Calc. for [$C_{14}H_{18}O_4Te$] **32**; 381 $[M]^+$, **33** *m/z* [$C_{14}H_{18}O_5Te$]; 393 $[M]^+$ and **34** *m/z* [$C_{14}H_{16}O_4Te$]; 377 $[M]^+$.

3. Synthesis of compound 22:[18] Compound **22** was prepared by a modified synthetic procedure. To the stirred solution of *in-situ* generated disodium telluride (sodium (1.25 g, 54.3 mmol) and tellurium (3.45 g, 27.1 mmol) in dry THF (80 mL) in presence of catalytic amount of naphthalene)[31] was added *β*-bromocyclohexenal **27b** (10.27 g, 54.3 mmol) under inert atmosphere at 0 °C. After stirring for 0.5 h at 0 °C, the reaction mixture was poured into water and workup was performed following a similar procedure as described for **29** to get an orange oily liquid. Purification by column chromatography (3% ethyl acetate/petroleum ether yielded the same four products as obtained from the reaction of **30**. The yield of four products are; **26** (1.26 g; 14%); **22** (0.82; 18%) **31**(1.11 g; 21%), fourth products (**32**, **33** and **34**): 1.40 g).

4. Synthesis of 35: To an ice cold solution of di-(2-formylcyclohexenyl)diselenide **28** (0.10 g, 0.27 mmol) in dry CCl_4, was added an excess of SO_2Cl_2 (0.08 g, 0.7 mmol) in CCl_4 (10 mL). The reaction mixture was allowed to stir for 1.5 h at room temperature. The resulting solution was concentrated and triturated with hexane to give **35** as yellowish white solid. Yield: 0.310 g (29%); mp 75-79 °C; ^{1}H NMR (400MHz, $CDCl_3$): δ 9.56 (s, -CHO, 1H), 3.08 (m, 2H), 2.79-2.74 (m, 2H), 1.91-1.82 (m, 4H); ^{13}C NMR ($CDCl_3$): δ 21.4, 22.6, 24.8, 32.9, 131.4, 186.2, 189.6; ^{77}Se NMR ($CDCl_3$): δ 1266; ESI-MS: *m/z* calcd. for C_7H_9OSeCl : 222.5; found: 188 $[M-Cl]^+$, (100%). Anal. Calcd. for C_7H_9OSeCl: C, 37.61; H, 4.06; found C, 37.2; H, 4.02.

5. Synthesis of 36: To a stirred solution of di-(2-formylcyclohexenyl)diselenide **28** (0.21 g, 0.56 mmol) in dry CCl_4 (10 ml) was added the CCl_4 solution of bromine (0.20 g, 1.2 mmol) at 0 °C. The reaction mixture was stirred for 1.5 h at room temperature and monitored by TLC. The resulting solution was concentrated to get brown-yellow liquid and kept in refrigerator to solidify. Analytically pure sample of **36** was obtained by the recrystallization of the solid with $CHCl_3$/pentane solution as a light yellow solid. Yield: 0.301 g (30%); mp 80-82 ^oC; ^1H NMR (400 MHz, $CDCl_3$): δ 9.43 (s, -CHO, 1H), 3.03-3.00 (m, 2H), 2.71-2.68 (m, 2H), 1.93-1.79 (m, 4H); ESI-MS *m/z* calcd. for C_7H_9OSeBr: 268; found: 188 $[M-Br]^+$, (100%); FT-IR υ 705, 1220, 1440, 1533, 1657, 2926 cm^{-1}. ^{77}Se NMR ($CDCl_3$): δ 1234; Anal. Calcd. for C_7H_9OSeBr: C, 31.37; H, 2.38; found C, 31.42; H, 2.28.

6. Synthesis of 37: To a stirred solution of di-(2-formylcyclohexenyl)diselenide **28** (0.11 g, 0.27 mmol) in dry CCl_4 (10 mL) was added a CCl_4 solution of iodine (0.07 g, 0.3 mmol) in carbon tetrachloride at 0 ^oC. The reaction mixture was allowed to warm up to room temperature and stirred for additional 2 h. The resulting solution was concentrated to obtain a violet crystalline product, which was recrystallized from $CHCl_3$-hexane mixture to give violet needles of **37**. Yield: 0.055 g (32%), mp 90-92 ^oC; ^1H NMR (400 MHz, $CDCl_3$): 9.08 (s, -CHO, 1H), 2.83-2.80 (*t*, J = 6.11 Hz, 2H), 2.59-2.57 (m, 2H), 1.85-1.80 (m, 4H); ^{13}C NMR ($CDCl_3$): δ 21.7, 24.6, 26.2, 42.4, 131.8, 171.5, 188.5; ^{77}Se NMR ($CDCl_3$): δ 1041. ESI-MS *m/z* calcd. for C_7H_9OSeI: 315; found: 188 $[M-I]^+$, (100%). Anal. Calcd. for C_7H_9OSeI: C, 26.69; H, 2.88; found C, 27.04; H, 2.48.

7. Synthesis of 38: To a stirred solution of di-(2-formylcyclohexenyl)telluride **22** (0.08 g, 0.2 mmol) in dichloromethane (7 mL) was added $Pd(C_6H_5CN)_2Cl_2$ (0.08 g, 0.2 mmol) and the reaction mixture was stirred for 45 min and monitored by TLC. The solvent was removed under vacuum to obtain a yellow solid which was recrystallized from dichloromethane/hexane to get yellow crystals. Yield: 0.079 g (41%); mp 135-137 ^oC; ^1H NMR ($CDCl_3$): δ(ppm) 9.59 (s, 4H), 3.25-3.20 (d, 4H), 2.97-2.92 (d, 4H), 2.59-2.58 (t, 8H,), 1.91-1.68 (m, 16H); ^{13}C NMR ($CDCl_3$): δ 21.3, 24.5, 28.8, 38.1, 141.5, 143.4, 193.3; ^{125}Te NMR ($CDCl_3$): δ 837. ESI-MS *m/z* calcd. for $[C_{28}H_{36}Cl_2O_4PdTe_2]$: 869; found 452 $[C_{14}H_{18}O_2PdTe]^+$; FT-IR ($\upsilon_{C=O}$) 1675 cm^{-1}; Anal. Calcd for $C_{28}H_{36}Te_2O_4PdCl_2$: C, 38.69; H, 4.18; found C, 38.10; H, 3.49.

8. Synthesis of 39: To a solution of di-(2-formylcyclohexenyl)telluride **22** (0.10 g, 0.03 mmol) in dichloromethane (7 mL) was added $PtCl_2$ (0.08 g, 0.03 mmol) and the reaction was carried out in a similar manner to that used for the synthesis of **38**. A deep red colored solution was obtained. The residue was kept in refrigerator to get red crystalline solid of **39**. Yield: 0.094 g (34%); mp. 151-153 °C; ^{1}H NMR ($CDCl_3$): δ(ppm) 9.91 (s, -CHO, 2H), 9.82 (s, -CHO, 2H) 3.09-3.04 (m, 4H), 2.83-2.78 (m, 4H), 2.62-2.50 (m, 8H), 1.85-1.67 (m, 16H); ^{13}C NMR ($CDCl_3$): δ 21.4, 24.3, 24.4, 27.5, 38.3, 141.5, 143.4, 143.9, 193.4; ^{125}Te NMR ($CDCl_3$): δ 818 ; (^1J (Te-Pt)= 631.5 Hz), ESI-MS *m/z* calcd. for $C_{28}H_{36}Te_2O_4PtCl_2$; 957; found: 958 $[M+H]^+$; 557 $[C_{14}H_{18}TeO_2PtCl+H]^+$, 238 $[C_7H_9TeO]^+$. FT-IR $\upsilon_{C=O}$ 1678, 1669 cm^{-1}; Anal. Calcd for $C_{28}H_{36}Te_2O_4PtCl_2.CH_2Cl_2$: C, 33.40; H, 3.67; found C, 33.50; H, 3.41.

9. Synthesis of 40: To a stirred solution of dry dichloromethane (10 mL) containing **26** (0.11 g, 0.33 mmol) was added $Pd(C_6H_5CN)_2Cl_2)$ (0.12 g, 0.30 mmol). The color of the reaction mixture changed from yellow to brownish red within 10 minutes. It was allowed to stir for additional 45 min and monitored by TLC. The solution was filtered through celite and resultant reaction mixture concentrated under vacuum. The residue was recrystallized from CH_2Cl_2 to get brown crystals of **40**. Yield: 0.097 g (29%); mp 155-157 °C; ^{1}H NMR ($CDCl_3$): δ(ppm) 9.83(s, -CHO, 1H), 9.79(s, -CHO, 1H), 6.08 (s(b), 2H), 3.49-3.37(m, 4H), 2.60-2.31 (m, 10H), 1.96-1.43 (m, 14H); ^{13}C NMR ($CDCl_3$): δ 21.6, 21.8, 23.8, 25.5, 31.8, 33.6, 34.1, 34.2, 125.4, 128.3, 129.2, 129.3, 129.5, 132.3, 137.5, 138.0, 138.3, 191.8; ^{125}Te NMR ($CDCl_3$): *δ* 685; ESI-MS *m/z* calcd. for $C_{28}H_{32}Te_2PdCl_2O_2$; 835.8; found: 505.0 $[M-L]^+$, 327.8 $[L]^+$ (L = ligand); FT-IR $\upsilon_{C=O}$ 2936, 1634, 1471, 1154, 1049, 991, 699 cm^{-1}; Anal. Calcd. for $C_{28}H_{32}Te_2Pd_2Cl_4O_2$: C, 33.28; H, 3.19; found C, 33.50; H, 3.37.

10. Synthesis of 41: Complex **41** was synthesized by the reaction of $PtCl_2$ (0.089 g, 0.33 mmol) with **26** (0.11 g, 0.33 mmol) using a similar method as used for the synthesis of Pd complex **38**. A brown precipitate obtained was dissolved in $CHCl_3$ and the solution filtered through celite. Yield: 0.097 g (63%); mp. 183-185 °C; ^{1}H NMR ($CDCl_3$): δ(ppm) 9.76 (s, CHO, 2H), 6.09 (s, 2H), 3.46-3.20 (m, 8H), 2.65-2.56 (m, 8H), 2.47-2.36(m, 6H), 2.02-1.79(m, 6H); ^{13}C NMR ($CDCl_3$): δ 22.1, 23.2, 23.5, 24.6, 24.7, 31.1, 33.1, 33.4, 34.2, 48.0, 123.4, 129.6, 133.1, 135.3, 138.0, 139.1, 191.3; ^{125}Te NMR ($CDCl_3$): δ 573; ESI-MS *m/z* calcd. for [$C_{14}H_{16}TePtCl_2O$]: 594; found 618.03 [M+Na]$^+$; FT-IR υ 2928, 1632, 1576, 1474, 1158, 939, 701 cm^{-1}. Anal. Calcd. for $C_{28}H_{32}Te_2PtCl_2O_2.CH_2Cl_2$: C, 34.60; H, 3.40; found C, 34.38; H, 3.19.

Computational details

All calculations were carried out using Gaussian09 suite of programs.[41] Full Geometry optimizations were performed at B3LYP/6-31+g(d) level. Orbital interactions were analyzed with Natural Bond Orbital **(**NBO) and Atoms In Molecules (AIM) calculations were carried using 6-311+g** basis set.[8f, 42, 54]

X-ray crystal structure determination

The single crystal X-ray diffraction measurements for compounds and **21**, **28, 29, 31**, **36** and **38-41** were performed on Oxford Diffraction Gemini diffraction measurement device with graphite monochromated Mo Kα radiation (λ = 0.7107 Å). The structures were determined by routine heavy-atom method using SHELXS 97[55] and refined by full-matrix least-squares with the non-hydrogen atom anisotropic and hydrogen atoms with fixed isotropic thermal parameters of 0.07 Å by means of SHELXS 97 program.[55] The heteroatom hydrogens were located from difference electron-density map and the rest was fixed at predetermined positions. Scattering factors were from common sources.[56] A riding model was chosen for refinement. The structure refinement parameters for compounds **21**, **28, 29**, **31**, **36** and **38-41** are given in Tables 4-6. The crystallographic data are given in Table 4-6.
CCDC- 1041180 (**21**)**,** CCDC-1041190 (**28**), CCDC-1041181 (**29**), CCDC-1041186 (**31**), CCDC-1041183 (**36**), CCDC-1041185 (**38**), and CCDC-1041187 (**39**), CCDC-1041188 (**40**), CCDC-1041189 (**41**),
contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif

Table 4. Crystal data and structure refinement for **21**, **28** and **29**

Compound	**21**	**28**	**29**
Empirical formula	$C_{14}H_{18}O_2S$	$C_{14}H_{18}O_2\,Se_2$	$C_{14}H_{18}O_2Se$
Formula weight	250.34	376.21	297.25
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/n$
a (Å)	11.0970(3)	8.4359(1)	11.2517(7)
b (Å)	8.2873(2)	7.9945(1)	8.3912(5)
c (Å)	14.6671(4)	21.4825(3)	14.8938
α (°)	90	90	90
β (°)	108.622(3)	91.702(2)	108.624(7)
γ (°)	90	90	90
V (Å^3)	1278.23(6)	1448.16(3)	1332.56(14)
Z	4	4	4
D (calcd) (Mg/m^3)	1.301	1.726	1.482
Absorption coefficient (mm^{-1})	0.241	6.319	2.806
Reflections collected	11014	6141	9870
Final R(F) [$I>2\sigma(I)$][a]	0.0395	0.0363	0.0630
wR(F2) indices [$I>2\sigma(I)$]	0.1057	0.0990	0.1017
Data / restraints / parameters	3250 / 0 / 154	3012/0/164	4435 / 15 / 177
Goodness-of-fit on F^2	1.026	1.075	1.005

[a] $R(Fo) = \Sigma||Fo| - |Fc||/\Sigma|Fo|$ and $wR(Fo^2) = \{\Sigma[w(Fo^2 - Fc^2)^2]/ \Sigma[w(Fc^2)^{1/2}$

Table 5**.** Crystal data and structure refinement for **31**, **36** and **38**

Compound	**31**	**36**	**39**
Empirical formula	$C_{14}H_{18}O_2Te$	C_7H_9BrOSe	$C_{28}H_{36}Cl_2O_4PtTe_2$
Formula weight	345.88	268.01	957.76
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/n$	P-1	$P2_1/c$
a (Å)	8.3511(5)	7.9977(11)	10.6364(3)
b (Å)	10.1970(8)	8.0789(7)	14.2022(4)
c (Å)	15.6047(1)	12.4832(13)	10.5132(3)
α (º)	90	80.322(8)	90
β (º)	10027(8)	78.575(10)	113.194(4)
γ (º)	90	81.320(9)	90
V (Å^3)	1294.64(2)	835.51(16)	1470.46(7)
Z	4	4	2
D (calcd) (Mg/m^3)	1.775	2.131	3.163
Absorption coefficient (mm^{-1})	18.037	11.126	26.201
Reflections collected	4548	4952	5681
Final R(F) [I>2σ(I)][a]	0.0709	0.1211	0.0366
wR(F2) indices [I>2σ(I)]	0.2011	0.3327	0.0878
Data / restraints / parameters	2560 / 51 / 177	3272/0/181	2970 / 0 / 169
Goodness-of-fit on F^2	1.085	1.136	1.011

[a] $R(Fo) = \Sigma||Fo| - |Fc||/\Sigma|Fo|$ and $wR(Fo^2) = \{\Sigma[w(Fo^2 - Fc^2)^2]/ \Sigma[w(Fc^2)^2\}^{1/2.}$

Table 6. Crystal data and structure refinement for **39**, **40** and **41**

Compound	**40**	**41**
Empirical formula	$C_{30}H_{36}Cl_8O_2Pd_2Te_2$	$C_{57}H_{65}Cl_7O4Pt_2Te_4$
Formula weight	1180.19	1962.80
Crystal system	Triclinic	Monoclinic
Space group	P-1	$P2_1/c$
a (Å)	8.649(4)	24.5246(10)
b (Å)	10.353(4)	13.3341(6)
c (Å)	11.416(5)	18.8162(7)
α (°)	64.524(11)	90
β (°)	89.03(2)	99.933(4)
γ (°)	88.03(2)	90
V (Å^3)	923.3(7)	6060.9(4)
Z	1	4
D (calcd) (Mg/m^3)	3.125	2.151
Absorption coefficient (mm^{-1})	3.133	26.588
Reflections collected	7026	9193
Final R(F) [I>2σ(I)][a]	0.0385	0.1445
wR(F^2) indices [I>2σ(I) [a]	0.0883	0.3428
Data / restraints / parameters	3275/0/169	12082 / 410 / 683
Goodness-of-fit on F^2	1.057	1.089

[a] $R(Fo) = ||Fo| - |Fc||/|Fo|$ and $wR(Fo^2) = \{\Sigma[w(Fo^2 - Fc^2)^2]/ [w(Fc^2)^2\}^{1/2.}$

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Highlights

→ Facile synthesis of alicyclic dichalcogenide and monochalcogenides stabilized by intramolecular Se···O coordination

→ The strength of Se···O intramolecular interactions in alicyclic diselenide and their derivatives is greater than that observed for the aromatic analogues

→ Pd(II) and Pt(II) metal complexes of alicyclic monotellurides isolated without the cleavage of Te-C bond