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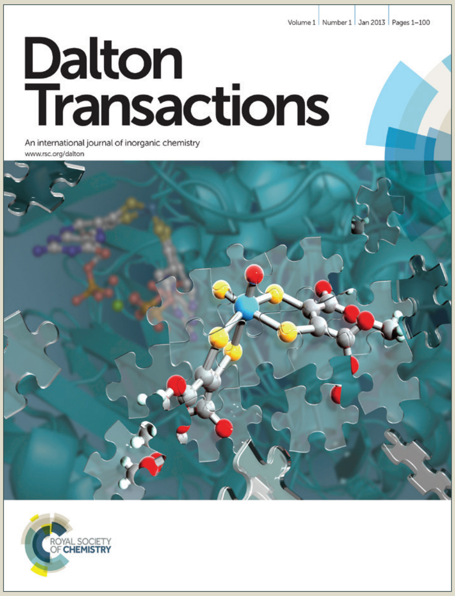

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Cyclopalladation of telluro ether ligands: Synthesis, reactivity and structural characterization

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Abstract

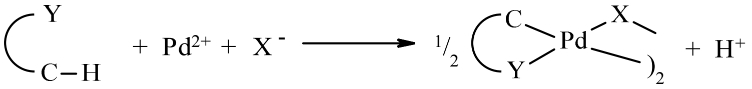
Treatment of [PdCl$_2$(PhCN)$_2$] with diaryl telluride in 1:2 molar ratio gave mononuclear palladium complexes, *trans*-[PdCl$_2$(TeR$_2$)$_2$] (**1**) (R = Mes (**1a**) (Mes = 2,4,6-trimethylphenyl), Ph (**1b**), *o*-tol (**1c**) (*o*-tol = *ortho*-tolyl)). Reaction of [PdCl$_2$(TeMes$_2$)$_2$] with one equivalent of [PdCl$_2$(PhCN)$_2$] or Na$_2$PdCl$_4$ with TeRR′ afforded chloro-bridged binuclear complexes, [Pd$_2$(μ-Cl)$_2$Cl$_2$(TeRR′)$_2$] (**2**) (R/R′ = Mes/Mes (**2a**); Mes/Ph (**2b**); Ph/Ph (**2c**)). Toluene-methanol solution of *trans*-[PdCl$_2$(TeMes$_2$)$_2$] on refluxing for 30 minutes yielded a binuclear cyclopalladated complex, [Pd$_2$(μ-Cl)$_2${CH$_2$C$_6$H$_2$(4,6-Me$_2$)TeMes)}$_2$] (**3**). When the refluxing was prolonged, a mononuclear complex *cis*-[PdCl$_2${MesTeCH$_2$C$_6$H$_2$(4,6-Me$_2$)TeMes}] (**4**) was isolated. Treatment of palladium acetate with TeMes$_2$ afforded an acetato-bridged analogue of **3**, [Pd$_2$(μ-OAc)$_2${CH$_2$C$_6$H$_2$(4,6-Me$_2$)TeMes}$_2$] (**5a**) together with a very minor component, a tetranuclear complex, [Pd(μ-OAc)(μ-TeMes)]$_4$ (**6**). This reaction with unsymmetrical tellurides, MesTeR also gave cyclopalladated complexes [Pd$_2$(μ-OAc)$_2${CH$_2$C$_6$H$_2$(4,6-Me$_2$)TeR}$_2$] (R = *o*-tol (**5b**) and Ph (**5c**)) in which 2-methyl of mesityl group of the telluride was exclusively metallated. The complex *trans*-[PdCl$_2$(TeMes$_2$)$_2$] on refluxing in xylene gave palladium telluride, Pd$_7$Te$_3$. These complexes were characterized by elemental analyses, IR and NMR (^{1}H, ^{13}C and ^{125}Te) spectroscopy. The molecular structures of *trans*-[PdCl$_2$(TeMes$_2$)$_2$] (**1a**), [Pd$_2$(μ-Cl)$_2$Cl$_2$(TeMes$_2$)$_2$].2acetone (**2a**.2acetone), *cis*-[PdCl$_2${MesTeCH$_2$C$_6$H$_2$(4,6-Me$_2$)TeMes}] (**4**), [Pd$_2$(μ-OAc)$_2${CH$_2$C$_6$H$_2$(4,6-Me$_2$)TeMes)}$_2$].toluene (**5a**.toluene), [Pd$_2$(μ-OAc)$_2${CH$_2$C$_6$H$_2$(4,6-Me$_2$)Tetol-*o*}$_2$] (**5b**) and [Pd(μ-OAc)(μ-TeMes)]$_4$ (**6**) were established by single crystal X-ray diffraction analyses. The mononuclear complex **1a** was isolated in two polymorphic forms each with *trans* configuration.

Keywords: Palladium, Telluro ether, Cyclopalladation, X-ray crystallography, Palladium tellurolate

Introduction

The chemistry of organopalladium compounds has witnessed a rapid growth during the past half century owing to their ease of synthesis, rich reaction chemistry and wide ranging applications in diverse areas. Among them cyclopalladated compounds or palladacycles represent an interesting family of the most popular and well investigated organopalladium derivatives.[1] These compounds remained in forefront ever since their initial isolation in mid 1960s by Cope and Siekman.[2] The growing interest in these compounds may be attributed to their applications in organic synthesis,[3, 4] catalysis[5-8] (*e.g.* $[Pd_2(\mu\text{-}OAc)_2\{o\text{-}tol_2PC_6H_4CH_2\text{-}o\}_2]$ (*o*-tol = *ortho*-tolyl) by Herrmann and co-workers) and materials science.[9, 10] These compounds are also encountered as reaction intermediates in palladium catalyzed organic transformations.[8, 11] Their unique metallomesogenic,[12] photo-physical[13] and antitumor[14] properties has provided further impetus to the progress of this area.

Over a period, a myriad of internally functionalized organic compounds containing neutral donor atom (e.g. N, P, As, O, S) have been utilized for cyclopalladation reaction (Scheme 1) leading to the formation of, in general, a four electron C-anionic donor ligand ($C^\frown Y$).[1, 8] Initially these organic molecules coordinate to the metal centre through neutral donor atom and it is believed that the C-H bond of the organic fragment is activated when it falls within the metal coordination plane.[3, 8] Thus the reactions with compounds containing lighter hetero-atom are quite facile while with the heavier hetero-atom containing compounds show little tendency to metalate. For instance, the effect of the size of the hetero-atom on metallation is evident in the reactions of Me_2ECH_2Ph (E = N, P, As, Sb). Both dimethyl benzylamine and dimethyl benzylphosphine (E = N, P)[15, 16] are metallated readily while dimethyl benzylarsine affords $[PdX_2(PhCH_2AsMe_2)_2]$, (X = Cl, Br, I).[17]



(X = Cl or OAc; Y = N, P, As, S donor atoms;
C-H = sp, sp^2, sp^3 carbon)

Scheme 1. Cyclopalladation of organic ligands

Cyclopalladation of a wide variety of organic compounds containing nitrogen and phosphorus as neutral donor atom has been extensively investigated.[1, 8] Among Group 16 donors, metallation of oxygen[18] and sulfur (thioethers, thioketones, etc.)[6, 19] compounds are well documented. However, with heavier chalcogen compounds, metallation of only a few organoselenium compounds (Bu^tSeCH_2Ph[7] and

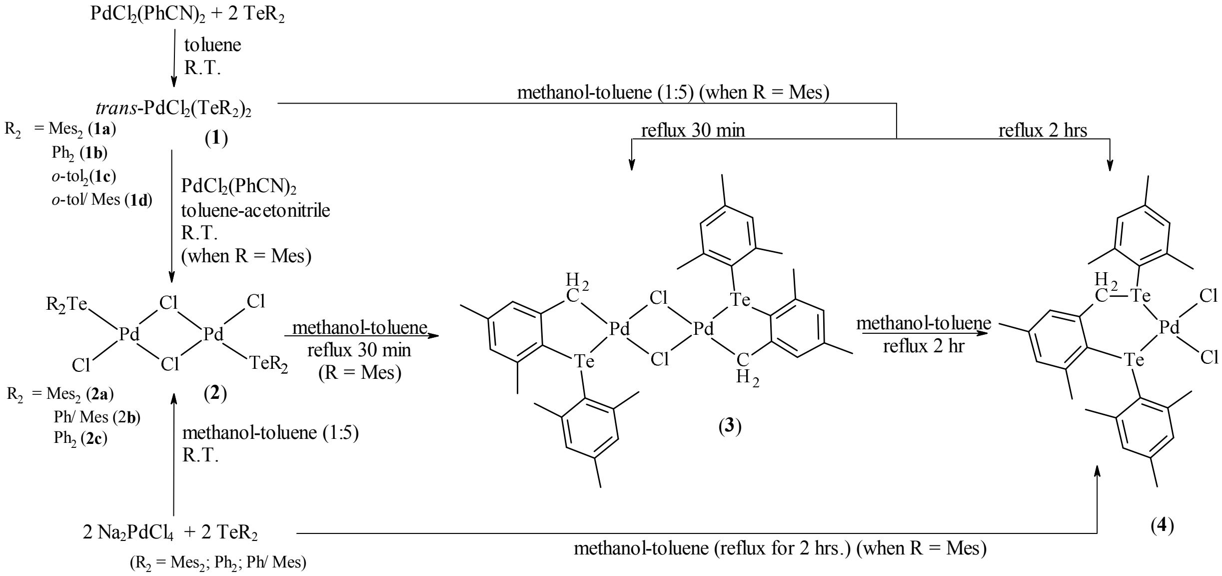
Mes_2Se[20]) has been described recently, whereas there is hardly any report on metallation of tellurium ligands. Such a limited exploration with heavier chalcogen compounds may possibly be attributed to either the formation of coordination complexes, $[PdX_2(ER_2)_2]$ (E = Se or Te), cleavage of the E-C bond or even complete decomposition of the complexes under metallation conditions. In a recent attempt by Singh and co-workers to metalate di-*o*-tolyltelluride lead to cleavage of the Te-C bond.[21] They isolated $[Pd(OAc)_2\{o\text{-tolTe})_2O\}]$ (*o*-tol = *ortho*-tolyl) and $[o\text{-tol}_2Pd_3(\mu\text{-OAc})_4\{Te(o\text{-tol})_2\}_2]$ formed by cleavage of Te-C bond of $o\text{-tol}_2Te$, rather than a metalated complex.[21] Interestingly the metalated compounds with heavier chalcogen ligand show higher catalytic activity than the lighter chalcogen compounds, *e.g.* $[Pd(\mu\text{-}OAc)(Bu^tECH_2C_6H_4)]_2$ (E = S or Se).[7]

In the light of the above, we have examined reactions of common palladium precursors ($[PdCl_2(PhCN)_2]$, Na_2PdCl_4, $[Pd(OAc)_2]_3$) used in cyclopalladation reactions with diorganotellurides and isolated a whole range of novel complexes by subtle variation in the reaction conditions. The complexes include simple coordination complexes, *trans*-$[PdCl_2(TeR_2)_2]$; intermediate binuclear complex with intramolecular C-H···Pd interaction, $[Pd_2(\mu\text{-Cl})_2Cl_2(TeMes_2)_2]$ (Mes = 2,4,6-trimethylpheny), cyclopalladated complexes, $[Pd_2(\mu\text{-X})_2\{CH_2C_6H_2(4,6\text{-Me}_2)TeR\}_2]$ (X= Cl, OAc; R = Mes, *o*-tol (*o*-tol = *ortho*-tolyl), Ph), complexes formed by Te-C bond cleavage, *cis*-$[PdCl_2\{MesTeCH_2C_6H_2(4,6\text{-Me}_2)TeMes\}]$, $[Pd(\mu\text{-OAc})(\mu\text{-TeMes})]_4$ to eventually palladium telluride as decomposition product. The results of this exploration are described herein.

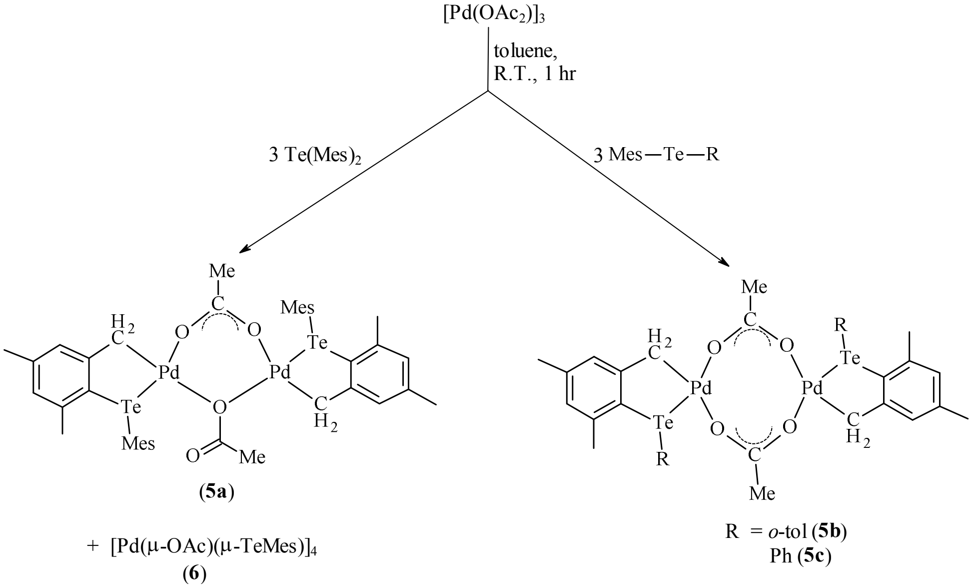
Results and discussion

Synthesis

Syntheses of various palladium complexes are depicted in Schemes 2 and 3. Treatment of $[PdCl_2(PhCN)_2]$ with diaryl telluride in 1:2 molar ratio in toluene at room temperature gave mononuclear palladium complexes, *trans*-$[PdCl_2(TeR_2)_2]$ (**1**) (R = Mes (**1a**) (Mes = 2,4,6-trimethylpheny, Ph (**1b**), *o*-tol (**1c**) (*o*-tol = *ortho*-tolyl)) as orange crystalline solids. The latter (R = Mes) when treated with one equivalent of $[PdCl_2(PhCN)_2]$ in toluene-acetonitrile mixture at room temperature afforded a chloro-bridged binuclear complex, $[Pd_2(\mu\text{-Cl})_2Cl_2(TeMes_2)_2]$ (**2a**). The complex **2a** can also be prepared by the reaction of Na_2PdCl_4 with $TeMes_2$ at room temperature in 79% yield. This reaction can be extended to prepare analogues of **2a** by employing MesTePh and Ph_2Te.



Scheme 2. Synthetic routes for palladium telluro ether complexes



Scheme 3. Synthesis of acetato bridged cycloplladated telluro ether complexes

When a toluene-methanol solution of *trans*-$[PdCl_2(TeMes_2)_2]$ (**1a**) was refluxed for ~ 30 minutes, a cyclopalladated binuclear complex, $[Pd_2(\mu\text{-}Cl)_2\{CH_2C_6H_2(4,\ 6\text{-}Me_2)TeMes\}_2]$ (**3**) was isolated as an orange powder in 75% yield. When refluxing was prolonged for two hrs a mononuclear complex *cis*-$[PdCl_2\{MesTeCH_2C_6H_2(Me_2\text{-}4,6)TeMes\}]$ (**4**) was isolated. The latter was also formed when a toluene-methanol solution of either *trans*-$[PdCl_2(TeMes_2)_2]$ or a 1:1 mixture of Na_2PdCl_4 and $TeMes_2$ was re-fluxed for 2 hrs. The complex **4** appears to be formed by a nucleophilic attack of a tellurolate ion (Mes-

Te$^-$), generated by Te-C bond cleavage,[22, 23] on methylene carbon of the cyclopalladated complex **3**. The formation of tellurolate ion from a telluro ether ligand has been noted previously[24] and also in the present study (see later, e.g. isolation of **6**). Attempt to prepare similar cyclopalladated complexes with *o*-tolTeMes, *o*-tol$_2$Te and Ph$_2$Te were unsuccessful. The solution of **1a** on prolonged refluxing (2 hrs) either in xylene or 2-ethoxy ethanol gave black powder which was identified as Pd_7Te_3 from powder X-ray diffraction pattern (JCPDS File no. 43-1294) (Supplementary Material). The product formed in 2-ethoxy ethanol was however contaminated with elemental tellurium. Recently, a telluro ether complex of palladium, $[PdCl\{C_6H_5(2\text{-}HOC_6H_4)CHNH(CH_2)_3TeC_6H_4OMe\text{-}4\}]$, was used for the preparation of Pd_3Te_2 nanoparticles.[25]

Treatment of palladium acetate with TeMes$_2$ in toluene at room temperature afforded an acetato-bridged analogue of **3**, $[Pd_2(\mu\text{-}OAc)_2\{CH_2C_6H_2(4,6\text{-}Me_2)TeMes\}_2]$ (**5a**) as a yellow crystalline solid together with a very minor component, a tetranuclear complex, $[Pd(\mu\text{-}OAc)(\mu\text{-}TeMes)]_4$ (**6**) (Scheme 3). This reaction with unsymmetrical telluro ether ligands, MesTeR (R = *o*-tol, Ph) also yielded cyclopalladated complexes $[Pd_2(\mu\text{-}OAc)_2\{CH_2C_6H_2(4,6\text{-}Me_2)TeR\}_2]$ (R = *o*-tol (**5b**) and Ph (**5c**)) in which 2-methyl of the mesityl group of the telluro ether ligand was exclusively metallated.

Cyclopalladation using telluro ether ligands containing at least one meistyl group was quite facile when $[Pd(OAc)_2]_3$ was used as the palladating agent, whereas the same took place with Na_2PdCl_4 or $[PdCl_2(PhCN)_2]$ only in case of Mes$_2$Te. This could be due to the fact that in the latter case only with Mes$_2$Te due to steric crowding of two bulky mesityl rings, one of the *ortho* C-H bond falls into the coordination plane of palladium as is evidenced in the molecular structure of **2a** (see later, Fig 3 (b)) leading to metallation with the generation of HCl as by-product. On the other hand, with $[Pd(OAc)_2]_3$, in the reaction medium via the η^2-bridging mode OAc$^-$ give a cyclic transition state by coordinating palladium with one oxygen and at the same time bringing one of the *ortho* C-H bond of methyl group of mesityl into the close proximity of palladium using other oxygen atom through C-H···O interaction and leads to activation of the C-H bond with the generation of HOAc as the by-product. HOAc being a weak conjugate of OAc$^-$ also makes the metallation energetically more feasible than strong acid; HCl generated in the case of Na_2PdCl_4 and have a strong interference with the formed M-C bond than HOAc.

Spectroscopy

The IR spectra of acetato-bridged metallated complexes showed absorptions at 1615, 1558 (**5a**)/ 1566 (**5b**) cm^{-1} attributable to bridging acetate groups. The ^{1}H NMR spectra displayed expected resonances. The methyl groups (at 2- and 6- positions) of the coordinated mesityl telluride were deshielded in the ^{1}H NMR spectra while they were shielded in the ^{13}C NMR spectra with reference to the corresponding free ligands. The cyclopalladated complexes showed a distinct AB pattern for the Pd-CH_2 protons at a chemical shift significantly downfield from that of the mesityl methyl groups (3.38 ppm, br, 2H (3); 3.36 ppm, 2H, $\Delta\nu_{AB}$ = 71 Hz, J_{AB} = 13 Hz (5a); 3.09 ppm, 2H, $\Delta\nu_{AB}$ = 24.6 Hz, J_{AB} = 12.7 Hz (**5b**)). Similar anisotropic behavior was also noted for analogous selenium complex, $[Pd_2(\mu\text{-}Cl)_2\{CH_2C_6H_2(4,6\text{-}Me_2)SeMes\}_2]$.[20] The CH_2 protons in **4** were also anisotropic and appeared as an AX pattern at 3.55 ppm with significantly large chemical shift difference (2H, $\Delta\nu_{AX}$ = 169 Hz, J_{AX} = 11 Hz).

The ^{125}Te{^{1}H} NMR spectra of these complexes displayed a single resonance which appeared at higher frequency with respect to the free ligand ($TeMes_2$, ^{125}Te δ = 260.8 ppm, Te(*o*-tol)$_2$, ^{125}Te δ = 499.3 ppm, $TePh_2$, ^{125}Te δ = 693.4 ppm, MesTe(*o*-tol) ^{125}Te δ = 336.8 ppm, MesTePh ^{125}Te δ = 427.2 ppm). The ^{125}Te NMR resonance was progressively deshielded from mononuclear (**1a**) (δ 489.1 ppm) to cyclopalladated derivative **3** (δ 644.0 ppm) through the binuclear **2a** (δ 575.0 ppm). Such a large deshielding (69 ppm) from binuclear complex **2a** to cyclopalladated complex **3** has also been noted from our group in the corresponding mesityl seleno ether derivatives (deshielded by 86 ppm in ^{77}Se resonance).[20] The effect of bridging ligand as well as the nature of R group on Te is also evident in cyclopalladated complexes. There is shielding of ~90 ppm of the ^{125}Te NMR resonance on replacing bridging chloride in **3** (δ 644.0 ppm) by acetate group (**5a**) (δ 554.1 ppm). Replacement of mesityl group on Te in **5a** by *ortho*-tolyl or phenyl groups results in successive deshielding of the resonance (**5b**, 592.2 ppm; **5c**, 690.4 ppm). Such changes could be attributed to the electron releasing methyl groups in the aryl ring which consequently increases electron density at the tellurium.

Crystallography

Molecular structures of *trans*-$[PdCl_2(TeMes_2)_2]$ (**1a**), $[Pd_2(\mu\text{-}Cl)_2Cl_2(TeMes_2)_2]$.2acetone (**2a**.2acetone), *cis*-$[PdCl_2\{MesTeCH_2C_6H_2(4,6\text{-}Me_2)TeMes\}]$ (**4**), $[Pd_2(\mu\text{-}OAc)_2\{CH_2C_6H_2(4,6\text{-}Me_2)TeMes\}_2]$.toluene (**5a**.toluene), $[Pd_2(\mu\text{-}OAc)_2\{CH_2C_6H_2(4,6\text{-}Me_2)Tetol\text{-}o\}_2]$ (**5b**) and $[Pd(\mu\text{-}OAc)(\mu\text{-}TeMes)]_4$ (**6**) were established by single crystal X-ray diffraction analyses and are shown in Figures 1-7. Selected inter-atomic parameters are summarized in Tables 1 - 7. Palladium atom in all these complexes acquires a distorted square planar configuration. The Pd-Te distances (2.47 – 2.59 Å) are well within the range reported for palladium-telluro ether complexes, $[PdCl\{OC_9H_6C(Me)=NCH_2CH_2TeC_6H_4OMe\text{-}4\}]$ (Pd-Te = 2.5025(7) Å)[26], $[PdCl_2\{4\text{-}BrC_3H_2N_2CH_2CH_2TeC_6H_4OMe\text{-}4\}]$ (Pd-Te = 2.512(6) Å)[27], $[Pd(TePh)_2(dppe)]$ (Pd-Te = 2.5871 -2.6704(8) Å[28] and $[tol_2Pd_3(\mu\text{-}OAc)_4(Tetol_2\text{-}o)_2]$ (Pd-Te = 2.5054 (5)

Å).[21] The Pd-C distances (~2.0Å) are in accord with the values reported for cyclopalladated complexes such as $[Pd_2(\mu\text{-}Cl)_2\{CH_2C_6H_2(4,6\text{-}Me_2)SeMes\}_2]$ (Pd-C = ~2.03 Å)[20] and $[Pd(OCH\text{-}C_4H_3N)(Bzq)]$ (Bzq = 7,8-benzoquinolyl) (Pd-C = 1.993 (3) Å).[29] The Te-C (~ 2.14 Å) bond distances are in conformity with the range reported in organotellurium compounds (e.g. Mes_2Te (Te-C = 2.140(3) Å),[30] $Te\{C_5H_3(Me\text{-}3)N\}_2$ (Te-C = 2.136(1) Å)[23] and $[Cd(TeMes)_2]_\infty$ (Te-C = 2.164(12) Å).[31]

The mononuclear complex, $[PdCl_2(TeMes_2)_2]$ (**1a**) was isolated in a *trans* configuration and showed polymorphism depending on the crystallization solvents. The two polymorphs, viz rectangular block and needle shaped crystals were isolated from acetonitrile-diethyl ether (monoclinic form, Fig. 1) and toluene-hexane (triclinic form, Fig. 2) mixture, respectively. The triclinic form described here also differs from the one reported earlier.[32] The two polymorphs essentially differ slightly in the inter-atomic parameters as well as in the relative orientation of the mesityl groups on tellurium. The Te-Pd-Te angle in the triclinic form is significantly reduced (~164°) from the ideal value of 180° while in the monoclinic form it is 180°. The Pd-Te-C angles in the monoclinic form are smaller than the triclinic form. The C-Te-C angle (~100° in the triclinic form and 102.5° in monoclinic form) are as observed in Mes_2Te (101.0(1)°).[30] In the monoclinic form the mesityl rings (C1-C9) and ($C1^i$-$C9^i$) are coplanar and are almost perpendicular (85.60°) to the Pd square plane ($Cl1Te1Pd1Te1^iCl1^i$), while the other mesityl rings (C10-C18) and ($C10^i$-$C18^i$) lie in plane parallel to each other which are nearly perpendicular to the Pd square plane (77.80°). The two mesityl rings attached to tellurium atom lie at an angel of 80.04°. There are weak secondary interaction between the chloride and the hydrogen atom of the acetonitrile molecule (Cl1…C25 = 2.719Å) as well as nitrogen and hydrogen (sp^2 (2.691Å) and sp^3 (2.718Å)) atom of nearby molecule (supplementary material). In the triclinic form the arrangement of the mesityl rings are completely different. The mesityl rings (C10-C18) and (C29-C36) are *syn* to the Pd square plane.

The binuclear complex, $[Pd_2(\mu\text{-}Cl)_2Cl_2(TeMes_2)_2]$ (**2a**) (Fig 3) crystallizes with two molecules of acetone and comprises of a rectangular planar four-membered chloro-bridged "$Pd_2(\mu\text{-}Cl)_2$" core; a configuration usually observed for the chloro-bridged complexes[1] with neutral monodentate group 16 ligands, eg. $[Pd_2(\mu\text{-}Cl)_2Cl_2(SeMes_2)_2]$.[20] Two telluro ether ligands are mutually *trans*, forming a *sym-trans* dimeric structure. The terminal Pd-Cl distances are marginally shorter (2.290(4) Å) than the bridging Pd-Cl distances (2.310(4), 2.403(4)Å). The Pd-Te distance is shorter than the one noted for the mononuclear complex, **1a**. This may be attributed to the weak *trans* influencing effect of chloro ligand *trans* to it. The C-Te-C angle (97.64°) is also reduced significantly from the mononuclear complex. The Pd…H17A-C17 distance (2.377 Å), which is significantly shorter than the van der Waal radii (2.83 Å), and the C17-

H17…Pd1 angle (171.19°) correspond to an anagostic interaction between palladium and the *ortho*-methyl hydrogen atom[33]. There is also a short contact between the terminal chloride and hydrogen atom (H17A) of *ortho* methyl group (Cl2...H17A-C17 = 2.925 Å).

The complex *cis*-$[PdCl_2\{MesTeCH_2C_6H_2(Me_2\text{-}4,6)TeMes\}]$ (**4**) (Fig. 4) is a discrete monomer in which coordination around palladium is defined by two *cis* chlorides and a chelating telluro ether ligand. The Pd-Te and Pd-Cl distances are slightly shorter and longer, respectively than **1a** owing to weak *trans* influencing chloride ligand *trans* to Te. The Pd-Te distances are well in agreement with the reported *cis* configured complexes such as *cis*-$[PdCl_2\{MeTe(C_4H_3E)\}_2]$ (E = O (Pd-Te = 2.530Å); S (Pd-Te = ~2.54Å))[34] and *cis*-$[PdCl_2\{$*meso*-$(TeC_6H_4OMe\text{-}4)_2CH_2\}]$ (Pd-Te = 2.518, 2.526Å).[35] The six-membered "PdTeCCCTe" ring is puckered. The Cl1 lies slightly (0.391Å) out of the Pd1 mean square plane.

The molecular structure of $[Pd_2(\mu\text{-}OAc)_2\{CH_2C_6H_2(4,6\text{-}Me_2)TeMes\}_2]$ (**5a**) (Fig. 5) is unique and distinctly different from bis acetato-bridged binuclear palladium complexes, $[Pd_2(\mu\text{-}OAc)_2X_2Y_2]$ reported thus far.[1] The molecule adopts a *sym-cis* configuration in which tellurium atoms are *trans* to anisobidentate acetate group. The Pd-Te distances are shorter than the one observed for mono- and bi-nuclear complexes described above and also from those found in $[Pd_3(o\text{-}tol)_2(\mu\text{-}OAc)_4\{Te(o\text{-}tol)_2\}_2]$ (Pd-Te = 2.5054(5)Å).[21] The Pd...Pd separation is longer than those reported in acetate-bridged binuclear complexes but is significantly shorter than the sum of the van der Waal radii (3.08 Å vs 3.26 Å, respectively).[1] In **5a** two palladium atoms are held together by two different types of bridging acetate groups; one acting in an anisobidentate fashion while the other bridges through only one oxygen atom, so as to give a six-membered "Pd(μ-OAc)(μ-O)Pd" ring rather than an eight-membered boat shaped "$Pd_2(\mu\text{-}OAc)_2$" ring usually observed. The second acetate group (O3-C39-C40-O4) is almost coplanar with Pd1 but almost perpendicular to Pd2 square planes. The distances between the O4 and Te1 and Te2 are 3.447 and 2.989 Å, respectively. The latter (O4-Te2) is significantly shorter than the sum of the van der Waal radii of oxygen and tellurium (3.58Å) indicating short secondary Te2...O4 interaction. Also the O4 is placed almost equidistant to neighbouring methyl groups in the unit cell (O4…H36C-C36 = 2.440 Å; O4…H16C-C16 = 2.663 Å; O4…H9B-C9 = 2.591 Å (adjacent molecule). Both Te1 and Te2 atoms are nearly coplanar with the bridging acetate group.

In contrast to **5a**, the complex, $[Pd_2(\mu\text{-}OAc)_2\{CH_2C_6H_2(4,6\text{-}Me_2)Tetol\text{-}o\}_2]$ (**5b**) (Fig. 6) adopts an usual acetate bridged structure with short Pd···Pd distance 2.8677(14)Å and boat shaped eight-membered "$Pd_2(\mu\text{-}OAc)_2$" ring. The two tellurium ligands are mutually *trans.* Methyl of tolyl rings and oxygen atoms show short contacts (C16-H16A…O1 = 2.749 Å and C32-H32A…O3 = 2.763 Å). The O2-Pd2 (2.097 Å) and O4-Pd1 (2.104 Å) (*trans* to the Te atom) distances are shorter than the O1-Pd1 (2.142 Å) and O3-Pd2 (2.164 Å) (*trans* to methylene groups).

The complex [Pd(μ-OAc)(μ-TeMes)]$_4$ (**6**), is a tetramer and adopts a paddle-wheel geometry. Two pairs of orthogonal acetate groups and two pairs of mesityl tellurolate ligands hold two different pairs of palladium atoms. The molecule contains two almost rectangular planes formed by Pd1-Pd2-Pd1^i-Pd2^i (Pd2-Pd1-Pd2^i = 93.17°, Pd1-Pd2-Pd1^i = 86.83; Pd1-Pd2^i = 3.696 Å, Pd1-Pd2 = 2.947 Å) and Te1-Te2-Te1^i-Te2^i (Te2-Te1-Te2^i = 89.42, Te1-Te2-Te1^i = 90.58, Te1-Te2 = 3.314 Å, Te1-Te2^i = 4.009 Å) which are nearly perpendicular (89.90°). The geometry around each palladium atom is defined by two oxygen atoms from two different acetate groups and two tellurolate ligands. The four palladium atoms form a rectangular plane with short Pd···Pd distances (bridged by two acetate groups) varying in the range 2.947 - 3.695Å, which lie well within the range reported in iso-structural chalcogenolate complexes, [Pd(μ-OAc)(μ-ER)]$_n$ (ER = SePh, Pd···Pd = 2.864(18)Å;[36] ER = *o*-tolSe, Pd···Pd = 2.8805(8)Å;[21] ER = SEt, Pd···Pd = 3.036, 3.194 Å[37]). The structures of palladium acetate complexes of composition [Pd(μ-OAc)(μ-ER)]$_n$ are influenced by the nature of R groups and ranges from bi-nuclear to tetra-nuclear. For example, [Pd(OAc)(ECH$_2$CH$_2$CH$_2$NMe$_2$)]$_2$.H$_2$O (E = S or Se)[38] and [Pd(OAc)(SCH$_2$CH$_2$NMe$_2$)]$_3$.3H$_2$O[39] are di- and tri-meric, respectively with terminal monodentate acetate groups and chelating bridging chalcogenlate ligands. In contrast complexes with chacogenolate ligands without internal functionalized organic group yield tetrameric derivatives.

Experimental section

Solvents were dried and distilled under a nitrogen atmosphere prior to use according to a literature method.[40] All the reactions were carried out in an argon atmosphere. Diaryl tellurides, RTeR′ were prepared by the reaction of RTeBr, obtained in-situ by bromination of diaryl ditellurides (R$_2$Te$_2$) with bromine in THF with an appropriate aryl magnesium bromide (R′MgBr) (supplementary material).[41] [PdCl$_2$(PhCN)$_2$][42] and [Pd(OAc)$_2$]$_3$[43] were prepared according to literature methods. Elemental analyses were carried out on a Carlo-Erba-1110 CHNS micro-analyzer. Melting points were determined in capillary tubes and are uncorrected. ^{1}H, ^{13}C{^{1}H} and ^{125}Te{^{1}H} NMR spectra were recorded on a Bruker Avance-II 300 NMR spectrometer operating at 300.1, 75.5 and 94.7 MHz, respectively. The chemical shifts are relative to an internal chloroform peak (δ 7.26 for ^{1}H and 77.0 ppm for ^{13}C) and external Me$_2$Te for ^{125}Te (secondary reference Ph$_2$Te$_2$, δ 421 ppm in C$_6$D$_6$).

Synthesis

trans-[$PdCl_2(TeMes_2)_2$] (**1a**)

To a toluene solution of [$PdCl_2(PhCN)_2$] (300 mg, 0.78 mmol), a solution of Mes_2Te (572 mg, 1.56 mmol) was added at room temperature with stirring which continued for 4 hr whereupon an orange-red precipitate formed. The latter was filtered and washed with hexane and diethyl ether, and extracted with acetonitrile. The concentrated acetonitrile solution (~2 ml) containing few drops of diethyl ether on slow evaporation at room temperature gave orange-red rectangular shaped crystals (550 mg, 77% yield); m.p. 178°C (dec). Anal calcd for $C_{36}H_{44}Cl_2PdTe_2$: C, 47.55; H, 4.88%. Found: C, 47.37; H, 4.86%. ^1H NMR ($CDCl_3$) δ: 2.23, 2.58 (s, Me); 6.86 (s, 3,5-CH). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 20.9, 27.2 (Me), 118.8 (Te-C), 129.3 (3,5-CH), 139.9, 143.6. $^{125}Te\{^1H\}$ NMR ($CDCl_3$) δ: 489.1 ppm.

trans-[$PdCl_2(TePh_2)_2$] (**1b**)

Prepared similar to **1a** and isolated as an orange–red crystalline solid in 74% yield; m.p. 160°C (dec). Anal calcd for $C_{24}H_{20}Cl_2PdTe_2$: C, 38.90; H, 2.72%. Found: C, 38.71; H, 2.70%. 1H NMR ($CDCl_3$) δ: 7.29-7.44 (m), 7.81 (d, 7.2 Hz) (Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 117.9 (C-Te), 129.7, 130.0, 137.0. $^{125}Te\{^1H\}$ NMR (CDCl3) δ: 749.8 ppm.

[$PdCl_2\{Te(o\text{-tol})_2\}_2$] (**1c**)

Prepared similar to **1a** and isolated in 58% yield; m. p. 195°C (dec). Anal calcd for $C_{28}H_{28}Cl_2PdTe_2$: C, 42.19; H, 3.54%. Found: C, 42.40; H, 3.17%. ^1H NMR ($CDCl_3$) δ: 2.54 (s, Me), 7.10(t, 7.2 Hz) 7.25 (d) 7.34 (t, 7.2 Hz), 7.84 (d, 7.2 Hz) (*o*-tol). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 25.5 (Me), 119.8 (C-Te), 127.4, 130.2, 130.3, 138.4, 142.4 (*o*-tol). $^{125}Te\{^1H\}$ NMR ($CDCl_3$) δ: 637 ppm.

[$PdCl_2(MesTetol\text{-}o)_2$] (**1d**)

Prepared similar to **1a** and isolated in 62% yield; m. p. 183-184 °C (dec). Anal calcd for $C_{32}H_{36}Cl_2PdTe_2$: C, 45.05; H, 4.25%. Found: C, 45.52; H, 4.00%. ^1H NMR ($CDCl_3$) δ: 2.31, 2.46, 2.76 (each s, Me), 7.01(s), 7.15-7.25 (m).

[$Pd_2(\mu\text{-}Cl)_2Cl_2(TeMes_2)_2$] (**2a**)

(i) To a methanolic solution (5 cm^3) of Na_2PdCl_4 (102 mg, 0.35 mmol), a toluene solution (25 cm^3) of Mes_2Te (131 mg, 0.36 mmol) was added with stirring at room temperature. The contents were stirred for 3 hrs at room temperature whereupon a dark-red precipitate formed which was filtered and washed with toluene. The precipitate was extracted with acetone. The volume of the solvent was reduced to 5 ml and hexane (1 ml) was added which on cooling at -5°C for several hrs gave red needle shaped crystals (150 mg, 79% yield), m.p. 178°C (dec). Anal calcd for $C_{36}H_{44}Cl_4Pd_2Te_2$: C, 39.79; H, 4.08%. Found: C, 39.71; H, 4.07%. ^{1}H NMR (CDCl3) δ: 2.24 (s, 1Me); 2.65 (s, 2Me), 6.88 (s, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$) δ: 20.9, 26.8 (Me), 116.8 (C-Te), 130.1 (3,5-CH), 141.0, 143.3. ^{125}Te{^{1}H} NMR ($CDCl_3$) δ: 575.0 ppm.

(ii) To a toluene-acetonitrile (1:1) solution of *trans*-[$PdCl_2(TeMes_2)_2$] (**1a**) (100 mg, 0.11 mmol), $PdCl_2(PhCN)_2$ (42 mg, 0.11 mmol) was added with stirring at room temperature which was continued for 5 hrs. The red precipitate formed during the reaction was filtered and washed with toluene and was processed similar to (i) and isolated in 71% yield. The NMR data were consistent with the above preparation.

[$Pd_2(\mu\text{-}Cl)_2Cl_2\{Te(Ph)Mes\}_2$] (**2b**)

This was prepared similar to **2a** method (i) and isolated as brown crystalline solid from acetone-hexane mixture at -5°C in 74% yield; m.p. 174°C (dec). Anal calcd for $C_{30}H_{32}Cl_4Pd_2Te_2$: C, 35.95; H, 3.22%. Found: C, 35.86; H, 3.22%. ^{1}H NMR (CDCl3) δ: 2.34 (s,1Me), 2.81 (s, 2Me), 7.04 (s, 3,5-CH, Mes), 7.19-7.44 (m, Ph). ^{125}Te{^{1}H} NMR (CDCl3) δ: 704.0 ppm.

[$Pd_2(\mu\text{-}Cl)_2Cl_2(TePh_2)_2$] (**2c**)

This was prepared in a manner similar to (**2a**) employing both methods (i) and modified (ii) under refluxing in toluene and was isolated as an orange-red crystalline solid from acetonitrile-diethyl ether mixture at room temperature in 66-73% yield, m.p. 142°C (dec). Anal calcd for $C_{24}H_{20}Cl_4Pd_2Te_2$: C, 31.39; H, 2.19%. Found: C, 31.32; H, 2.19%. ^{1}H NMR ($CDCl_3$) δ: 7.38 (t, 7.5 Hz), 7.49 (t, 7.2 Hz), 7.78 (d, 7.2 Hz). ^{125}Te{^{1}H} NMR ($CDCl_3$) δ: 823.5 ppm.

[$Pd_2(\mu\text{-}Cl)_2\{CH_2C_6H_2(4,6\text{-}Me_2)TeMes\}_2$] (**3**)

A toluene-methanol (5:1 v/v; 50 cm^3) solution of *trans*-[$PdCl_2(TeMes_2)_2$] (**1a**) (100 mg, 0.11 mmol) was refluxed for 30 min with stirring under an argon atmosphere whereupon an orange-red solution faded to orange color. The solvents were evaporated under vacuum and the residue was washed with petroleum ether, and then extracted with toluene. The solvent was reduced to 2 ml under vacuum, on addition of hexane (5 ml) the title complex precipitated out as an orange powder (42 mg, 75%), m.p. 164-169 °C (dec.). Anal calcd for $C_{36}H_{42}Cl_2Pd_2Te_2$: C, 42.66; H, 4.18%. Found: C, 42.52; H, 4.17%. ^{1}H NMR ($CDCl_3$) δ: 2.04 (s, 1Me), 2.25 (s, 1Me), 2.53 (s, 2Me), 3.38 (br, CH_2), 6.94 (s, 1H), 6.78 (s, 1H), 6.87 (s, 2H) (CH, Mes). ^{13}C{^{1}H} NMR ($CDCl_3$) δ: 20.9, 21.0, 22.9, 25.7, 27.2 (1Me), 29.7 (CH2, metallated), 127.4, 128.8 (3/5- CH of metallated), 129.1 (3,5-CH non-metallated), 140.3, 140.8, 141.2, 143.9 (quaternary carbons). ^{125}Te{^{1}H} NMR ($CDCl_3$) δ: 644.0 ppm.

The complex **3** could also be obtained when a toluene-methanol solution of [Pd_2(μ-Cl)$_2$$Cl_2$($TeMes_2$)$_2$] was refluxed for 30 min (^{125}Te{^{1}H} NMR ($CDCl_3$) δ: 644.0 ppm).

cis-[$PdCl_2${$MesTeCH_2C_6H_2$(4,6-Me_2)TeMes}] (**4**)

(i) A toluene-methanol solution of **3** was refluxed for 2 hrs and the colour of the solution darkened from orange to dark red. The solvents were evaporated under vacuum and the residue was washed with petroleum ether and extracted with toluene. The solvent was reduced to 2 ml and a few drops of hexane were added which on slow evaporation afforded dark-red crystals, m.p. 185°C (dec). Anal calcd for $C_{27}H_{32}Cl_2PdTe_2$: C, 41.10; H, 4.09%. Found, C, 41.20; H, 3.96%. ^{1}H NMR ($CDCl_3$) δ: 2.02, 2.22, 2.27, 2.50 (each s, 1Me), 2.47, 2.63 (br, s, each 2Me, 2,6-Me of Mes), 3.55 (AX pattern, CH_2 metallated, $\Delta\nu_{AX}$ = 169 Hz, J_{AX} = 11 Hz), 6.25, 6.83 (each s, 1H, 3,5-CH, metallated), 6.93 (s, 3,5-CH, Mes). ^{13}C{^{1}H} NMR ($CDCl_3$) δ: 20.5, 20.8, 25.3, 26.5 (1Me), 27.5, 28.5 (br, 2Me), 117.0, 117.6 (C-Te), 129.0, 129.2, 130.4, 130.9, 140.6, 140.9, 141.1, 142.3, 142.7, 144.3 ppm. ^{125}Te{^{1}H} NMR ($CDCl_3$) δ: 428.2 ppm.

(ii) A toluene-methanol solution of *trans*-[$PdCl_2$($TeMes_2$)$_2$] (150 mg, 0.16 mmol) was refluxed for 2 hrs which resulted into a dark-red solution. After processing in a similar way gave red crystals (45 mg, 35%). The NMR data were consistent with the product obtained in the above preparation.

(iii) To a methanolic solution of Na_2PdCl_4 (200 mg, 0.68 mmol), a toluene solution of $TeMes_2$ (254 mg, 0.69 mmol) was added with stirring and the whole was refluxed for 2 hrs. The solvents were evaporated under reduced pressure and the residue was washed with petroleum ether. The residue was extracted with toluene and recrystallized similarly as above (125 mg, 23%). Analytical and NMR data were consistent to the product obtained through (i).

[Pd_2(μ-OAc)$_2${$CH_2C_6H_2$(4,6-Me_2)TeMes}$_2$] (**5a**)

To a toluene solution of palladium acetate (200 mg, 0.30 mmol) a toluene solution of Mes_2Te (328 mg, 0.89 mmol) was added with stirring at room temperature which continued for 1 hr. The solution was passed through Celite to remove any decomposition products. The solution was concentrated to 5 ml and precipitated by adding petroleum ether. The precipitate was filtered out and washed with a small portion of petroleum ether and then recrystallized from toluene-hexane mixture (1:1, v/v) at room temperature to afford two different types of crystals, *viz* yellow rectangular blocks (260 mg, 55% yield), m. p. 138-139°C (dec) and a few red needle shaped crystals. The two were separated manually. The yellow crystals were characterized as the title complex (**5a**) while the red crystals could be characterized by single crystal X-ray diffraction analysis as a tetra-nuclear complex [Pd(μ-OAc)(μ-TeMes)]$_4$ (**6**). Anal calcd for (**5a**) $C_{40}H_{48}O_4Pd_2Te_2$: C, 45.29; H, 4.56%. Found: C, 44.00; H, 4.31%. ^{1}H NMR ($CDCl_3$, 400MHz) δ: 1.95-2.53 (overlapping singlets due to methyl groups of mesityl and acetate groups), 3.36 (AB pattern, CH_2 metallated, $\Delta\nu_{AB}$ = 71 Hz, J_{AB} = 13 Hz), 6.43, 6.60, 6.64, 6.77, 6.81, 6.86 (each br s of 3,5-CH of mesityl). ^{125}Te{^{1}H} NMR ($CDCl_3$) δ: 554.1 ppm.

$[Pd_2(\mu\text{-OAc})_2\{CH_2C_6H_2(4,6\text{-Me})_2Tetol\text{-}o\}_2]$ (**5b**)

Prepared similar to **5a** and isolated as orange crystals from acetonitrile-diethyl ether at -5°C in 63% yield, m. p. 140°C (dec). Anal calcd for $C_{36}H_{40}O_4Pd_2Te_2$: C, 43.04; H, 4.01%. Found: C, 43.05; H, 3.84%. ^{1}H NMR ($CDCl_3$) δ: 1.88 (s, OAc), 2.04, 2.14, 2.29 (each s, 1Me), 3.09 (AB pattern, CH_2 metallated, $\Delta\nu_{AB}$ = 24.6 Hz, J_{AB} = 12.7 Hz), 6.60 (s, 3,5-CH, Mes), 6.70-6.91 (m), 7.18 (br) (o-tol). ^{13}C{^{1}H} NMR ($CDCl_3$) δ: 21.2, 22.2, 23.4, 24.0, 24.2, (for Me, CH_2), 118.9 (C-Te), 126.6, 127.2, 128.7, 128.9, 130.4, 132.6, 140.6, 141.0, 142.2, 179.8 (C=O);^{125}Te{^{1}H} NMR ($CDCl_3$) δ: 592.2 ppm

$[Pd_2(\mu\text{-OAc})_2\{CH_2C_6H_2(4,6\text{-Me}_2)TePh\}_2]$ (**5c**)

Prepared similar to **5a** as a red powder in 45% yield, m. p. 147°C (dec). The complex tends to decompose and hence gave variable analysis. ^{125}Te{^{1}H} NMR ($CDCl_3$) δ: 690.4 ppm.

X-ray Crystallography

Single crystal X-ray data on *trans*-$[PdCl_2(TeMes_2)_2]$ (**1a**), $[Pd_2(\mu\text{-Cl})_2Cl_2(TeMes_2)_2]$.2 acetone (**2a**.2 acetone), *cis*-$[PdCl_2\{MesTeCH_2C_6H_2(4,6\text{-Me}_2)TeMes\}]$ (**4**), $[Pd_2(\mu\text{-OAc})_2\{CH_2C_6H_2(4,6\text{-Me}_2)TeMes\}_2]$.toluene (**5a**.toluene), $[Pd_2(\mu\text{-OAc})_2\{CH_2C_6H_2(4,6\text{-Me}_2)Tetol\text{-}o\}_2]$ (**5b**) and $[Pd(\mu\text{-OAc})(\mu\text{-TeMes})]_4$ (**6**) were collected on a Agilent SuperNova or Bruker APEX-II CCD diffractometer. Crystallographic data, together with data collection and refinement details are given in Tables S1 and S2 of supplementary material. All the data were corrected for Lorentz and polarization effects. The structures were solved by direct methods[44] and expanded using Fourier technique.[45] Hydrogen atoms were added to the parent atom with idealized geometry and refined isotropically. Molecular structures were drawn using ORTEP.[46]

Conclusion

In summary we have isolated a number of complexes formed in the reactions of telluro ethers with palladium precursors. By subtle variation in reaction conditions a variety of complexes, such as addition complexes (e.g. *trans*-$[PdCl_2(TeMes_2)_2]$), complexes showing secondary Pd…H interactions (e.g. $[Pd_2(\mu\text{-Cl})_2Cl_2(TeMes_2)_2]$), cyclometallated complexes (e.g. $[Pd_2(\mu\text{-OAc})_2\{CH_2C_6H_2(4,6\text{-Me}_2)TeMes\}_2]$), complexes formed by Te-C bond cleavage (e.g. [Pd(μ-OAc)(μ-TeMes)]$_4$) and finally leading to palladium telluride (Pd_7Te_3), have been isolated and structurally characterized. The cyclopalladation of telluroether ligands *via* benzyl C-H bond activation has also been demonstrated for the first time.

Supporting Information

CCDC Nos. 996454-996460 for *trans*-[PdCl$_2$(TeMes$_2$)$_2$].2CH$_3$CN (**1a**.2CH$_3$CN) (996459), *trans*-[PdCl$_2$(TeMes$_2$)$_2$].toluene (**1a**.toluene) (996458), [Pd$_2$(μ-Cl)$_2$Cl$_2$(TeMes$_2$)$_2$].2acetone (**2a**.2acetone) (996455), *cis*-[PdCl$_2${MesTeCH$_2$C$_6$H$_2$(4,6-Me$_2$)TeMes}] (**4**) (996460), [Pd$_2$(μ-OAc)$_2${CH$_2$C$_6$H$_2$(4,6-Me$_2$)TeMes}$_2$].toluene (**5a**.toluene) (996457), [Pd$_2$(μ-OAc)$_2${CH$_2$C$_6$H$_2$(4,6-Me$_2$)Tetol-*o*}$_2$] (**5b**) (996456) and [Pd(μ-OAc)(μ-TeMes)]$_4$ (**6**) (996454), respectively contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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Table 1. Selected bond lengths (Å) and bond angles (°) for monoclinic form of *trans*-[$PdCl_2(TeMes_2)_2$].2MeCN (**1a**.2MeCN)

Pd1-Cl1	2.3006(14)	Te1-C1	2.130(5)
Pd1-Te1	2.5817(3)	Te1-C10	2.137(5)
Cl1-Pd1-Cl1^i	180.00(11)	C1-Te1-Pd1	110.36(13)
Cl1-Pd1-Te1	83.78(4)	C10-Te1-Pd1	106.71(13)
Cl1-Pd1-Te1^i	96.22(4)	C1-Te1-C10	102.5(2)
Cl1^i-Pd1-Te1	96.22(4)	Te1-Pd1-Te1^i	180.000(15)
Cl1^i-Pd1-Te1^i	83.78(4)		

Table 2. Selected bond lengths (Å) and bond angles (°) for triclinic form of *trans*-[$PdCl_2(TeMes_2)_2$].toluene (**1a**.toluene)

Pd1-Cl1	2.290(2)	Te1-C1	2.149(6)
Pd1-Cl2	2.292(2)	Te1-C10	2.137(6)
Pd1-Te1	2.5951(6)	Te2-C19	2.143(8)
Pd1-Te2	2.5908(6)	Te2-C28	2.126(8)
Cl1-Pd1-Cl2	177.61(10)	C1-Te1-Pd1	109.92(17)
Cl1-Pd1-Te1	83.86(5)	C10-Te1-C1	100.2(3)
Cl1-Pd1-Te2	95.50(5)	C10-Te1-Pd1	113.57(18)
Cl2-Pd1-Te1	95.78(6)	C19-Te2-Pd1	112.0(2)
Cl2-Pd1-Te2	84.19(6)	C28-Te2-C19	100.2(3)
Te2-Pd1-Te1	163.97(3)	C28-Te2-Pd1	114.2(2)

Table 3. Selected bond lengths (Å) and bond angles (°) for $[Pd_2(\mu\text{-}Cl)_2Cl_2(TeMes_2)_2]$.2acetone (**2**.2acetone)

Cl1-Pd1	2.310(4)	C1-Te1	2.156(13)
Cl1-Pd1^{i}	2.403(4)	C10-Te1	2.119(14)
Cl2-Pd1	2.290(4)	Pd1-Te1	2.5067(13)
		Pd1-Pd1^{i}	3.421
Cl1-Pd1-Cl1^{i}	86.96(13)	Cl2-Pd1- Te1	83.47(11)
Cl1-Pd1-Te1	96.25(10)	Pd1-Te1-C1	108.4(3)
Cl1^{i}-Pd1- Te1	174.08(12)	C1-Te1-C10	97.6(5)
Cl1-Pd1-Cl2	177.78(17)	Pd1-Te1-C10	111.0(4)
Cl1^{i}-Pd1-Cl2	93.14(13)	Pd1-Cl1-Pd1^{i}	93.04(13)

Table 4. Selected bond lengths (Å) and bond angles (°) for *cis*-[PdCl$_2${MesTeCH$_2$C$_6$H$_2$(4,6-Me$_2$)TeMes}] (**4**)

Pd1-Te1	2.5402(3)	C1-Te1	2.151(4)
Pd1-Te2	2.5137(3)	C10-Te1	2.135(4)
Pd1-Cl1	2.3419(10)	C16-Te2	2.166(4)
Pd1-Cl2	2.3389(9)	C19-Te2	2.133(3)
Cl1-Pd1-Te1	85.97(3)	C1-Te1-Pd1	110.96(10)
Cl1-Pd1-Te2	172.31(3)	C10-Te1-Pd1	97.38(9)
Cl1-Pd1-Cl2	93.85(4)	C10-Te1-C1	100.76(14)
Cl2-Pd1-Te1	177.01(3)	C16-Te2-Pd1	105.18(9)
Cl2-Pd1-Te2	85.30(3)	C19-Te2-Pd1	113.44(9)
Te2-Pd1-Te1	95.278(11)	C19-Te2-C16	94.41(13)

Table 5. Selected bond lengths (Å) and bond angles (°) for $[Pd_2(\mu\text{-}OAc)_2\{CH_2C_6H_2(4,6\text{-}Me_2)TeMes\}_2]$.toluene (**5a**.toluene).

Pd1-O1	2.108(7)	Pd2-O2	2.097(7)
Pd1-O3	2.238(7)	Pd2-O3	2.272(8)
Pd1-C7	2.027(9)	Pd2-C27	1.999(10)
Pd1-Te1	2.4706(10)	Pd2-Te2	2.4845(9)
Te1-C1	2.133(10)	Te2-C19	2.090(10)
Te1-C10	2.140(11)	Te2-C28	2.152(9)
Pd1…Pd2	3.0831(10)		
O1-Pd1-C7	86.5(4)	O2-Pd2-C27	86.9(3)
O3-Pd1-O1	87.6(3)	O3-Pd2-O2	89.4(3)
Te1-Pd1-O1	172.29(19)	Te2-Pd2-O2	173.0(2)
Te1-Pd1-O3	98.8(2)	Te2-Pd2-O3	97.0(2)
O3-Pd1-C7	173.9(4)	O3-Pd2-C27	175.7(3)
Te1-Pd1-C7	86.9(3)	Te2-Pd2-C27	86.8(3)
Pd1-Te1-C1	94.0(3)	Pd2-Te2-C19	93.7(3)
Pd1-Te1-C10	107.4(3)	Pd2-Te2-C28	105.8(3)
Pd1-C7-C2	122.2(7)	Pd2-C27-C20	122.9(7)
Pd1-O1-C37	124.9(7)	Pd2-O2-C37	129.4(7)
Pd1-O3-C39	130.4(11)	Pd2-O3-C39	116.7(13)
		Pd2-O3-Pd1	86.3(3)

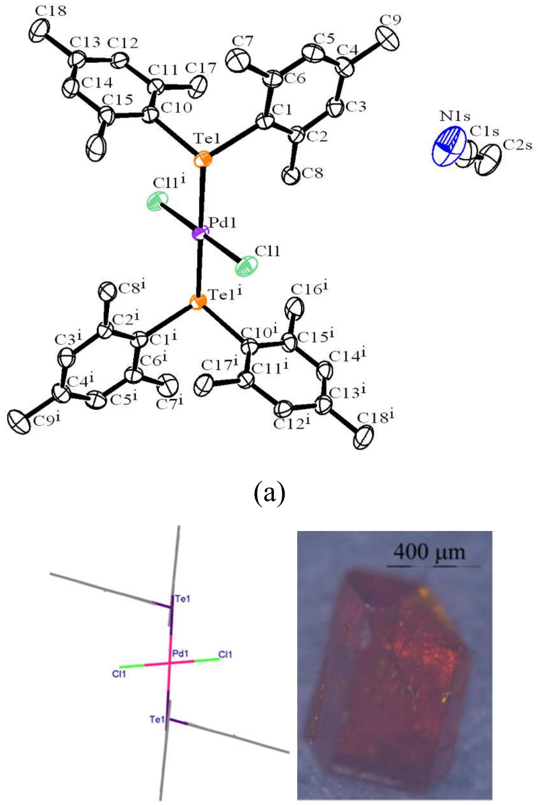
Table 6. Selected bond lengths (Å) and bond angles (°) for $[Pd_2(\mu\text{-}OAc)_2\{CH_2C_6H_2(4,6\text{-}Me)_2Tetol\text{-}o\}_2]$ (**5b**).

Te1-Pd1	2.4979(13)	Te2-Pd2	2.4926(13)
C7-Pd1	1.980(15)	C23-Pd2	2.007(14)
O1-Pd1	2.142(10)	O2-Pd2	2.097(10)
O4-Pd1	2.103(11)	O3-Pd2	2.164(10)
C1-Te1	2.120(13)	C17-Te2	2.104(12)
C10-Te1	2.122(12)	C26-Te2	2.152(13)
O1-C33	1.261(15)	O3-C35	1.248(18)
O2-C33	1.225(16)	O4-C35	1.246(18)
		Pd1…Pd2	2.8677(14)
O1-Pd1-O4	91.7(4)	O2-Pd2-O3	91.5(4)
O1-Pd1-C7	177.6(5)	O2-Pd2-C23	87.1(5)
O1-Pd1-Te1	94.2(3)	O2-Pd2-Te2	168.5(3)
O4-Pd1-C7	89.7(5)	O3-Pd2-C23	178.4(5)
O4-Pd1-Te1	173.9(3)	O3-Pd2-Te2	95.1(3)
C7-Pd1-Te1	84.4(4)	C23-Pd2-Te2	86.2(4)
Pd1-Te1-C1	92.4(4)	Pd2-Te2-C17	93.3(3)
Pd1-Te1-C10	106.6(3)	Pd2-Te2-C26	100.9(3)
Pd1-O1-C33	123.3(9)	Pd2-O2-C33	128.0(9)
Pd1-O4-C35	124.2(9)	Pd2-O3-C35	124.7(10)
C1-Te1-C10	99.6(5)	C17-Te2-C26	98.1(5)

Table 7. Selected bond lengths (Å) and bond angles (°) of [Pd(μ-OAc)(μ-TeMes)]$_4$ (**6**)

Pd1-O1	2.130(5)	Pd2-O2	2.117(5)
Pd1-O3	2.104(5)	Pd2-O4	2.100(5)
Pd1-Te1	2.5404(7)	Pd2-Te2	2.5299(6)
Pd1-Te2^{i}	2.5448(6)	Pd2-Te1^{i}	2.5374(7)
Te1-C1	2.149(7)	Te2-C10	2.154(7)
Te2^{i}-C10^{i}	2.154(7)	Te1i-C1^{i}	2.149(7)
Pd1^{i}-O1^{i}	2.130(5)	Pd2i-O2^{i}	2.117(5)
Pd1^{i}-O3^{i}	2.104(5)	Pd2i-O4^{i}	2.100(5)
Pd1^{i}-Te1^{i}	2.5404(7)	Pd2^{i}-Te1	2.5374(7)
Pd1^{i}-Te2	2.5448(6)	Pd2^{i}-Te2^{i}	2.5299(6)
Pd1···Pd2	2.9474(7)	Pd2^{i}-Pd1^{i}	2.9474(7)
Pd1…Pd2^{i}	3.695	Pd2-Pd1^{i}	3.695

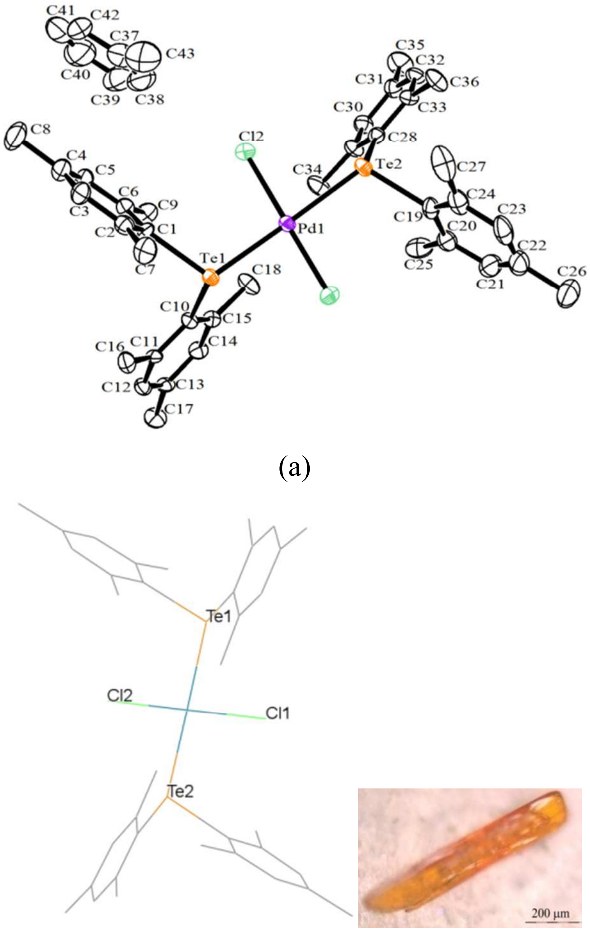
O1-Pd1-O3	87.7(2)	O2-Pd2-O4	88.3(2)
O1-Pd1-Te1	176.59(15)	O2-Pd2-Te2	177.60(15)
O1-Pd1-Te2^{i}	96.00(15)	O2-Pd2-Te1^{i}	96.20(16)
O3-Pd1-Te1	94.85(19)	O4-Pd2-Te2	93.78(17)
O3-Pd1-Te2^{i}	175.54(17)	O4-Pd2-Te1^{i}	175.42(18)
Te1-Pd1-Te2^{i}	81.347(19)	Te2-Pd2-Te1^{i}	81.694(19)
Pd1-Te1-C1	102.82(17)	Pd2-Te2-C10	103.63(17)
Pd1-Te2^{i}-C10^{i}	106.78(18)	Pd2-Te1^{i}-C1^{i}	107.59(18)
Pd1-Te1-Pd2	93.40(2)	Pd2-Te2-Pd1^{i}	93.47(2)
Pd1-Te2^{i}-Pd2^{i}	93.47(2)	Pd2-Te1^{i}-Pd1^{i}	93.40(2)
O1^{i}-Pd1^{i}-O3^{i}	87.7(2)	O2^{i}-Pd2^{i}-O4^{i}	88.3(2)
O1^{i}-Pd1^{i}-Te2	96.00(15)	O2^{i}-Pd2^{i}-Te1	96.20(16)
O1^{i}-Pd1^{i}-Te1^{i}	176.59(15)	O2^{i}-Pd2^{i}-Te2^{i}	93.78(17)
O3^{i}-Pd1^{i}-Te2	175.54(17)	O4^{i}-Pd2^{i}-Te1	175.42(18)
O3^{i}-Pd1^{i}-Te1^{i}	94.85(19)	O4^{i}-Pd2^{i}-Te2^{i}	93.78(17)
Te2-Pd1^{i}-Te1^{i}	81.347(19)	Te1-Pd2^{i}-Te2^{i}	81.694(19)



(a)

(b) (c)

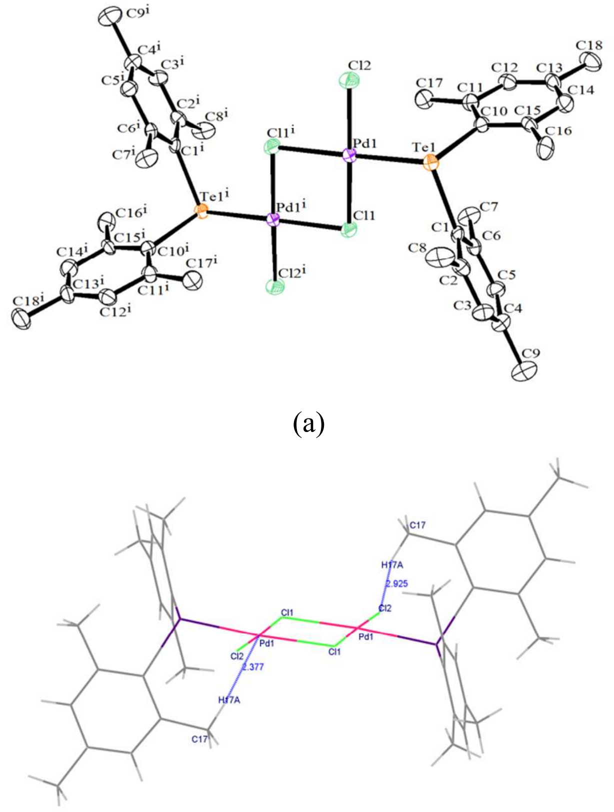
Fig 1. (a) ORTEP diagram of *trans*-[PdCl$_2$(TeMes$_2$)$_2$].2MeCN (**1a**.2MeCN) (25% probability). Hydrogen atoms are omitted for clarity, (b) view perpendicular to the Pd1 square plane, (c) Optical microscope image of **1a**.2MeCN crystallized from acetonitrile-diethyl ether.



(a)

(b) (c)

Fig 2. ORTEP diagram of *trans*-[$PdCl_2(TeMes_2)_2$].toluene (**1a**.toluene) (25% probability). Hydrogen atoms are omitted for clarity, (b) view perpendicular to the Pd1 square plane, (c) Optical microscope image of **1a**.toluene crystallized from toluene-hexane mixture.



(a)

(b)

Fig 3. ORTEP diagram of [$Pd_2(\mu\text{-}Cl)_2Cl_2(TeMes_2)_2$].2acetone (**2**.2acetone) (25% probability). Hydrogen atoms and solvent molecules are omitted for clarity, (b) intra molecular interactions

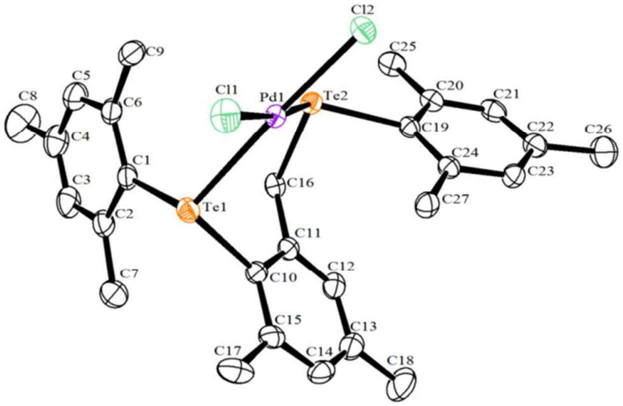


Fig 4. ORTEP diagram of *cis*-[PdCl$_2${MesTeCH$_2$C$_6$H$_2$(4,6-Me$_2$)TeMes}] (**4**) (25% probability). Hydrogen atoms are omitted for clarity.

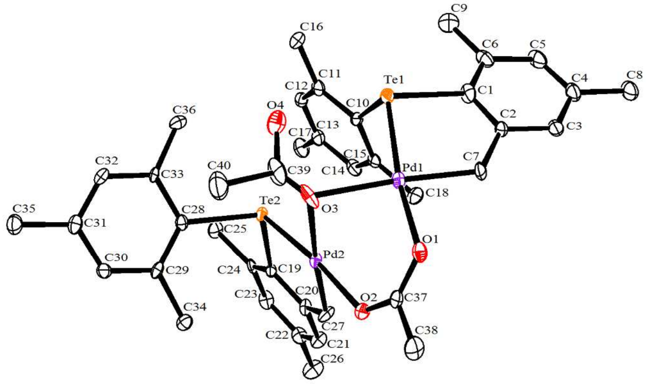


Fig 5. ORTEP diagram of $[\mathrm{Pd_2}(\mu\text{-OAc})_2\{\mathrm{CH_2C_6H_2}(4,6\text{-Me}_2)\mathrm{TeMes}\}_2]$.toluene (**5a**.toluene) (25% probability). Hydrogen atoms and toluene molecule are omitted for clarity.

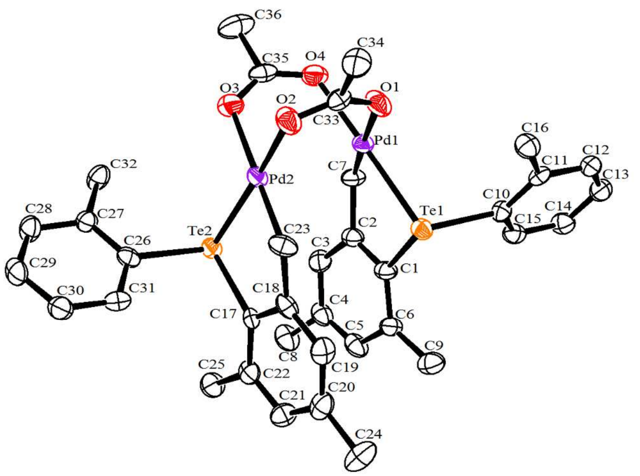
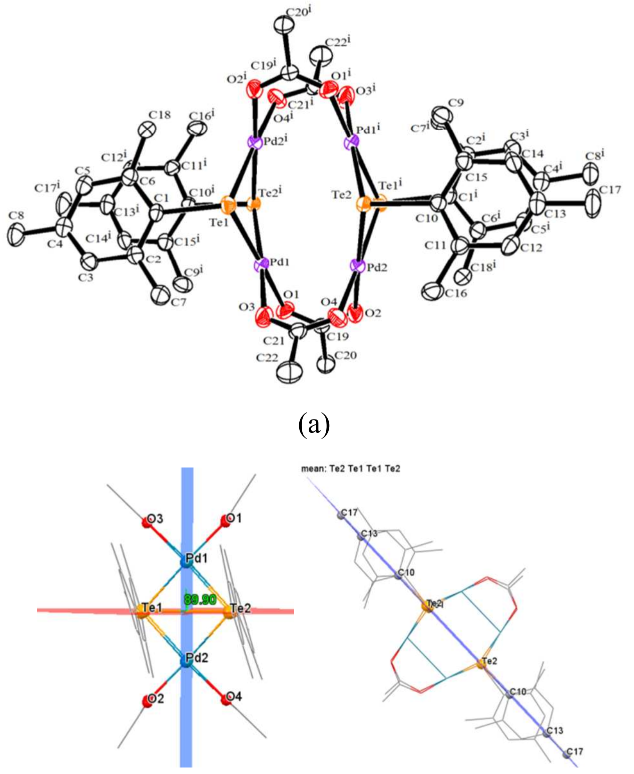


Fig 6. ORTEP diagram of $[\mathrm{Pd_2(\mu\text{-}OAc)_2\{CH_2C_6H_2(4,6\text{-}Me_2)Tetol}\text{-}\mathit{o}\}_2]$ (**5b**) (25% probability). Hydrogen atoms are omitted for clarity.



(a)

(b) (c)

Fig 7. (a) ORTEP diagram of [Pd(μ-OAc)(μ-TeMes)]$_4$ (**6**) (25% probability). Hydrogen atoms are omitted for clarity (b and c) orientations of atomic planes within the molecule

Table of Contents - Synopsis

Reactions of telluro ethers with common cyclopalladation precursors such as Na_2PdCl_4, $PdCl_2(PhCN)_2$ and $[Pd(OAc)_2]_3$, gave a variety of palladium complexes ranging from mononuclear, trans-$[PdCl_2(TeAr_2)_2]$ to binuclear $[Pd_2(\mu\text{-}Cl)_2Cl_2(TeArAr`)_2]$, cyclopalladated $[Pd_2(\mu\text{-}OAc)_2\{ArTeCH_2C_6H_2(4,6\text{-}Me_2)\}_2]$ and products formed by Te-C bond cleavage.

Table of Contents - Artwork