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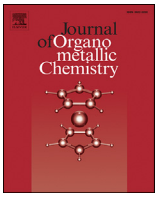

Role of anagostic interactions in cycloplatination of telluroethers: Synthesis and structural characterization

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ABSTRACT

Reactions of K_2PtCl_4 with TeRR′ gave complexes of composition $[PtCl_2(TeRR')_2]$ (R/R′ = Ph_2(**1a**), *o*-tol$_2$ (**1b**), Mes_2(**1c**), Ph/Mes (**1d**), *o*-tol/Mes (**1e**)). The complex $[PtCl_2(TeMes_2)_2]$ in refluxing THF afforded a mononuclear cyclometalated complex $[PtCl\{(CH_2C_6H_2Me_2\text{-}4,6)TeMes\}(TeMes_2)]$ (**2**). It tends to remain in equilibrium with a binuclear derivative $[Pt(\mu\text{-}Cl)\{(CH_2C_6H_2Me_2\text{-}4,6)TeMes\}]_2$ (**3**) in $CDCl_3$ solution. The complexes **1d** and **1e** did not undergo cyclometalation reaction under similar reaction conditions. The **2** on treatment with PPh_3 gave $[PtCl\{(CH_2C_6H_2Me_2\text{-}4,6)TeMes\}(PPh_3)]$ (**4**). All the complexes have been characterized by elemental analysis and NMR (^1H, ^{31}P, ^{125}Te, ^{195}Pt) spectroscopy. Anagostic interactions have been recognised for facilitation of cyclometalation reactions. The molecular structures of *trans*-$[PtCl_2(TeMes_2)_2]$ **(1c)**, *trans*-$[PtCl_2(PhTeMes)_2]$ **(1d)**, *trans*-$[PtCl_2(o\text{-}tolTeMes)_2]$ **(1e)**, $[PtCl\{(CH_2C_6H_2Me_2\text{-}4,6)TeMes\}(TeMes_2)]$ (**2**) and $[PtCl\{(CH_2C_6H_2Me_2\text{-}4,6)TeMes\}(PPh_3)]$ (**4**) have been established unambiguously by single crystal X-ray diffraction analyses.

1. Introduction

The coordination chemistry of platinum group metals with heavier chalcogen (Se or Te) ligands has witnessed a rapid growth during the past two decades or so [1–6]. The sustained and growing interest in these complexes stem from their utility in diverse areas like precursors for metal chalcogenides [7,8], homogeneous catalysts for organic transformations [9,10], in materials science [11] and as antitumour agents [12].

The coordination chemistry of tellurium ligands is gaining momentum as larger atomic radius and increased metallic character and high nucleophilicity of tellurium coupled with weak Te–C bond make their chemistry distinct from analogous sulphur and selenium ligands. Accordingly coordination chemistry of different families of tellurium ligands, such as diorganoditellurides (R_2Te_2) [13], diorganotellurides (telluroethers, R_2Te), tellurolates (RTe^-) [5], telluride (Te^{2-}) [1] and polytellurides (Te_n^{2-}) [14], has been explored. Among them telluroethers have been used as ligands for a long time and in fact the first telluroether complex, $[PtCl_2(TeBz_2)_2]$ was isolated by Fritzmann a century back [15]. Since then several simple telluroether complexes have been isolated and characterized [16–18]. Of late complexes with hybrid [19–21] and bidentate chelating telluroethers [17,22] have been synthesized. In several preparations involving telluroethers, products formed by the facile cleavage of Te–C bond, transmetallation as well as complete decomposition are well established. For instance, the reactions of palladium(0)/platinum(0) complexes, $[M(PEt_3)_n]$ (M = Pd or Pt; n = 3 or 4) with R_2Te afford oxidative addition products, *trans*-$[M(R)(TeR)(PEt_3)_2]$ [23]. Dealkylation of coordinated telluroether in *cis*-$[PdI_2\{o\text{-}MeTeC_6H_4TeMe\}]$ yielding a tetranuclear complex, $[Pd(\{o\text{-}C_6H_4(TeMe)Te\}I]_4$ has been reported [24]. Singh and co-workers have described transmetalation of telluroether in the reaction of $Te(C_6H_4CH_2NMe_2)_2$ with $PdCl_2(COD)$ affording a mixture of transmetalated products, $[Pd(\mu\text{-}Cl)(C_6H_4CH_2NMe_2)]_2$ and $[Te(\mu\text{-}Cl)(C_6H_4CH_2NMe_2)]_2$ [25]. In no case cyclometalation of telluroether ligand is reported. In an attempt to metalate di-*o*-tolyl telluride, Singh and co-workers isolated Te–C bond cleaved products, $[Pd(OAc)_2\{o\text{-}tolTe)_2O\}]$ and $[o\text{-}tol_2Pd_3(\mu\text{-}OAc)_4\{Te(o\text{-}tol)_2\}_2]$ (*o*-tol = *ortho*-tolyl) [26]. Recently, we have reported cyclopalladation of dimesityl telluride (Mes_2Te) using simple palladation precursors, like Na_2PdCl_4, $[Pd(OAc)_2]_3$ [27]. In general cyclometalation with palladium is quite facile whereas similar reactions with metals like platinum are often sluggish [1]. To assess the generality of cyclometalation of telluroether ligands, we have

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examined reactions with platinum complexes. Cyclometalation of telluroether ligands is shown to be equally facile with platinum. It is noted that anagostic interaction between the telluroether ligand and the metal centre facilitate cyclometalation. The results of this work are reported herein.

2. Results and discussion

The reactions of K_2PtCl_4 with telluroethers afforded $[PtCl_2\{TeRR'\}_2]$ (R = R′ = Ph (**1a**); *o*-tol (**1b**); Mes (**1c**); R ≠ R′ = Ph, Mes (**1d**) and *o*-tol, Mes (**1e**)). The complexes **1a**, **1b**, **1d** and **1e** on refluxing in THF for an hour did not show any change while the complex **1c** on refluxing in THF yielded a mononuclear complex $[PtCl\{(CH_2C_6H_2Me_2\text{-}4,6)TeMes\}(TeMes_2)]$ (**2**) in which one of the telluroether ligand is cyclometalated (Scheme 1). The complex **1c,** however, remained unchanged in refluxing toluene-methanol mixture in contrast to analogous palladium derivative which cyclometalate under these conditions [27]. Surprisingly, metalation of the mesityl methyl group in **1e** does not take place even in refluxing toluene-methanol mixture. Such contrasting behaviour of **1c**, **1d** and **1e** is evident from the non-bonding Pt⋯H interactions (anagostic interactions [28]) (see later).

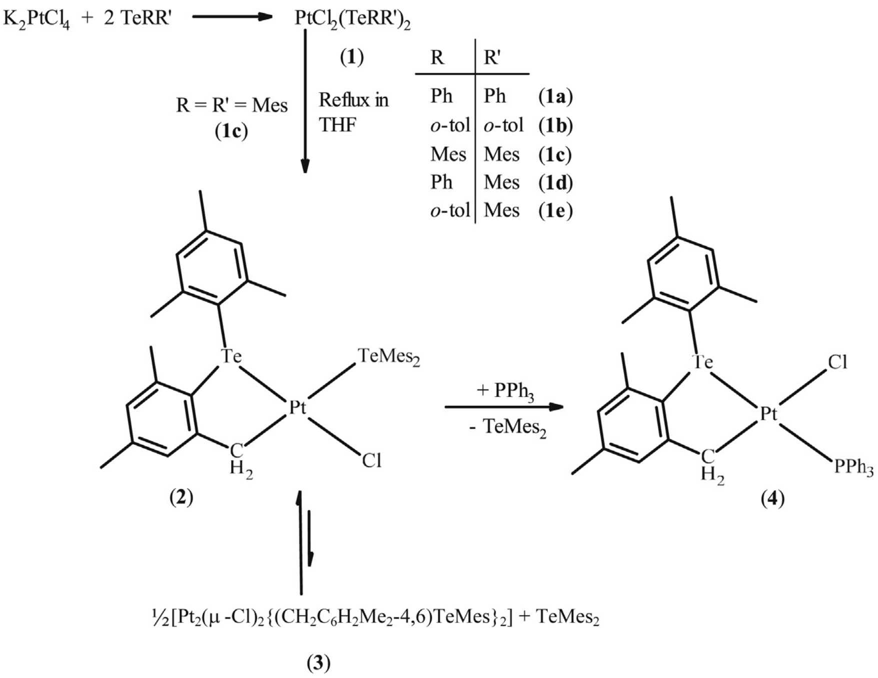
Monodentate telluroether complexes, $[PtCl_2(TeRR')_2]$ (R = R′ = Me, Et, ^{n}Pr, CH_2CH_2Ph, CH_2SiMe_3, Ph) are known to be formed as *cis* isomer which in solution exists as a mixture of *cis* and *trans* isomers [17,18,29,30]. The relative ratio of *cis* and *trans* isomers in solution depends on the nature of the organic groups attached to tellurium and the solvent. The $^{125}Te\{^1H\}$ and $^{195}Pt\{^1H\}$ NMR spectra of **1a** and **1b** in $CDCl_3$ exhibited two sets of resonances attributable to *cis* and *trans* isomeric forms; the *cis* being the predominant isomer. This is in accordance with the earlier observations [17]. The $^{125}Te\{^1H\}$ and $^{195}Pt\{^1H\}$ NMR spectra of **1c** displayed single resonances. The magnitude of $^1J(^{195}Pt\text{–}^{125}Te)$ is in accordance with the *trans* form [17,18,30]. The spectra of **1d** and **1e** (Supplementary information, Figs. S1 and S2), however, exhibited two closely spaced resonances. Tellurium with stereo-chemically active lone pair of electrons is chiral and therefore four enantiomers (*viz.* RR/SS and RS/SR) are expected for each (*cis* and *trans*) isomeric forms. The observed magnitude of $^1J(^{195}Pt\text{–}^{125}Te)$ coupling constants for two resonances are in conformity with the *trans* form [17,18] and are assigned to the expected enantiomers.

The $^{125}Te\{^1H\}$ NMR spectrum (Fig. 1) of **2** displayed five signals including one for free telluroether ligand ($TeMes_2$ at δ 260 ppm). The other four resonances were flanked with platinum satellites. The $^{195}Pt\{^1H\}$NMR spectrum exhibited two signals at −4286 (major) and −4450 (minor) ppm. The observed spectral pattern is indicative of existence of two species in solution, viz. **2** and a dimeric complex **3** formed by dissociation of the coordinated telluroether ligand from **2** (Scheme 1). Thus the $^{125}Te\{^1H\}$ NMR resonance at 336 ppm with $^1J(^{195}Pt\text{–}^{125}Te)$ of 612 Hz is assigned to the coordinated $TeMes_2$ while the resonance at 592 ppm with $^1J(^{195}Pt\text{–}^{125}Te)$ of 1528 Hz is attributed to metalated tellurium ligand of **2**. The remaining ^{125}Te NMR signals at 600 ppm with $^1J(^{195}Pt\text{–}^{125}Te)$ of 1192 Hz and 424 with $^1J(^{195}Pt\text{–}^{125}Te)$ of 788 Hz could be due to *cis* and *trans* isomers of **3**. Dissociation of $TeMes_2$ from **2** could be due to weakening of Pt–Te linkage owing to the presence of strong *trans* influencing metalated carbon atom *trans* to it.

To arrest dissociation of **2** in solution, the coordinated telluroether ligand was substituted by triphenylphosphine to give $[PtCl\{(CH_2C_6H_2Me_2\text{-}4,6)TeMes\}(PPh_3)]$ (**4**). The **4** displayed a single ^{31}P resonance with associated platinum satellites ($^1J(^{195}Pt\text{–}^{31}P)$ = 3945 Hz). The ^{125}Te NMR spectrum exhibited a doublet at δ 555 ppm due to coupling with phosphorus nucleus ($^2J(^{125}Te\text{–}^{31}P)$ = 455 Hz) (Supplementary information Fig. S3). The doublet was flanked by platinum satellites with $^1J(^{195}Pt\text{–}^{125}Te)$ = 677 Hz. The observed magnitude of coupling constants is indicative of a configuration with the neutral ligands (P and Te) *trans* to each other which is further confirmed by X-ray structural analysis (see later). It is worth noting that in **2** the neutral ligands (two Te donor atoms) are *cis* disposed.

3. Crystallography

The molecular structures of *trans*-$[PtCl_2\{Te(R)Mes\}_2]$ (R = Mes (**1c**), Ph (**1d**) or *o*-tol (**1e**)), $[PtCl\{(CH_2C_6H_2Me_2\text{-}4,6)$



Scheme 1. Reactions of K_2PtCl_4 with telluroethers.

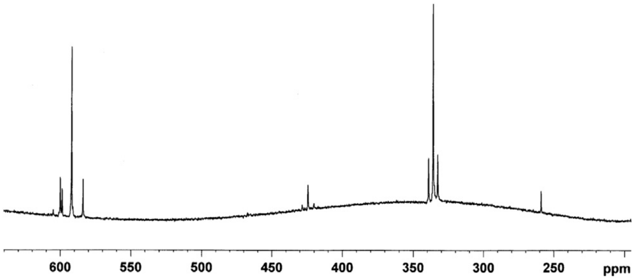


Fig. 1. $^{125}Te\{^1H\}$ NMR spectrum of$[PtCl\{(CH_2C_6H_2Me_2\text{-}4,6)TeMes\}(TeMes_2)]$ (**2**) in $CDCl_3$.

$TeMes\}(TeMes_2)]$ (**2**) and $[PtCl\{(CH_2C_6H_2Me_2\text{-}4,6)TeMes\}(PPh_3)]$ (**4**) were established by single crystal X-ray diffraction analyses and are shown in Figs. 2–6. Selected inter-atomic parameters are summarized in Tables 1–5. The central metal atom in these complexes adopts a square planar configuration. The Te–C distances (2.107 (12) - 2.151 (14) Å) are as expected [31,32].

There are two different types of molecules in the crystal lattice of **1c** which differ slightly in the relative orientation of the mesityl rings in the two molecules. Interestingly different polymorphic forms for the corresponding palladium complex, $[PdCl_2(TeMes_2)_2]$ have been isolated and structurally characterized [27]. The dichloro complexes $[PtCl_2\{Te(R)Mes\}_2]$ (**1d** and **1e**) are iso-structural and adopt a *trans* configuration defined by two neutral telluroether ligands and two chloro ligands. The Pt–Te and Pt–Cl distances in all these complexes are in accordance with the *trans* configured telluroether complexes, such as *trans*-$[PtCl_2\{Te(CH_2CH_2)_2O\}_2]$ (Pt–Te = 2.5945 (3)Å) [31], *trans*-$[PtCl_2\{Te(CH_2SiMe_3)_2\}_2]$ (Pt–Te = 2.5807 (6) Å; Pt–Cl = 2.309 (2) Å [18] and $[PtCl\{(TeC_6H_4OEt\text{-}4)CH_2CH_2\}_2NH)]Cl$ (Pt-Te$_{av}$ = 2.56 Å; Pt–Cl = 2.306 (4) Å) [33]. However in *cis* configured complexes the Pt–Te bond is shortened as a consequence the Pt–Cl bond is elongated (*e.g., cis*-$[PtCl_2\{(Bu^nTeCH_2)_2SiMe_2\}]$; Pt-Te$_{av}$ = 2.50 Å, Pt-Cl$_{av}$ = 2.34 Å [34]. Lengthening of Pt–Te distance in the *trans* complexes is in accordance with the stronger *trans* influence of tellurium than that of chloride. One of the Te–C bonds is marginally shorter than the other Te–C bond in the coordinated telluroether. The mesityl rings of telluroether ligands in **1d** and **1e** lie opposite each other with respect to the metal square plane.

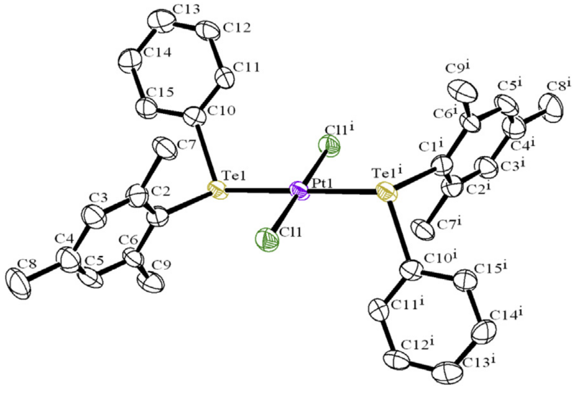


Fig. 3. ORTEP drawing of trans-$[PtCl_2\{Te(Ph)Mes\}_2]$ (**1d**) with atomic numbering scheme (H atoms omitted for clarity).

The interesting feature in the structure of **1c** is the Pt … H–C interactions which are significantly longer in the case of **1d** and **1e**. These interactions can be characterized as anagostic interactions which have M···H distances of ~2.3–2.9 Å and M-H-C angles of ~110–170° [28] and have implication in C–H bond activation. In general, based on the M … H distance and the M … H–C angle three different types of M … H–C interaction are encountered, viz. i) agostic, ii) anagostic and iii) hydrogen bonding. The former is usually encountered in the case of d^6 metal complexes while the anagostic interactions are noted with d^8 square planar complexes. Clearly the presence of anagostic interaction in **1c** facilitate C–H bond activation leading to cyclometalation, while the absence of such interaction, as in **1d** and **1e**, does not result in cyclometalation. A similar situation has been reported for palladium complexes. The $[PdCl_2(TeMes_2)_2]$ cyclometalate in refluxing toluene-methanol solution while $[PdCl_2(Te(o\text{-}tolMes)_2]$ and $[PdCl_2(o\text{-}tol_2Te)_2]$ fail to metalate under similar conditions [27].

The platinum atom in $[PtCl\{(CH_2C_6H_2Me_2\text{-}4,6)TeMes\}(TeMes_2)]$ (**2**) adopts a distorted square planar configuration and is defined by "Te_2CCl" donor set with the neutral telluroether ($TeMes_2$) ligand

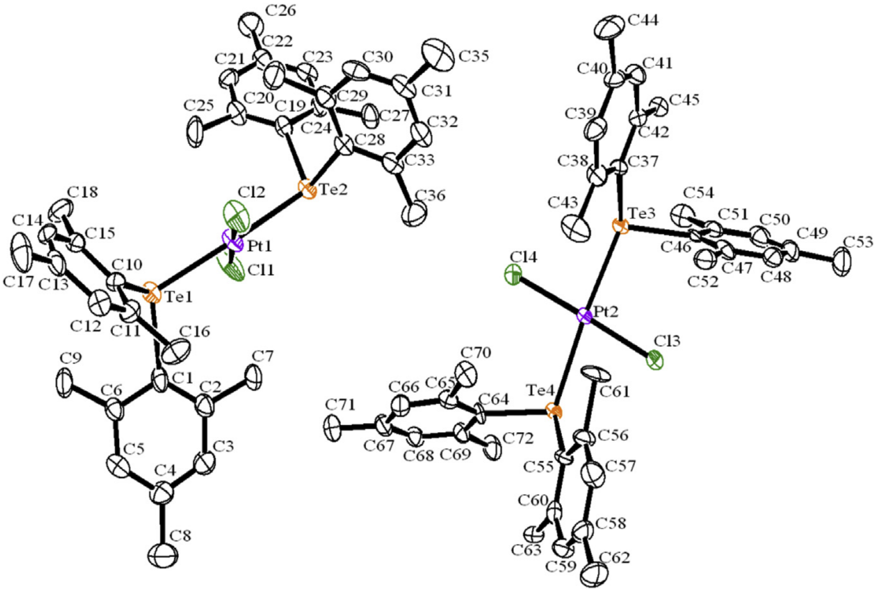


Fig. 2. ORTEP drawing of *trans*-$[PtCl_2(TeMes_2)_2]$ (**1c**) with atomic numbering scheme (H atoms omitted for clarity).

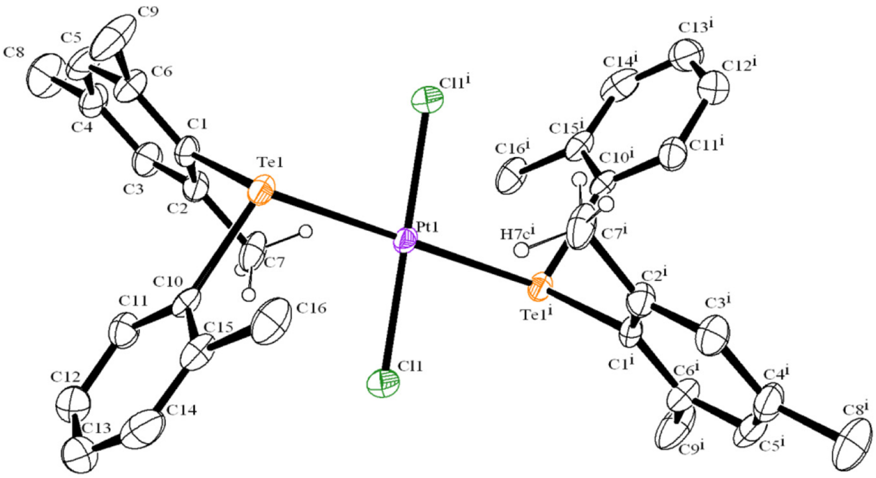


Fig. 4. ORTEP drawing of *trans*-[PtCl$_2${Te(*o*-tol)Mes}$_2$] (**1e**) with atomic numbering scheme (H atoms omitted for clarity).

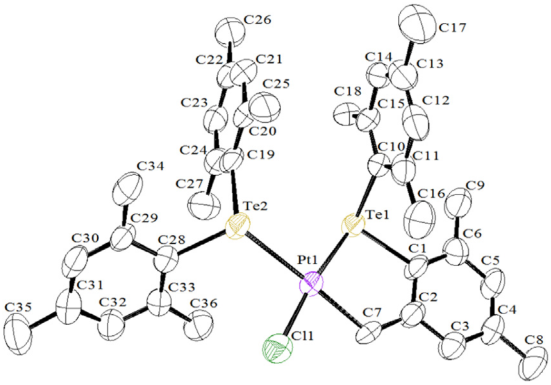


Fig. 5. ORTEP drawing of [PtCl{(CH$_2$C$_6$H$_2$Me$_2$-4,6)TeMes}(TeMes$_2$)] (**2**) with atomic numbering scheme (H atoms omitted for clarity).

trans to the Pt-Carbon bond. The Pt—Te distance of metalated telluroether ligand is shorter than the neutral TeMes$_2$. This is owing to the strong *trans* influence of the cyclometalated carbon and weak *trans* influence of the chloride. The Pt—C distance (2.084(12) Å) is well in agreement with the values reported for metalated platinum complexes [1]. The C—Te—C angle (~101°) on coordination is little influenced from its value for the free ligand, TeMes$_2$ (101.0(1)°) [35]. The mesityl ring on Te is nearly perpendicular to this ring. The metalated mesityl ring plane lies at an angle of 14.06° with the metal square plane rendering the metalated five-membered "PtTeCCC" ring in puckered conformation.

The R-factor of [PtCl{(CH$_2$C$_6$H$_2$Me$_2$-4,6)TeMes}(PPh$_3$)] (**4**) is large due to presence of disordered aromatic rings, but the overall chemical structure supports the conclusions drawn from NMR data. The crystal lattice of [PtCl{(CH$_2$C$_6$H$_2$Me$_2$-4,6)TeMes}(PPh$_3$)] (**4**) shows two independent molecules which differ slightly in their interatomic parameters. The platinum(II) center in each molecule adopts a distorted square planar geometry with a "TeCPCl"

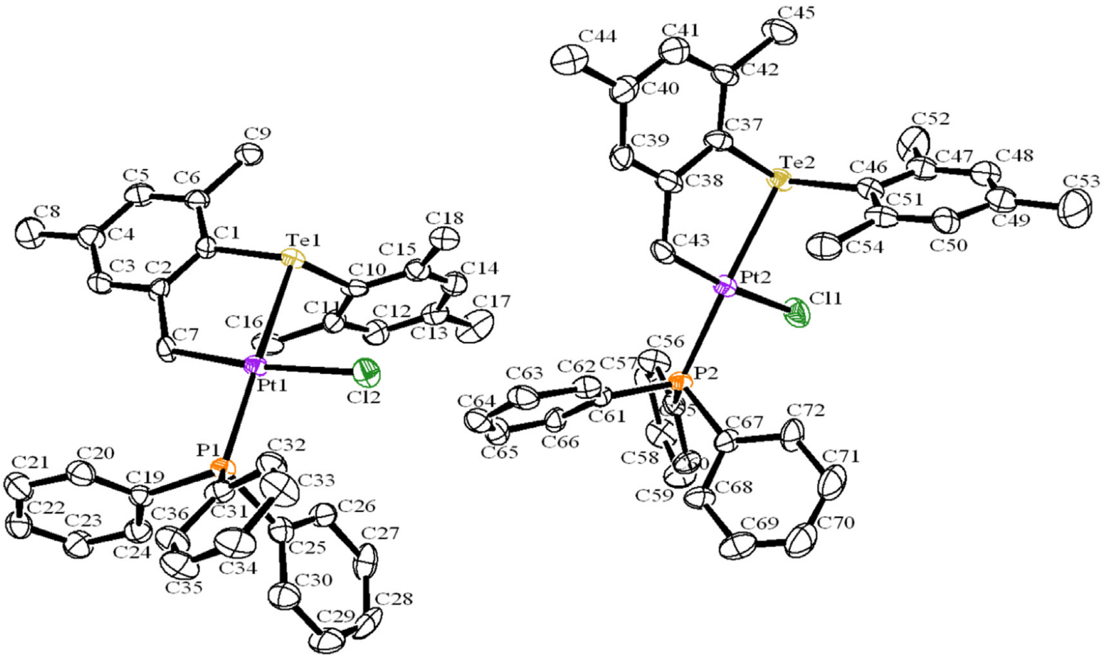


Fig. 6. ORTEP drawing of [PtCl{(CH$_2$C$_6$H$_2$Me$_2$-4,6)TeMes}(PPh$_3$)] (**4**) with atomic numbering scheme (H atoms omitted for clarity).

Table 1
Selected inter-atomic parameters (Å, °) for *trans*-[PtCl$_2$(TeMes$_2$)$_2$] (**1c**).

Pt1−Te1	2.5717(13)	Pt2−Te3	2.5786(11)
Pt1−Te2	2.5589(12)	Pt2−Te4	2.5763(11)
Pt1−Cl1	2.320(5)	Pt2−Cl3	2.289(5)
Pt1−Cl2	2.275(5)	Pt2−Cl4	2.301(5)
Te1−C1	2.14(2)	Te3−C37	2.161(16)
Te1−C10	2.143(18)	Te3−C46	2.115(13)
Te2−C19	2.150(18)	Te4−C55	2.168(19)
Te2−C28	2.110(17)	Te4−C64	2.121(13)
Cl1−Pt1−Cl2	179.1(3)	Cl3−Pt2−Cl4	174.1(2)
Cl1−Pt1−Te1	84.07(14)	Cl3−Pt2−Te3	94.66(12)
Cl1−Pt1−Te2	83.19(13)	Cl3−Pt2−Te4	80.63(12)
Cl2−Pt1−Te1	96.25(15)	Cl4−Pt2−Te3	85.99(12)
Cl2−Pt1−Te2	96.56(15)	Cl4−Pt2−Te4	97.62(13)
Te1−Pt1−Te2	166.41(5)	Te3−Pt2−Te4	168.39(5)
Pt1−Te1−C1	113.8(4)	Pt2−Te3−C37	115.7(5)
Pt1−Te1−C10	109.2(4)	Pt2−Te3−C46	107.4(4)
Pt1−Te2−C19	108.2(4)	Pt2−Te4−C55	113.6(4)
Pt1−Te2−C28	113.8(5)	Pt2−Te4−C64	111.9(4)
C1−Te1−C10	99.8(7)	C37−Te3−C46	98.5(6)
C19−Te2−C28	101.6(7)	C55−Te3−C64	97.7(6)
Pt1−Te1−C1−C2	1.58	Pt2−Te3−C37−C38	−2.74
Pt1−Te1−C1−C6	−176.94	Pt2−Te3−C37−C42	−177.98
Pt1−Te1−C10−C11	−77.75	Pt2−Te3−C46−C47	−65.69
Pt1−Te1−C10−C15	102.23	Pt2−Te3−C46−C51	112.65
Pt1−Te2−C19−C20	6.33	Pt2−Te4−C55−C56	3.01
Pt1−Te2−C19−C24	−164.71	Pt2−Te4−C55−C60	−170.04
Pt1−Te2−C28−C29	−67.03	Pt2−Te4−C64−C65	−67.4
Pt1−Te2−C28−C33	113.81	Pt2−Te4−C64−C69	115.06

Table 3
Selected bond length (Å) and angles (°) for [PtCl{(CH$_2$C$_6$H$_2$Me$_2$-4,6)TeMes}(TeMes$_2$)] (**2**).

Pt1−Te1	2.4870(11)	Te1−C1	2.121(12)
Pt1−Te2	2.6138(10)	Te1−C10	2.141(13)
Pt1−Cl1	2.342(4)	Te2−C19	2.151(14)
Pt1−C7	2.084(12)	Te2−C28	2.112(14)
C7−Pt1−Cl1	87.3(4)	C1−Te1−C10	100.8(5)
C7−Pt1−Te1	86.7(4)	C1−Te1−Pt1	93.4(4)
Cl1−Pt1−Te1	173.59(10)	C10−Te1−Pt1	105.9(4)
C7−Pt1−Te2	172.4(4)	C28−Te2−C19	100.9(5)
Cl1−Pt1−Te2	86.46(9)	C28−Te2−Pt1	112.7(4)
Te1−Pt1−Te2	99.34(3)	C19−Te2−Pt1	113.7(3)

coordination core [36]. The neutral ligands (Te and P) are mutually *trans* with P−Pt−Te angle of 175.50(11) and 177.37(12) °. The five-membered cyclometalated ring is almost planar.

A comparison of all the above structures (Table 5) shows increase in steric bulkiness of the groups on tellurium leads to gradually decrease of the torsion angles Pt1−Te−C1−C2 from **1d** to **1e** to **1c** leading to increase in proximity of the methyl group C7 with the metal centre. This may lead to favourable anagostic interactions resulting in cyclometalation of ligands with bulky groups while others despite the presence of bulky mesityl group show reluctance under similar conditions.

4. Conclusion

In summary platinum(II) telluroether complexes have been synthesized and characterized by NMR spectroscopy and X-ray crystallography. The complexes with sterically bulky organic groups on tellurium tend to exist as *trans* isomers, while ligands with smaller R groups yield *cis* isomers which isomerise to *trans* form in solution. The complexes with asymmetric telluroethers exist as diastereomers which can readily be identified from their ^{125}Te/^{195}Pt NMR spectra. The role of anagostic interaction in cycloplatination reactions has been demonstrated.

5. Experimental section

Solvents were dried and distilled under a nitrogen atmosphere prior to use according to a literature method [37]. All the reactions were carried out in an argon atmosphere. Diaryltellurides, ArTeAr' were prepared by the reaction of ArTeBr, obtained *in-situ* by bromination of diaryl ditellurides (Ar$_2$Te$_2$) with bromine in THF, with an appropriate aryl magnesium bromide (Supplementary material) [38]. Elemental analyses were carried out on a Thermo Fischer Flash EA 1112 CHNS micro-analyser. Melting points were determined in capillary tubes and are uncorrected. ^{1}H, ^{13}C{^{1}H},^{125}Te {^{1}H} and ^{195}Pt{^{1}H} NMR spectra were recorded on a BrukerAvance-II 300 (300.1, 75.5, 94.7 and 64.5 MHz, respectively) and Bruker Ascend TM-400 (400, 100.61, 126.24, 86.02 MHz, respectively) NMR spectrometers. 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$_6$) and external Na$_2$PtCl$_6$ in D$_2$O.

6. Synthesis

6.1. *cis-[PtCl$_2$(TePh$_2$)$_2$] (**1a**)*

To an aqueous solution of K$_2$PtCl$_4$ (100 mg, 0.24 mmol), a toluene-acetone solution of diphenyl telluride (135 mg, 0.475 mmol) was added and the reaction mixtures were stirred at room temperature for 12 h. The acetone was removed under vacuum and the organic layer was separated out and washed with

Table 2
Selected bond length (Å) and angles (°) of *trans*-[PtCl$_2${Te(R)Mes}$_2$].

	trans-[PtCl$_2${Te(Ph)Mes}$_2$] (**1d**)	*trans*-[PtCl$_2${Te(*o*-tol)Mes}$_2$] (**1e**)
Pt1−Te1	2.5785(13)	2.5771(7)
Pt1−Cl1	2.287(6)	2.309(3)
Te1−C1	2.10(2)	2.131(12)
Te1−C10	2.11(2)	2.107(12)
Te1−Pt1−Te1^i	180	180
Te1−Pt1−Cl1	93.75(16)	95.81(8)
Cl1−Pt1−Te1^i	86.25(16)	84.19(8)
(Cl1−Pt1−Te1)		
Cl1−Pt1−Cl1^i	180	180
Pt1−Te1−C1	110.4(6)	109.4(4)
Pt1−Te1−C10	106.3(6)	108.2(3)
C1−Te1−C10	95.9(9)	96.7(5)
Pt1−Te1−C1−C2	−58.31	31.47
Pt1−Te1−C1−C6	121.65	−147.69
Pt1−Te1−C10−C11	−19.50	−101.12
Pt1−Te1−C10−C15	−163.58	79.54

Table 4
Selected bond length (Å) and angles (°) for [PtCl{(CH$_2$C$_6$H$_2$Me$_2$-4,6)TeMes}(PPh$_3$)] (**4**).

Pt1–P1	2.268(4)	Pt2–P2	2.273(4)
Pt1–Cl2	2.412(5)	Pt2–Cl1	2.410(5)
Pt1–Te1	2.5504(11)	Pt2–Te2	2.5410(12)
Pt1–C7	2.029(14)	Pt2–C43	2.09(2)
Te1–C1	2.080(17)	Te2–C37	2.15(2)
Te1–C10	2.161(17)	Te2–C46	2.13(2)
P1–Pt1–Cl2	94.49(15)	P2–Pt2–Cl1	91.07(17)
P1–Pt1–Te1	175.50(11)	P2–Pt2–Te2	177.37(12)
P1–Pt1–C7	91.8(4)	P2–Pt2–C43	94.8(5)
Cl2–Pt1–Te1	86.25(11)	Cl1–Pt2–Te2	86.35(13)
Cl2–Pt1–C7	173.4(5)	Cl1–Pt2–C43	174.0(5)
Te1–Pt1–C7	87.6(4)	Te2–Pt2–C43	87.8(4)
Pt1–C7–C2	119.2(10)	Pt2–C43–C38	119.1(12)
Pt1–Te1–C1	92.5(5)	Pt2–Te2–C37	93.0(4)
Pt1–Te1–C10	104.2(4)	Pt2–Te2–C46	107.7(4)
C1–Te1–C10	102.2(7)	C37–Te2–C46	103.0(7)

distilled water and dried over anhydrous Na$_2$SO$_4$. The clear solution was passed through Cellite and concentrated to 5 ml. The title complex was precipitated as a greenish yellow powder by addition of hexane and then was washed with hexane and diethyl ether and dried, (Yield: 123 mg, 61%), m.p. 196 °C (dec). Anal. calcd. for C$_{24}$H$_{20}$Cl$_2$PtTe$_2$: C, 34.75; H, 2.42%. Found: C, 34.31; H, 2.40%. ^{1}H NMR (CDCl$_3$) δ: 7.22–7.27 (m), 7.35–7.40 (m), 7.61–7.64 (m) [Ph] ppm. ^{125}Te{^{1}H} NMR (CDCl$_3$) δ: 717 (major, ^{1}J(^{195}Pt–^{125}Te) = 1329 Hz) and 728 (minor) ppm. ^{195}Pt{^{1}H} NMR (CDCl$_3$) δ: −3650 (major), −3653 (minor). When a CDCl$_3$ solution of the complex is left for longer duration of acquisition additional peaks in the ^{125}Te{^{1}H} and ^{195}Pt{^{1}H} NMR spectra were observed which could be due to dissociation in solution.

6.2. *trans-[PtCl$_2${(Te(tol-o)$_2$}$_2$] (**1b**)*

Prepared similar to **1a** and recrystallized from dichloromethane–hexane as yellow needles (Yield: 155 mg, 73%); m. p. >210 °C. Anal. calcd. for C$_{28}$H$_{28}$Cl$_2$PtTe$_2$: C, 37.97; H, 3.19%, Found: C, 37.23; H, 3.16.%. ^{1}H NMR (CDCl$_3$) δ: 2.25, 2.56 (each s); 7.08–7.15 (m), 7.24–7.36 (m); 7.79 (dd, 1.2, 7.5 Hz); 7.88 (d,d, 1.2, 7.5 Hz) ppm. ^{125}Te{^{1}H} NMR (CDCl$_3$) δ: 622 (^{1}J(^{195}Pt–^{125}Te) = 793 Hz) ppm; when this solution was left for overnight a new additional peak appeared in ^{125}Te NMR spectrumatδ: 605 (^{1}J(^{195}Pt–^{125}Te) = 1357 Hz) ppm while ^{195}Pt{^{1}H} NMR (CDCl$_3$) showed two resonances at δ: −3717, −4324 ppm.

6.3. *trans-[PtCl$_2$(TeMes$_2$)$_2$] (**1c**)*

Prepared similar to **1a** and recrystallized from dichloromethane-hexane in 64% yield as light orange crystalline solid; m.p. 180 °C. Anal. calcd. for C$_{36}$H$_{44}$Cl$_2$PtTe$_2$: C, 43.33; H, 4.44%. Found: C, 43.64; H, 4.87%. ^{1}H NMR (CDCl3) δ: 2.24 (s, 4-Me); 2.61 (s, 2,6-Me); 6.85 (s, 3,5-CH). ^{13}C{^{1}H} NMR (CDCl$_3$)δ: 20.9, 26.8, 116.8 (Te–C), 129.3 (3,5-CH), 139.8, 143.6. ^{125}Te{^{1}H} NMR (CDCl$_3$) δ: 467 (^{1}J(^{195}Pt–^{125}Te) = 379 Hz) ppm. ^{195}Pt{^{1}H} NMR (CDCl$_3$) δ: −3449 (^{1}J(^{195}Pt–^{125}Te) = 359 Hz) ppm.

6.4. *trans-[PtCl$_2$(PhTeMes)$_2$] (**1d**)*

Prepared similar to **1a** and recrystallized from dichloromethane-hexane in 75% yield as orange crystals; m. p. 198 °C (dec). Anal. calcd. for C$_{30}$H$_{32}$Cl$_2$PtTe$_2$: C, 39.43; H, 3.53%. Found: C, 39.07; H, 3.45%. ^{1}H NMR (CDCl$_3$) δ: 2.29 (s, 4-Me), 2.68 (s, 2,6-Me); 6.96 (s, 3,5-CH); 7.30 (br, m); 7.59 (br) (Ph). ^{125}Te{^{1}H} NMR (CDCl$_3$) δ: 575 (^{1}J(^{195}Pt–^{125}Te) = 366 Hz), 576 (^{1}J(Pt–Te) = 369 Hz) ppm. ^{195}Pt{^{1}H} NMR (CDCl$_3$) δ: −3555, −3557 ppm.

6.5. *trans-[PtCl$_2$(o-tolTeMes)$_2$] (**1e**)*

Prepared similar to **1a** and recrystallized from dichloromethane-hexane in 70% yield as orange crystals; m. p. > 200 °C. Anal. calcd. for C$_{32}$H$_{36}$Cl$_2$PtTe$_2$: C, 40.81; H, 3.85%. Found: C,40.65; H, 3.78%. ^{1}H NMR (CDCl$_3$) δ: 2.29, 2.30 (each s, 4-Me of Mes), 2.45, 2.48 (each s, 2-Me of tol); 2.72, 2.74 (each s, 2,6-Me of Mes); 6.95, 6.97 (each s, 3,5-CH of Mes); 7.02–7.22 (m, tol); 7.51, 7.64 (each d, 7.8 Hz, tol) ppm. ^{125}Te{^{1}H} NMR (CDCl$_3$) δ: 541; 543 (^{1}J(^{195}Pt–^{125}Te) = 515 Hz) ppm. ^{195}Pt{^{1}H} NMR (CDCl$_3$) δ: −3611, −3615 ppm.

6.6. *[PtCl{(CH$_2$C$_6$H$_2$Me$_2$-4,6)TeMes}(TeMes$_2$)] (**2**)*

A THF (~25 ml) solution of *trans*-[PtCl$_2$(TeMes$_2$)$_2$] (60 mg, 0.06 mmol) was refluxed with stirring for 2 h under an argon atmosphere whereupon the initial orange colour faded. After cooling the solution, the solvent was evaporated under reduced pressure to give a yellow residue which was washed with hexane and recrystallized from dichloromethane-hexane mixture as red prismatic crystals (Yield: 40 mg, 70%); m.p. 182 °C (dec). Anal. calcd. for C$_{36}$H$_{43}$ClPtTe$_2$: C, 44.97; H, 4.51%. Found: C, 45.02; H, 4.61%. ^{1}H NMR (CDCl$_3$) δ: 2.02, 2.19, 2.24, 2.27, 2.34, 2.53 (each s for Me); 4.0 (J$_{AX}$ = 16.8, Δν$_{AX}$ = 105.8 Hz; metalated CH$_2$); 6.66 (s, 4,6-CH of Mes of metalated); 6.71 (s, 4,6-CH, Mes$_2$Te); 6.86, 7.04 (CH of metalated ring) ppm.^{125}Te{^{1}H} NMR (CDCl$_3$) δ: 336 (^{1}J(^{195}Pt–^{125}Te) = 612 Hz); 592 (^{1}J(^{195}Pt–^{125}Te) = 1528 Hz) ppm; for the dimer: 424 (^{1}J(^{195}Pt–^{125}Te) = 788 Hz) and 600 (^{1}J(^{195}Pt–^{125}Te) = 1192 Hz); 260(s, TeMes$_2$) ppm. ^{195}Pt{^{1}H} NMR (CDCl$_3$) δ: −4286 (minor); −4450 (major).

6.7. *[PtCl{(CH$_2$C$_6$H$_2$Me$_2$-4,6)TeMes}(PPh$_3$)] (**4**)*

To a dichloromethane solution of **2** (45 mg, 0.047 mmol) a

Table 5
Secondary C–H … M interactions with the metal centre (Å/°)[a].

	trans-PtCl$_2$(PhTeMes)$_2$ (**1d**)	*trans*-PtCl$_2$(*o*-tolTeMes)$_2$ (**1e**)	*trans*-PtCl$_2$(TeMes$_2$)$_2$ (**1c**)	
			Molecule A	Molecule B
C7–H7c … Pt1	3.114	2.850	2.794	2.689
∠C7–H7c-Pt1	157.06	119.37	122.89	134.74
Pt1–Te1–C1–C2	−58.31	31.47	1.58	−2.74
Pt1–Cl1	2.286	2.309	2.320	2.289
∠Cl1–Pt1–Cl2	180	180	179.06	174.08
Pt1–Te1	2.578	2.577	2.572	2.579
∠Te1–Pt1–Te2	180	180	166.41	168.39
Mean sq. plane-M			0.042	0.180

[a] The distances have been noted down using mercury program, hence do not have esds.

Table 6
Crystallographic and Structural Refinement Data for *trans*-$[PtCl_2\{Te(R)Mes\}_2]$ (R = Mes, Ph, *o*-tol), $[PtCl\{(CH_2C_6H_2Me_2\text{-}4,6)TeMes\}(TeMes_2)]$ and $[PtCl\{(CH_2C_6H_2Me_2\text{-}4,6)TeMes\}PPh_3]$.

	trans- $[PtCl_2\{Te(Ph)Mes\}_2]$ (**1d**)	*trans*-$[PtCl_2\{Te(o\text{-}tol)Mes\}_2]$ (**1e**)	*trans*-$[PtCl_2\{TeMes\}_2]$ (**1c**)	$[PtCl\{(CH_2C_6H_2Me_2\text{-}4,6)TeMes\}(TeMes_2)]$ (**2**)	$[PtCl\{(CH_2C_6H_2Me_2\text{-}4,6)TeMes\}(PPh_3)]$ (**4**)
Formula	$C_{30}H_{32}Cl_2PtTe_2$	$C_{32}H_{36}Cl_2PtTe_2$	$C_{36}H_{44}Cl_2PtTe_2$	$C_{36}H_{43}ClPtTe_2$	$C_{36}H_{36}ClPPtTe$
M	913.74	941.80	997.90	961.44	857.76
Size(mm)	0.73 × 0.45 × 0.12	0.20 × 0.20 × 0.10	0.078 × 0.180 × 0.400	0.27 × 0.15 × 0.08	0.19 × 0.39 × 0.87
Crystal system	triclinic	monoclinic	triclinic	monoclinic	triclinic
Space group	$P\overline{1}$	$P2_1/c$	$P\overline{1}$	$P2_1/n$	$P\overline{1}$
a/Å	8.3863(7)	12.2222(7)	12.2279(4)	12.3617 (3)	9.2579(3)
b/Å	8.8308(9)	9.8439(6)	15.9978(5)	15.0672(3)	18.5589(8)
c/Å	11.8748(15)	14.6962(9)	18.9292(6)	18.7395(4)	20.6306(9)
α/°	68.588(11)	–	84.313(3)	–	106.161(4)
β/°	76.008(9)	113.953(7)	83.183(3)	100.793(2)	97.925(3)
γ/°	68.321(9)	–	86.493(3)	–	101.363(3)
V/Å^3	754.98(16)	1615.88(19)	3654.1(2)	3428.60(13)	3267.2(2)
Z	1	2	4	4	4
d_{calc}/g cm^{-3}	2.010	1.936	1.814	1.863	1.744
μ (mm^{-1})/F(000)	25.378/428	23.737/888	21.034/1904	21.689/1832	16.317/1656
θ for data collection/°	4.0580 to 69.3280	3.958 to 70.405	2.779 to 70.106	3.791 to 69.987	2.841to 69.969
Limiting indices	$-10 \le h \le 9$ $-10 \le k \le 10$ $-14 \le l \le 14$	$-14 \le h \le 12$ $-11 \le k \le 11$ $-12 \le l \le 17$	$-14 \le h \le 14$ $-19 \le k \le 18$ $-22 \le l \le 17$	$-14 \le h \le 12$ $-17 \le k \le 18$ $-22 \le l \le 19$	$-11 \le h \le 8$ $-22 \le k \le 22$ $-25 \le l \le 23$
No. of unique reflns	2784	3028	13593	6364	12159
No. of obsd reflns with I > 2σ(I)	1745	2659	10182	5045	8245
Data/restraints/parameters	2784/0/165	3028/0/173	13593/6/764	6364/0/372	12159/0/731
Final R_1, ωR_2 indices	0.0872/0.2304	0.0707/0.2022	0.0877/0.2597	0.0763/0.2246	0.1158/0.3000
R_1, ωR_2 (all data)	0.1237/0.2778	0.0759/0.2068	0.1102/0.2790	0.0891/0.2351	0.1436/0.3379
Goodness of fit on F^2	1.022	1.075	1.064	1.077	1.160
Largest diff. peak and hole (e.Å^{-3})	2.629 and −2.121	3.698 to −1.831	4.711 to −2.702	3.950 to −2.023	4.681 to −4.816

solution of triphenylphosphine (13 mg; 0.05 mmol) was added with stirring under argon. After stirring the reactants for 3 h at room temperature, the solvent was evaporated under vacuum and the residue was washed with hexane. The complex on recrystallization from acetone −hexane (1:1) mixture at room temperature gave pale yellow rod like crystals (27 mg, 67%); m. p. 167 °C. Anal. calcd. for $C_{36}H_{36}ClPPtTe$: C, 50.41; H, 4.23%. Found: C, 50.63; H, 4.21%. ^1H NMR ($CDCl_3$) δ:2.12, 2.26, 2.28 (each s, 1 Me), 2.58 (s, 2Me); 2.89 (br, CH_2), 6.47, 6.68 (each s; 1CH); 6.87 (s, 2CH); 7.44 (m, 7.74–7.81 (m) (Ph). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: 23.6 ($^1J(^{195}Pt-^{31}P)$ = 3945 Hz; $^2J(^{125}Te-^{31}P)$ = 456 Hz) ppm.$^{125}Te\{^1H\}$ NMR ($CDCl_3$) δ: 555 ($^1J(^{195}Pt-^{125}Te)$ = 677 Hz; $^2J(^{125}Te-^{31}P)$ = 455 Hz) ppm.

7. X-ray crystallography

Single crystal X-ray data on *trans*-$[PtCl_2(TeMes_2)_2]$ **(1c)**, *trans*-$[PtCl_2(PhTeMes)_2]$ **(1d)**, *trans*-$[PtCl_2(o\text{-}tolTeMes)_2]$ **(1e)**, $[PtCl\{(CH_2C_6H_2Me_2\text{-}4,6)TeMes\}(TeMes_2)]$ (**2**) and $[PtCl\{(CH_2C_6H_2Me_2\text{-}4,6)TeMes\}(PPh_3)]$ (**4**) were collected on a Agilent SuperNova CCD diffractometer. Crystallographic data, together with data collection and refinement details are given in Table 6. All the data were corrected for Lorentz and polarization effects. The structures were solved by direct methods [39] and expanded using Fourier technique [40]. Hydrogen atoms were added to the parent atom with idealized geometry and refined isotropically. Molecular structures were drawn using ORTEP [41].

Supporting information

CCDC-Nos. 1043744–1043748 for *trans*-$[PtCl_2(TeMes_2)_2]$ (**1c**), $[PtCl\{(CH_2C_6H_2Me_2\text{-}4,6)TeMes\}(PPh_3)]$ (**4**), *trans*-$[PtCl_2(PhTeMes)_2]$ (**1d**), *trans*-$[PtCl_2(o\text{-}tolTeMes)_2]$ (**1e**) and $[PtCl\{(CH_2C_6H_2Me_2\text{-}4,6)TeMes\}(TeMes_2)]$ (**2**), 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, CambridgeCB2 1EZ, UK [Fax: + 44–1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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