# **Inorganic Chemistry**

# Platinum-Mediated Activation of Coordinated Organonitriles by Telluroethers in Tetrahydrofuran: Isolation, Structural Characterization, and Density Functional Theory Analysis of Intermediate Complexes

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**Supporting Information** 

**ABSTRACT:** The reactions of  $[PtCl_2(NCR)_2]$  with telluroethers (ArAr'Te) in organic solvents have been investigated. The reactions in dichloromethane yield  $[PtCl_2(TeArAr')_2]$ , while those in tetrahydrofuran (THF) give different products depending on the steric demands of the aryl groups on tellurium, the molarity of the reactants, and the reaction conditions. The reactions between  $[PtCl_2(PhCN)_2]$  and TeArAr' in 1:1 molar ratio at room temperature in THF yield several products, like  $[PtCl_2(TeArAr')_2]$  (Ar/Ar' = Ph/Ph, *o*-tol/Mes, Mes/Mes),  $[PtCl_2(PhCN)\{NC(O)Ph[TeMes(o-tol)]\}]$ , and  $[PtCl_2\{NC-(O)Ph(TeMes_2)\}_2]$ . The reaction with TeMes\_2 in refluxing THF gave  $[PtCl_2\{NC(Ph)C_4H_7O\}\{NC(O)Ph(TeMes_2)\}]$  and  $[PtCl(TeMes_2)-\{Te(Mes)CH_2C_6H_2Me_2\}]$ , depending on the duration of heating. Reaction of  $[PtCl_2(PhCN)_2]$  with TeArMes afforded  $[PtCl_2-PtCl_2(PhCN)_2]$ 



 $(TeArMes)_2$  (Ar = Ph, o-tol, and Mes), the formation of which decreased with increasing steric demand of the Ar group, together with [PtCl<sub>2</sub>{NC(O)Ph(TeArMes)}\_2]. The telluroether in the latter binds to nitrogen, and tellurium exists in the formal oxidation state of +4 (from XPS). The tellurium in these complexes exhibits secondary interactions with platinum  $(J(^{195}Pt-^{125}Te) = 309-347 \text{ Hz})$  and with the carbonyl oxygen. These complexes slowly dissociate in solution to give [PtCl<sub>2</sub>(TeMesAr){NC(O)Ph(TeMesAr)}], finally leading to the formation of [PtCl<sub>2</sub>(TeMesAr)<sub>2</sub>]. Molecular structures of *trans*-[PtCl<sub>2</sub>(PhCN){NC(O)Ph[TeMes(o-tol)]}], *trans*-[PtCl<sub>2</sub>{NC(O)Ph(TeMes<sub>2</sub>)}<sub>2</sub>], *trans*-[PtCl<sub>2</sub>{NC(O)Ph(TeMes<sub>2</sub>)}], *trans*-[PtCl<sub>2</sub>{NC(O)Ph(TeMes<sub>2</sub>)}], *trans*-[PtCl<sub>2</sub>{NC(O)Ph(TeMes<sub>2</sub>)}], and [PtCl(Te-o-tol){NC(O)Ph}<sub>2</sub>] have been unambiguously established by single-crystal X-ray diffraction analyses. Density functional theory calculations for some of the complexes were performed, and geometrical parameters are in good agreement with the values obtained from X-ray analyses.

# INTRODUCTION

During the past two decades or so, organotellurium chemistry has made great strides in diverse areas, with applications in organic synthesis<sup>1</sup> and organocatalysis,<sup>2</sup> as metal complexes in catalysis,<sup>3</sup> in ligand chemistry,<sup>4–7</sup> as precursors for metal tellurides,<sup>8</sup> and in pharmacology.<sup>9–11</sup> Recent developments in the coordination chemistry of tellurium ligands have defied the general belief that it would be similar to that of sulfur and selenium.<sup>12</sup> Of late, not only have several dissimilarities between tellurium coordination chemistry and that of sulfur/ selenium been recognized, but also numerous unprecedented results have been reported. Isolation of  $[Pt(Te)-(TeC_5H_4N)_2(PPh_3)]$ , containing bare Te<sup>0</sup> as a ligand, from the reaction of  $Pt(PPh_3)_4$  with  $py_2Te_2$  is an example of unprecedented formation of such complexes.<sup>13</sup> Telluroether complexes of platinum group metals have been known for nearly a century,  $[PtCl_2(TeBz_2)_2]$  being the first complex isolated by Fritzmann<sup>14</sup> in 1915, and later Chatt and co-workers<sup>15,16</sup> investigated with Et<sub>2</sub>Te and Pr<sub>2</sub>Te complexes. The palladium/platinum complexes are usually isolated either by reaction between  $M'_2MCl_4$  and a telluroether in water (eq  $1)^{17-20}$  or by treatment of  $[MCl_2(R'CN)_2]$  (R' = Me or Ph) with a telluroether in an organic solvent (dichloromethane, DCM (CH<sub>2</sub>Cl<sub>2</sub>), or tetrahydrofuran, THF)<sup>20–23</sup> (eq 2). The substitution reaction in the latter is believed to involve attack of the telluroether at the metal center.<sup>23</sup>

$$M'_2MCl_4 + 2TeAr_2 \xrightarrow{H_2O} [MCl_2(TeAr_2)_2] + 2M'Cl$$
 (1)

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Scheme 1. Reactions between [PtCl<sub>2</sub>(PhCN)<sub>2</sub>] and Te(Ar)Mes in 1:1 Stoichiometry in THF



Scheme 2. Reactions between [PtCl<sub>2</sub>(PhCN)<sub>2</sub>] and Te(Ar)Mes in 1:2 Stoichiometry in THF at Room Temperature



$$[MCl_{2}(R'CN)_{2}] + 2TeAr_{2}$$

$$\xrightarrow{\text{organic solvent}} [MCl_{2}(TeAr_{2})_{2}] + 2R'CN \qquad (2)$$

To study cycloplatination of telluroether ligands, recently we have isolated  $[PtCl_2(TeArAr')_2]$  complexes by employing the reaction between an aqueous solution of K<sub>2</sub>PtCl<sub>4</sub> and telluroether in an acetone mixture (eq 1).<sup>24</sup> Since the separation of the final products from the biphasic reaction medium was a tedious process, we thought to employ a reaction route involving  $[PtCl_2(PhCN)_2]$  (eq 2) and telluroether in an organic solvent. While the reaction with simple telluroethers gave the desired products, as has been reported

earlier,<sup>20–23</sup> to our surprise, with a bulky telluroether (e.g., TeMes<sub>2</sub>) formation of other intermediate complexes could be detected by <sup>125</sup>Te NMR spectroscopy. This led us to examine these reactions systematically by varying solvent, molarity of the reactants, steric demands of the organic groups on tellurium, and temperature. The results of this work are reported herein.

# RESULTS AND DISCUSSION

Reactions of  $[PtCl_2(PhCN)_2]$  (1a) with telluroethers TeArAr' (2) in 1:2 stoichiometry in DCM over 48 h afforded the expected *cis/trans*- $[PtCl_2(TeArAr')_2]$  (3) in 60–83% yield as isolated from the reaction of K<sub>2</sub>PtCl<sub>4</sub> with the telluroether in water–acetone mixture. With asymmetric telluroethers, dia-

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Figure 1. <sup>125</sup>Te NMR spectra of a reaction between  $[PtCl_2(PhCN)_2]$  and TeMes<sub>2</sub> in 1:2 molar ratio in THF monitored with time: (a) 24 h, (b) 3 d, and (c) 7 d. Spectra were recorded in CDCl<sub>3</sub>.

stereomers are formed. As the steric demand of organic group on tellurium increases, the reactions tend to be slower. Thus, in the case of TeMes<sub>2</sub>, unreacted  $[PtCl_2(PhCN)_2]$  was noted in solution by <sup>195</sup>Pt NMR spectroscopy even after 48 h of reaction.

Since the reactions involving bulky telluroethers were sluggish in DCM, another commonly used solvent, viz. THF was used. Surprisingly the reactions were more complex giving several products formed by the initial attack of telluroether on the coordinated benzonitrile rather than the platinum center. To understand the reaction profile, reactions between  $[PtCl_2-(PhCN)_2]$  and telluroethers in 1:1 and 1:2 stoichiometry in THF were examined under different reaction conditions.

Reactions of  $[PtCl_2(PhCN)_2]$  (1a) with TeArMes (Ar = mesityl, *o*-tolyl, phenyl) in 1:1 ratio in THF afforded different products depending on the steric demand of the Ar group (Scheme 1). When Ar was phenyl, expected mononuclear complex *trans*- $[PtCl_2{Te(Ph)(Mes)}_2]$  (3b) was formed exclusively. When the steric demand of the Ar group increased from phenyl to *o*-tolyl, two products were isolated, viz. *trans*- $[PtCl_2{Te(o-tol)(Mes)}_2]$  (3d) as a minor fraction and *trans*- $[PtCl_2(PhCN){NC(O)Ph(Te(Mes)o-tol)}]$  (4; see later for structure), formed by the attack of telluroether on one of the coordinated benzonitrile, as a major fraction. On further increasing the steric demand of Ar group from *o*-tolyl to mesityl, again two products were isolated, *trans*- $[PtCl_2(TeMes_2)_2]$  (3e) as a minor fraction and a product formed by the attack of telluroether on both the coordinated

benzonitriles, trans-[PtCl<sub>2</sub>{NC(O)Ph(TeMes<sub>2</sub>)}<sub>2</sub>] (5), as a major fraction (see later for structure). When this reaction was carried out in refluxing THF, different products were isolated, depending on the duration of refluxing. The reaction mixture on refluxing for 30 min yielded a single product, trans- $[PtCl_2{NC(Ph)C_4H_7O}{NC(O)Ph(TeMes_2)}]$  (6; see later for structure) wherein one of the coordinated benzonitrile is activated by THF molecule (C-H ortho to oxygen) while the other coordinated benzonitrile is attacked by the telluroether. When refluxing prolonged for 3 h, a mixture of products were formed which were separated using diethyl ether. The ether soluble component was characterized by NMR spectroscopy as cycloplatinated complex [PtCl(TeMes<sub>2</sub>){Te(Mes)- $CH_2C_6H_2Me_2$ ] (7) while the ether insoluble part contained  $[PtCl_2(PhCN)_2]$  (1a) and  $[Pt_2Cl_2(\mu-Cl)_2(TeMes_2)_2]$  (8) as confirmed by <sup>125</sup>Te and <sup>195</sup>Pt NMR spectroscopy. Recently we have described the formation of 7 from 3e in refluxing THF.<sup>24</sup>

Having examined the reactions of  $[PtCl_2(PhCN)_2]$  (1a) with TeArMes in 1:1 stochiometry, it was imperative to assess the reactivity with 1:2 Pt to Te ratio (Scheme 2). The reaction of  $[PtCl_2(PhCN)_2]$  with TePhMes in 1:2 stoichiometry in THF at room temperature afforded expected complex 3b. The reaction of Te(*o*-tol)Mes with  $[PtCl_2(PhCN)_2]$  gave two products, viz.  $[PtCl_2{Te(o-tol)Mes}_2]$  (3d) as a minor fraction and a complex formed by the attack of telluroether on both the coordinated benzonitrile *trans*- $[PtCl_2{NC(O)Ph{Te(o-tol)-Mes}_2]$  (9; see later for structure) as a major constituent. The 9 decomposes slowly in solution. Thus, when 9 was left for recrystallization in acetone at room temperature along with the crystals of 9, 3d was also formed as precipitate together with the colorless crystals of  $[PtCl(Te-o-tol){NC(O)Ph}_2]$  (11). This indicates that in the reaction medium initially the complex 9 is formed, which is converted gradually into the more stable 3d via the cleavage of Pt-N bond with concomitant formation of stable Pt-Te linkage. All the three complexes (3d, 9, and 11) were separated manually. Interestingly the reaction of [PtCl<sub>2</sub>(PhCN)<sub>2</sub>] with TeMes<sub>2</sub> yielded different products depending on the duration of the reaction which was monitored by <sup>125</sup>Te NMR spectroscopy (Figure 1). Initially a complex generated by telluroether attack on coordinated benzonitrile, was formed in 24 h, although other products, viz. 3e and 10, also existed in solution (Figure 1). When this reaction continued for 72 h, in addition to this complex and 3e, the concentration of trans-[PtCl<sub>2</sub>(TeMes<sub>2</sub>){NC(O)Ph- $(TeMes_2)$ ] (10) increased significantly, and 10 could be isolated from solution (see later for structure). On prolonging the reaction for a week, bis-telluroether complex 3e existed in more than 90% yield (Figure 1). Therefore, from the above time dependent complexation history it is clear that initial reaction of telluroether takes place at the coordinated benzonitrile rather than at platinum center followed by stepwise rearrangement. All these intermediate complexes could be isolated and characterized with sterically demanding telluroether, whereas with non-steriaclly hindered telluroethers, such intermediates, which might have formed, could not be detected, and only the substitution products,  $trans-[PtCl_2(TeArAr')_2]$ , were isolated.

In order to assess generality of the reaction, organonitriles differeing in the nature of organic substituents were examined. Thus, the reactions between  $[PtCl_2(RCN)_2]$  (R = Me, 4-MeC<sub>6</sub>H<sub>4</sub>, 4-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>) with two equivalents of TeMes<sub>2</sub> in THF at room temperature were carried out and were monitored by <sup>125</sup>Te NMR spectroscopy. In every case reaction proceeds in a manner similar to benzonitrile. In the <sup>125</sup>Te NMR spectra resonances due to *trans*-[PtCl<sub>2</sub>{NC(O)R(TeMes<sub>2</sub>)}<sub>2</sub>] and *trans*-[PtCl<sub>2</sub>(TeMes<sub>2</sub>){NC(O)R(TeMes<sub>2</sub>)}] (Supporting Information, Figures S1–S3) were observed and even in one case *trans*-[PtCl<sub>2</sub>{NC(O)Me(TeMes<sub>2</sub>)}<sub>2</sub>] (12) was isolated and structurally characterized.

To compare the reactivity of bulky telluroether with palladium benzonitrile complex, a reaction of  $[PdCl_2(PhCN)_2]$  with TeMes<sub>2</sub> in 1:2 molar ratio in THF at room temperature afforded expected product *trans*- $[PdCl_2(TeMes_2)_2]$  as revealed by <sup>1</sup>H and <sup>125</sup>Te NMR spectroscopy.<sup>20</sup>

Activation of C-N bond of metal ligated organonitriles by a variety of nucleophiles, and to a lesser extent with electrophiles, have been investigated extensively during the past two decades or so.<sup>25-31</sup> Both protic (e.g., ROH, RSH, oximes, etc.) and aprotic nucleophiles have been shown to react with coordinated organonitrile to yield a variety of compounds containing new C-C and C-X (X = N, P, O, S) bonds. Activation of nitriles by telluroethers in THF to give kinetically labile imide complexes, described here, represents the first example of the formation of  $N = TeR_2$  linkage. A possible route could be the initial attack of telluroether on nitrile carbon atom to give Te-C=N-Pt linkage. The latter is attacked by THF oxygen on carbon and simultaneous migration of TeArAr' to nitrogen leads to Pt-N(TeArAr')C(=O)R linkage. This has been reaffirmed by DFT calculations (Figure S4). Since Pt-N(TeArAr')C(=O)R linkage does not form in moist DCM, the source is attributed to THF. The C-H activation of the ortho-position of  $\text{THF}^{32}$  as noted for **6** and extrusion of oxygen from  $\text{THF}^{33,34}$  is well documented in literature.

Spectroscopy. The NMR spectral data (<sup>1</sup>H, <sup>125</sup>Te, and  $^{195}\text{Pt})$  for  $[\text{PtCl}_2(\text{TeArAr'})_2]$  and for 7 are in accord with those reported recently by us.<sup>24</sup> The <sup>1</sup>H NMR spectra of 4-10 displayed resonances and peak multiplicities as expected. Both the ortho protons of phenyl of benzonitrile resonances are significantly deshielded ( $\delta \sim 8.25$  ppm,  $\sim 7.2$  Hz). The <sup>13</sup>C NMR spectra exhibited, in addition to the expected resonances, a signal at ~180 ppm due to C=O group. The  $^{125}$ Te NMR spectra of the complexes containing "NC(O)Ph(TeAr'Mes)" (4, 5, 6, 9, and 10) as a ligand exhibited a resonance in the region,  $\delta$  907–959 ppm and were flanked by <sup>195</sup>Pt satellites with  $I(^{195}Pt-^{125}Te)$  in the range 309–347 Hz. The <sup>125</sup>Te NMR resonances are significantly deshielded from the corresponding signal for both coordinated telluroethers as well as cyclometalated telluroether ligands. The magnitude of platinumtellurium coupling is comparable to the trans-[PtCl<sub>2</sub>-(TeArAr')<sub>2</sub>]. The observed <sup>125</sup>Te NMR chemical shift range for 4, 5, 6, 9, and 10 is indicative of tellurium in a higher formal oxidation state, as has been noted for organotellurium(IV) complexes,<sup>35</sup> such as  $(Et_2NCOCH_2)_2TeCl_2$  ( $\delta^{125}Te = 806$  ppm);<sup>36a</sup> (5,7-Cl<sub>2</sub>-8-Me<sub>2</sub>NC<sub>10</sub>H<sub>4</sub>)<sub>2</sub>TeCl<sub>2</sub> ( $\delta^{125}Te = 1031.3$  ppm).<sup>36b</sup> Recently, Lin and Gabbaï described several platinum complexes of Te(o-C<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub>)<sub>2</sub> ( $\delta^{125}$ Te = 580 ppm) in which tellurium undergoes oxidation with formal oxidation state III/ IV and showed <sup>125</sup>Te NMR chemical shift >1000 ppm.<sup>37</sup> The <sup>195</sup>Pt NMR resonances for these complexes are also deshielded with respect to the corresponding signal for  $[PtCl_2(TeArAr')_2]$ .

The X-ray photoelectron spectra of *trans*- $[PtCl_2{NC(O)Ph-(TeMes_2)}_2]$  (5) was recorded with an aim to find out the chemical state of tellurium and platinum. Figure 2 shows the



Figure 2. Te(3d) and Pt(4f) X-ray photoelectron spectrum of *trans*-[ $PtCl_{2}\{NC(O)Ph(TeMes_{2})\}_{2}$ ] (5).

core-level Te 3d and Pt 4f spectra. Two groups of peaks at 575.1 and 585.5 eV were assigned to Te( $3d_{5/2}$ ) and Te( $3d_{3/2}$ ), respectively. Similarly, the peaks for Pt( $4f_{7/2}$ ) and Pt( $4f_{5/2}$ ) were observed at 72.4 and 75.7 eV, respectively. The binding energies of Te(3d) and Pt(4f) indicate that the chemical states of tellurium and platinum are Te(IV)<sup>38</sup> and Pt(II),<sup>39</sup> respectively.

**Crystallography.** The molecular structures of *trans*-[PtCl<sub>2</sub>-(PhCN)[NC(O)Ph{TeMes(o-tol)}] (4), *trans*-[PtCl<sub>2</sub>{NC-(O)Ph(TeMes<sub>2</sub>)}<sub>2</sub>] (5), *trans*-[PtCl<sub>2</sub>{NC(Ph)C<sub>4</sub>H<sub>7</sub>O}{NC-

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(O)Ph(TeMes<sub>2</sub>)}] (6), trans-[PtCl<sub>2</sub>{NC(O)Ph(TeMes-otol)}<sub>2</sub>] (9), trans-[PtCl<sub>2</sub>(TeMes<sub>2</sub>){NC(O)Ph(TeMes<sub>2</sub>)}] (10), [PtCl(Te-o-tol){NC(O)Ph}<sub>2</sub>] (11), and trans-[PtCl<sub>2</sub>-{NC(O)Me(TeMes<sub>2</sub>)}<sub>2</sub>] (12) were established unambiguously by single-crystal X-ray diffraction analyses. ORTEP drawing are shown in Figures 3–9, while the selected inter-atomic parameters are summarized in Tables S1–S7.



Figure 3. ORTEP drawing of  $trans-[PtCl_2(PhCN){NC(O)Ph-(TeMes-o-tol)}]$  (4) with atomic numbering scheme (drawn with 25% probablility ellipsoids; H atoms are omitted for clarity).



Figure 4. ORTEP drawing of trans-[PtCl<sub>2</sub>{NC(O)Ph(TeMes<sub>2</sub>)}<sub>2</sub>]· 4H<sub>2</sub>O (5·4H<sub>2</sub>O) with atomic numbering scheme (drawn with 25% probablility ellipsoids; H atoms and solvent molecules are omitted for clarity).

The two *trans* chloride and two neutral donor (N or/and Te) ligands define the coordination environment around platinum. There is slight deviation of various angles involving platinum from idealized square planar configuration of central platinum atom in these complexes. The Pt–Cl distances (2.281(6)-2.318(7) Å) are well in agreement with those reported in mononuclear *trans*-PtCl<sub>2</sub>L<sub>2</sub> complexes, such as *trans*-[PtCl<sub>2</sub>-



Figure 5. ORTEP drawing of *trans*- $[PtCl_{2}{NC(Ph)C_{4}H_{7}O}{NC(O)-Ph(TeMes_{2})}]$  (6) with atomic numbering scheme (drawn with 25% probability ellipsoids; H atoms are omitted for clarity).



Figure 6. ORTEP drawing of  $trans-[PtCl_{NC}(O)Ph{Te(o-tol)-Mes}_{2}]$  (9) with atomic numbering scheme (drawn with 25% probability ellipsoids; H atoms are omitted for clarity).

{Te(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub>}<sub>2</sub>] (2.309(2) Å)<sup>23</sup> and *trans*-[PtCl<sub>2</sub>(Te-{(CH<sub>2</sub>CH<sub>2</sub>)O}<sub>2</sub>)] (2.3169(9) Å).<sup>40</sup> The Pt–N distances (1.966(13)–2.06(2) Å) are in accord with the values reported for [Pt<sub>2</sub>( $\mu$ -Br)<sub>2</sub>(diimine)<sub>2</sub>]<sup>2+</sup> (Pt–N = 1.992(2), 2.001(2) Å,<sup>41</sup> but are longer than those found in complexes in which nitrogen is *trans* to the strong *trans* influencing ligands, e.g., [PtCl-(ECH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)(PR<sub>3</sub>)] (E/PR<sub>3</sub> = Se/PEt<sub>3</sub>, 2.160(7) Å; Te/ PMePh<sub>2</sub>, 2.182(4) Å).<sup>42</sup> The Pt–Te distance (2.520(2) Å) is well in agreement with those found in *trans*-[PtCl<sub>2</sub>(TeRR')<sub>2</sub>].<sup>24</sup>

The Te–C distances (2.08(3)-2.183(13) Å) are as expected.<sup>24,40,43</sup> The Te–N bond lengths (1.97-2.06 Å) in these complexes can be compared with those reported in diorganotellurimides (R<sub>2</sub>Te=NR').<sup>44</sup> The observed distances indicate dipolar character as is usually observed in tellurium imides.<sup>44</sup> These distances are significantly shorter than those found for intramolecular Te…N secondary bonding interactions.<sup>45</sup> The Te–O distances (2.510(13)-2.690(12) Å) are significantly longer than those expected for single tellurium–



Figure 7. ORTEP drawing of trans-[PtCl<sub>2</sub>(TeMes<sub>2</sub>){NC(O)Ph-(TeMes<sub>2</sub>)}] (10) with atomic numbering scheme (drawn with 25% probability ellipsoids; H atoms are omitted for clarity).



Figure 8. ORTEP drawing of *trans*- $[PtCl_2\{NC(O)Me(TeMes_2)\}_2]$ . 2CH<sub>2</sub>Cl<sub>2</sub> (12·2CH<sub>2</sub>Cl<sub>2</sub>) with atomic numbering scheme (drawn with 25% probablility ellipsoids; H atoms are omitted for clarity).

oxygen bond lengths but are indicative of intramolecular secondary Te···O bonding interactions.<sup>45</sup> The Pt---Te distances fall in the range 3.320(3)-3.5150(13) Å which are shorter than the sum of van der Waals radii of platinum and tellurium (3.81 Å). This suggests that there is platinum-tellurium nonbonding interaction which facilitates the formation of Pt-telluroether linkage.

The C–Te–C angles  $(94.4-100.2^{\circ})$  are reduced from the free telluroether (e.g., TeMes<sub>2</sub>,  $101.0(1)^{\circ}$ ).<sup>46</sup> This angle is little influenced on coordination with platinum.<sup>24</sup> The Te–N–C angles show little variation ( $101.6-104.1^{\circ}$ ), and the Pt–N–C angles fall in a rather large range ( $120(2)-130.4(12)^{\circ}$ ). The carbon–oxygen bond lengths (1.23(4)-1.30(2) Å) are of double bond character.

The complex  $[PtCl(Te-o-tol){NC(O)Ph}_2]$  (11, Figure 9) comprises a distorted square-planar platinum atom with a "N2ClTe" coordination core. The two nitrogen atoms of the amide group are mutually *trans*. The deviations of the N1–Pt1–N2 and Cl1–Pt1–Te1 angles from linearity are rather small. The two five- membered chelate rings "Pt1Te1O1C1N1" and "Pt1Te1O2C8N2" are coplanar. The phenyl rings of the amide groups are slightly out of the plane and are little tilted in the opposite directions from this plane. The coplanarity of the two chelate rings and short bite angle of the amide ligands



(b)

Figure 9. (a) ORTEP drawing of  $[PtCl(o-tolTe){NC(O)Ph}_2]$ . CH<sub>2</sub>Cl<sub>2</sub> (11·CH<sub>2</sub>Cl<sub>2</sub>) (drawn with 25% probability ellipsoids; H atoms and solvent molecules are omitted for clarity). (b) Intermolecular interaction in 11.

appear to be responsible for unusually short Pt-Te distance (2.4503(10) Å) reported thus far.<sup>12</sup> The other bond distances involving platinum (Pt-N and Pt-Cl) are normal. The tellurium atom adopts a distorted trigonal bipyramidal configuration defined by the platinum, o-tolyl ring and a lone pair of electrons at the equatorial positions while the two oxygen atoms occupying the axial sites. The Te-C and Te-O distances are as expected. Tellurium(IV) as a ligand has been described recently and complexes in general have Te-Cl linkages.<sup>37,47</sup> The present complex represents the first example where organotellurium(IV) acetoxy compound acts as a ligand. Recently Singh and co-workers have isolated a palladium complex [{ $(o-tol-Te)_2O$ }Pd( $\mu$ -OAc)<sub>2</sub>] containing tellurenic anhydride as a ligand.<sup>48</sup> The X-ray crystallographic structural parameters of [PtCl(Te-o-tol){NC(O)Ph}<sub>2</sub>] are in accordance with the data obtained from the DFT calculations. Interstingly, electron density contours/charge density distribution (Figures S5 and S6) reveals that there is an extensive delocalization of electron density along the "PtCl(Te){NC(O)Ph}2" unit and leads to  $\pi - \pi$  stacking with the separation of 3.56 Å (Figure 9b).

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Density Functional Theory Calculations. The optimized geometry of trans- $[PtCl_2(TeArAr')_2]$  (4, 5, 9) is given in Figure S7. The calculated geometrical parameters (bond lengths and bond angles) show good agreement with those obtained from X-ray crystallographic data (Tables S1-S7). The reaction between  $[PtCl_2(PhCN)_2]$  and telluroether may lead to the formation of tellurium amides and/or imides. In order to assess the possibility of formation of tellurium amides, an amide analogue of  $trans-[PtCl_2{NC(O)Ph(TeMes_2)}_2]$  was also optimized and the relaxed geometry is shown in Figure S8. The amide analogue shows larger separation between tellurium and the nitrogen center (Te-N, 2.93 Å) than the tellurium imide (Te-N, 2.09 Å) derivative. The C-Te-C angle in tellurium imide and amide structure is 94.8° and 99.5°, respectively. This indicates that amide structure has C-Te-C angle close to that of free telluroether. Based on the comparison between crystallographic data and theoretical results, it can be inferred that the reactions between  $[PtCl_2(PhCN)_2]$  and telluroethers would result in the formation of tellurium imide rather than a tellurium amide linkage. The relative charge density for the plane >Te--N--C=O unit of 5 is shown in Figure 10. The remarkably high



**Figure 10.** Relative charge density for the plane having >Te—N— C=O unit in the *trans*-[PtCl<sub>2</sub>{NC(O)Ph(TeMes<sub>2</sub>)}<sub>2</sub>]. Inset picture shows the plane from another angle.

formal positive charge on tellurium is found in the Mullikan and Lowdin charge analysis and further reconfirmed from the plot of total electron density contours (Figure 11). The theoretical calculation (Figure 10) and the single-crystal X-ray analysis (Figure 4) indicate that the Te-N-C=O unit is coplanar, with a dihedral angel of  $\sim 2^{\circ}$  (O1-C1-N1-Te1,  $-2.1(15)^{\circ}$ ). The relative charge density calculation (Figure 10) suggests that the electron cloude is delocalized throughout the Te-N-C-O bond. The delocaloization is further extended into the phenyl ring due to its planarity with the Te-N-C= O unit. The above delocalization is also supported by O1-C1, C1-N1, and N1-Te1 bond distances which are intermediate to the corresponding single and double bond distances. It is clear from Figure 11 that the valence electron density around tellurium is negligible indicating significant positive charge on tellurium which is in agreement with the X-ray photoelectron spectroscopy (XPS) results indicating +4 oxidation state of tellurium. Molecular orbital (MO) analysis for the frontier MOs of trans- $[PtCl_2{NC(O)Ph(TeMes_2)}_2]$  (5) shows that HOMO and LUMO have major contributions from platinum metal atom (Figure S9). Tellurium atomic orbitals are



Figure 11. Total electron density contours (contour value 0.1) for the *trans*- $[PtCl_2{NC(O)Ph(TeMes_2)}_2]$ .

appearing in LUMO+1 molecular orbital. Since the molecular arrangement of 4, 6, and 9 are similar to 5, it could be inferred that the formal charge on tellurium and platinum in all these complexes are +4 and +2 along with the above-described delocalization of charge, respectively.

It is worth mentioning that in the present study, the reactions between  $[PtCl_2(PhCN)_2]$  and TeMes<sub>2</sub>, addition of telluroether to PhCN ligand take place with the formation of imide complex **5**. However, Vigo and co-workers<sup>23</sup> reported that the recation between  $[PtCl_2(PhCN)_2]$  and Te(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub>}<sub>2</sub> yields *cis*-[PtCl<sub>2</sub>{Te(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub>}<sub>2</sub>] by substitution of PhCN ligand. Therefore, in order to access the likewise possibility of any ligand substitution product (*instead of addition product, i.e., amide or imide complex*) in the reaction of  $[PtCl_2(PhCN)_2]$  with TeMes<sub>2</sub>, a substituted counterpart products were considered and optimized without any constraint and the optimized relaxed geometry is shown in Figure S10. It is found that formation of addition product, *i.e., amide/imide complex*, is thermodynamically more favorable in comparison to the formation of substitution product PtCl<sub>2</sub>(TeMes)<sub>2</sub>.

# EXPERIMENTAL SECTION

Solvents were dried and distilled under a nitrogen atmosphere prior to use according to a literature method.<sup>49</sup> All the reactions were carried out under an argon atmosphere. Diaryltellurides, ArTeAr', were prepared by the reaction of ArTeBr, obtained in situ by bromination of diarylditellurides (Ar<sub>2</sub>Te<sub>2</sub>) with bromine in THF, with an appropriate aryl magnesium bromide (see Supporting Information for details).<sup>50</sup> Elemental analyses were carried out on a Thermo Fischer Flash EA 1112 CHNS microanalyzer. Melting points were determined in capillary tubes and are uncorrected.  $^1H,\ ^{13}C\{^1H\},\ ^{125}Te\{^1H\},$  and <sup>195</sup>Pt{<sup>1</sup>H} NMR spectra were recorded on a Bruker Avance-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 internal chloroform peak ( $\delta$  7.26 ppm for <sup>1</sup>H and 77.0 ppm for <sup>13</sup>C) and external Me<sub>2</sub>Te for <sup>12</sup> Te (secondary reference  $Ph_2Te_2$ ,  $\delta$  421 ppm in  $C_6D_6$ ) and external Na<sub>2</sub>PtCl<sub>6</sub> in D<sub>2</sub>O for <sup>195</sup>Pt. X-ray photoelectron spectrum of trans- $[PtCl_{2}{NC(O)Ph(TeMes_{2})}_{2}]$  (5) was recorded on a SPECS instrument with 385 W, 13.85 kV, and 175.6 nA (sample current) Al  $K\alpha$  (1486.6 eV) duel anode, with a PHOBIOS 100/150 Delay Line

Detector (DLD), and with pass energy of 50. The C 1S peak (284.6 eV) was used as an internal reference for the absolute binding energy calculation.

X-ray Crystallography. Single-crystal X-ray data on trans-[PtCl<sub>2</sub>(PhCN){NC(O)Ph(Te(Mes)o-tol)}] (4), trans-[PtCl<sub>2</sub>{NC-(O)Ph(TeMes<sub>2</sub>)}<sub>2</sub>] (5), trans-[PtCl<sub>2</sub>{NC(Ph)C<sub>4</sub>H<sub>7</sub>O}{NC(O)Ph-(TeMes<sub>2</sub>)}] (6), trans-[PtCl<sub>2</sub>{NC(Ph)C<sub>4</sub>H<sub>7</sub>O}{NC(O)Ph{Te(o-tol)Mes}}<sub>2</sub>] (9) trans-[PtCl<sub>2</sub>(TeMes<sub>2</sub>){NC(O)Ph(TeMes<sub>2</sub>)}] (10), [PtCl(Te-o-tol)-{NC(O)Ph}<sub>2</sub>] (11), and trans-[PtCl<sub>2</sub>{NC(O)Me(TeMes<sub>2</sub>)}<sub>2</sub>] (12) were collected on Agilent Super Nova CCD and Rigaku AFC7S diffractometers at room temperature (298 ± 2 K). Crystallographic data, together with data collection and refinement details, are given in Table S8. All the data were corrected for Lorentz and polarization effects. The structures were solved by direct methods<sup>51</sup> and expanded using Fourier technique.<sup>52</sup> Hydrogen atoms were added to the parent atom with idealized geometry and refined isotropically. Molecular structures were drawn using ORTEP.<sup>53</sup>

**Density Functional Theory Calculations.** Theoretical calculations on 4, 5, 9, and 11 were carried out using the *ab initio* molecular orbital theory-based LCAO approach as implemented in the GAMESS software.<sup>54</sup> Geometry optimization (without any symmetry constraint) was done using the hybrid exchange correlation energy functional commonly known as B3-LYP.<sup>54–56</sup> The notation B3 implies threeparameter Becke exchange functional, and LYP indicates correlation functional as described by Lee, Yang, and Parr. Selected calculations were also carried out using the PBE0 functional, and the results were found to be analogous (Table S9). To ensure the local minima, frequency calculations were carried out. While a standard split-valence with polarization functions (6-31G(d)) was employed as basis set for all low-*Z* elements, the SBKJC standard basis set was used for platinum and tellurium.

**Synthesis.** Reactions between  $[PtCl_2(PhCN)_2]$  and ArTeAr' in 1:2 ratio in DCM are given in the Supporting Information.

Reactions between  $[PtCl_2(PhCN)_2]$  and TeArMes in 1:1 Ratio in THF. (i). Reaction with TePhMes. To a THF solution of  $[PtCl_2(PhCN)_2]$  (100 mg, 0.21 mmol) was added mesityl phenyl telluride (72 mg, 0.22 mmol), and the reaction mixture was stirred for 6 h at room temperature. The solution was dried and washed with diethyl ether. The complex was extracted with DCM and recrystallized from a DCM-hexane (5:1) mixture, which on slow evaporation afforded  $[PtCl_2\{Te(Ph)Mes\}_2]$  (3b) in 38% (75 mg) yield. Microanalysis and NMR data are consistent with those of the sample prepared in DCM (Supporting Information).

(ii). Reaction with Te(o-tol)Mes. The reaction was carried out by a method similar to that described above for reaction with TePhMes. The residue was extracted with diethyl ether, and the insoluble part was identified as  $[PtCl_2{Te(o-tol)Mes}_2]$  (3d, yield ~5%, by NMR data). The ether extract on evaporation afforded *trans*- $[PtCl_2(PhCN)-{NC(O)Ph[Te(o-tol)Mes]}]$  (4, yield 41%) which was recrystallized from acetone-hexane mixture as light yellow crystals. Anal. Calcd for  $C_{30}H_{28}Cl_2N_2OPtTe: C, 43.61; H, 3.42; N, 3.39\%$ . Found: C, 43.52; H, 3.41; N, 3.45%. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  2.29 (s, 4-Me of Mes), 2.38 (s, 2-Me of tol), 2.64 (s, 2,6-Me of Mes), 6.98 (s, 3,5-CH of Mes), 7.38-7.86 (m), 8.73-8.77 (m, aryl) ppm. <sup>125</sup>Te{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  937 ( $J(^{195}Pt-^{125}Te) = 317$  Hz) ppm.

(*iii*). Reaction with TeMes<sub>2</sub>. This reaction on stirring at room temperature gave different products depending on the duration of the reaction.

(a) At room temperature: The reaction was carried out by a method similar to that described above, and the residue was recrystallized from an acetone–hexane mixture. The orange crystals of *trans*-[PtCl<sub>2</sub>{NC-(O)Ph(TeMes<sub>2</sub>)}<sub>2</sub>] (5, yield 28%) were separated out, and the mother liquor on further reduction of the solvent afforded crystals of *trans*-[PtCl<sub>2</sub>(TeMes<sub>2</sub>)<sub>2</sub>] (3e, yield <5%, mp >200 °C, characterized from NMR). Characterization data for 5: Anal. Calcd for C<sub>50</sub>H<sub>54</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>2</sub>PtTe<sub>2</sub>: C, 48.58; H, 4.40; N, 2.27%. Found: C, 48.25; H, 4.33; N, 2.30%. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  2.21 (s, 4-Me), 2.39 (s, 2,6-Me<sub>2</sub>), 6.70 (s, 3,5-CH), 7.16 (t, 7.8 Hz), 7.36 (m), 8.24 (d, 7.2 Hz) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): 21.0, 22.4 (s, Me), 127.4, 128.6, 130.2, 130.3, 130.7, 133.9 (56 Hz), 140.6, 143.6, 182.3 (C=O) ppm.

<sup>125</sup>Te{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  959 ( $J(^{195}Pt-^{125}Te) = 347$  Hz) ppm. <sup>195</sup>Pt{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  -3079 ppm.

(b) Refluxed for 30 min: The reaction between  $[PtCl_2(PhCN)_2]$ (100 mg, 0.21 mmol) and dimesityl telluride (79 mg, 0.21 mmol) was carried out similar to the above under reflux for 30 min in THF. After drying under vacuum, the residue was washed with hexane and extracted with diethyl ether. The solvent was evaporated in vacuum to give a pale yellow powder of *trans*- $[PtCl_2\{NC(Ph)C_4H_7O\}\{NC(O)-Ph(TeMes_2)\}]$  (6, yield 70 mg, 35%, mp 179–180 °C). Anal. Calcd for C<sub>36</sub>H<sub>39</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>2</sub>PtTe: C, 46.68; H, 4.25; N, 3.02%. Found: C, 47.00; H, 4.20; N, 2.85%. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  2.21, 2.27 (each s, Me), 2.60 (br), 3.54–3.78 (m), 5.18 (br, C<sub>4</sub>H<sub>7</sub>O), 6.95 (s, C<sub>6</sub>H<sub>2</sub>Me<sub>3</sub>), 7.28–7.50 (m), 8.58–8.65 (m, aryl) ppm. <sup>125</sup>Te{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  946 ppm. <sup>195</sup>Pt{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  –1861 ppm.

(c) Refluxed for 3 h: The reaction between  $[PtCl_2(PhCN)_2]$  (100 mg, 0.21 mmol) and dimesityl telluride (79 mg, 0.21 mmol) was carried out similar to the above under reflux for 3 h in THF. The solvent was evaporated under vacuum, and the residue was extracted from diethyl ether, leaving behind an insoluble part which was soluble in acetone.

The diethyl ether extract on evaporation gave an orange powder, [PtCl(TeMes<sub>2</sub>){Te(Mes)CH<sub>2</sub>C<sub>6</sub>H<sub>2</sub>Me<sub>2</sub>}] (7), which could be recrystallized from an acetonitrile-diethyl ether mixture at room temperature (yield 29%, mp 180 °C). Anal. Calcd for C<sub>36</sub>H<sub>43</sub>ClPtTe<sub>2</sub>: C, 44.97; H, 4.51%. Found: C, 45.01; H, 4.53%. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  2.02, 2.19, 2.24, 2.27, 2.34, 2.53 (each s for Me), 4.0 ( $J_{AX}$  = 16.8,  $\Delta \nu_{AX}$  = 105.8 Hz; metalated CH<sub>2</sub>), 6.66 (s, 3,5-CH of Mes of metalated), 6.71 (s, 3,5-CH of TeMes<sub>2</sub>), 6.86, 7.04 (CH of metalated ring) ppm. <sup>125</sup>Te{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  336 (<sup>1</sup>J(<sup>195</sup>Pt-<sup>125</sup>Te) = 622 Hz), 592 (<sup>1</sup>J(<sup>195</sup>Pt-<sup>125</sup>Te) = 1545 Hz), 598 (~5% due to dimer), 259 (TeMes<sub>2</sub>) ppm.

The acetone extract on evapaoration gave a yellow powder comprising  $[Pt_2Cl_2(\mu-Cl)_2(TeMes_2)_2]$  (8) and  $[PtCl_2(PhCN)_2]$  (1a) as inferred from NMR data. <sup>125</sup>Te{<sup>1</sup>H} NMR (CDCl\_3):  $\delta$  425 (<sup>1</sup>J(<sup>195</sup>Pt-<sup>125</sup>Te) = 1052 Hz) ppm (due to 8). <sup>195</sup>Pt{<sup>1</sup>H} NMR (CDCl\_3):  $\delta$  -3083 (due to 8) and -2336 (due to 1a) ppm.

Reactions between  $[PtCl_2(PhCN)_2]$  and TeArMes in 1:2 Ratio in THF. (i). Reaction with TePhMes. The reaction was carried out in a manner similar to that of  $[PtCl_2(PhCN)_2]$  and TePhMes described above using  $[PtCl_2(PhCN)_2]$  (100 mg, 0.21 mmol) and mesityl phenyl telluride (140 mg, 0.43 mmol) in THF at room temperature. The product after recrystallization was characterized as  $[PtCl_2{Te(Ph)-Mes}_2]$  (3b, yield 153 mg, 77%).

(ii). Reaction with Te(o-tol)Mes. The reaction was carried out in a manner similar to that of  $[PtCl_2(PhCN)_2]$  and Te(o-tol)Mes described above. The residue was extracted with diethyl ether, and the insoluble part was identified as  $[PtCl_2\{Te(o-tol)Mes\}_2]$  (3d, yield ~10%, NMR data were consistent with those of the sample prepared in DCM). The ether extract on evaporation afforded *trans*- $[PtCl_2(NC-(O)Ph\{Te(o-tol)Mes\})_2]$  (9) and was recrystallized from acetone–hexane (8:1) mixture at room temperature as orange crystals (yield 67%, mp 179 °C). Anal. Calcd for  $C_{46}H_{46}Cl_2N_2O_2PtTe_2$ : C, 46.82; H, 3.93; N, 2.37%. Found: C, 46.77; H, 4.00; N, 2.40%. <sup>1</sup>H NMR (CDCl\_3):  $\delta$  2.13 (s, 4-Me of Mes), 2.18 (s, 2-Me of tol), 2.43 (s, 2,6-Me of Mes), 6.64 (s, 3,5-CH of Mes), 7.09–7.23 (m), 7.30–7.35 (m), 7.90 (d, 7.8 Hz), 8.18 (d, 7.5 Hz, tol) ppm. <sup>125</sup>Te{<sup>1</sup>H} NMR (CDCl\_3):  $\delta$  907 ppm. <sup>195</sup>Pt{<sup>1</sup>H} NMR (CDCl\_3):  $\delta$  -1525 ppm.

When **9** was left in acetone–hexane at room temperature in open for recrystallization, colorless crystals of  $[PtCl(Teo-tol)\{NC(O)Ph\}_2]$  (**11**) were isolated. Anal. Calcd for  $C_{21}H_{17}ClN_2O_2PtTe: C, 36.69; H, 2.49; N, 4.07\%. Found: C, 36.43; H, 2.53; N, 3.99\%. <sup>1</sup>H NMR (CDCl<sub>3</sub>): <math>\delta$  2.93 (s, 2-Me), 7.32, 7.38 (t, 7.5 Hz), 7.49 (t, 6.9 Hz, 4-CH of Ph and tol), 7.72 (d, 8.1 Hz, 2,6-CH of Ph), 8.22 (d, 7.8 Hz, 6-CH of tol) ppm. <sup>125</sup>Te{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  633 ppm. <sup>195</sup>Pt{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  –3188 ppm.

(iii). Reaction with TeMes<sub>2</sub>. This reaction on stirring at room temperature gave different products depending on the duration of the reaction.

(a) 24 h reaction time: The reactants  $[PtCl_2(PhCN)_2]$  (100 mg, 0.21 mmol) and dimesityl telluride (158 mg, 0.43 mmol) in THF were

stirred for 24 h at room temperature. The solvent was evaporated under vacuum and the residue was extracted with diethyl ether from which *trans*-[PtCl<sub>2</sub>{NC(O)Ph(TeMes<sub>2</sub>)}<sub>2</sub>] (5, yield 37%) was isolated and characterized by NMR spectroscopy. The supernantant exhibited <sup>125</sup>Te NMR spectrum showing resonance due to 3e, 5, and 10, together with a small amount of TeMes<sub>2</sub>.

(b) 72 h reaction time: The contents of another reaction were stirred for 72 h followed by evaporation of the solvent. The residue was washed with diethyl ether and extracted with acetone. The acetone extract on drying gave trans-[PtCl<sub>2</sub>(TeMes<sub>2</sub>){NC(O)Ph(TeMes<sub>2</sub>)}] (10) and was recrystallized from acetone—hexane (10:1) as colorless crystals (yield: 39%), mp 190 °C. Anal. Calcd for C<sub>43</sub>H<sub>49</sub>Cl<sub>2</sub>NOPtTe<sub>2</sub>: C, 46.23; H, 4.42; N, 1.25%. Found: C, 46.31; H, 4.41; N, 1.27%. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  2.21 (s, 2,4,6-Me of NTeMes<sub>2</sub>), 2.29 (s, 4-Me of TeMes<sub>2</sub>), 2.59 (br, s, 2,6-Me of TeMes<sub>2</sub>)), 6.70 (s, 3,5-CH of NTeMes<sub>2</sub>), 6.91 (s, 3,5-CH of TeMes<sub>2</sub>), 7.41–7.54 (m, 3,4,5-CH of Ph), 8.49 (d, 7.2 Hz, 2,6-CH of Ph) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$ 20.8, 21.0, 22.8, 26.1, 127.8, 128.9, 129.3, 130.2, 130.7, 134.7, 139.3, 141.5, 143.4, 183.4 (C=O) ppm. <sup>125</sup>Te{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  418 (<sup>1</sup>J(<sup>195</sup>Pt-<sup>125</sup>Te) = 1638 Hz), 939 (J(<sup>195</sup>Pt-<sup>125</sup>Te) = 309 Hz) ppm. <sup>195</sup>Pt{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  –2701 ppm.

(c) 7 d reaction time: The contents of another reaction were stirred for 7 days followed by evaporation of the solvent. The residue was washed with hexane–diethyl ether (1:1) mixture and extracted with diethyl ether. The ether extract after drying under vacuum affored **3e** as characterized by <sup>125</sup>Te NMR spectroscopy:  $\delta$  467 ppm (<sup>1</sup>J(<sup>195</sup>Pt–<sup>125</sup>Te) = 377 Hz).

# CONCLUSIONS

From the foregoing results, it can be concluded that the reactions of telluroether with commonly used platinum precursors,  $[PtCl_2(RCN)_2]$ , in dichloromethane yield the desired substitution products, [PtCl<sub>2</sub>(TeAr<sub>2</sub>)<sub>2</sub>], but in tetrahydrofuran such reactions proceed through a complex intermediate species which can be isolated and structurally characterized in the case of telluroethers containing sterically demanding organic groups. These intermediate species are formed by sequential attack of telluroether on coordinated nitrile, mediated by the platinum center, to generate [PtCl<sub>2</sub>- $(RCN)(NC(O)R{TeAr_2})$  and  $[PtCl_2(NC(O)R{TeAr_2})_2]$ . Tellurium in these species is in the formal oxidation state of +4 and shows intramolecular interactions both with oxygen and platinum. The interaction with platinum occurs in solution, as one can observe J(Pt-Te) coupling in <sup>125</sup>Te NMR spectra. These species slowly decompose in a stepwise manner to generate  $[PtCl_2(TeAr_2){NC(O)R(TeAr_2)}]$  and  $[PtCl_2 (TeAr_2)_2$ ].

#### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b02024. CCDC Nos. 1416145–1416150 and 1419452 contain the crystallographic data for 12, 5, 10, 9, 4, 6, and 11, respectively. These files 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].

Details of telluroethers synthesis, purification and characterizations, reactions of telluroethers with  $[PtCl_2-(PhCN)_2]$  in DCM and characterization data, selected interatomic parameters (Tables S1–S7), crystallographic and refinement data (Table S8), and Figures S1–S10 (PDF)

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#### Notes

The authors declare no competing financial interest.

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### REFERENCES

(1) Comasseto, J. V.; Cunha, R. L. O. R.; Clososki, G. C. Comprehensive Organometallic Chemistry III **2007**, *9*, 587–648.

- (2) McGarrigle, E. M.; Myers, E. L.; Illa, O.; Shaw, M. A.; Riches, S. L.; Aggarwal, V. K. *Chem. Rev.* **2007**, *107*, 5841–5883.
- (3) Kumar, A.; Rao, G. K.; Kumar, S.; Singh, A. K. Organometallics 2014, 33, 2921–2943.
- (4) Gysling, H. J. Coord. Chem. Rev. 1982, 42, 133-244.
- (5) Arnold, J. Prog. Inorg. Chem. 1995, 43, 353-417.
- (6) Singh, A. K.; Sharma, S. Coord. Chem. Rev. 2000, 209, 49-98.
- (7) Levason, W.; Orchard, S. D.; Reid, G. Coord. Chem. Rev. 2002, 225, 159–199.
- (8) Sharma, R. K.; Kedarnath, G.; Jain, V. K.; Wadawale, A.; Pillai, C. G. S.; Nalliath, M.; Vishwanadh, B. Dalton Trans. **2011**, 40, 9194–9201.
- (9) Nogueira, C. W.; Zeni, G.; Rocha, J. B. T. Chem. Rev. 2004, 104, 6255-6286.
- (10) Tiekink, E. R. T. Dalton Trans. 2012, 41, 6390-6395.
- (11) Amorati, R.; Valgimigli, L.; Dinér, P.; Bakhtiari, K.; Saeedi, M.; Engman, L. *Chem. - Eur. J.* **2013**, *19*, 7510–7522.
- (12) Jain, V. K.; Chauhan, R. S. Coord. Chem. Rev. 2016, 306, 270-301.
- (13) Chauhan, R. S.; Kedarnath, G.; Wadawale, A.; Munoz-Castro, A.; Arratia-Perez, R.; Jain, V. K.; Kaim, W. *Inorg. Chem.* **2010**, *49*, 4179–4185.
- (14) Fritzmann, E. J. Russ. Phys. Chem. Soc. 1915, 47, 588.
- (15) Chatt, J.; Venanzi, L. M. J. Chem. Soc. 1955, 2787–2793. Chatt,

J.; Venanzi, L. M. J. Chem. Soc. 1955, 3858-3864.

- (16) Chatt, J.; Duncanson, L. A.; Venanzi, L. M. J. Chem. Soc. **1955**, 4456–4460. Chatt, J.; Duncanson, L. A.; Venanzi, L. M. J. Chem. Soc. **1955**, 4461–4469.
- (17) Chatt, J.; Venanzi, L. M. J. Chem. Soc. 1957, 2351-2356.
- (18) Adams, D. M.; Chatt, J.; Gerratt, J.; Westland, A. D. J. Chem. Soc. 1964, 734-739.
- (19) Gysling, H. J.; Zumbulyadis, N.; Robertson, J. A. J. Organomet. Chem. 1981, 209, C41-C44.
- (20) Kolay, S.; Kumar, M.; Wadawale, A.; Das, D.; Jain, V. K. Dalton
- Trans. 2014, 43, 16056–16065. (21) Kemmitt, T.; Levason, W. Inorg. Chem. 1990, 29, 731–735.
- (21) Kemmut, 1.; Levason, W. morg. Chem. 1990, 29, 751–755.
- (22) Knorr, M.; Guyon, F.; Jourdain, I.; Kneifel, S.; Frenzel, J.; Strohmann, C. Inorg. Chim. Acta 2003, 350, 455-466.
- (23) Vigo, L.; Oilunkaniemi, R.; Laitinen, R. S. Eur. J. Inorg. Chem. 2008, 2008, 284–290.
- (24) Kolay, S.; Kumar, M.; Wadawale, A.; Das, D.; Jain, V. K. J. Organomet. Chem. 2015, 794, 40-47.
- (25) Michelin, R. A.; Mozzon, M.; Bertani, R. Coord. Chem. Rev. 1996, 147, 299-338.
- (26) Kukushkin, V. Y.; Pombeiro, A. J. L. Chem. Rev. 2002, 102, 1771–1802.
- (27) Pombeiro, A. J. L.; Kukushkin, V. Y. In *Comprehensive Coordination Chemistry II*; Lever, A. B. P., Vol. Ed.; 2004; p: 639.
- (28) Bolotin, D. S.; Bokach, N. A.; Haukka, M.; Kukushkin, V. Y. Inorg. Chem. 2012, 51, 5950–5964.
- (29) Lasri, J.; Kuznetsov, M. L.; Guedes da Silva, M. F. C.; Pombeiro, A. J. L. Inorg. Chem. **2012**, *51*, 10774–10786.

Article

- (30) Bolotin, D. S.; Bokach, N. A.; Kritchenkov, A. S.; Haukka, M.; Kukushkin, V. Y. *Inorg. Chem.* **2013**, *52*, 6378–6389.
- (31) Gupta, V.; Karthik, V.; Anantharaman, G. Dalton Trans. 2015, 44, 758-766.
- (32) Pünner, F.; Hilt, G. Chem. Commun. 2014, 50, 7310-7313.
- (33) Korobkov, I.; Gambarotta, S.; Yap, G. P. A. Organometallics 2001, 20, 2552–2559.
- (34) Clayden, J. Nat. Chem. 2010, 2, 523-524.
- (35) Duddeck, H.; Biallaβ, A. Magn. Reson. Chem. **1994**, 32, 303-311.
- (36) (a) Misra, S.; Chauhan, A. K. S.; Singh, P.; Srivastava, R. C.;
- Duthie, A.; Butcher, R. J. Dalton Trans. 2010, 39, 2637-2643.
- (b) Beckmann, J.; Bolsinger, J.; Duthie, A.; Finke, P. Dalton Trans. **2013**, 42, 12193–12202.
- (37) Lin, T. P.; Gabbaï, F. P. J. Am. Chem. Soc. 2012, 134, 12230-12238.
- (38) Konno, H.; Yamamoto, Y. Bull. Chem. Soc. Jpn. **1988**, 61, 2990–2992.
- (39) Hammond, J. S.; Winograd, N. J. Electroanal. Chem. Interfacial Electrochem. 1977, 78, 55–69.
- (40) Singh, A. K.; Kadarkaraisamy, M.; Husebye, S.; Tornroos, K. W. J. Chem. Res. **2000**, 2000, 64–65.
- (41) Oblad, P. F.; Bercaw, J. E.; Hazari, N.; Labinger, J. A. Organometallics 2010, 29, 789-794.
- (42) Dey, S.; Jain, V. K.; Knödler, A.; Klein, A.; Kaim, W.; Záliš, S. Inorg. Chem. **2002**, 41, 2864–2870.
- (43) Singh, A. K.; Kumar, J. S.; Butcher, R. J. Inorg. Chim. Acta 2001, 312, 163-169.
- (44) Chivers, T. J. Chem. Soc., Dalton Trans. 1996, 1185-1194.
- (45) Sudha, N.; Singh, H. B. Coord. Chem. Rev. **1994**, 135/136, 469–515.
- (46) Klapötke, T. M.; Krumm, B.; Mayer, P.; Polborn, K.; Schwab, I. Z. Anorg. Allg. Chem. **2005**, 631, 2677–2682.
- (47) Torubaev, Y.; Pasynskii, A.; Mathur, P. Coord. Chem. Rev. 2012, 256, 709-721.
- (48) Chakraborty, T.; Sharma, S.; Singh, H. B.; Butcher, R. J. Organometallics 2011, 30, 2525-2530.
- (49) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. Purification of Laboratory Chemicals, 2nd ed.; Pergamon: Oxford, 1980.
- (50) Petragnani, N.; Torres, L.; Wynne, K. J. J. Organomet. Chem. 1975, 92, 185-189.
- (51) SIR92: Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli, M. *J. Appl. Crystallogr.* **1994**, *27*, 435–436.
- (52) SHELX: Sheldrick, G. M. Acta Crystallogr., Sect. A: Found. Crystallogr. 2008, 64, 112–122.
- (53) Johnson, C. K. ORTEP-II, Report ORNL-5136; Oak Ridge National Laboratory, Oak Ridge, TN, 1976.
- (54) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. J. Comput. Chem. **1993**, *14*, 1347–1363.
- (55) Becke, A. D. Phys. Rev. A: At., Mol., Opt. Phys. 1988, 38, 3098-3100.
- (56) Lee, C.; Yang, W.; Parr, R. G. Phys. Rev. B: Condens. Matter Mater. Phys. **1988**, 37, 785–789.