

# Synthesis and single crystal X-ray structure of the first cationic Pd(II) complex of a tellurium-containing polyaza macrocycle: contrasting reactions of Pd(II) and Pt(II) with a 22-membered macrocyclic Schiff base

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The reaction of the tellurium containing macrocyclic Schiff base **1** with Pd(PhCN)<sub>2</sub>Cl<sub>2</sub> and NH<sub>4</sub>PF<sub>6</sub> gives the expected cationic complex [Pd<sup>II</sup>1][PF<sub>6</sub>]<sub>2</sub>; by contrast the reaction of **1** with Pt(cod)Cl<sub>2</sub> proceeds via novel transmetalation to yield an organoplatinum complex.

The chemistry of macrocycles bearing nitrogen or sulfur atoms has been very well developed.<sup>1</sup> The considerable effort which has been directed towards studying the coordination chemistry of polythio crowns in recent years has established that these macrocyclic ligands exhibit very different coordinating properties from their acyclic counterparts. This is principally due to the greater σ-donor effects caused by their cyclic nature which has facilitated stabilization of a wide range of metal ions in relatively unusual oxidation states. Polyselenoether macrocycles have an equally good potential to serve as ligands, however, the number of known polyselenoether macrocycles is very small.<sup>2</sup>

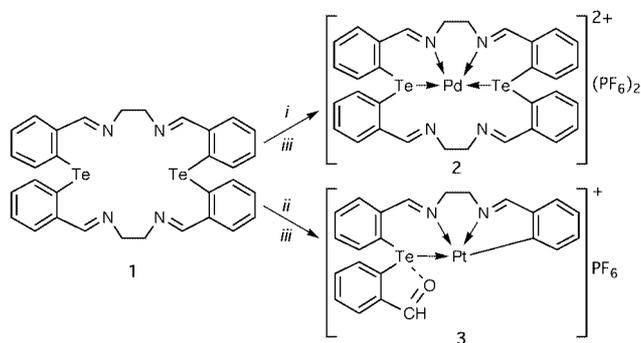
Recent studies by Levason *et al.* and others have established that the acyclic telluroether ligands are significantly better σ-donors compared to the lighter group 16 congeners.<sup>3</sup> Despite this, extension of this type of chemistry to the corresponding tellurium macrocycles is virtually unknown. A few notable examples include, 21-telluraporphyrins<sup>4a</sup> and 1,1,5,5,9,9-hexachloro-1,5,9-tritelluracyclododecane.<sup>4b</sup> Recently we have reported an easy, high yield template free synthesis, structure and preliminary coordination behaviour of the novel tellurium azamacrocyclic **1**.<sup>4c</sup> The high yield and template free synthesis of **1** arises from intramolecular Te...N interactions in the macrocyclic ring.<sup>4c</sup> In continuation of this work, we report here, the synthesis and structure of the first cationic Pd(II) complex of the tellurium containing macrocyclic Schiff base **1** and the contrasting reaction of Pt(cod)Cl<sub>2</sub> with **1**. Both complexes **2** and **3** have been characterized by <sup>1</sup>H, <sup>13</sup>C, <sup>125</sup>Te NMR, mass and X-ray crystallography.

The reaction of **1** with 1 equivalent of Pd(PhCN)<sub>2</sub>Cl<sub>2</sub> in CHCl<sub>3</sub> afforded a reddish yellow powder which was dissolved in methanol and treated with an excess of NH<sub>4</sub>PF<sub>6</sub> to give the yellow complex **2** (Scheme 1). Slow diffusion of diethyl ether

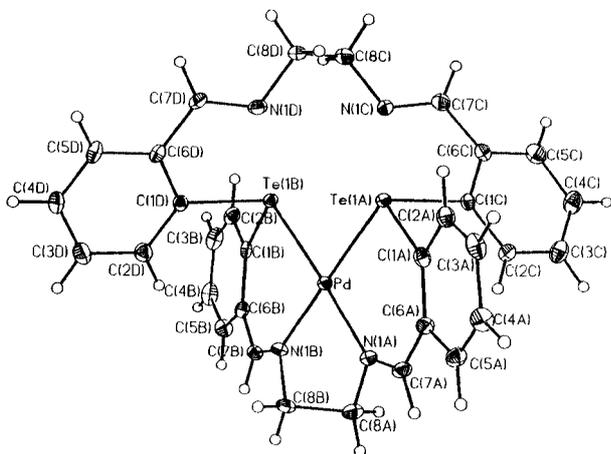
into an acetonitrile solution of this complex afforded yellow needles of **2**. This complex is fairly soluble in MeCN, MeNO<sub>2</sub>, acetone, DMF and DMSO but insoluble in common chlorinated solvents. The IR spectrum of the complex confirmed the presence of PF<sub>6</sub><sup>-</sup> [ $\nu(\text{P-F})$  836,  $\delta(\text{F-P-F})$  556 cm<sup>-1</sup>] and showed a peak at 1639.8 cm<sup>-1</sup> corresponding to the azomethine stretching frequency. The <sup>1</sup>H NMR spectrum of complex **2** exhibited two peaks in equal intensity at 8.99 and 8.82 ppm for the azomethine protons. The <sup>13</sup>C NMR spectrum showed two signals for the azomethine carbons at 170.81 and 163.76 ppm and for the methylene carbons at 58.11 and 63.75 ppm, suggesting coordination through only two imine nitrogens. However, the <sup>125</sup>Te NMR spectrum showed a single deshielded signal at 739.96 ppm *cf.* 607.1 ppm for the free ligand **1**<sup>4c</sup> thus indicating the coordination of Te to Pd and the presence of an identical environment around both the tellurium atoms. Elemental analysis data for complex **2** suggested the formation of a 1 : 1 product. The FAB mass spectrum of **2** showed a highest mass peak at *m/z* 977 corresponding to 2<sup>+</sup> - PF<sub>6</sub><sup>-</sup>. Hence a formulation of [Pd<sup>II</sup>1][PF<sub>6</sub>]<sub>2</sub> for the complex is suggested. The structure was further confirmed by single crystal X-ray diffraction studies.<sup>‡</sup>

Interestingly, a similar reaction of **1** with Pt(cod)Cl<sub>2</sub> in dichloromethane yielded a reddish brown precipitate of the complex **3**<sup>‡</sup> (Scheme 1) which could be recrystallized by slow evaporation from acetonitrile. The IR spectrum of **3** showed peaks consistent with the presence of  $\nu(\text{C=O})$  and  $\nu(\text{C=N})$  stretching frequencies at 1697 and 1647 cm<sup>-1</sup>, respectively. The peak at 10.24 ppm in the <sup>1</sup>H NMR spectrum of **3** was assigned to an aldehydic proton. In addition, two peaks at 9.17 and 8.73 ppm were observed for the azomethine protons. The <sup>125</sup>Te NMR spectrum showed a high intensity peak at 708.39 ppm and a low intensity peak at 684.12 ppm. Similar behaviour has been observed for [Pt([16]aneSe<sub>4</sub>)](PF<sub>6</sub>)<sub>2</sub> by Reid and coworkers who observed two resonances for <sup>77</sup>Se at 187 and 147 ppm in MeCN at 300 K.<sup>5</sup> These authors suggested the presence of at least two invertomers in solution. The FAB mass spectrum showed a highest peak at *m/z* 665 corresponding to 3<sup>+</sup> - PF<sub>6</sub><sup>-</sup>. Elemental analysis also suggested the formation of complex **3** the structure of which was confirmed from X-ray crystallographic studies.<sup>‡</sup> The novel organoplatinum complex **3** results from facile C-Te bond cleavage and transmetalation. McWhinnie *et al.*, we and others have observed a similar transfer of organic groups from tellurium to another metal in the reactions of HgCl<sub>2</sub>,<sup>4c,6</sup> copper salts,<sup>7</sup> Pd(II)<sup>8,9</sup> and Pt(II)<sup>3d,9</sup> with telluroethers. The facile cleavage of the C-Te bond is due to strong N → Te intramolecular interactions which activate the *trans* C-Te bond.

A view of the cation of the Pd(II) complex **2** is shown in Fig. 1. The cation adopts a four coordinate geometry, with coordination by two nitrogen and two tellurium atoms. The N-Pd-N, Te-Pd-Te and N-Pd-Te angles are close to 90 and 180°. The Pd-Te(1A) and Pd-Te(1B) bond distances of 2.5443(7) and 2.5483(7) Å are comparable to the Pd(1)-Te(1) and Pd(2)-Te(3) distances of 2.540(2) and 2.549(20) Å,



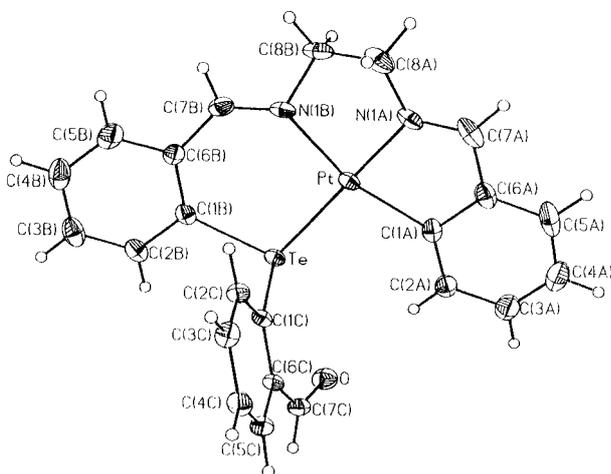
**Scheme 1** Reagents and conditions: i, Pd(PhCN)<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, 2 h; ii, Pt(cod)Cl<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>, 16 h; iii, MeOH, NH<sub>4</sub>PF<sub>6</sub>, room temp.



**Fig. 1** An ORTEP diagram of Pd complex **2**. Selected bond lengths (Å) and angles (°): Te(1A)–Pd 2.5443(7), Te(1B)–Pd 2.5483(7), Pd–N(1A) 2.097(6), Pd–N(1B) 2.099(6), Te(1A)–N(1C) 2.739, Te(1B)–N(1D) 2.737, Te(1A)···Te(1B) 3.591, N(1B)–Pd–Te(1A) 176.9(2), N(1A)–Pd–Te(1B) 175.9(2), Te(1A)–Pd–Te(1B) 89.68(2), N(1A)–Pd–Te(1A) 94.4(2), N(1B)–Pd–Te(1B) 93.1(2), N(1A)–Pd–N(1B) 82.8(2).

respectively, in  $[\{Pd(C_6H_4(TeMe)Te-o)I\}_4]$ .<sup>8</sup> The Te···N distances of 2.739 and 2.737 Å are well within the van der Waals distance (3.7 Å following Pauling<sup>10</sup>) and the Te–C–C–N moieties are planar. The tellurium is acting simultaneously as a Lewis acid and Lewis base. The Te···Te transannular bond distance of 3.591 Å is significantly shorter than the sum of the van der Waals radii (4.4 Å). This distance is also shorter than the transannular Te···Te bond distance (4.979 Å)<sup>4c</sup> in free ligand **1**.

The cation of complex **3** is shown in Fig. 2. The structure shows square planar geometry around the Pt(II) ion with coordination of carbon, tellurium and two nitrogen atoms. The angles around the Pt(II) ion lie in the range 80–100° and 162–177°, indicating the distorted square planar geometry. The Pt–Te bond distance of 2.5180(6) Å is comparable with the Pt–Te distance of 2.512(1) Å in  $[Pt\{(NC_2H_4-2-(CH_2)_2-Te-C_6H_4-4-OMe)Cl_2\}]$ .<sup>11</sup> The intramolecular Te···O distance of 3.004 Å implies a weak coordination of oxygen to tellurium as it is significantly shorter than the sum of the van der Waals radii (3.6 Å) of Te and O. However, this bond distance is longer than the mean tellurium–oxygen distance of 2.76 Å observed in bis(*o*-formylphenyl)diteLLuride.<sup>12</sup> In addition, the cations are linked into weak dimers by weak intermolecular Te···Pt contacts (3.483 Å). Complex **3** is the first example of a structurally characterized organoplatinum complex having both



**Fig. 2** An ORTEP diagram of Pt complex **3**. Selected bond lengths (Å) and angles (°): Pt–N(1A) 1.994(7), Pt–N(1B) 2.087(7), Pt–C(1A) 2.028(8), Pt–Te 2.5180(6), Te···O 3.004, Te···Pt 3.483; N(1A)–Pt–N(1B) 82.4(3), C(1A)–Pt–N(1B) 162.4(3), N(1A)–Pt–Te 177.0(2), N(1A)–Pt–C(1A) 80.3(4), N(1B)–Pt–Te 96.8(2), Te–Pt–C(1A) 100.7(2).

intramolecular Te→Pt and intermolecular Pt···Te interactions.

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## Notes and references

† Analytical data: **2** yield, 0.13 g (87%), mp 202–204 °C (decomp.); Anal. (C<sub>32</sub>H<sub>28</sub>N<sub>4</sub>Te<sub>2</sub>Pd<sub>2</sub>F<sub>12</sub>, 1120.16). Calc.: C, 34.29; H, 2.52; N, 5.00. Found: C, 34.42; H, 2.45; N, 5.13%. **3** Yield 0.060 g (46%), mp 260–262 °C (decomp.); Anal. (C<sub>23</sub>H<sub>19</sub>N<sub>2</sub>TePtOPF<sub>6</sub>, 807.07). Calc.: C, 34.23; H, 2.37; N, 3.47. Found: C, 34.24; H, 2.43; N, 3.45%.

‡ Crystal data: for **2**: C<sub>32</sub>H<sub>28</sub>N<sub>4</sub>Te<sub>2</sub>Pd<sub>2</sub>F<sub>12</sub>, *M* = 1120.12; monoclinic, space group *P*2<sub>1</sub>/*n*, *a* = 8.2250(10), *b* = 21.280(4), *c* = 21.150(4) Å, *V* = 3691.9(11) Å<sup>3</sup>, *Z* = 4, 8490 reflections collected, 8467 independent reflections (*R*<sub>int</sub> = 0.0155), *D*<sub>c</sub> = 2.015 Mg m<sup>-3</sup>, *R*(*R*<sub>w</sub>) = 0.0512(0.1162).

For **3**: C<sub>23</sub>H<sub>19</sub>F<sub>6</sub>N<sub>2</sub>OPPtTe, *M* = 807.06; monoclinic, *P*2<sub>1</sub>/*n*, *a* = 12.3253(14), *b* = 14.6557(14), *c* = 13.4054(11) Å, *V* = 2403.4(4) Å<sup>3</sup>, *Z* = 4, 5352 reflections collected, 5108 independent reflections (*R*<sub>int</sub> = 0.0225), *D*<sub>c</sub> = 2.230 Mg m<sup>-3</sup>, *R*(*R*<sub>w</sub>) = 0.0422(0.1071). CCDC 182/1501.

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