

Oxidative addition of cyclic 1-oxa-5,6-ditellurasprirooctane to platinum(0) complexes†‡

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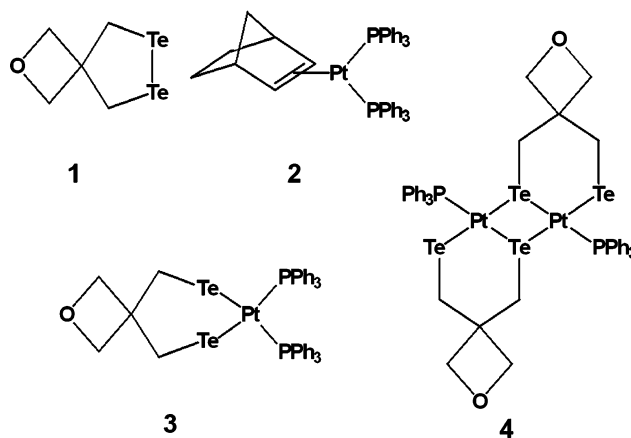
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The oxidative addition of cyclic ditelluride 1-oxa-5,6-ditellurasprirooctane, $\text{Te}_2\text{C}_5\text{H}_8\text{O}$, to bis(triphenylphosphine)-(norbornene)platinum(0), $[\text{Pt}(\text{PPh}_3)_2(\eta^2\text{-nb})]$, and to [1,8-bis-(diphenylphosphino)naphthalene](norbornene)platinum(0), $[\text{Pt}(\text{dppn})(\eta^2\text{-nb})]$, lead to the formation of dinuclear and mononuclear tellurolato platinum(II) complexes, respectively, as a consequence of Te–Te bond cleavage; no Te–C bond cleavage was observed.

The oxidative addition of organic dichalcogenides to low valent transition metal centres generally results in the cleavage of the chalcogen–chalcogen bond and formation of chalcogenolato complexes.¹ In case of ditellurides, however, competitive cleavage of the Te–C bond may take place upon oxidative addition,² as comprehensively discussed for the reactions of telluroethers and silyl tellurides with tetrakis(triorganophosphine)platinum.³ The oxidative addition of dichalcogenides to Pt(0) or Pd(0) centers seems to be an important step in the catalytic formation of C–E (E = S, Se, Te) bonds from dichalcogenides, and finds utility in regioselective and stereospecific organic synthetic chemistry.⁴

The present study involving a cyclic ditelluride 1-oxa-5,6-ditellurasprirooctane (**1**)⁵ was undertaken in order to gain more information about the competitive cleavage of the Te–Te and Te–C bonds to the Pt(0) center. As a source of platinum(0), we have used bis(triphenylphosphine)(norbornene)platinum(0) (**2**)⁶ that is relatively convenient to handle. Since the first structurally characterised mononuclear platinumtellurolato complex containing a bidentate tellurolato ligand turned out to be stable,⁷ the products in the reaction of **1** and **2** can also be expected to be stable.

Initially, the reaction of equimolar amounts of **1** and **2** in toluene produces mononuclear platinum(II) complex *cis*- $[\text{Pt}(\text{Te}_2\text{C}_5\text{H}_8\text{O})(\text{PPh}_3)_2]$ (**3**) which forms the dinuclear complex $[\text{Pt}_2(\text{Te}_2\text{C}_5\text{H}_8\text{O})_2(\text{PPh}_3)_4]$ (**4**) (see Scheme 1). The reaction was monitored by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. At first, three resonances were observed at 12.7 ppm ($^1J_{\text{Pt-P}} = 2906$ Hz), 13.8 ppm ($^1J_{\text{Pt-P}} = 3355$ Hz), and at –4.7 ppm. The last resonance was assigned to free PPh_3 . Within three hours, the resonance at 12.7 ppm completely disappeared, while the intensities of two other resonances increased.



Scheme 1

The resonance at 12.7 ppm can be assigned to the mononuclear complex **3**. The $^1J_{\text{Pt-P}}$ coupling constant of 2906 Hz is consistent with the related mononuclear complexes *cis*- $[\text{Pt}(o\text{-Te}_2\text{C}_6\text{H}_4)(\text{PPh}_3)_2]$ (2990 Hz),⁷ *cis*- $[\text{Pt}(1,2\text{-Te}_2\text{C}_5\text{H}_6)(\text{PPh}_3)_2]$ (2860 Hz),⁷ *cis*- $[\text{Pt}(\text{TePh})_2(\text{dppe})]$ (dppe = 1,2-bis(diphenylphosphino)ethane) (2896 Hz),⁸ and *cis*- $[\text{Pt}\{\text{Te}(\text{C}_4\text{H}_5\text{S})\}_2(\text{dppe})]$ (2907 Hz).⁸

The formation of free PPh_3 , and the larger $^1J_{\text{Pt-P}}$ coupling constant (3355 Hz) of the resonance at 13.8 ppm indicate the formation of the dinuclear complex **4**. While no data are available to facilitate the direct comparison between the coupling constants of corresponding mononuclear and dinuclear platinum tellurolato complexes, the magnitude and trends in the coupling constants can be inferred from those of the related selenolato complexes. The value of $^1J_{\text{Pt-P}}$ coupling is 3070 Hz for *cis*- $[\text{Pt}\{\text{Se}(\text{C}_4\text{H}_5\text{S})\}_2(\text{PPh}_3)_2]$ ⁹ and 2824 Hz for $[\{\mu\text{-}\eta^1\text{-Fe}(\eta\text{-C}_5\text{H}_5\text{Se})_2\}\text{Pt}(\text{P}^n\text{Bu}_3)_2]$,¹⁰ while the corresponding values of dinuclear $[\text{Pt}_2\{\text{Se}(\text{C}_4\text{H}_5\text{S})\}_4(\text{PPh}_3)_2]$ and $[\{\mu\text{-}\eta^1\text{-Fe}(\eta\text{-C}_5\text{H}_5\text{Se})_2\}_2\text{Pt}_2(\text{P}^n\text{Bu}_3)_2]$ are 3422 Hz⁹ and 3225 Hz,¹⁰ respectively. Consistently with this inference, the ^{195}Pt NMR spectrum of **4** exhibits a doublet at –5748 ppm due to the coupling of a ^{195}Pt nucleus to one ^{31}P nucleus ($^1J_{\text{Pt-P}} = 3355$ Hz).

The ^{125}Te NMR spectrum of **4** exhibits two resonances at 75 and –313 ppm. The high field resonance can be assigned to the bridging tellurium and the low field resonance to the nominally terminal tellurium.⁸

The ^1H – ^1H COSY spectrum of **4** displays in the range 2.2 to 4.2 ppm eight groups of resonance signals, which are assigned to the eight diastereotopic protons. The doublets at 3.6, 3.7, 4.0 and 4.1 ppm are attributed to the four protons of the oxetane ring and four broader signals with typical platinum satellites at 2.3, 2.7, 2.9 and 3.4 ppm to the methylene protons next to the tellurium atoms, respectively.

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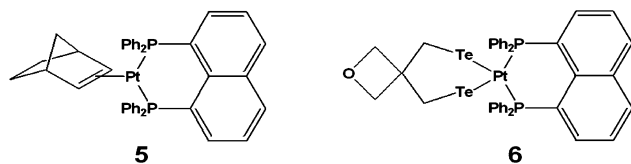
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^1H – ^{13}C HSQC analysis of **4**, allows the assignment of the ^{13}C resonances at 81.4 and 82.3 ppm to the methylene carbon atoms of the oxetane ring. The resonance signal of the quarternary carbon atom is detected at 43.5 ppm, whereas the signals at 7.1 and 23.6 ppm are attributed to the methylene carbon atoms directly bonded to the tellurium atoms.

The formation of the dinuclear complex can be avoided by treating **1** with platinum(0) complex **5**⁶ containing the bidentate phosphine ligand dppn [1,8-bis(diphenylphosphino)naphthalene] (see Scheme 2). The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the reaction mixture exhibits one resonance at –2.3 ppm showing ^{195}Pt and ^{125}Te satellites. The corresponding coupling constants are $^1J_{\text{P-Pt}} = 2554$ Hz and $^2J_{\text{P-Te}} = 70$ Hz. The ^{195}Pt NMR spectrum shows a triplet at –4955 ppm and the ^{125}Te NMR spectrum exhibits one resonance at –71 ppm. The coupling constant $^1J_{\text{Te-Pt}} = 820$ Hz is obtainable from both spectra. These resonances can be assigned to the compound **6**. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum exhibits three resonances due to the ditellurolato ligand.



Scheme 2

X-Ray quality crystals of $4\text{-C}_7\text{H}_8$ and **6** are obtained by diffusion of *n*-pentane into solutions of **4** and **6** in toluene–dichloromethane (1 : 1) at 4 °C.^{‡§} The crystal structures of the two complexes are shown in Fig. 1 and 2 together with selected bond parameter data.[‡]

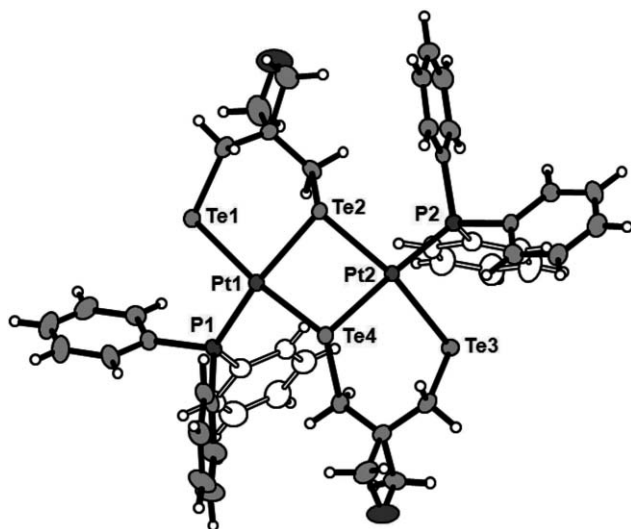


Fig. 1 The molecular structure of $[\text{Pt}_2(\mu\text{-Te}_2\text{C}_5\text{H}_8\text{O})_2(\text{PPh}_3)_2]$ (**4**). The thermal ellipsoids have been drawn at 50% probability level. Selected bond lengths (Å) and angles (°): Pt1–Te1 2.6001(9), Pt1–Te2 2.6311(10), Pt1–Te4 2.6048(9), Pt2–Te2 2.6150(8), Pt2–Te3 2.6163(10), Pt2–Te4 2.6109(8), Pt1–P1 2.260(2), Pt2–P2 2.255(2); Te1–Pt1–Te2 92.66(4), Te1–Pt1–Te4 170.94(2), Te2–Pt1–Te4 79.44(3), P1–Pt1–Te1 92.16(6), P1–Pt1–Te2 169.90(4), P1–Pt1–Te4 96.34(6), Te2–Pt2–Te3 167.71(2), Te2–Pt2–Te4 79.62(4), Te3–Pt2–Te4 91.58(4), P2–Pt2–Te2 103.24(6), P2–Pt2–Te3 85.93(6), P2–Pt2–Te4 176.35(6).

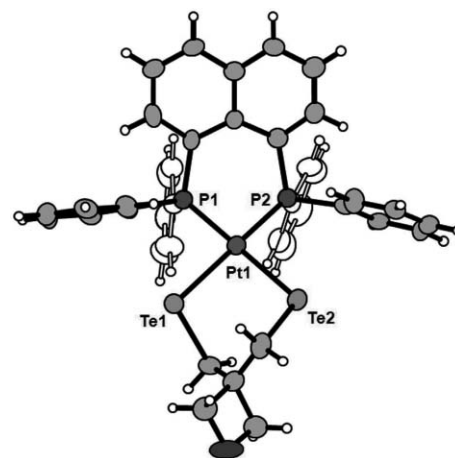


Fig. 2 The molecular structure of $[\text{Pt}(\text{Te}_2\text{C}_5\text{H}_8\text{O})\{(\text{PPh}_3)_2(\text{C}_{10}\text{H}_6)\}]$ (**6**). The thermal ellipsoids have been drawn at 50% probability level. Selected bond lengths (Å) and angles (°): Pt1–Te1 2.6231(6), Pt1–Te2 2.6304(7), Pt1–P1 2.259(2), Pt1–P2 2.249(2); Te1–Pt1–Te2 90.77(3), P1–Pt1–Te1 92.44(5), P1–Pt1–Te2 171.17(4), P2–Pt1–Te1 178.92(4), P2–Pt1–Te2 88.56(5).

Both lattices are composed of discrete complexes with each platinum atom exhibiting a distorted square-planar coordination environment ($\Sigma = 360.35$ and 360.60° for **4** and $\Sigma = 360.12$ for **6**). In particular, the individual bond angles in **4** deviate significantly from the ideal value of 90° (see Fig. 1). The two square-planes of **4** have a hinged arrangement with an angle of $129.27(2)^\circ$ between the planes.

Five of the six Pt–Te bond lengths in **4** are close to each other ranging from 2.6001(9)–2.6163(10) Å, the bridging Pt1–Te2 distance of 2.6311(10) Å being significantly longer. They can be compared to the Pt–Te bond lengths in dinuclear $[\text{Pt}_2(\text{TePh})(\mu\text{-TePh})_2(\text{PEt}_3)_2(\eta^5\text{-2-CB}_{10}\text{H}_{11})]$.¹¹ The bridging and terminal Pt–Te bonds involving the $\text{Pt}(\text{TePh})(\mu\text{-TePh})_2(\text{PEt}_3)$ fragment span a range of 2.6113(7)–2.6225(7) Å. Interestingly, the terminal Pt–Te bond is the longest in this case. All Pt–Te bonds involving the platinum atom as a vertex in the *closo*-1-carba-2-platinadodecaborane structure are longer.

The Pt–Te bond lengths in mononuclear **6** are 2.6231(6) and 2.6304(7) Å. They can be compared with those in *cis*- $[\text{Pt}(1,2\text{-Te}_2\text{C}_6\text{H}_4)(\text{PPh}_3)_2]$ [2.586(1) and 2.592(1) Å],⁷ *cis*- $[\text{Pt}(\text{TeCF}_3)_2(\text{PPh}_3)_2]$ [2.649(1) Å],¹⁰ $[\text{Pt}(\text{TeAr})_2(\text{dppe})]$ (Ar = phenyl, 2-thienyl) [2.6053(6)–2.6594(9) Å],¹² and *trans*- $[\text{Pt}\{\text{TeCO}(4\text{-MeC}_6\text{H}_4)\}_2(\text{PEt}_3)_2]$ [2.632(2) Å].¹³

All observed products, **3**, **4**, and **6** are formed *via* the cleavage of the Te–Te bond upon oxidative addition. The formation of the dinuclear complex **4** is consistent with computational predictions that tellurolato complexes of platinum and palladium have a higher tendency to form dinuclear complexes than their corresponding thiolato and selenolato complexes.¹⁴

The oxidative addition of diselenides to platinum(0) complexes results in mononuclear *cis*-platinumdiselenolato complexes, which isomerize fast to *trans*-isomers. The same reactions using palladium(0) complexes afford dinuclear complexes.⁹ It has recently been reported that palladium(0) complexes show better catalytic activity in the addition of diselenides to alkynes than platinum(0) complexes, one possible reason being the fast formation of dinuclear selenolato complexes.¹⁵ Whether dinuclear tellurolato

platinum complexes such as **4** exhibit catalytic activity comparable to dinuclear thiolato- and selenolatopalladium complexes is an open question and requires further study.

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Notes and references

§ The crystal data for **4** (C_7H_8) and **6** were collected on a Nonius Kappa CCD diffractometer at 120(2) K using Mo- K_α radiation ($\lambda = 0.71073 \text{ \AA}$). The structures were solved by direct methods¹⁶ and refined on F^2 .¹⁷ The calculated hydrogen atoms were included in the final refinement (the phenyl rings: C–H = 0.95 Å; the methylene groups: C–H = 0.99 Å). Crystal data for $\text{C}_{33}\text{H}_{54}\text{O}_2\text{P}_2\text{Pt}_2\text{Te}_4$ (**4**, C_7H_8): $M = 1685.48$, triclinic, space group $P\bar{1}$, $a = 11.904(2)$, $b = 15.039(3)$, $c = 16.760(3) \text{ \AA}$, $\alpha = 86.35(3)^\circ$, $\beta = 81.87(3)^\circ$, $\gamma = 67.62(3)^\circ$; $U = 2746.4(10) \text{ \AA}^3$; $Z = 2$; $D_c = 2.038 \text{ g cm}^{-3}$, $F(000) = 1564$; $\mu(\text{Mo-K}_\alpha) = 7.265 \text{ mm}^{-1}$, crystal dimensions $0.20 \times 0.15 \times 0.15 \text{ mm}$. Reflections (40175 total, 10607 unique, θ range $2.97\text{--}26.00^\circ$, $R_{\text{int}} = 0.0850$), the final $R_1 = 0.0493$ and $wR_2 = 0.1350$ [9866 reflections with $F_o > 4\sigma(F_o)$] ($R_1 = 0.0520$ and $wR_2 = 0.1375$ all data). Crystal data for $\text{C}_{39}\text{H}_{54}\text{OP}_2\text{PtTe}_2$ (**6**): $M = 1030.89$, monoclinic, space group $P2_1/n$, $a = 16.993(3)$, $b = 10.613(2)$, $c = 18.855(4) \text{ \AA}$, $\beta = 92.74(3)^\circ$; $U = 3396.7(12) \text{ \AA}^3$; $Z = 4$; $D_c = 2.016 \text{ g cm}^{-3}$, $F(000) = 1952$; $\mu(\text{Mo-K}_\alpha) = 5.940 \text{ mm}^{-1}$, crystal dimensions $0.20 \times 0.20 \times 0.15 \text{ mm}$. Reflections (30157 total, 6582 unique, θ range $3.07\text{--}26.00^\circ$, $R_{\text{int}} = 0.1040$), the final $R_1 = 0.0570$ and $wR_2 = 0.1441$ [6214 reflections with $F_o > 4\sigma(F_o)$] ($R_1 = 0.0604$ and $wR_2 = 0.1522$ all data).

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