

Synthesis and Structural, Electrochemical and NMR Analysis of the $[\{\text{Pt}(\text{PEt}_3)_2\}_2\text{Te}_2]^n$ Series ($n = 0, 2+$) and the Bicapped Triplatinum $[\{\text{Pt}(\text{PEt}_3)_2\}_3(\mu_3\text{-Te})_2]^{2+}$ Dication: Te–Te Bond Formation in a *cyclo*-Pt₂Te₂ Core upon a Chemically Reversible Two-electron Oxidation

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Room-temperature reactions of three $[\text{Pt}_3(\text{CO})_6]_n^{2-}$ dianions ($n = 3, 4, 5$) with TePEt_3 in tetrahydrofuran (containing $[\text{AsPh}_4]^+\text{Cl}^-$) give rise to the 32-electron $[\{\text{Pt}(\text{PEt}_3)_2\}_2(\mu_2\text{-Te})_2]$ **1**, the 30-electron $[\{\text{Pt}(\text{PEt}_3)_2\}_2(\mu_2\text{-Te}_2)]^{2+}$ dication **2** and the 48-electron $[\{\text{Pt}(\text{PEt}_3)_2\}_3(\mu_3\text{-Te})_2]^{2+}$ dication **3** which were characterized by X-ray diffraction, electrochemical and multinuclear (¹H, ¹³C, ¹⁹F, ³¹P, ¹⁹⁵Pt) NMR measurements; a chemical two-electron oxidation of **1**, which has a planar *cyclo*-Pt₂Te₂ core, quantitatively produces **2** with a highly bent *bicyclo*-Pt₂Te₂ core due to the formation of an electron-pair Te–Te bond (which can be reversibly cleaved upon chemical reduction to reconvert **2** into **1**).

An attempt to obtain high-nuclearity platinum carbonyl telluride clusters by separate reactions of three (triangular metal)-stacking $[\text{Pt}_3(\text{CO})_6]_n^{2-}$ dianions ($n = 3, 4, 5$)¹ with TePEt_3 in tetrahydrofuran (thf) containing $[\text{AsPh}_4]^+\text{Cl}^-$ resulted instead in cluster degradation to give primarily red $[\{\text{Pt}(\text{PEt}_3)_2\}_2(\mu_2\text{-Te})_2]$ **1** (ca. 80% yield) along with Cl^- , $[\text{SbF}_6]^-$, and/or $[\text{PF}_6]^-$, salts of the deep red-brown $[\{\text{Pt}(\text{PEt}_3)_2\}_2(\mu_2\text{-Te}_2)]^{2+}$ **2** (ca. 2% yield) and green-brown $[\{\text{Pt}(\text{PEt}_3)_2\}_3(\mu_3\text{-Te})_2]^{2+}$ **3** (ca. 15% yield). Characterization of these products by X-ray crystallography,[†] cyclic voltammetry,[‡] and multinuclear (¹H, ¹³C, ¹⁹F, ³¹P, ¹⁹⁵Pt)

NMR analyses[‡] has revealed intriguing structural-bonding relationships. In fact, the chemically reversible oxidation of **1** to **2** provides the first illustration of a *cyclo*-M₂E₂ dimeric system (M = transition metal; E = main-group atom) undergoing E–E (instead of M–M) bond formation upon a two-electron chemical oxidation. In an analogous fashion, the 34-electron $[\text{Fe}_2(\text{CO})_6(\mu_2\text{-S})_2]^{2-}$ dianion,³ which contains a bent, (Fe–Fe)-bonded *bicyclo*-Fe₂S₂ core, can be reversibly oxidized to the neutral 32-electron $[\text{Fe}_2(\text{CO})_6(\mu_2\text{-S}_2)]$ which has an (S–S)-bonded *closo*-tetrahedral *tricyclo*-Fe₂S₂ core.⁴

The molecular geometry of **1** (Fig. 1) consists of a four-membered Pt₂Te₂ ring with two tricyclophosphine ligands coordinated to each Pt^{II}; the resulting (PtP₂)₂Te₂ architecture of centrosymmetric C_i - $\bar{1}$ site and planar D_{2h} - mmm symmetry is virtually identical to that of the corresponding PPh₃-derivative $[\{\text{Pt}(\text{PPh}_3)_2\}_2(\mu_2\text{-Te})_2]$ (of crystallographic C_{2v} site symmetry), previously obtained (in ca. 20% yield) from the reaction of $[\text{NBu}_4]^+[\text{Hg}_4\text{Te}_{12}]^{4-}$ with $\text{Pt}(\text{PPh}_3)_4$ in dimethylformamide (DMF).⁵ Of prime interest is a comparison of its molecular parameters with those of the isostructural palladium analogue, $[\{\text{Pd}(\text{PEt}_3)_2\}_2(\mu_2\text{-Te})_2]$ **4**, which was isolated in 10% yield from the room-temperature reaction of $\text{Pd}(\text{PPh}_3)_4$ and TePEt_3 .⁶ The congeneric replacement in **4** of the two second-row d⁸ M^{II} atoms (M = Pd) by third-row M^{II} atoms (M = Pt) in **1** causes the following average changes in molecular geometry: (i) a 0.04 Å-shorter M–P bond length in **1**; in contrast, the M–Te distances are virtually identical (<0.01 Å difference); (ii) large compensatory angular variations between the crystallographically planar M₂Te₂ rhombi involving a 5.1°-larger acute Te–M–Te bond angle of 77.0° in **1** that is exactly counterbalanced by a 5.1°-smaller obtuse M–Te–M bond angle of 103.0° in **1**. The larger acute Te–M–Te bond angle in **1** results in its nonbonding Te...Te distance being 0.20 Å longer, and (iii) the 1.8°-larger obtuse P–M–P bond angle of 106.0° in **1**. In light of the small size difference between second- and third-row transition metal congeners due to the lanthanide-contraction effect,⁷ the marked differences between the mean M–P distances and acute Te–M–Te bond angles in **1** and **4** appear to be highly significant. The less acute Te–M–Te bond angle in **1** can be rationalized in terms of greater interorbital electron-pair interactions which favour a wider (less acute) Te–M–Te bond angle in Pt^{II} on account of its greater effective nuclear charge; the significantly smaller M–P distances in **1** suggests that Pt^{II} forms stronger σ-bonds with corresponding phosphine ligands than does Pd^{II} in structurally analogous complexes (presumably owing to relativistic stabilization effects⁸).

Although cyclic voltammograms (CVs) of **1** exhibit an irreversible oxidation wave, chemical oxidation of **1** with two equivalents of $[\text{Fe}(\text{C}_5\text{H}_5)_2]^+[\text{SbF}_6]^-$ in CH_2Cl_2 gives rise in quantitative yield to the $[\{\text{Pt}(\text{PEt}_3)_2\}_2(\mu_2\text{-Te}_2)]^{2+}$ dication **2** in which an electron-pair Te–Te bond (rather than a Pt–Pt bond) is formed; **2** was also obtained directly (60% yield) as the PF_6^- salt from the reaction of $\text{Pt}(\text{cod})\text{Cl}_2$ (cod = cycloocta-1,5-

[†] Crystal data for **1**: $[\{\text{Pt}(\text{PEt}_3)_2\}_2(\mu_2\text{-Te})_2]$, monoclinic, $P2_1/n$, $a = 10.094(3)$, $b = 13.290(4)$, $c = 13.781(4)$ Å, $\beta = 109.32(2)^\circ$, $Z = 2$, 2568 reflections were observed at -80°C , $R = 0.0494$, $R_w = 0.0510$.

For **2a**: $[\text{Pt}_2\text{Te}_2(\text{PEt}_3)_4]^{2+}[\text{PF}_6]_2 \cdot 2\text{CH}_2\text{Cl}_2$, monoclinic, $P2/c$, $a = 14.268(3)$, $b = 7.915(9)$, $c = 22.023(6)$ Å, $\beta = 91.55(2)^\circ$, $Z = 2$, 3021 reflections were observed at 25°C , $R = 0.0806$, $R_w = 0.0712$.

For **2b**: $[\text{Pt}_2\text{Te}_2(\text{PEt}_3)_4]^{2+}[\text{SbF}_6]_2 \cdot 2\text{CH}_2\text{Cl}_2$, monoclinic, $P2/c$, $a = 14.268(6)$, $b = 8.036(3)$, $c = 22.513(7)$ Å, $\beta = 92.01(2)^\circ$, $Z = 2$, 4521 reflections were observed at -80°C , $R = 0.0495$, $R_w = 0.0545$.

For **3a**: $[\{\text{Pt}(\text{PEt}_3)_2\}_3(\mu_3\text{-Te})_2]^{2+}[\text{PF}_6]_2$, orthorhombic, $P2_12_12_1$, $a = 13.608(3)$, $b = 19.015(4)$, $c = 23.427(5)$ Å, $Z = 4$, 2638 reflections were observed at 25°C , $R = 0.0903$, $R_w = 0.0805$.

For **3b**: $[\{\text{Pt}(\text{PEt}_3)_2\}_3(\mu_3\text{-Te})_2]^{2+}[\text{Cl}]_2 \cdot \text{Me}_2\text{CO}$, monoclinic, $P2_1/n$, $a = 10.839(3)$, $b = 25.124(9)$, $c = 22.350(8)$ Å, $\beta = 102.31(2)^\circ$, $Z = 4$, 7084 reflections were observed at -80°C , $R = 0.0682$, $R_w = 0.0697$.

All the structures were refined by use of SHELXTL PLUS. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

[‡] Electrochemical/NMR data: CVs of **1** in CH_2Cl_2 exhibit an irreversible oxidation wave at +400 mV and an irreversible reduction wave at -1025 mV [vs. saturated calomel electrode (SCE)]. CVs of **2a** in CH_2Cl_2 display two quasi-reversible reduction waves with similar relative peak-current heights at $E_{1/2}$ values of -267 mV ($\Delta E_p = 70$ mV) and -527 mV ($\Delta E_p = 64$ mV). A CV of **3** in CH_2Cl_2 gave no discernible waves. ³¹P NMR spectrum of **1**: 298 K, C_6D_6 , H_3PO_4 ext, δ 1.4 [s, $J(\text{Pt}-\text{P})$ 3031 Hz]; ¹⁹⁵Pt NMR spectrum of **1**: 298 K, $[\text{H}_6]\text{acetone}$, Na_2PtCl_6 in D_2O ext, δ -5380.2 [t, $J(\text{P}-\text{Pt})$ 2935 Hz]. ¹H NMR spectrum of **1** (200 MHz; C_6D_6): δ 1.18, 2.01 (Et). ¹³C NMR spectrum of **1** (270 MHz; C_6D_6): δ 8.3, 16.6 (Et). ³¹P spectrum of **2a**: 298 K, $[\text{H}_6]\text{acetone}$, H_3PO_4 ext, δ 17.3 [s, $J(\text{Pt}-\text{P})$ 3564 Hz]; ¹⁹⁵Pt NMR spectrum of **2a**: 298 K, $[\text{H}_6]\text{acetone}$, Na_2PtCl_6 in D_2O ext, δ -4298.7 [t, $J(\text{P}-\text{Pt})$ 3485 Hz]. ¹⁹F NMR spectrum of **2a**: 298 K, $[\text{H}_6]\text{acetone}$, CFCl_3 ext, δ 28.9, 27.4 [d, $J(\text{P}-\text{F})$ 712 Hz]. ³¹P NMR spectrum of **3a**: 298 K, $[\text{H}_6]\text{acetone}$, H_3PO_4 ext, δ 3.7 [s, $J(\text{Pt}-\text{P})$ 3238 Hz]; this most intense resonance is due to the isotopomer with no magnetically active platinum-195 and is consistent with that in the ³¹P spectrum of the $[\text{Pt}_3(\text{PMe}_2\text{Ph})_6(\mu_3\text{-S})_2]^{2+}$ dication obtained by Bushnell *et al.*¹¹ ¹⁹⁵Pt NMR spectrum of **3a**: 298 K, $[\text{H}_6]$ acetone, Na_2PtCl_6 in D_2O ext, δ -5044.2 [t, $J(\text{P}-\text{Pt})$ 3233 Hz]; this most intense triplet is due to coupling of a single magnetically active platinum with two directly bonded phosphorus nuclei and is consistent with that in the ¹⁹⁵Pt spectrum of the $[\text{Pt}_3(\text{PMe}_2\text{Ph})_6(\mu_3\text{-S})_2]^{2+}$ dication obtained by Bushnell *et al.*¹¹

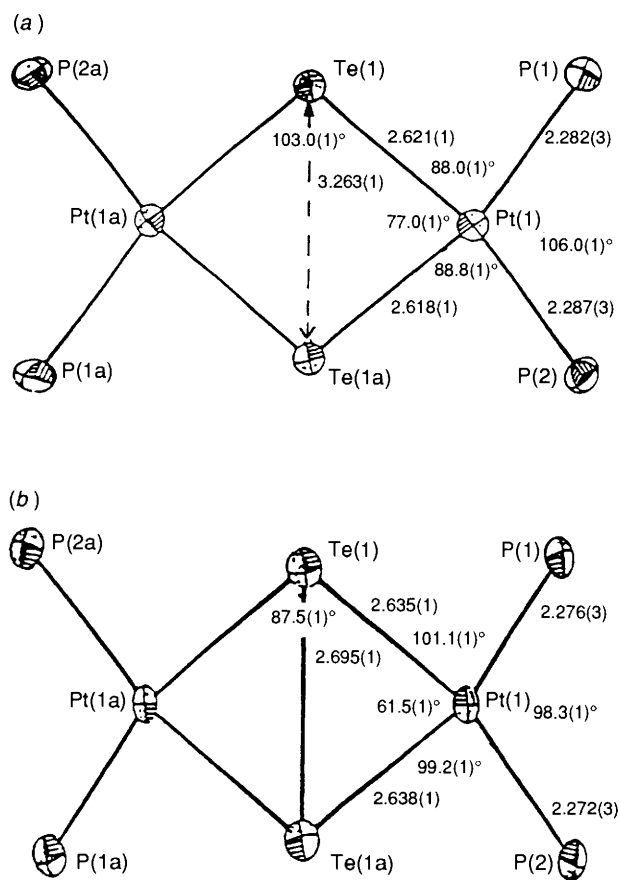


Fig. 1 Configurations of (a) the planar $(\text{PtP}_2)_2\text{Te}_2$ framework of $[\{\text{Pt}(\text{PEt}_3)_2\}_2(\mu_2\text{-Te})_2]$ **1**, which has crystallographic C_2 and pseudo D_{2h} - mmm symmetry; and (b) the butterfly $(\text{PtP}_2)_2\text{Te}_2$ framework (dihedral angle, 107°) of the oxidized $[\{\text{Pt}(\text{PEt}_3)_2\}_2(\mu_2\text{-Te})_2]^{2+}$ dication **2** (in the dichloromethane-solvated $[\text{SbF}_6]^-$ salt **2b**) which has C_{2v} and pseudo C_{2v} - $2mm$ symmetry

diene) and TIPF_6 with TePtEt_3 in thf. A structural comparison (Fig. 1) shows that the two-electron oxidation of **1** to **2** causes a 0.57 \AA decrease in the Te-Te distance from a nonbonding length of $3.263(1) \text{ \AA}$ to a bonding length of $2.695(1) \text{ \AA}$, which is comparable to the electron-pair bond length of $2.712(2) \text{ \AA}$ in diphenyl ditelluride.⁹ Another major change in the planar $(\text{PtP}_2)_2\text{Te}_2$ framework of **1** upon oxidation is a large folding of the two P_2PtTe_2 planes along the common Te-Te axis to give a highly bent butterfly C_{2v} - $2mm$ geometry (dihedral angle, 107°) in **2**.

Particularly noteworthy is that CVs of **2** display two quasi-reversible reduction waves and that reduction of **2** with two equivalents of either cobaltocene or K-benzophenone quantitatively reconverts **2** into **1**. Extensive attempts to isolate the species formed from the first reduction have been unsuccessful. The dissimilar electrochemical behaviour of **1** and **2** suggests that a large change in geometry of the planar $(\text{PtP}_2)_2\text{Te}_2$ framework of **1** is associated with the irreversible electron-transfer oxidation process but only a small structural reorganization of the bent $(\text{PtP}_2)_2\text{Te}_2$ architecture of **2** occurs during the quasi-reversible electron-transfer reduction processes. We conclude that the second quasi-reversible reduction in the CVs of **2** gives rise to a 'bent' $(\text{PtP}_2)_2\text{Te}_2$ geometry of **1** whose rate of irreversible structural transformation to the solid-state 'planar' geometry is slow relative to the electron-transfer rate. Supporting evidence that **1** can possess a 'bent' geometry in solution is given by the fact that the solid-state configuration of the neutral $[\{\text{Pt}(\text{PMe}_2\text{Ph})_2\}_2$ -

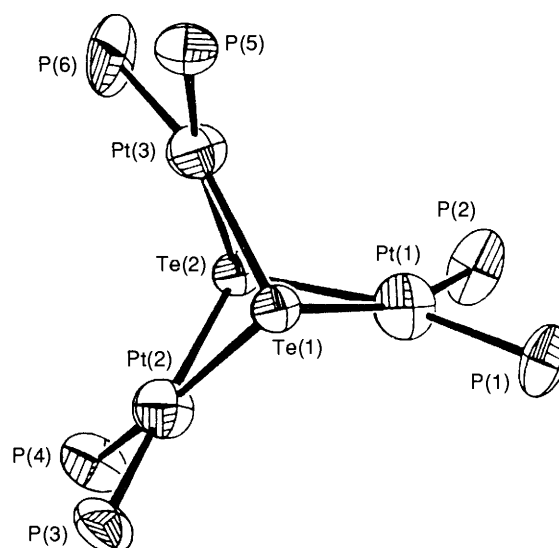


Fig. 2 Configuration of the trigonal bipyramidal $(\text{PtP}_2)_3\text{Te}_2$ architecture of the $[\{\text{Pt}(\text{PEt}_3)_2\}_3(\mu_3\text{-Te})_2]^{2+}$ dication **3** in both the $[\text{PF}_6]^-$ salt **3a** and the acetone-solvated chloride salt **3b**. Mean values of individual distances (\AA) and bond angles ($^\circ$) (whose numbers are enclosed in square brackets) for the $\text{Pt}_3\text{P}_6\text{Te}_2$ core under pseudo D_{3h} - $62m$ site symmetry in **3a** and **3b** (values given in parentheses) are: Te-Te, [1] $3.172(2)$ [$3.234(2)$]; Pt-Pt, [3] 3.577 (3.597); Pt-Te, [6] 2.604 (2.633); Pt-P, [6] 2.278 (2.286); P-Pt-P, [3] 99.9 (99.0); Pt-Te-Pt, [6], 86.8 (86.2)

$(\mu_2\text{-S})_2]$ **5**, which is electronically equivalent to **1**, has a highly bent $(\text{PtP}_2)_2\text{S}_2$ framework (dihedral angle, 121°) with a nonbonding S...S distance of 3.06 \AA ;¹⁰ an operational test of this proposal would be to carry out an electrochemical study of **5** to determine whether it undergoes reversible oxidation to the (S-S)-bonded dication.

The third product, $[\{\text{Pt}(\text{PEt}_3)_2\}_3(\mu_3\text{-Te})_2]^{2+}$ **3**, was alternatively obtained in ca. 70% yield by the addition of $\text{Ni}(\text{cod})_2$ to the reaction of $\text{Pt}(\text{cod})\text{Cl}_2$ and TIPF_6 with TePEt_3 . Its pseudo- D_{3h} geometry (Fig. 2) consists of a trigonal bipyramidal Pt_3Te_2 core with each Pt atom additionally linked to two triethylphosphine ligands in a square-planar coordination. The resulting configuration may also be viewed as three square-planar *cis*- PtP_2Te_2 moieties, which are symmetry-related by a pseudo threefold axis passing through the two common triply bridging Te atoms. This $[\text{M}_3\text{L}_6(\mu_3\text{-X})_2]^{2+}$ -type structure has also been adopted by several other electronically equivalent trimetal-disulfide complexes including $[\text{Pt}_3(\text{PMe}_2\text{Ph})_6(\mu_3\text{-S})_2]^{2+}$,¹¹ $[\text{Pd}_3(\text{PMe}_3)_6(\mu_3\text{-S})_2]^{2+}$,¹² and $[\text{Ni}_3(\text{PEt}_3)_6(\mu_3\text{-S})_2]^{2+}$.¹³

Although the electron-localized configuration of each square-planar platinum atom in **1** and **3** is unambiguously described as $d^8 \text{ Pt}^{\text{II}}$, that in **2** is not unequivocal. From an electronic viewpoint, **2** may be formally described in terms of two possible oxidation-state models: (i) the interaction of a Te_2^{2-} fragment with two square-planar $d^8 \text{ Pt}^{\text{II}}$; or alternatively, (ii) the interaction of a Te_2^{2+} fragment with two reduced trigonal-planar $d^{10} \text{ Pt}^0$, which requires internal electron reorganization¹⁴ involving simultaneous oxidation of both Te^{2-} in **1** to Te_2^{2+} in **2**. In an effort to discriminate between these two limiting models, a comparison of the ^{195}Pt , ^{31}P NMR parameters of **1** and **2** with those of trigonal-planar $\text{Pt}(\text{PEt}_3)_3$, *cis*- $\text{Pt}(\text{PEt}_3)_2\text{Cl}_2$ and other related platinum phosphine complexes^{11,15} was made. The NMR data do not permit us to distinguish between these oxidation-state models; from a valence-bond viewpoint, the $\text{Pt}^{\text{II}}\text{-Te}_2^{2-}$ description is preferred.

The electron counts of 32 for **1** and 48 for **3** (rather than the usual values of 36 and 54, respectively) are completely consistent with these dimetal and trimetal species possessing

no metal-metal bonds (in accordance with their observed nonbonding distances) because each square-planar d^8 Pt^{II} metal conforms to a 16-electron count rather than the normal 18-electron closed-shell electronic configuration. The 30-electron count for **2** is a consequence of an electron-pair Te-Te bond (instead of a metal-metal bond) being formed.

Details of the syntheses will be published later in connection with research in progress on related compounds.

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