

### Formation of Novel 'Phosphite' Metallacycles via Selective Ring Opening of Pt(II)- or Pd(II)-coordinated Tri- and Di-azaphospholes

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The tetramerization of azaphospholes can either be favoured or hindered by coordination to various metal centres [1] and in general it appears that such coordination also influences addition reactions of the P=N bond. For the tri- and di-azaphospholes 1 and 2 both  $\sigma$ -P and  $\sigma$ -N coordination modes have recently been realized [2]. During further studies of the coordination behaviour of 1 and 2 we have observed a multistep selective ring opening reaction with methanol that is clearly induced by metal coordination. These reactions employing Pd(II) and Pt(II) substrates are now reported, together with an X-ray diffraction study of one of the unusual six-membered metallacyclic compounds that are generated in the final step.

1,5-dimethyl-1,2,4,3-triazaphosphole 1 reacts with  $trans$ -[Et<sub>3</sub>PPtCl<sub>2</sub>]<sub>2</sub> to afford the oxygen- and moisture-sensitive complex 3\*\*. The 1:1 Pt(PEt<sub>3</sub>)Cl<sub>2</sub>/1 stoichiometry was deduced from micro-analytical results and is supported by <sup>31</sup>P and <sup>195</sup>Pt NMR data\*\*, which furthermore indicated a dimeric formulation. Complex 3 is not ionic (based on conductivity measurements in CH<sub>2</sub>Cl<sub>2</sub>) and the <sup>31</sup>P NMR spectrum points clearly to an asymmetric structure with  $\sigma$ -P coordination of each ligand 1 to one of the two platinum centres. Together with coupling data (e.g. J(Pt, Pt) ~ 0 Hz) it may be concluded that the triazaphospholes (either as separate units or linked together) are functioning here as the bridging groups between two five-coordinate platinum centres.

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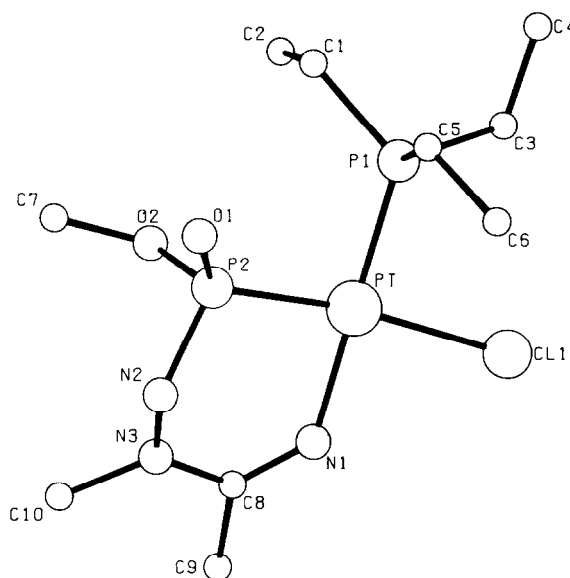


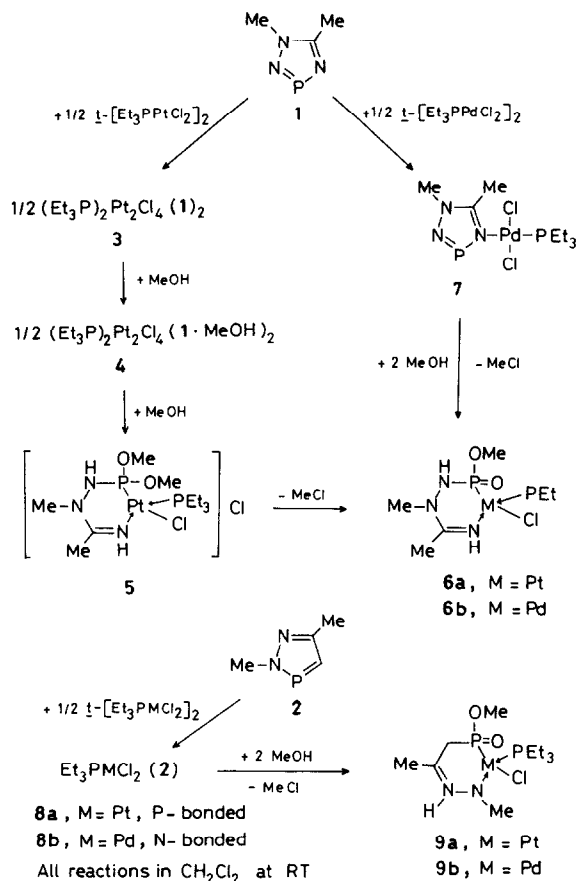
Fig. 1. The molecular structure of 6a [PtP(=O)(OMe)N(H)-N(Me)C(Me)=NH(Cl)(PEt<sub>3</sub>)]. Some relevant geometrical parameters are: Pt–P1 2.244(4), Pt–P2 2.198(5), Pt–Cl1 2.404(6), Pt–N1 2.08(2), P2–N2 1.71(2), N2–N3 1.38(2), N3–C8 1.37(3), C8–N1 1.30(3) Å; Pt–P2–N2 108.5(7), P2–N2–N3 119(2), N2–N3–C8 124(2), N3–C8–N1 121(2), C8–N1–Pt 134(2), N1–Pt–P2 89.2(6), P1–Pt–Cl1 94.4(2)°.

\*\*P- or N-bonding of 1 and 2 to metal centres is determined by comparison of <sup>31</sup>P and <sup>1</sup>H NMR data for the free and coordinated ligands. P<sub>A</sub> and P<sub>B</sub> are P-atom labels for PEt<sub>3</sub> ligands and P1<sub>A</sub>, P1<sub>B</sub> and P2 are those for azaphospholes. Some relevant NMR data (<sup>195</sup>Pt, 21.4 MHz [5]; <sup>31</sup>P, H<sub>3</sub>PO<sub>4</sub> ref., positive shift values are to higher frequency) in CDCl<sub>3</sub>: 3 (asym. dinuclear): <sup>31</sup>P 10.9 (P<sub>A</sub>), 14.3 (P<sub>B</sub>), 93.1 (P1<sub>A</sub>) and 104.8 (P1<sub>B</sub>); <sup>195</sup>Pt 251 (Pt<sub>1</sub>) and 218 (Pt<sub>2</sub>). [<sup>1</sup>J(P<sub>A</sub>-Pt<sub>1</sub>) 3135, <sup>1</sup>J(P<sub>B</sub>-Pt<sub>2</sub>) 3472, <sup>1</sup>J(P1<sub>A</sub>-Pt<sub>2</sub>) 5220, <sup>1</sup>J(P1<sub>B</sub>-Pt<sub>1</sub>) 5970, <sup>n</sup>J(P1<sub>A</sub>-Pt<sub>1</sub>) ~ 20, <sup>n</sup>J(P1<sub>B</sub>-Pt<sub>2</sub>) 88, <sup>n</sup>J(P<sub>A</sub>-P1<sub>A</sub>) 4, <sup>2</sup>J(P<sub>A</sub>-P1<sub>B</sub>) 23, <sup>2</sup>J(P<sub>B</sub>-P1<sub>A</sub>) 18 and <sup>n</sup>J(P1<sub>A</sub>-P1<sub>B</sub>) 14]. 4 (symm. dinuclear): <sup>31</sup>P 12.6 (P<sub>A</sub>, m), <sup>1</sup>J(PtP) 3045, and 63.4 (P1<sub>A</sub>, m), <sup>1</sup>J(PtP) 5606, <sup>2</sup>J(PtP) 62 <sup>195</sup>Pt 144. 5 (monomer.): <sup>31</sup>P 10.2 (P<sub>A</sub>, d), <sup>1</sup>J(PtP) 3045 and 75.7 (P1<sub>A</sub>, d), <sup>1</sup>J(PtP) 5682, [<sup>2</sup>J(P<sub>A</sub>-P1<sub>A</sub>) 26]; <sup>195</sup>Pt 19 6a (monomer.): <sup>31</sup>P 9.6 (P<sub>A</sub>, d), <sup>1</sup>J(PtP) 3559 and 36.1 (P1<sub>A</sub>, d), <sup>1</sup>J(PtP) 4974, [<sup>2</sup>J(P<sub>A</sub>-P1<sub>A</sub>) 28.5]. 6b (monomer.): <sup>31</sup>P 30.4 (P<sub>A</sub>, d) and 72.3 (P1<sub>A</sub>, d), [<sup>2</sup>J(P<sub>A</sub>-P1<sub>A</sub>) 10]. 7 (monomer.): <sup>31</sup>P 35.6 (P<sub>A</sub>) and 245.9 (P1<sub>A</sub>); <sup>1</sup>H 3.0 (CMe) and 4.05 (NMe). 8a (monomer.): 16.8 (P<sub>A</sub>, d), <sup>1</sup>J(PtP) 2960 and 166.1 (P2, d), <sup>1</sup>J(PtP) 4676, [<sup>2</sup>J(P<sub>A</sub>-P2) 25]. 8b (monomer.): <sup>31</sup>P 36.2 (P<sub>A</sub>) and 236.5 (P2). 9a (monomer.): <sup>31</sup>P 9.6 (P<sub>A</sub>, d), <sup>1</sup>J(PtP) 3657 and 65.2 (P2, d), <sup>1</sup>J(PtP) 4442, [<sup>2</sup>J(P<sub>A</sub>-P2) [23]. 9b (monomer.): <sup>31</sup>P 30.4 (P<sub>A</sub>, d) and 98.4 (P2, d), [<sup>2</sup>J(P<sub>A</sub>-P2) 9].

Satisfactory microanalytical data have been obtained for complexes 3, 6a, 6b, 7, 8a and 8b. <sup>1</sup>H NMR data and further <sup>31</sup>P NMR data for complexes in the Scheme (which are available from the authors) will be reported in a full paper.

With excess methanol, **3** affords in a slow reaction that proceeds in a stepwise manner *via* an isolable dimeric complex **4** and a mononuclear intermediate **5** (*vide infra*), a new monomeric complex **6a** ( $M/Z = 513$ , FD mass spectrometry) which contains a  $\text{PEt}_3\text{-PtCl}$  unit [ $^{31}\text{P}$  and  $^{195}\text{Pt}$  NMR, IR ( $\nu_{\text{PtCl}} = 264 \text{ cm}^{-1}$ )]. The single crystal X-ray structure of **6a** shows (Fig. 1)<sup>†</sup> that through the combined effect of two molecules of methanol the triazaphosphole ring of **1** has been opened at a P–N bond and with insertion of Pt has been closed to form a six membered metallacyclic system. By comparison with corresponding bonds in **1** [3] there is in the ring of **6a** a lengthening of C8–N3 (1.37(3) Å) and N2–N3 (1.38(2) Å) to what are typical single bonds and a shortened C8–N1 separation (1.30(3) Å) corresponding to that of a double bond. The bond angles of the ring atoms define a planar environment for C8, N1 and Pt with a (pseudo)tetrahedral one for the remainder.

These structural data are consistent with the illustrated bonding situation for **6a** in the scheme. The transformation of **3** (containing two differently coordinated **1** units) to **6a** begins with addition of MeOH to a specific P–N bond of both ring systems and generation of a MeO–P–N–H unit. The resulting complex **4** can be isolated from the 1:2 molar reaction of MeOH with **3** and is a dinuclear species with a symmetric structure (see NMR data)\*\*. Further addition of MeOH causes monomerization with insertion of the coordinated platinum into the ring, leading to formation of a cationic chelate species **5** which has only been identified by NMR data *in situ*. In what may then be considered a Michaelis Arbusov reaction, elimination of MeCl from **5** leads to oxidation of the P atom and generation of **6a**. The above reaction appears to be of general scope. Thus, the mononuclear palladium complex **7**\*\* with a *trans* Cl configuration ( $\nu_{\text{PdCl}} = 347 \text{ cm}^{-1}$ ) and N-bonded **1** (see footnote) affords with MeOH a complex, **6b**, which is exactly analogous to the Pt species **6a**. Furthermore, from the 2,5-dimethyl-1,2,3-diazaphosphole, **2**, one obtains a P-bonded *cis* Pt complex, **8a**, ( $\nu_{\text{PtCl}} = 319$  and  $282 \text{ cm}^{-1}$ ) and a N-bonded *trans* Pd complex, **8b**, ( $\nu_{\text{PdCl}} = 349 \text{ cm}^{-1}$ ) which react with two equivalents of MeOH, *via* intermediates, to produce the corresponding six-membered rings **9a** and **9b**. Although the free aza-



phospholes **1** and **2** do exhibit addition equilibria with MeOH [4] it is nevertheless the  $d^8$  metal centres here which are functioning as templates for the highly specific ring expansion reactions that lead to formation of novel 'phosphite' metallacycles.

## References

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<sup>†</sup>Crystal data:  $\text{C}_{10}\text{H}_{26}\text{ClN}_3\text{O}_2\text{P}_2\text{Pt}$ ,  $M = 512.83$ . Monoclinic,  $a = 10.223(1)$ ,  $b = 21.720(4)$ ,  $c = 7.987(1)$  Å,  $\beta = 102.30(1)^\circ$ ,  $U = 1733 \text{ \AA}^3$ ,  $Z = 4$ ,  $D_c = 1.96 \text{ g cm}^{-3}$ , space group  $P4/n$ , Mo-K $\alpha$  radiation. The structure is based on 2714 independent reflections [ $I \geq 2.5\sigma(I)$ ]. The non-hydrogen atoms were located using Patterson and Fourier methods and their parameters refined to  $R = 0.063$  with Pt and Cl having anisotropic temperature factors. Further refinement is in progress.