Inorganica Chimica Acta, *85* (1984) L33–L34

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

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Received November 25, 1983

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 σ-P and σ-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*-$[Et_3PPtCl_2]_2$ to afford the oxygen- and moisture-sensitive complex **3****. The 1:1 $Pt(PEt_3)Cl_2$/**1** stoichiometry was deduced from micro-analytical results and is supported by ^{31}P and ^{195}Pt NMR data**, which furthermore indicated a dimeric formulation. Complex **3** is not ionic (based on conductivity measurements in CH_2Cl_2) and the ^{31}P NMR spectrum points clearly to an asymmetric structure with σ-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.

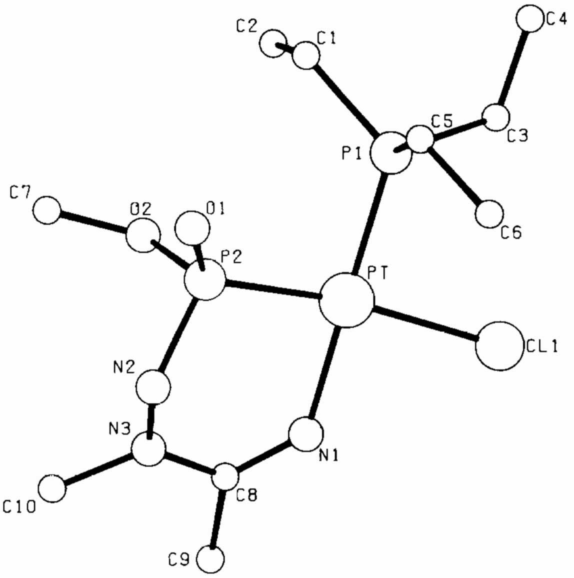

Fig. 1. The molecular structure of **6a** $[\overline{PtP(=O)(OMe)N(H)N(Me)C(Me)=N}H(Cl)(PEt_3)]$. Some relevant geometrical parameters are: Pt–P1 2.244(4), Pt–P2 2.198(5), Pt–Cl1 2.404(6), Pt–N1 2.08(2), P2–N2 1.71(2), N2–N3 1.38(2), N3–C8 1.37(3), C8–N1 1.30(3) A; Pt–P2–N2 108.5(7), P2–N2–N3 119(2), 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)°.

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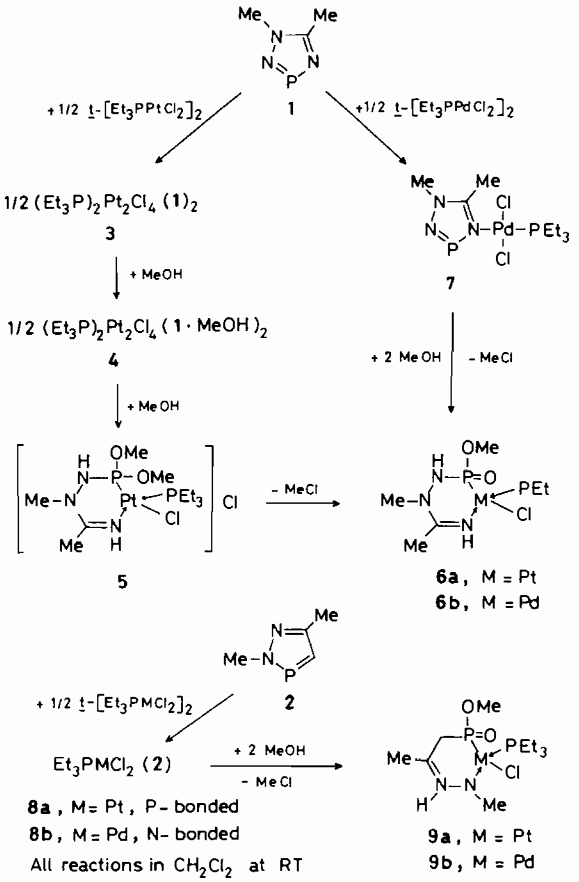
P- or N-bonding of **1 and **2** to metal centres is determined by comparison of ^{31}P and ^{1}H NMR data for the free and coordinated ligands. P_A and P_B are P-atom labels for PEt_3 ligands and $P1_A$, $P1_B$ and **P2** are those for azaphospholes. Some relevant NMR data (^{195}Pt, 21.4 MHz [5]; ^{31}P, H_3PO_4 ref., positive shift values are to higher frequency) in $CDCl_3$: **3** (asym. dinuclear): ^{31}P 10.9 (P_A), 14.3 (P_B), 93.1 ($P1_A$) and 104.8 ($P1_B$); ^{195}Pt 251 (Pt_1) and 218 (Pt_2), [$^{1}J(P_A$-$Pt_1)$ 3135, $^{1}J(P_BPt_2)$ 3472, $^{1}J(P1_APt_2)$ 5220, $^{1}J(P1_BPt_1)$ 5970, $^{n}J(P1_APt_1)$ ~ 20, $^{n}J(P1_BPt_2)$ 88, $^{n}J(P_AP1_A)$ 4, $^{2}J(P_AP1_B)$ 23, $^{2}J(P_BP1_A)$ 18 and $^{n}J(P1_AP1_B)$ 14]. **4** (symm. dinuclear): ^{31}P 12.6 (P_A, m, ^{1}J(PtP) 3045), and 63.4 ($P1_A$, m, ^{1}J(PtP) 5606, ^{2}J(PtP) 62) ^{195}Pt 144. **5** (monomer.): ^{31}P 10.2 (P_A, d, ^{1}J(PtP) 3045) and 75.7 ($P1_A$, d, ^{1}J(PtP) 5682), [$^{2}J(P_AP1_A)$ 26]; ^{195}Pt 19 **6a** (monomer.): ^{31}P 9.6 (P_A, d, ^{1}J(PtP) 3559) and 36.1 ($P1_A$, d, ^{1}J(PtP) 4974), [$^{2}J(P_AP1_A)$ 28.5]. **6b** (monomer.): ^{31}P 30.4 (P_A, d) and 72.3 ($P1_A$, d), [$^{2}J(P_AP1_A)$ 10]. 7 (monomer.): ^{31}P 35.6 (P_A) and 245.9 ($P1_A$); ^{1}H 3.0 (*C*Me) and 4.05 (*N*Me). **8a** (monomer.): 16.8 (P_A, d, ^{1}J(PtP) 2960) and 166.1 (**P2**, d, ^{1}J(PtP) 4676), [^{2}J-(P_A**P2**) 25]. **8b** (monomer.): ^{31}P 36.2 (P_A) and 236.5 (**P2**). 9a (monomer.): ^{31}P 9.6 (P_A, d, ^{1}J(PtP) 3657) and 65.2 (**P2**, d, ^{1}J(PtP) 4442), [$^{2}J(P_A$**P2**) [23]. **9b** (monomer.): ^{31}P 30.4 (P_A, d) and 98.4 (**P2**, d), [$^{4}J(P_A$**P2**) 9].

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

0020-1693/84/$3.00

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 PEt_3-PtCl unit [^{31}P and ^{195}Pt NMR, IR (ν_{PtCl} = 264 cm^{-1})]. The single crystal X-ray structure of **6a** shows (Fig. 1)[†] 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 (ν_{PdCl} = 347 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**, (ν_{PtCl} = 319 and 282 cm^{-1}) and a N-bonded *trans* Pd complex, **8b**, (ν_{PdCl} = 349 cm^{-1}) which react with two equivalents of MeOH, *via* intermediates, to produce the corresponding six-membered rings **9a** and **9b**. Although the free azaphospholes **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.



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[†] Crystal data: $C_{10}H_{26}ClN_3O_2P_2Pt$, M = 512.83. Monoclinic, a = 10.223(1), b = 21.720(4), c = 7.987(1) Å, β = 102.30(1)°, U = 1733 Å^3, Z = 4, D_c = 1.96 g cm^{-3}, space group $P4/n$, Mo-K_α radiation. The structure is based on 2714 independent reflections [$I \geqslant 2.5\sigma(I)$]. 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.