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# Platinum-mediated oxidative P–O coupling of white phosphorus and alcohols: an ab initio study

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Received 9 February 2000; accepted 22 May 2000

## Abstract

Ab initio quantum chemical investigations of the oxidative P–O coupling of white phosphorus and alcohol have been carried out by the model platinum complexes  $[\text{PtCl}_3(\text{CH}_3\text{OH})(\eta^2\text{-P}_4)]^+$  (**1**),  $[\text{PtCl}_3(\text{CH}_3\text{OH})(\eta^2\text{-P}_4)]^-$  (**2**),  $[\text{PtBr}_3(\text{CH}_3\text{OH})(\eta^2\text{-P}_4)]^+$  (**3**),  $[\text{PtBr}_3(\text{CH}_3\text{OH})(\eta^2\text{-P}_4)]^-$  (**4**) and  $[\text{PtClBr}_2(\text{CH}_3\text{OH})(\eta^2\text{-P}_4)]^+$  (**5**) applying the B3PW91 model of density functional theory. According to the performed geometry optimizations, both the tetrahedral  $\text{P}_4$  and  $\text{CH}_3\text{OH}$  molecules are deformed and activated in complexes **1**–**5**. The results of the calculated total atomic charge (TAC) and overlap population (OP) show that the better conditions accounting for the nucleophilic attack of the  $\text{P}_4$  molecule by the alkoxide ion, that is originated from the coordinated  $\text{CH}_3\text{OH}$  molecule, are found in the cationic Pt(IV)  $\eta^2\text{-P}_4$  complexes **1**, **3** and **5**. In these molecules, the coordinated  $\text{P}_4$  molecule acts as an electron-pair acceptor and easily reacts with the alkoxide ligand. The results of the present calculations agree with the experimental observation indicating that the P–O coupling reaction between  $\text{P}_4$  and ROH, which affords trialkylphosphates, proceeds only in the presence of a Pt(IV)( $\eta^2\text{-P}_4$ ) intermediate complexes. The halide ligands, which complete the coordination sphere around Pt, do not directly participate in the reaction. However, they are active components of the catalytic cycle because they promote the reaction via nucleophilic assistance to the alcohol deprotonation step. © 2000 Elsevier Science S.A. All rights reserved.

**Keywords:** Ab initio study; Platinum complexes; White phosphorus complexes

## 1. Introduction

White phosphorus,  $\text{P}_4$ , is the precursor of many useful organophosphorus compounds, which are currently manufactured through a multistep process based on phosphorus chloride and oxychloride as starting materials. Among the different organophosphorics, trialkyl phosphates,  $\text{PO}(\text{OR})_3$ , that are produced in multi-tons amount, are noticeably relevant and are widely employed in different technological areas as extractors of rare and radioactive elements, inhibitors of metal

corrosion and polymer burning, additives to combustible and lubricating materials, brake-liquids, etc.

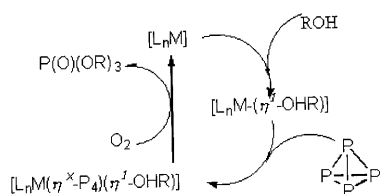
For most organophosphorus compounds, the traditional synthesis of  $\text{PO}(\text{OR})_3$  is based on the preliminary oxidative chlorination of  $\text{P}_4$  followed by the phosphorylation of the alcohol by phosphorus oxychloride. A sketch illustrating the overall process is presented in Eq. (1):



This productive cycle demands consumption of highly toxic  $\text{Cl}_2$  and causes the emission of toxic HCl into the atmosphere with consequent serious environmental impact. For this reason, the search for an

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Scheme 1.

alternative technology, which does not use  $\text{PCl}_3$  as starting reagent for the preparation of organophosphorics, is attracting considerable industrial and environmental interest.

Relevant progress in this area was recently obtained by Ya. Dorfman et al. [1] who developed a 'chlorine free', and therefore more environmentally friendly, method for the preparation of trialkylphosphates. Dorfman's technology is based on the catalytic activation and functionalization of white phosphorus in alcohol/arene solutions of Cu(II) or Fe(III) salts under mild reaction conditions and uses dioxygen as a cheap and efficient oxidant (see Scheme 1). The structure and activity of Cu catalyst was computed previously by using semiempirical quantum chemical methods<sup>1</sup> [2]. The geometry of calculated Cu complexes was fixed (single point calculations), but the real displacement of ligands in the coordination sphere near the central atom was not estimated. The new and powerful possibilities offered by ab initio quantum chemical density functional theory (DFT) methods [3], that evaluate electron correlations, as well as by Berny geometry optimization procedure [4], allowed us to investigate the real displacement and the electronic structure of the ligands in the coordination sphere around the active catalyst. Based on these investigations, it has been possible to shed some light on the complicated first steps of the oxidative phosphorylation of alcohols catalyzed by transition metal catalysts.

The white allotrope of elemental phosphorus,  $\text{P}_4$ , due to the presence of both lone  $\sigma$ -electron pairs and empty d-orbitals, displays rich coordination chemistry and its bonding properties are well documented. During the last two decades, plenty of literature has been accumulated on  $\text{P}_4$  activation by transition-metal moieties [5]. In particular, examples of phosphorus complexes exhibiting both  $\eta^2$ - [6] and  $\eta^1$ -coordination<sup>2</sup> [7] have been described, while the possibility to form complexes via a  $\eta^3$ -coordination has been postulated on the basis of theoretical arguments [8]. When an  $\eta^2$ -coordination is attained, as in  $[\text{RhCl}(\text{P}_4)(\text{PPh}_3)_2]$ , the edge of the  $\eta^2$ -co-

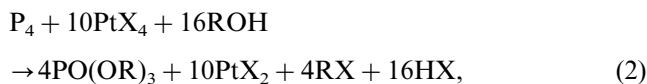
ordinated  $\text{P}_4$  molecule opens by 0.25 Å [6a]. Upon coordination, the proclivity of the  $\text{P}_4$  molecule to undergo heterolytic reaction increases considerably thus making the coordinated  $\text{P}_4$  molecule more suitable to react with different organic and inorganic species [9].

## 2. Experimental

In the search for a more efficient approach to the catalytic functionalization of white phosphorus, it has been demonstrated that the phosphorylation of alcohols by  $\text{P}_4$  can be mediated not only by Cu and Fe species but also by a variety of Pt, Pd, Ru salts and complexes. Noticeably, on substituting Pt(IV) with Pt(II), the reactions are not observed, indicating that a highly oxidised metal is the best promoter to accomplish the phosphorylation reaction [10].

In this article a variety of platinum complexes, that are thought to be relevant models for representing the key intermediate in the first step of the oxidative P–O coupling of white phosphorus and alcohols promoted by Pt(IV) salts, have been calculated by ab initio quantum chemical methods. A clear-cut indication that only the oxidized Pt(IV)  $\eta^2$ - $\text{P}_4$  complex is capable of promoting the P–O coupling step from alcohols and  $\text{P}_4$  has been obtained.

Pt(IV) salts are able to accomplish the oxidative P–O coupling of white phosphorus with alcohol as indicated in the general reaction:



$\text{X} = \text{Cl}, \text{Br}, \text{R} = \text{Butyl}, \text{Pentyl}$

Assuming that the coordination polyhedron of the key-intermediate platinum complex should include both the 'ingredients' of the catalytic phosphorylation reaction (i.e. alcohol and white phosphorus), we have considered the Pt(IV) complexes  $[\text{PtCl}_3(\text{CH}_3\text{OH})(\eta^2\text{-P}_4)]^+$  (1) and  $[\text{PtBr}_3(\text{CH}_3\text{OH})(\eta^2\text{-P}_4)]^+$  (3) ( $\text{CH}_3\text{OH}$  is the simplest alcohol), as good candidates for taking the role of active species in the present process. In order to explain the reasons for the lack of catalytic activity shown by Pt(II) salts and therefore to stress the importance of the oxidation state of the metal, the related Pt(II) complexes  $[\text{PtCl}_3(\text{CH}_3\text{OH})(\eta^2\text{-P}_4)]^-$  (2),  $[\text{PtBr}_3(\text{CH}_3\text{OH})(\eta^2\text{-P}_4)]^-$  (4) and  $[\text{PtClBr}_2(\text{CH}_3\text{OH})(\eta^2\text{-P}_4)]^+$  (5) were also computed.

Although complexes 1 and 3 have never been isolated from the reaction mixtures or even detected by spectroscopic techniques, they should be reasonably considered as possible intermediates in the phosphorylation process. In fact, the real geometry of the intermediate modelled by complexes 1–5 and the dynamic of the distortion of the tetrahedral  $\text{P}_4$  molecule in the phos-

<sup>1</sup> The mechanism of Cu-promoted phosphorylation of alcohols by white phosphorus was investigated by experimental techniques and semiempirical quantum chemical CNDO computation.

<sup>2</sup> Few  $\text{P}_4$ -complexes have been so far synthesized.

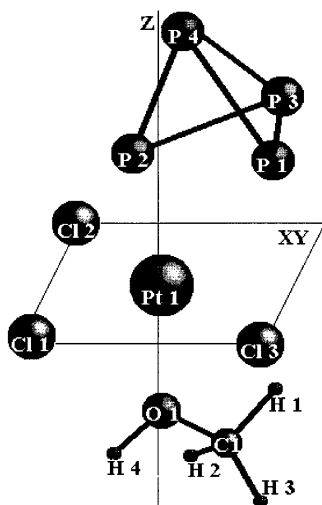


Fig. 1. Drawing of  $[\text{PtCl}_3(\text{CH}_3\text{OH})(\eta^2\text{-P}_4)]^+$  (**1**) showing the final optimized geometry obtained starting from *cis* or *trans* conformations.

phorylation process mediated by platinum can not be independently verified by experimental conditions. Therefore, quantum mechanical investigation is the only possible way to study how the reagents (alcohol and white phosphorus) are activated and understand which factors favour the oxidative P–O coupling of the two reagents in the assumed intermediate complexes **1–5**.

### 3. Results

The energy of the main configuration of Pt ( $[\text{Xe}]4f^{14}5d^96s^1$ ), does not much differ from  $[\text{Xe}]4f^{14}5d^86s^16p^1$ . The latter configuration leads to an octahedral hybridisation around Pt, and has been employed for designing the initial starting geometries of the complexes **1–5** with data and methods taken from reference [2] and the ligands displaced along the axes XYZ (Fig. 1)<sup>3</sup>. The platinum–ligands separations have been considered approximately equal to the sum of the covalent radii (CR) [11], while the initial starting geometries of **1–5** were adjusted using the Berny full geometry optimization algorithm [4] until stationary points on the potential surfaces were found. The minimum on the potential energy surface was searched until force gradient and displacement values become smaller than thresholds installed in GAUSSIAN-94 program package [12].

<sup>3</sup> The labeling scheme adopted for the atoms in **1** (see Fig. 1) and **2** is as follows: Pt1, tetraphosphorus atoms: P1, P2, P3, and P4, chloride ligands: Cl, Cl2 and Cl3, methanol: O1, C1, H1, H2, H3 and H4. In complexes **3** and **4** the labeling adopted was the same as in **1**, **2** but Cl was replaced by Br.

Complexes **1–5** differ in the oxidation state of the central atom (Pt(II) in **2** and **4**; Pt(IV) in **1**, **3** and **5**). In addition, the possibility of different arrangements of the  $\text{P}_4$  and ROH ligands with respect to central atom should be considered to account for the existence of different conformational isomers of the modeling complexes. When the angle (*A*) (see Fig. 1) between the tetraphosphorus ligand atom P1, the central Pt atom and the atom O1 of coordinated alcohol molecule is approximately equal to  $90^\circ$ , we refer to this conformation as *cis* whereas, when the above angle is equal to  $180^\circ$ , we refer to a *trans* conformation.

The full Berny geometry optimization procedure for the complexes **1–5** was performed for each pair of *trans* and *cis* conformers. However, the calculations carried out for the two possible conformers lead to approximately the same final geometry and we did not find any relevant difference between two conformers in the understanding of both the Pt-mediated  $\text{P}_4$  activation and the P–O coupling reaction. For example, the final total energy of optimized **1** complex starting from *cis* conformation is only  $0.06 \text{ kcal mol}^{-1}$  lower in comparison with final optimized total energy starting from *trans* arrangement. The above-mentioned angle *A* becomes equal to  $126.99^\circ$  starting from *cis* arrangement and equal to  $127.01^\circ$  starting from *trans* conformation. Nevertheless, the analysis of the total energies for the two types of conformer in all complexes indicates that the *cis* conformation is more favored for the starting of optimization procedure. Thus, only the results concerning the optimized conformers starting from *cis* arrangement are presented in this paper.

Theoretical investigation of complex **1 cis** and **3 cis** by geometry optimization proved that the  $\text{P}_4$  molecule becomes a deformed pyramid resembling a partially folded kite-like structure due to the coordination of the central atom and the ligand in the polar environment inside the coordination sphere. The most important result was that the distance between the two P atoms ( $\eta^2\text{-P}_4$ ) in **1 cis** became 2.705 and in **3 cis** is 2.755 Å (Table 1).

The interatomic distance between the P(2) and Pt atoms is approximately equal to the sum of their CR, while the distance P(1)–Pt is longer (Table 1). It implies that only the P(2) and Pt atoms form chemical bond.

### 4. Discussion

One of the goals of the present study is to understand the factors favoring the nucleophilic attack of the  $\text{P}_4$  molecule by the alkoxide ion by applying quantum mechanical methods. This nucleophilic attack represents the initial step of the alcohol-phosphorylation process. Although such P–O bonding step may originate through an intramolecular or an intermolecular

process, we think reasonable to hypothesize a metal-mediated intramolecular process, and thus we assume that the alkoxide attacking the  $P_4$  ligand originates from a coordinated alcohol molecule.

Relevant points to understand the whole process deal with the overall picture of the bonding interaction of  $P_4$  with the platinum metal. In this regard, our geometry optimization shows that the  $P_4$  molecule in the complexes **1–5** undergoes a significant pyramidal deformation similar to a partially folded kite-like structure (Fig. 1). As expected,  $P_4$  coordination resulted in the elongation of the P(1)–P(2) bond of the  $\eta^2$ - $P_4$  ligand. As an example, for **1**, our calculations indicate that the P(1)–P(2) separation increase to 2.705 Å in the computed complex (the experimental value of P–P bond is equal to 2.21 in the separate  $P_4$  molecule [13] [14]). The OP value between these P–P atoms in **1** decreases to –0.041 with respect to the value of 0.136 calculated for the separate  $P_4$  molecule. Similar results were obtained also for **2** (P(1)–P(2) opens to 3.074 Å and the OP decreases to –0.115) and for the bromide derivatives **3** and **4** in which the coordinated P(1)–P(2) bond length increases to 2.787 and 3.072 Å, respectively, with OP values –0.051 and –0.114, respectively. Therefore,

Table 1

The bond lengths (Å) in optimized **1 cis** and **3 cis** complexes when the stationary points on the potential surface have been found

Bond	Experimental	<b>1 cis</b> complex	<b>3 cis</b> complex
P(1)–P(2)	2.21 <sup>a</sup>	2.705	2.755
P(1)–P(4)	2.21	2.367	2.376
P(1)–P(3)	2.21	2.367	2.376
P(2)–P(4)	2.21	2.441	2.445
P(2)–P(3)	2.21	2.441	2.445
P(4)–P(3)	2.21 <sup>a</sup>	2.582	2.60
Pt(1)–P(1)	2.47 <sup>b</sup>	2.531	2.556
Pt(1)–P(2)	2.47 <sup>b</sup>	2.477	2.465
Pt(1)–Cl(1), (–Br(1))	2.36, (2.51) <sup>b</sup>	2.365	2.514
Pt(1)–Cl(2), (–Br(2))	2.36, (2.51) <sup>b</sup>	2.397	2.538
Pt(1)–Cl(3), (–Br(3))	2.36, (2.51) <sup>b</sup>	2.397	2.538
Pt(1)–O(1)	2.01 <sup>b</sup>	2.104	2.131
O(1)–C(1)	1.50 <sup>b</sup>	1.477	1.477
O(1)–H(4)	1.10 <sup>b</sup>	0.977	0.976

<sup>a</sup> Experimental bonds for separate  $P_4$  molecule are taken from [13,14].

<sup>b</sup> Sum of experimental CR are taken from [11].

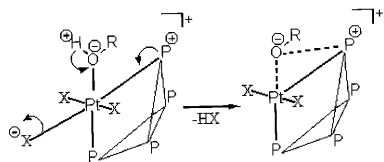


Fig. 2. The proposed mechanism of oxidative P–O coupling reaction.

there is no doubt that the geometry optimization of the model complexes **1–4**, points to a genuine cleavage of the coordinated P(1)–P(2) edge and then suggests a strong coordination of an  $\eta^2$ - $P_4$  molecule to the Pt atom.

In complex **1**, the calculated Pt(1)–P(1) and Pt(1)–P(2) bond lengths are 2.477 and 2.531 Å, respectively, which are in good agreement with the sum of the CR (2.47 Å) [11]. Our calculations on this model complex show also a small positive OP value for both Pt–P bonds (0.003 and 0.015). Similar results have been obtained for complex **3**, for which OP values 0.017 and 0.029 have been calculated. The different values of Pt(1)–P(1) and Pt(1)–P(2) bond lengths and OP may be due to an unsymmetrical coordination of  $P_4$  to the Pt atom, which could reflect different strengths in the coordinated P–P edge of the  $\eta^2$ - $P_4$  ligand. Following this assumption, it is possible to rationalize why one of the two Pt-bonded P atoms in complexes **1** and **3** easy undergo the nucleophilic attack of the alkoxide ion (see Fig. 2). In contrast, in complexes **2** and **4** (which contain a Pt(II) atom), the calculated interatomic distances between the metal and the two coordinated P atoms, give the values of 2.39 and 2.42 Å, which are smaller than the sum of covalent radii (2.473 Å). Moreover, the calculated OP values for the Pt–P bonds are equal to 0.270/0.280 and 0.279/0.302, for **2** and **4**, respectively. As a large localization of electron density in the Pt–P bonds reduces the electron coupling on P–O bond, this fact does not support complexes **2** and **4** for representing the key-intermediate in the phosphorylation reaction.

The three Cl (or Br) atoms are strongly coordinated to Pt in **1–4** complexes (with OP values ranging from 0.076 to 0.490). In all the investigated complexes a weak intramolecular interaction is established between Cl(1) (or Br(1)) and the proton H(14) of the *cis*-alcohol. The positive OP values for Cl(1)–H(4) bond are 0.013 (**1**) and 0.113 (**2**), respectively. The corresponding values for the Br(1)–H(4) bond are 0.010 (**3**) and 0.086 (**4**), respectively. Such ‘hydrogen-bonding’ interaction between the Pt-coordinated chloride Cl(1) (or bromide Br(1)) and the proton H(4) represents a favorable condition to account for the deprotonation of the alcohol ligand and the neat transfer of the alkoxide ion to the proximal phosphorus atom. The ultimate result of this likely concerted process is the formation of a first P–O bond with conjoint elimination of one equivalent of HX. A non-innocent role can therefore be assigned to the halide ligands which behave as weak bases capable of accepting protons from the coordinated alcohol and then assisting the stepwise transfer of up to three OR groups to the same tetraphosphorus molecule. A similar calculation was made once more for complex  $[PtClBr_2(CH_3OH)(\eta^2-P_4)]^+$  (**5**) which shows good  $P_4$  ligand destruction and effective alcohol molecule deprotonation.

Once the alcohol molecule is coordinated to platinum, it becomes more reactive and ready to participate in the P–O bond formation due to the increasing of the difference of absolute values of TAC ( $\Delta q$ ) on the O and H atoms of the O–H bond. The relatively large value of this difference promotes the alcohol deprotonation in the polar environment created in the coordination pocket surrounding the platinum atom. Our calculations indicate that the  $\Delta q$  value for the O–H bond is 0.935 electron charge (e) in complex **2**, 1.045 e in the **1** complex, while such value in separate CH<sub>3</sub>OH molecule. In complexes **3** and **4** values of 1.033 and 0.932 e, respectively, are figured out. As a consequence, in all the investigated complexes, the alcohol-deprotonation step should be possible.

In complexes **2** and **4** the sum of TAC over the P<sub>4</sub> molecule has the slight positive values of 0.338 and 0.308 e, respectively, while in complexes **1** and **3** the same TAC values become largely positive: 1.219 and 1.099 e, respectively. Thus, in complexes **1** and **3**, the coordinated P<sub>4</sub> molecule behaves as a stronger acceptor of negative charge and, at least in part, this feature explains how one of the Pt-activated phosphorus atoms efficiently undergoes the intramolecular attack of the methoxide ion.

In keeping with this result, we have also found that the OP value of Pt–O in complex **1** is negative (–0.005) but it becomes slightly positive for complex **3** (0.012) and even more positive for complexes **2** (0.029) and **4** (0.029). Such findings contribute to explain why the CH<sub>3</sub>O<sup>–</sup> anion more easily migrates to the proximal P-atom in the Pt(IV) complexes than in the Pt(II) complexes causing the disruption of the Pt– $\eta^2$ -P<sub>4</sub> cluster.

In summary, all our observations indicate that complexes **1** and **3** are nicely tailored for modeling the key-intermediate species responsible for accomplishing the first P–O bond-making step during the oxidative phosphorylation of alcohol mediated by a platinum complex. Therefore, the overall processes can be viewed as a cascade of elementary process in which: (1) the P<sub>4</sub> molecule coordinates to platinum affording a distorted  $\eta^2$ -P<sub>4</sub> complex; (2) in the Pt( $\eta^2$ -P<sub>4</sub>) assembly, one of two Pt–P bonds is relatively weak; (3) the OP concerning the Cl(1)–H(4) and Br(1)–H(4) bonds is positive; (4) the  $\Delta q(\text{OH})$  value of the coordinated methanol is relatively large; (5) the TAC value on the coordinated P<sub>4</sub> molecule is largely positive; (6) the OP value on the Pt–O bond is small.

In contrast, notwithstanding favorable requisites to promote the deprotonation step of the coordinated alcohol, the overall calculation on the Pt(II) compounds **2** and **4** point to a stronger coordination between the Pt atom and the  $\eta^2$ -coordinated P<sub>4</sub> and between Pt and the CH<sub>3</sub>O<sup>–</sup> anion. These strong coordination bonds make unlikely the occurrence of an intramolecular nucleophilic attack of the alkoxide group in the case of Pt(II) species and support the experimental results suggesting

that the phosphorylation reaction proceeds only in the presence of Pt (IV) to give alkylphosphates. Finally, the halide ligands do not directly participate in the oxidative P–O coupling but they are active components of the reaction providing nucleophilic assistance to the alcohol deprotonation step, and according to our calculations chloride ligand is more reactive than bromide in this step.

## 5. Calculation methods

In this paper the model complexes **1–5** have been calculated and investigated using the ab initio quantum chemical DFT method in the framework of Becke's three parameter hybrid method [15] and Perdew/Wang 91 gradient-corrected correlation functional [16] (abbreviation B3PW91) model in the LanL2DZ [17] basis set using GAUSSIAN-94, Revision E.2 package [12].

The summation of Mulliken occupation matrix elements inside of atom blocs gives the values of condensed to atoms all electrons [12] [18]. Of particular relevance are the values of off-diagonal Mulliken occupation matrix elements that are multiplied by two (because matrix is symmetrical and the same off-diagonal element between two atoms in the Mulliken matrix appears twice). These values show OP between atoms. A positive OP value points to the presence of a bonding between atoms, while a negative OP value indicates antibonding. The number of electrons in an atom diminished by the value of gross orbital population gives the value of the total atomic charge [12,18].

## Acknowledgements

We dedicate this paper to the memory of Professor Ya.A. Dorfman (1938–1996) and Doctor D.M. Doroshkevich (1950–1995), initiators and experts of this research in IOCE, Almaty. European Commission contracts ERBIC15CT960746 and Lithuanian State Science and Education Foundation supported our research described in this paper. Authors thank Dr N.A. Kotov and Oklahoma State University, Computer Center, Stillwater, OK 74078, USA for the cooperation in using DEC-AXP-OSF/1 computer and for GAUSSIAN-94 Revision E.2 package [12].

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