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P_4 Activation with Pt^0 Metal Centers: Selective Formation of a Dinuclear $\{Pt_2(\mu,\eta^{2:2}\text{-}P_2)\}$ Complex

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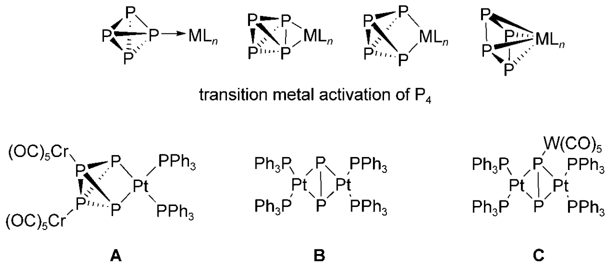
White phosphorus (P_4) is the common basis for organophosphorus compounds, by means of a multistep sequence, involving oxidation with chlorine gas as the first step. A more environmentally friendly derivatization of P_4 is highly desirable, and has been sought for the past decades.[1] In fact, the coordination chemistry of P_4 has been studied in depth since the seminal report of its reactivity toward Wilkinson's catalyst in 1971.[2] However, almost all the early studies after this date used harsh conditions (thermal or photochemical) resulting in unpredictable P_4 fragmentation.[3] It was later recognized that carefully designed transition-metal precursors, which provide a single coordination site under "soft conditions" could lead to η^1 coordination of P_4, which in this case acts as a "typical" phosphine ligand.[4] In particular; Peruzzini et al. have studied extensively the reactivity of Ru complexes of such η^1 derivatives, and shown possible functionalization.[5] On the other hand, when two coordination sites are made available, insertion of the metal center in a P–P bond is typically observed, resulting in the formal oxidation of the metal center, and concomitant reduction of P_4. Yet again, the outcome of the reaction is not very predictable (Scheme 1).[6]



Scheme 1. Various activations of P_4.

First investigations of the reaction of P_4 with electron-rich Pt^0 precursors, such as $[Pt(PPh_3)_2(CH_2CH_2)]$ or $[Pt(PPh_3)_4]$, were done by Scheer et al., who showed that the use of a stabilizing $\{Cr(CO)_5\}$ fragment was required to control the reactivity and to isolate the trimetallic complex $[Pt(PPh_3)_2(\mu^3,\eta^{2:1:1}\text{-}P_4)\{Cr(CO)_5\}_2]$ (**A**).[7] Schäfer and Binder synthesized a $\{Pt_2(\mu,\eta^{2:2}\text{-}P_2)\}$ complex **B** from a Pt^{II} precursor and $LiP(SiMe_3)_2$, showing that the "P_2" fragment[8] could be stabilized by two Pt centers.[9] Much more recently, Cummins et al. have reported on the generation of a related $\{(P_2)W(CO)_5\}$ transient molecule from a diphosphaazide niobium complex.[10] This fragment was efficiently trapped by two $\{Pt(PPh_3)_2\}$ fragments from the $[Pt(PPh_3)_2(CH_2CH_2)]$ complex to form $[\{Pt(PPh_3)_2\}_2(\mu^3,\eta^{2:2:1}\text{-}P_2)\{W(CO)_5\}]$ (**C**).[11] Most importantly, these "P_2" fragments have been trapped by cyclohexadiene to form phosphorus containing tetracyclic species, rare examples of functionalization under very mild conditions.[11,12]

We present here the use of 14-electron complexes of Pt^0 that simultaneously provide two sites of coordination and a d^{10} configuration, which result in a strong activation of P_4. We show that the use of a bidentate diphosphine ligand (vs. two phosphines) allows the isolation of a novel dinuclear $[\{Pt(dppp)\}_2(\mu,\eta^{2:2}\text{-}P_2)]$ complex (dppp = 1,3-bis(diphenylphosphino)propane). A DFT study which rationalizes the formation of this complex as well as its precise electronic structure is also presented.

In a first approach, the known $[Pt(PCy_3)_2]$ complex was selected as the Pt^0 precursor. The slow addition of stoichiometric amounts of P_4 at −78 °C resulted in a very fast and uncontrollable reaction, leading to a black solution. The ^{31}P NMR spectrum of the crude mixture showed the absence of the signal of P_4 and the starting complex and the sole presence of free PCy_3. Based on our previous report that a stoichiometric amount of P_4 reacted with $[Ni(cod)_2]$ (cod = 1,5-cyclooctadiene) to form the corresponding nickel phosphide species,[13] we reasoned that a platinum phosphide spe-

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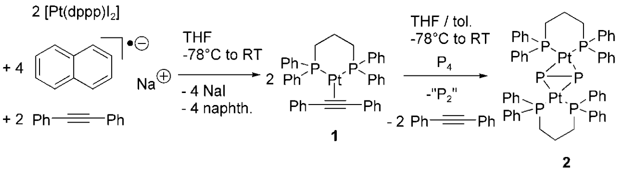
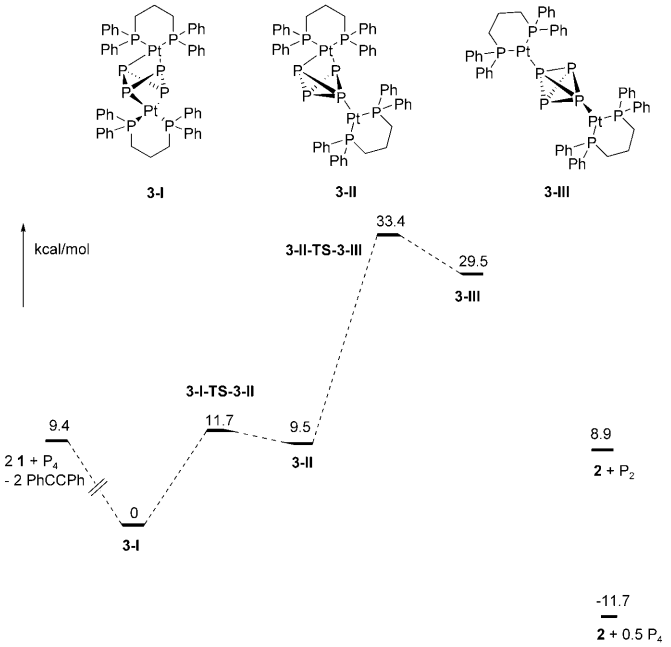
cies was formed in this case. Although disappointing, this result showed that an unsaturated, electron-rich Pt^0 complex readily reacted with P$_4$. The PCy$_3$ ligand is therefore a poor ligand for the desired system, not allowing the stabilization of any metal complex. It was then hypothesized that a bidentate ligand would bring more stability to the system. Unfortunately, the corresponding 14 electron complexes are known not to be stable at room temperature, readily inserting CH bonds. We postulated that such a species, however, might be generated at low temperature and could be trapped by P$_4$. The [Pt(dppp)I$_2$] complex was therefore reduced at −78 °C with two equivalents of Na/naphthalene, followed by the addition of a solution of P$_4$ in toluene. The mixture was slowly warmed back to room temperature and resulted in the formation of a single new Pt complex, but with the appearance of large amounts of free dppp, as evidenced by ^{31}P NMR spectroscopy. Addition of a two-electron donor, diphenyl acetylene, in order to stabilize the Pt^0 formed upon reduction, proved to be beneficial to the outcome of the reaction. Indeed, the reaction, either in one pot from the Pt^{II} or from isolated [Pt(dppp)(PhCCPh)] (**1**) with 0.5 equivalents of P$_4$ resulted in the formation of a single Pt complex **2** [Eq. (1)]. The formation of this complex is accompanied by the appearance of a red precipitate, being apparently oligomers of phosphorus atoms.[14] This by product results from the extrusion of "P$_2$" from each P$_4$ species.[15]



(1)

The formulation of complex **2** as a $\{Pt_2(\mu,\eta^{2:2}\text{-}P_2)\}$ complex is readily evidenced by the ^{31}P NMR spectrum (see the Supporting Information). Indeed, it is characterized by a triplet (^2J(P,P) = 21.8 Hz), with Pt satellites (^1J(Pt,P) = 3356 Hz), at −0.1 ppm, and a quintet at 49.3 ppm (^2J(P,P) = 21.8 Hz), which did not show any Pt satellites.[16] Further proof of the formulation of complex **2** was provided by ^{1}H and ^{13}C NMR spectroscopic measurements, as well as elemental analysis and most importantly an X-ray diffraction study (vide infra). The kinetics of the formation of complex **2** is quite slow, being complete after only three days at room temperature, which prompted us to follow the formation and disappearance of intermediates. In fact, only one intermediate was observed during the whole process. This intermediate, **3**, was the major product already after 2 h at room temperature with the concomitant decrease of the P$_4$ signal (−521 ppm). Importantly, no red phosphorus was observed at this point. This intermediate is characterized by a singlet with Pt satellites (^1J(Pt,P) = 2082 Hz), at −0.1 ppm and a complex signal centered on a singlet at −334 ppm (see the Supporting Information). Interestingly, only one signal was observed for the P$_4$ fragment, suggesting either a fast dynamic process equilibrating all the P centers at room temperature, or a static configuration in which the same electronic environment is found for the four P centers. A variable-temperature NMR experiment provided an argument in favor of the second hypothesis. Indeed, the same spectrum was observed even at 200 K.[17] Yet, one still could envision a fast process even at this low temperature. A DFT study was therefore carried out to both compare the energies of the various complexes postulated for the intermediates, and to propose a rational reaction pathway.

The Gaussian 03 set of programs[18] was used for this study. Optimizations were conducted on the real molecules using the B3PW91 functional, and the 6-31G* basis set for H, C, P and Def2-TZVP for the Pt center. These calculations provide data in full accord with the experimental facts. The free-energy profile is presented as the mechanism involves reactions between several molecules (Scheme 2). First, elimination of the alkyne from the Pt^0 precursor **1** by P$_4$ is shown to be an exothermic process. Most interestingly, the three potential intermediates involving the P$_4$ fragment, **3-I**, **3-II**, and **3-III**, are shown to possess very different energies, with the insertion of the two Pt centers in two P−P bonds (in **3-I**) being strongly favored over the simple coordination (in **3-III**). In light of this, one can reasonably assume that the intermediate observed by ^{31}P NMR spectroscopy is **3-I**. The final step of the mechanism involves the elimination of a "P$_2$" fragment from a complex to form complex **2**. Experimentally, this P$_2$ fragment appears as oligomers of phosphorus atoms. However, for our purposes, these oligomers are not readily modeled and the elimination of the high-energy fragment P$_2$ was first calculated instead. Not surprisingly, it is not favorable being above **3-I** by 8.9 kcal mol^{-1}. On the other hand, when 0.5 P$_4$ was calculated to be elimi-



Scheme 2. Free-energy profile of potential structures for intermediate **3**.

nated, the reaction was strongly favored. As the formation of oligomers of phosphorus atoms is expected to be even more likely than P_4, our calculations predict this elimination process to be highly favorable.

As mentioned above, final proof of the structure for complex **2** was provided by an X-ray diffraction study (Figure 1).[19] It was obtained from a slow diffusion of hexanes into a solution of complex **2** in THF.

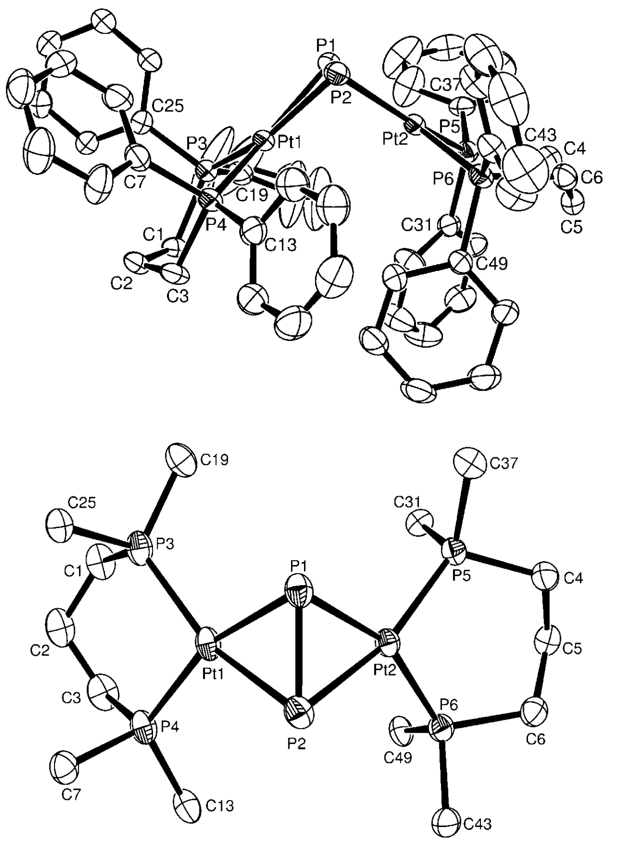


Figure 1. Molecular structure of complex **2a** with thermal ellipsoids depicted at 50% probability. Hydrogen atoms (top) and phenyl groups (bottom) have been omitted for clarity. Selected distances [Å] and angles [°]: P1–P2 2.125(2); Pt1–P1 2.391(1); Pt1–P2 2.371(1); Pt2–P1 2.391(1); Pt2–P2 2.384(1); Pt1–P3 2.258(1); Pt1–P4 2.270(1); Pt2–P5 2.267(1); Pt2–P6 2.266(1); P1-Pt1-P2 53.02(4); P3-Pt1-P4 96.08(4); P1-Pt2-P2 52.86(4); P5-Pt2-P6 95.06(4) Pt1-P1-P2-Pt2 99.39(3).

In fact, two independent molecules are found in the unit cell: **2a** and **2b** (see the Supporting Information for the structure of **2b**). The bond lengths and angles are identical (within experimental error) for the two molecules. They differ only in the dihedral angle Pt-P-P-Pt between the two Pt centers and the P–P bridge: Pt1-P1-P2-Pt2 99.39(3)° in **2a** vs. Pt3-P7-P8-Pt4 96.55(3)° in **2b**. Evidently, the presence of two different geometries in the solid state shows that a slight variation of the dihedral angle does not change the overall energy of the system to a great extent. The most important point is the geometry at the Pt center, which is square planar, consistent with an oxidized Pt^{II} center. The P1–P2 bond length at 2.125(2) Å is much shorter than the P–P bond lengths in P_4 (2.21 Å), which conveys a multiple bond character. The Pt–P (P_2 bridge) bond lengths of 2.384 Å (av) are quite long, and point to a weak Pt–P bond.[11,20] The Pt–P (to the diphosphine ligand) bond lengths of 2.265 Å (av) are in the usual range for diphosphine–Pt^{II} complexes.

In this complex, two Pt^{II} centers are therefore present, which point a strong electronic transfer from the initial Pt^0 center to the P_2 fragment to form a highly reduced P_2^{4-} moiety. A precise analysis of the electronics of this system was carried out by using DFT calculations. Note that the geometry of the calculated complex is in excellent agreement with the observed structure in terms of bond lengths and angles. In fact, the calculation predicts a dihedral angle of 104.0°, in between the two angles experimentally observed. The analysis of the highest occupied molecular orbitals show that four of them (HOMO, HOMO−1, HOMO−2, and HOMO−4) possess large coefficients on the P atoms of the bridge, confirming the high electron density over these two atoms (see Figure 2 for the HOMO, see the Supporting Information for the other orbitals). A charge decomposition analysis (CDA) was performed in order to quantify the participation of the "P_2" fragment in each of these five highest orbitals. Complex **2** was separated in three fragments: two "{(dppp)Pt}" and a P_2 fragment, each being in its geometry found in the complex. Each orbital then results from the mixing of the appropriate fragment orbitals of the three fragments. The results are found in Table 1.

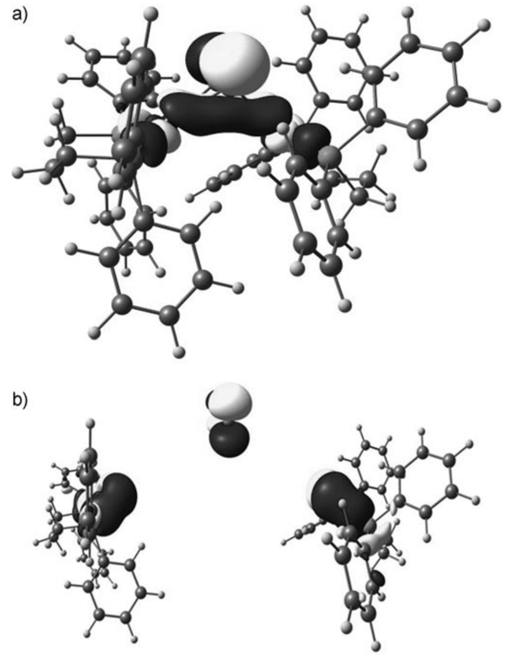


Figure 2. CDA of the HOMO of compound **2**. a) Homo of compound **2**. b) HOFO (fragment Pt1)−LUFO+1 (fragment P2)−HOFO (fragment Pt2).

Table 1. CDA analysis of the HOMOs of compound **2**.

Orbital	Fragment "Pt_1" [%]	Fragment "P_2" [%]	Fragment "Pt_2" [%]
HOMO	29	41	30
HOMO−1	18	52	30
HOMO−2	35	39	26
HOMO−3	40	20	40
HOMO−4	27	52	21

For example, the HOMO orbital mainly results from the combination of the d_{xy} orbital of the "Pt_1" fragment (29%), a π* orbital fragment of the "P_2" fragment (40%) and the $d_{x'y'}$ orbital of the "Pt_2" fragment (30%; Figure 2, see the Supporting Information for the decomposition of other orbitals). These calculations show that the electron density in the P_2 fragment ranges from 39% to 52% in the highest orbitals.

The reactivity of this complex **2** is therefore expected to be nucleophilic, because of the high electron density at the two phosphorus centers. Preliminary tests toward various electrophiles showed the lone pairs at phosphorus to be readily accessible to coordination.

In conclusion, the strong activation of white phosphorus by an unsaturated, electron-rich, Pt center (**1**) is presented here. It resulted in the splitting of the initial P_4 molecule into polymeric red phosphorus and a formally P_2^{4-} coordinated fragment. The mechanism of this transformation was calculated by DFT, which corroborated the experimental facts. Most importantly, DFT calculations point out the high electron density at the bridging P atoms in four high-energy orbitals. Preliminary reactivity results showed the accessibility of the P lone pairs, opening the way for further functionalization of the activated fragment. Studies in this direction are pursued in our group.

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Keywords: coordination modes • main group elements • phosphorus • platinum • structure elucidation

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