Atomic Level Mechanism of the White Phosphorous Demolition by Di-iodine

Carlo Mealli, Andrea Ienco,* Maurizio Peruzzini and Gabriele Manca*

*Istituto di Chimica dei Composti Organometallici – Consiglio Nazionale delle Ricerche (CNR-ICCOM), Via Madonna del Piano 10, 50019, Sesto Fiorentino (FI), Italy.

A detailed mechanism of the I₂-induced transformation of white phosphorus into P_l₃ emerges from a DFT analysis. The multi-step process implies at any stage one P-P and two I-I bond cleavages, associated to the formation of two P-I bonds plus an *in situ* generated brand new I₂ molecule. Significant electron transfer between atoms is observed at any step, but the reactions better define as *concerted* rather than redox. Along the steepest descent to the product, no significant barrier is encountered except for the very first P₄ activation, which costs +14.6 kcal mol⁻¹. At the atomic level, one first I₂ molecule, a typical mild oxidant, is first involved in a linear halogen bonding interaction (XB) with one P donor, while its terminal I atom is engaged in an additional XB adduct with a second I₂. Significant electron transfer through the combined diatomics allows the external I atom of the dangling I₃ grouping to convey electrons into the σ* level of one P-P bond with its consequent cleavage. This implies at some point the appearance of a six-membered ring, which alternative switches its bonding and no-bonding interactions. The final transformation of the P₂I₄ diphosphine into two P_l₃ phosphines is enlightening also for the specific role of the I substituents. In fact, it is proved that an organo-diphosphine analogue hardly undergoes the separation of two phosphines, as reported in literature. This is attributable to the particularly high donor power of the carbo-substituted P atoms, which prevents the *concertedness* of the reaction but favors charge separation in an unreactive ion pair.
Introduction

The interconversion between various allotropes of elemental phosphorus depends on several factors, in particular temperature and pressure but also the involvement of other chemical species.\(^1\) Our group has dedicated much attention to the molecular white phosphorus, \(\text{P}_4\), and its behavior toward transition-metal fragments from both the experimental and theoretical viewpoints.\(^2\) Such a know-how is also deemed important for interpreting the behavior of other P allotropes such as that of the polymeric red\(^3\) and black\(^4\) phosphorus. In particular, our interest is being presently attracted by the latter, as the precursor of the 2D material, phosphorene, which is obtainable upon exfoliation of the black phosphorus.\(^5\) As a matter of fact, we are currently involved in a project\(^6\) aimed at exploring the functionalization of the rugged phosphorene sheets with organic and inorganic species. As in \(\text{P}_4\), all the phosphorene \(sp^3\) P-atoms are pyramidally connected to other three equivalent ones, hence a good understanding of the white phosphorus reactivity may offer an interpretational key for the behavior of the other allotropes. For instance, it has emerged that phosphoro-philic di-iodine molecules contribute to the transformation of red phosphorus into the more ordered black allotrope,\(^7\) thus suggesting that also in this case some P-P bonds cleave and recombine in a different structure with still pyramidal atoms.

In solution, molecular \(\text{P}_4\) molecule is known to be transformed by \(\text{I}_2\) into four \(\text{PI}_3\) molecules, as summarized by Eq. 1.\(^8,9\)

\[
\text{P}_4 + 6\text{I}_2 \rightarrow 4\text{PI}_3 \quad \text{Eq. 1}
\]

In spite of the relatively small number of involved atoms, no detailed atomic level mechanism of the process has been reported as yet. Only a limited number of reaction’s intermediates emerged from NMR spectroscopic studies,\(^10\) while more species have remained undisclosed, likely for their short lifetime. Since modern computational chemistry allows the detection of even feeble stationary points (including transition states), we present here a reconstruction of the multi-step process of Eq. 1 based on a series of sequential energy profiles. In particular, since the diphosphine \(\text{P}_2\text{I}_4\) is perhaps the best
experimentally characterized intermediate in the process, and possibly the most immediate precursor of the \( \text{PI}_3 \), Eq. 1 was split in two sequential parts, such as Eq. 2 and Eq. 3, respectively.

\[
P_4 + 4\text{I}_2 \rightarrow 2\text{P}_2\text{I}_4 \quad \text{Eq. 2}
\]

\[
\text{P}_2\text{I}_4 + \text{I}_2 \rightarrow 2\text{PI}_3 \quad \text{Eq. 3}
\]

As an emblematic step, Eq. 3 suggests the inner P-P \( \sigma \) bond cleavage, accompanied by the I-I one to give two new P-I bonds, thus suggesting a formal 2+2 symmetry forbidden reaction. From the orbital viewpoint, these implies the interconversion of \( \sigma \) bonding into \( \sigma^* \) MOs or the other way around, with an invariably difficult electron transfer between the levels. Another doubt concerns the reported method of synthesis for \( \text{P}_2\text{I}_4 \), based on the disproportionation of the \( \text{PI}_3 \). By assuming that Eq. 3, in the given form is reverse, there would be again a problem of forbidden symmetry, to the point that one starts doubting on the correct proposition of Eq. 3. An occurrence of similar problems also for some of the steps summarized in Eq. 1 cannot be a priori excluded.

With the previous points in mind, an in silico DFT analysis of the whole process was attempted to monitor the mode of electron redistribution and its implications for redox behaviors. The latter is more probable for the parallel \( \text{P}_4+\text{O}_2 \) stepwise process, given the larger electronegativity difference between the atoms. In fact, in the derivatives \( \text{P}_4\text{O}_6 \) and \( \text{P}_4\text{O}_{10} \) the electrons are preferentially assigned to the oxygen atoms implying that the phosphorus oxidation state evolves from the zero value in \( \text{P}_4 \) to +3 and +5, respectively. Such a conclusion appears more questionable for the reactivity of \( \text{P}_4 \) with \( \text{I}_2 \), given that the larger electropositivity of the element is closer to that of phosphorus. On the other hand, the participation of \( \text{I}_2 \) in redox processes is rather general, a previous example studied by us being the oxidation of classic 44e\(^-\) phosphide bridged Pt\(_3\) clusters to 42e\(^-\) derivatives with the reduced iodides as terminal ligands.

In our computational approach to the \( \text{P}_4 \) activation, the DFT-D functional was used, since the dispersion forces help detecting particularly feeble adducts, some of which are endergonic and clearly disfavored by entropy. In particular, the latter highlight incipient Halogen Bonding (XB), still far from its canonic formulation emerging in frozen crystal structures, which clearly indicate the
occurrence of a major electron density redistribution. In any case, the feeble adducts are fundamental to monitor the energy profile of any given step, characterized by the dynamic evolution of the XB species, which encompasses at some point the features found in frozen crystal structures and beyond them. For this, the calculations were based on the dichloromethane PCM model, in the search of consecutive minima and transition states, in order to gain a complete picture of the progressive electron redistribution at the linear P-I-I assembly and eventually to the P-P bond to be cleaved.

All the steps contributing to Eq. 1 seem to imply a concerted process, mainly because of the relatively low basicity of the various P atoms interacting with di-iodine. The point also holds for the allegedly final activation of P2I4 to give P13 (Eq. 3), but we became somewhat dubious about the result, after reading a recent paper by Cummins and coworkers, who showed how some related organo-substituted diphosphine does not afford any phosphine product with I2. Eventually, a reasonable explanation of the difference has been found and will be presented toward the end of this paper, while here we anticipate that it most likely depends on the donor power locally available at the atoms of the P-P bond on whether the latter may be cleaved or not.

Other studies in the literature concern the P4 + I2 reactivity in presence of additional co-reactants. For instance, the role of the Ag+ cation in the homoleptic silver complex [(P₄)₂Ag]⁺ and others has been summarized in a review article. Otherwise, the P₄ activation has been performed in presence of carbene moieties, which afford partial but incomplete P-P demolition and formation of the P=P double bond. The latter feature is never observed by us, excluding such a possibility in our mechanism (vide infra). In other cases, the reaction is promoted by organic radicals including a transition metal fragment such the Cp(CO)₂Fe, originated from the homolysis of its dimeric precursor and carrying an unpaired spin at the d⁷ metal. In this regard, other authors have remarked how an unassisted P₄+I₂ reaction excludes the access to any radical species. Also, the calculations corroborated such a result, since our attempts of isolating reaction radical intermediates invariably failed.
A final point concerns the various energy profiles, which emerged from tested analyses of the possible, alternative steps. Most of them occur with evident energy gains and the lack of substantial barriers, with the most important exception of the very first $P_4$ activation, estimated to be as large as $+14.6$ kcal mol$^{-1}$, with an approximate half one later in the process. This implies that the $P_4$ demolition requires in any case an initial but not excessive activation energy, after which it proceeds rather smoothly to the end.

**Experimental section**

All the compounds were optimized, within the Gaussian09 program$^{25}$ by using the hybrid density functional B97-D.$^{15}$ The dispersion forces in the latter are fundamental for allowing some aggregation of the species with consequent definition of the step profiles. All the free energies, derived after the calculations of the vibrational frequencies, refer to a temperature of 298 K. All the calculations were based on the CPCM model$^{17}$ for the dichloromethane solvent, most typically used in the various experiments. The basis set 6-31G inclusive of polarization functions was basically used, although as a simplification the Stuttgart/Dresden (SDD) pseudo-potential$^{26}$ was used for iodine. This appears to be at the origin of some overestimation of the calculated distances vs. the experimentally available ones. The coordinates of the optimized structures and their energetic parameters are reported in the Supporting Information.

**Results and discussion**

**General aspects of the reactivity between white phosphorus and di-iodine**

Eq. 1 is as exergonic as $-76.4$ kcal mol$^{-1}$, of which $-47.4$ kcal mol$^{-1}$ are for the double diphosphine’s production in Eq. 2. The final derivation of the $PI_3$ product (Eq. 3) affords a further free energy gain of $-14.5$ kcal mol$^{-1}$ per $P_2I_4$ molecule. The computational analysis started with the initial formation of the di-iodine adduct with $P_4$ and continued with other subsequent derivatives, whose evolution was
monitored by series of relaxed scans of reasonable reaction’s coordinates. All the encountered key points were then fully optimized, as minima or transition states, thus allowing precise stepwise profiles, based on structural motifs most of which are present in the literature.

To facilitate the reading of the paper, all the steps, detected through the strategy, are anticipated in Fig. 1 and refer to the evolution of the $P_4$ skeleton, without addressing yet the role of di-iodine molecules to be illustrated case by case. Also, Fig. 1 is subdivided in two main streams, with the left side one essentially representing the succession of the Eq.s 2 and 3, while the right side is indicative of possible alternative steps. Cut down to the bone, each step mainly corresponds to a new P-P cleavage, hence it is identified by a progressive Roman number, which is accompanied by an alphabetic character in the case of alternative routes.

Fig. 1 Flow chart showing the computed phosphorus intermediates in the process of Eq. 1. The mode of action of the $I_2$ reactants are similar at the various steps and will be separately illustrated.
The diphosphine cleavage in Eq. 3 occurs twice in the left side cascade, but only once at the right side, where some PI₃ product forms at earlier stages, suggesting Eq. 4 in place of Eq. 2.

\[ \text{P}_4 + 5\text{I}_2 \rightarrow \text{P}_2\text{I}_4 + 2\text{PI}_3 \]  
Eq. 4

The energy evaluation of the overall Eq. 4, shows that the P₂I₄ diphosphine formation is more exergonic than that through Eq. 2 (-61.9 vs. -47.4 kcal mol⁻¹), but only for a half amount of the product, since, as expected, the energy balance of the whole process must be the same. The following detailed analyses show that basically any step implies a nucleophilic interaction of an electron pair at P₄ (or one of the fragments derived from its degradation) with I₂ molecule(s). Some behavior difference arises because the P donor power is not constant but varies with local geometry and interconnections. For instance, the original P₄ basicity is the smallest detected, likely due to its strained tetrahedral structure. In any case, however, any incipient P⁻·I-I adduct is linear, already suggesting a native Halogen Bonding (XB), which can be still far from its classic equilibrium features, emerging from frozen crystal structures. The latter are generalized with a generic D base (the P lone pair in our case) and a X-Y halogen donor or a X₂ dihalogen, one of which is I₂ itself.¹⁶ The stronger is the base, the larger the P-I bonding interaction, while the I⁻·I elongation is enhanced with accumulation of the electron density at the most external I atom, closer to an iodide. According to the XB definition,¹⁶ the residual I⁻·I interaction is mainly of electrostatic forces, which somehow hide the electron transfer and/or polarization effects occurred to reach the point. On the other hand, the monitoring of the evolution from the initial adduct as well as the underpinning of the ultimate XB scission have been scarcely documented up to now. Moreover, the steps of the P₄ reactivity are peculiar not because of the actual heterotypic scission of the terminal iodide at the end of each step, but for the subsequent P-P cleavage associated to the formation of two new P-I bonds. Previously, we have already addressed some other peculiar behavior of XB adducts formed at a metal center upon the I₂ addition to a chloride ligand, which is intriguingly substituted by an \textit{in situ} formed less electronegative iodide.²⁷,²⁸ Also in this case, the key information was extracted by the computational
monitoring of the system’s evolution involving a XB dynamism. The general electronic underpinnings of the latter are briefly summarized in the next section.

**Dynamic aspects of the Halogen Bonding (XB)**

In a typical D\(^{6+}\)-X-\(\cdots\)-X\(^{5-}\) XB interaction (where D is a generic base), the scission of the terminal halide is controlled by the D’s donor power. It has been found that the latter is also related to the surrounding crystalline environment, as it has emerged from a number of X-ray structures, with an asymmetric I\(^{-}\) anion in place of the symmetric expected one.\(^{29}\) This may be seen as a peculiar XB species, where the more distal lateral iodide has for some reason accumulated a larger electron density, hence has a somewhat lower donor power than its trans-axial analogue. Our proposed explanation\(^{27}\) was based on the different interactions made by the lateral I\(^{-}\) atoms with the surrounding cations in the cell. Thus, the more affected I atom is forced a higher accumulation of electron density and behaves as a weaker donor toward the associated I\(_2\) moiety. The extent of the effect varies crystal to crystal, as shown by the various degrees of I\(^{-}\) asymmetry in different structures. Consequently, the asymmetric I\(^{-}\) species are like snapshots along the dynamic evolution path of XB. To further clarify the point, we refer to some of our experimental and theoretical analyses\(^{27,28}\) of generic D\(^{+}\)-I-\(\cdots\)-I adducts. The larger is the D donor power, the more electron density is drifted into the I\(_2\) \(\sigma^*\) level, which behaves as the unique acceptor because of its relatively low energy. The consequence is that the abstraction of the terminal iodide is progressively easier, especially if facilitated by the presence of a polar solvent. For instance, this occurs in the preparation of organo iodo-compounds from a strong donor such as a carbo-anion and I\(_2\), where the dynamism of the XB intermediate is particularly relevant.\(^{30}\) As mentioned, even a XI\(_2\)\(^{-}\) mixed trihalide (formally similar to an asymmetric I\(^{-}\)) may undergo a dynamic electron redistribution to the point that a coordinated Cl-I-I\(^{-}\) trihalide separates one iodide from the heterodiatomic I-Cl, which was experimentally detected by Raman spectra.\(^{28}\)

To generalize the expected trends of electronic redistribution in linear XB system, we stress the qualitative implications of the generic HOMO in Scheme 1.\(^{27}\) In the latter, the \(sp\) hybridization of the
central atom depends on the lateral donor powers. Only for a fully symmetric triiodide, the central p orbital is uninvolved, with the s orbital alone being equally antibonding, hence repulsive at both sides because of its formal population. This is consistent with the intrinsic hypervalent character of the symmetric trihalides and more in general XB, because the feature persists upon asymmetrization.

**Scheme 1** HOMO of a generic halogen bonded Y-X-D species suggesting the stretching trends.

The control of the relative power of the lateral donors is responsible for the p mixing, which reinforces the bonding of the stronger donor to the central atom. Conversely, a large sp lobe develops toward the opposite weaker donor, which is most likely the terminal halide of the XB system. The latter is affected by bond stretching, if not an actual scission. The fact that HOMO has larger contributions in the antibonding area, implies a corresponding electron density accumulation, with increasing possibility of the terminal halide scission, especially with the support of an abstractor.

**The limiting adducts of an organo-phosphine with di-iodine**

The previously indicated trends of XB interactions are experimentally corroborated by the available structures of the 1:1 and 1:2 adducts of the organo-phosphine $\text{P}^\text{iPr}_3$ with di-iodine.$^{32,33}$ Already in $\text{P}^\text{iPr}_3\text{I}_2$ of Fig. 2a,$^{32}$ the I-I distance of 3.38 Å is definitely weakened with respect to the free diatomic of 2.73 Å, while the P-I bond could be considered as single (2.41 Å).

![Experimental structures of $\text{P}^\text{iPr}_3\text{I}_2$ (a) and $\text{P}^\text{iPr}_3\text{2I}_2$ (b) with red and italics geometric parameters, while the black ones are those of the corresponding optimized $\text{P(CH}_3)_3$ models.](image)

**Fig. 2** Experimental structures of $\text{P}^\text{iPr}_3\text{I}_2$ (a) and $\text{P}^\text{iPr}_3\text{2I}_2$ (b) with red and italics geometric parameters, while the black ones are those of the corresponding optimized $\text{P(CH}_3)_3$ models.
The mentioned experimental values (*in red italics*) are satisfactorily reproduced in the DFT optimized model \( \text{P(CH}_3\text{)}_3\text{I}_2 \), shown in bold in Fig. 2a.\(^{34}\) Moreover, the distal I atom is found to have the -0.7 charge, consisting with the realistic XB character of the adduct. The structure of the 1:2 \( \text{PPr}_3\text{2I}_2 \) adduct in Fig. 2b\(^{33}\) indicates that a second and residually acidic \( \text{I}_2 \) molecule has the possibility of acting as a real extractor of the first formed iodide, as indicated by the large and non-bonding I\(^-\)-I separation of 3.71 Å, attained by the first molecule and the \( \pm 0.92 \) charge separation of the phosphonium and tri-iodide counterions. As a matter of fact, the optimized model best formulates as the ion pair \([\text{P(CH}_3\text{)}_3\text{I}^+\text{I}_3^-]\), although the computed I\(^-\)-I and P-I distances and the I\(^+\) asymmetry are somewhat more pronounced than in the experimental data. A better consistency instead concerns the P-I\(^-\)-I angle of 167.1° and 171.1° in the experimental and *in silico* 1:2 species, respectively. The latter deviation from linearity confirms some lost XB character of the first adduct, after the formation of the classic I\(^+\) species. In any case, the computed free energies of the \( \text{P(CH}_3\text{)}_3\) adducts are consistent with a very high donor power of the organo substituted phosphines. In fact, \( \text{P(CH}_3\text{)}_3\text{I}_2 \) is already as exergonic as -23.5 kcal mol\(^-1\), while the 1:2 adduct gains an additional -7.8 kcal mol\(^-1\). Consider that in this respect the aggregation of up to three molecules is entropically penalized up to the estimated value of +16.7 kcal mol\(^-1\), which is nonetheless overwhelmed by the highly exothermic electron transfer in these species. The entropy seems instead to favor the physical separation of the counterions \( \text{PR}_3\text{I}^+ \) and I\(^+\) by the endergonic amount of -5.6 kcal mol\(^-1\). An important conclusion about the phosphine’s adducts is the occurrence of an actual 1e\(^-\) redox process independently from the actual separations of the counterions \([\text{P(CH}_3\text{)}_3\text{I}^+\text{I}_3^-]\) or their combination as an ion pair. Such a picture greatly differs from any of those encountered in the overall \( \text{P}_4 \) demolition by \( \text{I}_2 \), because of the limited possibilities of electron transfer with scarcely dative P atoms, such as the I-substituted ones. The point will reappear frequently in the subsequent discussion.
Domino evolution of the \( P_4 \) reactivity

Independently from the routes in Fig. 1, the large exergonic balance of the overall process is consistent with its easy experimental occurrence. The possible barriers at the various steps have not been yet remarked, but they are either small or absent in most cases, except in the very early stages (e.g., steps I or IIA) for reasons to be clarified. Importantly, the general mode of attack of a \( P \) lone pair into \( I_2 \) compares with that already illustrated in Fig. 2 relative to the collinear interaction of an organophosphine lone pair with a diatomic, with further enhancement of electron transfer upon the addition of a second one. This occurs also at the various steps of the \( P_4 \) activation with the basic difference that the less dative \( P \) atom transfers a reduced amount of electrons, without preventing the further evolution of the systems in the forms of a new \( P-P \) bond cleavage. In contrast, the latter event will be shown to be definitely more difficult upon a large shift of the electron density, which leads to an apparently inert ion pair. These aspects, as well as other problems, encountered step by step, will be addressed in the following discussion.

First \( P-P \) bond cleavage in \( P_4 \)

Since no adduct between \( I_2 \) and \( P_4 \), 1, has ever been experimentally reported or detected, its identification was attempted in silico. To have more chances of identifying such a feeble adduct, the DFT-D functional\(^{15} \) was adopted, also because the dispersion forces have already enabled us to detect some otherwise metastable metallo-organic initiator of catalytic processes for the transformation of azides.\(^{35} \) Also in this case, an initial minimum of formula \( P_4I_2 \), 1\( I_2 \) (at the left side of Fig. 3) was optimized, although endergonic by as much as +6.2 kcal mol\(^{-1} \). Any lone pair of a \( P_4 \) tetrahedron is a potential donor, as shown for instance by its behavior as a \( \eta^1 \) ligand toward a vacant \( \sigma \) metal acceptor. An example is the complex \( [(np3)\text{Ni}(\eta^1-P_4)] \) (where \( np3 = N(CH_2CH_2PPh_2)_3 \)).\(^{36} \) first reported by our institute, which was followed by others \( \eta^1-P_4 \) complexes.\(^2 \) Conversely, no structure documents the dative interaction of \( P_4 \) toward \( I_2 \), whose residual acceptor capabilities are given by its \( \sigma^* \) level. As a matter of fact, the latter must be higher in energy than any reasonable metal \( \sigma \) hybrid with \( d \) character.
Fig. 3 Optimized adducts between $\text{P}_4$ and one or two $\text{I}_2$ molecule(s).

It is evident that in $\text{1-1}_2$ the dative interaction is still very poor, although its incipient XB character is indicated by the collinearity of the $\text{P} \cdots \text{I}$ and I-I vectors. The lengths of the latter however (3.23 and 2.79 Å, respectively) prove a minimum electron redistribution, which suggested to look for possible alternatives. Thus, by assuming residual basicity for any bent and strained P-P linkage, the species $\text{1-}(\text{I}_2)_{\text{br}}$, at the center of Fig. 3, was optimized with $\text{I}_2$ in perpendicular orientation. Also, in this case the diatomic seems minimally perturbed in view of the two large P-I\textsubscript{bridge} distances of 3.64 Å. On the other hand, a 0.05 Å P-P elongation and the now smaller endergonic balance of +3.9 kcal mol\(^{-1}\) suggested us to insist with the modeling, hence a second diatomic was added with the hope of increasing the electron withdrawing from $\text{P}_4$, as noticed for the phoshine’s bis-adduct of Fig. 2b. As a matter of fact, the new species $\text{1-2I}_2$, at the right side of Fig. 3, was equally optimized starting from either one of the mono-adducts $\text{1}_1\text{I}_2$ or $\text{1-}(\text{I}_2)_{\text{br}}$. An enhanced electron redistribution is indicated by the 0.04 Å stretching of the first added $\text{I}_2$, while its terminal $\text{I}_1^*$ atom is already forming a quasi-orthogonal $\text{I}_3$ grouping. Also, the 0.03 Å elongation of the $\text{P}_1$-$\text{P}_2$ bridged bond and the average ~ 0.15 Å shortening of the P-I\textsubscript{bridge} distances are indicative of some activation as well as the almost null free energy cost of the adduct (only +0.7 kcal mol\(^{-1}\)). In trying to guess how the species $\text{1-2I}_2$ may further evolve toward the expected P-P cleavage, we noticed the large spatial freedom of the terminal $\text{I}_3$ grouping. Hence we tested, as a possible reaction coordinate, the shortening of the $\text{I}_2^- \cdots \text{P}_2$ distance down to a bonding value. The corresponding relaxed scan from 8.47 to 2.55 Å highlighted a promising profile, since the initial energy loss of only 10 kcal mol\(^{-1}\) later converted in a double size energy gain,
all through reasonable chemical species. In fact, the encountered key points could be then fully optimized, affording for step I the precise free energy profile of Fig. 4. Indeed, such a strategy based of relaxed scans and full optimizations allowed to construct the Fig. 1 chart. Fig. 4 starts at the left with the separated P₄ and I₂ reactants, which assemble into the adducts 1(I₂)br and 12I₂ of Fig. 3 with a total energy cost of +4.6 kcal mol⁻¹. Another +10.0 kcal mol⁻¹ must be added to reach the transition state (1-2)TS, whose overall barrier of +14.6 kcal mol⁻¹ is the highest in the overall P₄ demolition process, which hence requires an activation energy to be triggered. Remarkably at (1-2)TS, the first added I₂ molecule is stretched by 3.45 Å, suggesting that an important electron delocalization has already occurred, as also underlined by the 0.6 Å shortening of the P-I bridging linkages, still almost symmetric. On the other hand, the I₁-I₁* vector is no more perpendicular to P₁-P₂, but reoriented to align the terminal I₂ atom of the I₃ grouping with the P₁-P₂ linkage (angle of 171°).

![Fig. 4 Profile of step I for the first activation of P₄ by two I₂ molecules (free energies in kcal mol⁻¹).](image)

Although at (1-2)TS the I₂…P₂ separation is still as large as 4.20 Å, it seems that some iodine electron density may start transferring into the P₁-P₂ σ* level, as also indicated by the 2.57 Å P₁-P₂ elongation. An effect of this sort for the P-P bond weakening was previously remarked by other authors.³⁷ Also, the vibrations of the unique imaginary frequency for (1-2)TS is indicative of the intended I₂…P₂ bond shortening. Another point to remark that the mentioned 3.45 Å elongation of the first added diatomic is still ~0.3 Å shorter than that of the organo phosphine aggregate P¹Pr₃2I₂ of
Fig. 2b, hence one cannot yet propose an ion pair formulation for it, a point, whose importance will become more evident later.

After (1-2)rs, the P1-P2 bond definitely cleaves, as it emerges from the two subsequent minima, namely the metastable adduct IP4I2, 2I2, and the isolated butterfly 2. The obtainment of the former species is exergonic by -20.3 kcal mol⁻¹, while another -2.0 kcal mol⁻¹ are gained on dismantling the residual XB interaction which holds together 2 with the I2 molecule. The nature of the latter must be stressed, because generated in situ from the two original I2 molecules, cooperating in the step. Such an event will be repeatedly observed throughout the P4 demolition, stressing in particular the fundamental importance of having di-iodine in a constant double amount with respect to the phosphorous reactant.38

In closing the description of step I, we address the chemical reliability of the butterfly 2 based on the data of the literature and in the CCDC database.29 From previous NMR investigation of the P4+X2 reaction in CS2 (X = Cl, Br),10b the formation of distinct butterfly isomers emerged. In the latter, the two X substituents may point in either opposite direction (as in 2) or hang both over the butterfly’s cavity. The former isomer was 4:1 more abundant, although the information for X=I is definitely less clear in this respect. Also, various structures of the carbo-substituted RP4R analogues are known in isomeric forms.59 To find possible implications for our system, an optimization of the isomer alternative to 2 was found to be +12.2 kcal mol⁻¹ less stable (see Fig. S1) and moreover the interconversion energy is as high as +35 kcal mol⁻¹. These results suggested to continue the analysis of any possible steps II, exclusively starting from the isomer 2.

**First considerations on the plausible concerted mechanism of the P₄ demolition**

From the results outlined up to now, the following indications emerge:

i) the P-P cleavage does not exclusively produce an I-substituted derivative of P₄ but also a brand new I₂ molecule. The latter is indicated as I⁻-I⁺ to imply its generation from two distinct I-I⁺
diatomics, whose I atoms form the new P-I linkages. Implicitly, step I corresponds to the termolecular reaction, indicated by Eq. 5, which affords two products. By the same token, the ultimate and emblematic diphosphine cleavage in Eq. 3, better formulates as Eq. 3’, as well as many other intermediate steps.

\[
P_4 + 2 \text{I}^- \rightarrow \text{IP}_4 + \text{I}^- \text{I}^* \quad \text{Eq. 5}
\]

\[
P_2\text{I}_4 + 2 \text{I}^- \rightarrow 2\text{PI}_3 + \text{I}^- \text{I}^* \quad \text{Eq. 3'}
\]

Certainly, the continuously reformed I2 molecules are reutilized in the process, so that overall Eq. 1 does not necessarily imply a double number of diatomics (e.g. 12 rather than 6), while it is fundamental that the amount of di-iodine is constantly doubled compared to any P-based reactant.

ii) the mechanistic study implies that step I and the following ones involve the combination of 3+3 bond breakings/makings, in place of the assumed 2+2 one;

iii) the species (1-2)rs in Fig. 4 adumbrates a distorted six-membered P2I4 ring (this is the only case also featuring an endocyclic connection, such as the I1-P2 one), while somewhat more regular rings will appear at the subsequent steps. Importantly, the sides of the ring convert into two distinct sets 3+3 bonds/no-bonds when moving in alternative directions with respect to TS or a point in its proximity (see below). This apparently corroborates the idea of concertedness, implying a significant electron density redistribution between any pair of adjacent connections. With regard to this, it has been already mentioned that the P-P cleavage seems promoted by the \(\sigma^*\) population, which the 4e/2c configuration implying initial repulsion, which is eventually mitigated since the bonding and antibonding electron pairs become local and reoriented P lone pairs;

iv) the concerted mechanism is in particular attributable to the relatively low donor power of the P atoms, such as those of P4 or its iodine-derivatives. In contrast, the larger donor power of organo-substituted analogues induces, as in the case of the phosphines in Fig. 2, a significant charge separation at the I2 reactant(s), with the resulting ion pair having no further possibility of concerted evolution. The most evident difference between the two situations will emerge, toward the end of the paper, from the behavior of the two differently substituted diphosphines (vide infra).
Second P-P bond cleavage

From the butterfly 2, the P₄ demolition may continue in two possible ways, given that the P-P bond to be cleaved may be either the hinge (step IIa)⁴⁰ or a peripheral one (step IIb). The former is closer to any one of the P₄ precursor, given that its atoms all form P-P bonds, hence one may predicts a difficult aggregation with the I₂ molecule(s). As a matter of fact, step IIa encounters some, but not insurmountable, difficulty, which seem to favor the alternative step IIb.

Cleavage of the IP₄I butterfly’s hinge (step IIa)

Although the initial aggregate (2·2I₂)ₜₜ could be reasonably expected to have the P-P edge bridged by I₂, as in 1·2I₂ of Fig. 4, the feature is not found in the profile of Fig. 5, given that only one P atom (P₃) is associated to two I₂ molecules.

![Diagram of Step IIa](image)

**Fig. 5** Step IIa for the di-iodine attack on hinge of the butterfly 2 to give the final puckered four-membered ring 3. (Free energies in kcal mol⁻¹).

Apparently, the P basicity must be somewhat larger, possibly due the less strained character of the P-P bond. A more effective interaction is confirmed by the P₃-I₃ and I₃···I₃* distances of 2.67 and 3.05 Å, respectively, which are indicative of somewhat more pronounced effects than in any adduct of 1. Moreover, (2·2I₂)ₜₜ has the about halved energy cost of +2.2 kcal mol⁻¹. Also, the externally dangling I₃ grouping is again suited for the relaxed scan analysis based on the I₄···P₄ shortening. This allowed the optimization of the key points down to the cleavage of the P-P hinge and beyond it. The
precise profile features at (2-3)_{RS} the second significant barrier detected in the whole process. Its +8.4 kcal mol\(^{-1}\) height is about halved with respect to (1-2)_{RS}, while a significant difference is of lack of bridge-bonding at the P-P linkage to be cleaved. The first diatomic is instead practically cleaved at 3.90 Å, with the quasi-symmetric terminal I\(_3\) grouping is already significantly charged (-0.7). The P\(_4\)-P\(_3\) bond is not however significantly stretched (2.37 Å), apparently because the I\(_4\)···P\(_4\)-P\(_3\) angle of 153° is still somewhat bent to limit the electron transfer into the P\(_4\)-P\(_3\) σ* level. Most likely, the situations change on the following descent from TS, given that the distance becomes as large as 3.10 Å in the product (PI)\(_4\), 3, with the shape of a puckered four-membered ring. As usual, the product 3 is preceded by an adduct (3I\(_2\) in Fig. S2), where the in situ formed I\(_3\)*-I\(_4\)* diatomic is still slightly interacting. The estimated free energy gains are -17.6 kcal mol\(^{-1}\) at 3I\(_2\) and -19.6 kcal mol\(^{-1}\) upon separation of the components.

The chemical reliability of 3 is also assessed by some analogues in the literature, although the species did not emerge from the previous NMR studies.\(^{10}\) In any case, the stereochemistry of 3 is peculiar for the two pairs of consecutive P-I linkages (not even parallel to each other), which simultaneously point to opposite sides of the ring. No other example of this is instead present in the CCDC,\(^{29}\) which in no case has a P\(_4\) ring with only halogen substituents, but at most two of them in the species P\(_4\)I\(_2\)(SiR\(_3\))\(_2\).\(^{41}\) Since other structures feature pairs of trans-diagonal organo-substituents at the same side of the P\(_4\) ring, we computationally tested such a stereochemistry also for (PI)\(_4\). Hence, the corresponding species 3’ in Fig. S3 was compared with that of 3, in order to find out an insignificant energy difference of only < 1 kcal mol\(^{-1}\) with a negligible interconversion barrier, as shown by the flat PES near TS. On the other hand, the unique relevance of 3 vs. 3’ clearly emerged on analyzing the subsequent step IIIa (see below), which is unique, given that the terminal I\(_3\) rearrangement is highly hindered by the substituents, when starting from 3’.

**Cleavage of one peripheral P-P linkage of the IP\(_4\)I butterfly (step IIIb)**

The aggregation of two I\(_2\) molecules is less unhindered at one I-substituted P atom of 2, possibly because the flexibility of the terminal P-I vector confers a larger degree of basicity to the P lone pair.
Indeed, the aggregate (2·2I₂)periph is less endergonic than the (2·2I₂)hinge one, as it emerges from the comparison of Fig. 5 and 6. Also, the analogue of (2·2I₂)periph involving the P₂ rather than the P₁ atom has been discarded because the terminal I₃ rearrangement would be hindered by the P₁-I₁ linkage already oriented over the cavity of the butterfly. Hence, step IIb uniquely proceeds as shown in Fig. 6, almost being also barrierless. In fact, a destabilization of only +0.6 kcal mol⁻¹ was estimated by our initial scan, which showed a plateau around (2·4)₄₃, which could not be fully optimized. After the latter, our strategy afforded the detailed energy profile of Fig. 6, still apparently consistent with a concerted mechanism.

![Diagram](image)

**Fig. 6** Step IIb for the I₂ attack on one external I-substituted atom of the butterfly 2. The species (2·4)₄₃, resulting from a relaxed scan, could not be fully optimized for lying on a flat plateau, indicated by the helical connection. (Free energies in kcal mol⁻¹).

Although the evolution of the butterfly 2 seems easier through step IIb, step IIa cannot be automatically excluded under the conditions for triggering the P₄ activation, since the barrier, is only half of that already passed at step I. On the other hand, the missing barrier for step IIb seems to imply a subsequent energy gain of only -10.6 kcal mol⁻¹ at the species 4I₂ (see Fig. S4), with an additional -1.5 kcal mol⁻¹ gained for the ultimate separation of 4. The latter can be synthetically formulated as I₂P₃I₂, to indicate at the right a P₃ ring with three exocyclic bonds, i.e., two equally oriented P-I ones and another P-PI₂ one in opposite direction with respect to the triangle. Again, experimental analogues are known with organo- in place of halogen substituents. Perhaps, the most related species is RCIP-P₃CIR with R being a substituted phenyl ring. In some cases, the two
substituents at the same side of the P₃ ring are interconnected by a chain,⁴³ while in 4 two adjacent P-I linkages are not exactly parallel to avoid a close contact.

**Third P-P bond cleavage**

The cascade of steps through the general mechanism continues from both products of the steps IIa and IIb, provided that 3 can be effectively formed in spite of the barriers to be passed. In this case, the left side cascade of Fig. 1, may continue with the opening of the (PI)₄ ring to give the chain P4I₆, 5, with two terminal PI₂ groupings (step IIIa). Conversely at the right side, the three-membered cycle 4 may follow alternative paths, such as the steps IIIb and IIIc, depending on the phosphorus/di-iodine docking mode. In the former case, the three-membered ring (PI)₃, 6, may form together with a dissociating (PI)₃ phosphine 7 or, in the latter, the tripod-like dendrimer P(PI₂)₃, 8, is consequent to the opening of the P₃ cycle at the bond involving the I-substituted P atoms.

**Opening of the four-membered ring (PI)₄ (step IIIa)**

The stereochemistry of the intermediate 3, based on the precursor 2, can in principle afford different adducts of the type 3·2I₂. The one shown at the left side of Fig. 7 does not encounter hindrance problems in the important I₃ grouping rearrangement.

![Fig. 7 Step IIIa for transforming 3 into the open chain product 5. (Free energies in kcal mol⁻¹).](image_url)

Remarkably, 3·2I₂ is the first exergonic aggregate encountered in the present P₄ chemistry (-3.8 kcal mol⁻¹), implying that the donor power of the P₁ atom has become larger. This is also corroborated
by the more evidently perturbed P₁-I₅ and I₅-I₅* distances of 2.56 and 3.10 Å, respectively. Also in this case, our strategy afforded a reliable energy profile, which includes the low lying transition state (3-5)ₚₛ (+2.5 kcal mol⁻¹). The latter is -1.3 kcal mol⁻¹ more stable than the separated reactants, suggesting an essentially barrierless evolution. The -0.6 charge of the terminal I₃ unit at TS is again consistent with a concerted electron transfer, which determines the cleavage of the P₄-P₅ bond to give the open chain P₄I₆, 5, stabilized by -11.8 kcal mol⁻¹.

As usual, the intermediate 5I₂ precedes the final mentioned product upon release of the in situ generated I₂ molecule with the exergonic balance of -3.7 kcal mol⁻¹. The still rather closed I₆-P₄-P₁ angle of 135° at (3-5)ₚₛ indicates as still poor activation of the P₄-P₁ bond, still as short as 2.36 Å. On the other hand, the electron flow into its σ* level becomes possibly on the descent to 5I₂, once again consistently with the concerted mechanism.

**Alternative steps IIIb and IIIc from 4**

As the product of step IIb, I₂P₃I₂ may aggregate two I₂ molecules in different manners to afford the species (4₂I₂)ₐ, (4₂I₂)ₐ and (4₂I₂)ₐ of Fig. 8, whose energy balances are similarly exergonic, namely -2.7, -3.9 and -0.3 kcal mol⁻¹, respectively.

![Fig. 8 Optimized structures of the isomeric adducts between I₂P₃I₂, 4 and two I₂ molecules.](image)

Both (4₂I₂)ₐ and (4₂I₂)ₐ may be almost equivalent precursors of the P₁-P₄ cleavage with separation of the phosphine PI₃, 7, from the cycle (PI)₃, 6. Fig. 9 shows the profile of the step IIIb only departing from (4₂I₂)ₐ. On the other hand, the aggregate (4₂I₂)ₐ could in principle have the
chance of undergoing the triangular P₃ ring opening at either the P₄-P₂ or P₄-P₃ linkage to give the four-membered open chain 1₃P₃-P₃-P₄-P₁₂, 5. The latter process is inhibited by the two P-I vectors departing from the ring, which hinder the I₁ rearrangement. Conversely, the P₂-P₃ side may open up starting from (4₂I₂)c to afford the dendrimer P₁₃P₁₂, 8, as shown by the profile of step IIIc in Fig. 10. The mentioned possibilities are here described in some detail.

**Fragmentation of the P₄ skeleton in 4 to give the P₁₃ and the ring (P₁₃)₃ (step IIIb)**

The cleavage of the P₁-P₃ exocyclic bond in (4₂I₂)a is monitored in Fig. 9. The encountered +5.3 kcal mol⁻¹ barrier at (4-6)ₜₛ is in actuality as small as +1.4 kcal mol⁻¹ given that the aggregation of the components in (4₂I₂)a is somewhat exergonic (-3.9 kcal mol⁻¹). This is because of the relatively good basicity of the exocyclic atom P₁, which determines the actual cleavage of the first I₅-I₅* diatomic at TS (separation of 3.96 Å), hence a significant charge delocalization at the terminal I₃ grouping, which is not too asymmetric given the 2.95 and 3.12 Å distances.

**Fig. 9** Step IIIb for the first cracking of the P₄ skeleton into a P₁₃, 7 and the (P₁₃)₃ ring 6. (Free energies in kcal mol⁻¹).

The situation is not to dissimilar from that of R₃P₂I₂ in Fig. 2b, although it is improper to discuss of an ion pair formulation, since the terminal I₆ atom is already at 3.08 Å from the P₄ atom, consistently with the idea of a concerted at work.
The next intermediate is still an aggregate, namely 61:7, where the newly formed I₅*-I₆*diatomic holds this time together two distinct molecules. Clearly, there is no direct interaction between the latter as shown by the large P₄-P₁ separation of 3.47 Å, but in any case this allows an energy gain of -6.8 kcal mol⁻¹, which almost doubles (another -5.5 kcal mol⁻¹) with the final scission of the three molecular components. In this case, the process seems particularly favored by entropy, whose contribution is evaluated to be about -17 kcal mol⁻¹. The formation of the first of the four expected PI₃ molecules in the overall process is remarkable for preceding that of the diphosphine P₂I₄, till now considered its natural precursor. An early presence of PI₃ could be possibly presumed on the basis of the early NMR data, although not explicitly proved.¹⁰

Opening of the three-membered ring in 4 to give the dendrimer 8 (step IIIc)

The P₃-P₂ cyclic bond in (42I₂)₆ does not encounter hindrance problems on its cleavage, because the terminal I₃ grouping occupies the space opposite to the two P-I linkages, as shown in Fig. 10. As the least stable of the isomers in Fig. 8, (42I₂)₆ reaches the transition state (4-8)rs with a cost of only +2.1 kcal mol⁻¹, which is reduced to +1.8 kcal mol⁻¹ with respect to its separated components.

**Fig. 10** Step IIIc for the opening of the cycle I₂P-P₃I₂, 4, to give the dendrimer P(PI₂)₃, 8. (Free energies in kcal mol⁻¹).

The (4-8)rs stereochemistry is particularly remarkable for allowing an easy identification of the P₂I₄ six membered ring, which switches the 3+3 formed/broken linkages in the ideal *concerted* nature of the process. In this case, not only the turning TS point is easily reached but also its subsequent descent to the dendrimer 8 seems smooth because of the total energy gain of -14.1 kcal mol⁻¹, of
which -3.2 kcal mol\(^{-1}\) are associated to the scission of the intermediate \(8\cdot I_2\). Again, halogenated species such as \(8\) have not been structurally characterized, but again the molecular type is supported by related tripodal triphosphanes with organic substituents.\(^{44}\)

**Fourth P-P bond cleavage**

In both cascades of Fig. 1, there remain three of the six original P-P bonds to be cleaved. The precursor at the left side is the open chain \(P_4I_6\), 5, which in principle may be cracked in the middle to give two \(P_2I_4\) diphosphines or allow the scission of a \(PI_3\) phosphine from the chain \(P_3I_5\), 10. At the right side, the fourth P-P cleavage may occur at either the ring \((PI)_3\), 6, or the dendrimer \(P(PI_2)_3\), 8, which equally afford the chain 10.

**Chain-breaking at \(P_4I_6\) (step IVa).** Alternative conformations of 5 are possible as shown by the structure of some organo-substituted \(P_4\) chains in the CCDC.\(^{29}\) In some cases, the chain is overall planar with zig-zag conformation,\(^{45}\) while in other is puckered and similar to a trapezoid, in which one of the cyclic sides has opened up without a major conformational rearrangement.\(^{46}\) The latter seems to be the case of compound 5, which derives from the closed cycle 3 without any significant conformational change (see step IIIa in Fig. 7). In other words, the product 5 maintains a chelate shape. This in principle causes some repulsion between the terminal P lone pairs, which is somewhat mitigated by a torsion around the central P\(_2\)-P\(_3\) linkage (the corresponding PPPP dihedral angle is 125°). In this manner, the \(P_4\) chain stabilizes, whereas its potential adduct with two \(I_2\) molecules at one lateral P atom encounters major stereochemical problems, which emerge from its attempted optimization. This is clearly indicated by the corresponding species \(5\cdot 2I_2\)\(^{4}\) (Fig. S5) with illogic chemical features. For instance, one I atom is found bridging between the two lateral P atoms with an energy cost of about +10 kcal mol\(^{-1}\), hence the species was abandoned as a precursor of the chain breaking. In contrast, the adduct \(5\cdot 2I_2\) involving an inner P atom of 5 has a stabilization energy of -4.4 kcal mol\(^{-1}\) and was used as the starting point of step IVa. For the sake of brevity, the corresponding
standard profile is presented in the SI (Fig. S6) and highlights the central split of 5 into the two \( \text{P}_2\text{I}_4 \) molecules, 9, through a practically barrier-less process and an overall energy gain of -15.3 kcal mol\(^{-1}\). As expected, an intermediate with the \textit{in situ} formed \( \text{I}_2 \) molecule, namely \( 9\text{I}_2\text{I}_2 \), precedes the final dissociation of the molecular components, which is exergonic by -4.4 kcal mol\(^{-1}\), likely because of the favourable entropy.

It is worth mentioning at this point an additional feature of \( 5\text{I}_2\text{I}_2 \), which has been overlooked until the submission of this paper. Namely, the species is not only the precursor of the diphosphine 9, but it alternatively affords the separation of the phosphine 7 from the shorter chain \( \text{P}_3\text{I}_5 \), 10, whose behavior will be illustrated below. Importantly, this shows the till now missing an interlink between the two cascades in Fig. 1. Very briefly, the alternative step starting from \( 5\text{I}_2\text{I}_2 \), whose detailed profile IVa-bis is shown in Fig. S7, is also smooth, for having the \( (5\text{-}10)_{\text{TS}} \) -0.9 kcal mol\(^{-1}\) lower than the reactants and a subsequent free energy gain of -14.1 kcal mol\(^{-1}\). The new results lead to the conclusion that the final product \( \text{PI}_3 \) is in any case partially attainable even before diphosphine 9 achievement.

**Opening of the three-membered ring 6 in step IVb**

At the right side of Fig. 1, the 4\(^\text{th} \) P-P cleavage may start from the \( (\text{PI})_3 \) ring. The observed conformation of the latter with all the I substituents at the same side is somewhat unusual and it is most likely imposed by that of precursor 4 (see step IIIb in Fig. 9). As a matter of fact, the known organo-substituted \( \text{P}_3 \) analogues have the 2+1 distribution of the substituents\(^{47}\) and also a calculation for such a \( (\text{PI})_3 \) isomer shows a larger stability of -3.9 kcal mol\(^{-1}\). Also, no interconversion of the isomer seems possible in view of a free energy cost >25 kcal mol\(^{-1}\). The computed profile for step IVb in Fig. S8 shows that the initial adduct \( 6\text{I}_2\text{I}_2 \) leaves large space for the rearrangement of the terminal \( \text{I}_3 \) grouping and the eventual formation of the open chain \( \text{P}_3\text{I}_5 \), 10. Also, the mechanism is usual with a small barrier of +2.5 kcal mol\(^{-1}\) to be passed at the transition state \( (6\text{-}10)_{\text{TS}} \), followed by an overall energy gain of -18.4 kcal mol\(^{-1}\). NMR evidences of \( \text{P}_3\text{I}_5 \) has been provided,\(^{48}\) while it is worth mentioning that other similar halogenated chains have been recognized as relevant in the chemistry of small \( \text{P}_n \) units.\(^{33,44}\)
Alternative generation of the phosphine 7 and the chain 10 from the dendrimer 8 (step IVc)

The pyramidal dendrimer $\text{P(PI}_2)_3$, obtained through step IIIc, can add two di-iodine molecules at either the central P atom, $(\text{8}_2\text{I}_2)_{\text{centr}}$, or one of the terminal ones, $(\text{8}_2\text{I}_2)_{\text{lat}}$. From both precursors one may expect the analogous $\text{P}_{\text{centr}}$-$\text{P}_{\text{lat}}$ bond cleavage but, since $(\text{8}_2\text{I}_2)_{\text{centr}}$ is more stable by -5.0 kcal mol$^{-1}$, it was the isomer of choice for step IVc. A new cracking of the $\text{P}_4$ skeleton generates the phosphine 7 and the open chain 10, which at this point appears to have various modes of formation. The profile of the step IVc in Fig. S9 confirms its unquestionable feasibility, given that $(\text{8-10})_{\text{TS}}$ lies -3.2 kcal mol$^{-1}$ lower than the separated reactants and the overall exergonic balance is -17.2 kcal mol$^{-1}$, consistently with the concerted mechanism.

Final P-P cleavages (steps V and VI)

The two last P-P cleavages are equivalent at the left side cascade of Fig. 1 with the generation of four phosphines, 7, from two diphosphines, 9. At the right side, no $\text{P}_2\text{I}_4$ molecule has yet formed at the 4$^{th}$ P-P cleavage, while one fourth of the $\text{PI}_3$ product is already present (it has alternatively formed through step IIIb or IVc). The amount of phosphine doubles at step V through the cracking of the chain 10, hence still excluding the mandatory involvement of the diphosphine for its formation. The latter is instead produced with the mentioned 5$^{th}$ P-P cleavage at the right side, which is in any case based on the cracking of 10, as shown by the subsequent profile.

Cracking at step V of the open chain 10

Irrespective from its formation, the three-membered chain 10 easily undergoes a P-P cleavage under the general mechanism. The profile of Fig. S10 assumes that the di-iodine molecule is anchored at the central P atom, although a lateral aggregation should not be dramatically different. The $(\text{10-9/7})_{\text{TS}}$ is again more stable than the separated reactants and from it the splitting of 9 and 7 occurs with an overall energy gain of -14.3 kcal mol$^{-1}$, of which -4.0 kcal mol$^{-1}$ are for the final scission of the ter-molecular intermediate $\text{91I}_2\text{7}$ of Fig. 11, for the particularly favourable entropic contribution.
**Fig. 11** Optimized structure of ter-molecular intermediate $9\text{I}_\text{2}\text{7}$.  

The just outlined process prompts an interesting comparison with the inverse, Ag$^+$ promoted, combination of PI$_3$ and P$_2$I$_4$ to give the cationic open chain P$_3$I$_6^+$. In the lack of a detailed reaction’s profile, Scheme 2a suggests how the AgI precipitation may favour the extraction of one iodide from PI$_3$, with the consequent orbital vacancy at the PI$_2^+$ grouping being saturated by a P$_2$I$_4$ lone pair and the formation of the new P-P bond.

![Scheme 2](image)

**Scheme 2** Comparison of the acidic action of Ag$^+$ vs. I$_2$ in the potential formation of the cationic chain P$_3$I$_6^+$.  

A similar role could be exerted by the residual I$_2$ acidity (see Scheme 2b), which could in principle extract an iodide from PI$_3$ and give I$_3^-$, hence the ion pair I$_3^-$/P$_3$I$_6^+$. The intermediate $9\text{I}_\text{2}\text{7}$ of Fig. 11 would be the turning point of the reaction, which is energetically penalized in forming the P-P bond formation, hence excluding the cationic chain P$_3$I$_6^+$ (Fig. S10).

**The ultimate I$_2$-promoted transformation of the diphosphine P$_2$I$_4$ into PI$_3$ and the inhibition for organo-substituted analogues**  

The diphosphine’s dissociation step to give PI$_3$ is a ter-molecular process, as it already emerged by the proposal of Eq. 3$'$ vs. Eq. 3. The latter implies a 2+2 addition, which is a symmetry forbidden
reaction,\textsuperscript{11} because of the inter-crossing of the $\sigma$ and $\sigma^*$ levels along the pathway and the high energy costs to invert the population. On the other hand, the concept of $\sigma$ bond metathesis\textsuperscript{49} has been raised for some organometallic compounds of $d^0$ elements, which interchanging some coordination bonds associated to the alternative formation/cleavage of metal–element bonds, while the inverse behaviour applies to the associated element–element bonds. Possibly, some relation with Eq. 3 may be established because of the electronic equivalence between the P atoms and $d^0$ metals, but the point has not been further pursued. Conversely, we insisted with the general picture emerging from the various $P_4$ demolition steps, which is based on the 3:3 and not the 2:2 ratio of broken/formed bonds.

As a matter of fact, $P_2I_4$ behaves in the known manner toward di-iodine, while other organo-diphosphine analogues do not undergo the P-P cleavage under the action of I$_2$. We refer in particular to the species $P_2$(dmb)$_2$, \textit{11}, recently reported by Cummins \textit{et al.}\textsuperscript{18} where dmb are chains of four carbon atoms, which close two cycles by sharing the same P-P linkage. For the comparative calculations in Fig. 12, the realistic model of \textit{11} was preferred to the simpler diphosphine $P_2$(CH$_3$)$_4$ one. A first important difference concerns the initial 1:1 adduct 9I$_2$ vs. 11I$_2$. As a matter of fact, an organo-substituted P atom must be a stronger donor, more effectively perturbing the added I$_2$ molecule, as already noticed for the phosphine adduct $PR_3$I$_2$ of Fig. 2a.\textsuperscript{50} Thus, the I$_{11}$-I$_{11}^*$ elongation in 11I$_2$ is definitely larger than in 9I$_2$ (3.31 vs. 2.97 Å), while P$_1$-I$_{11}$ distance is closer to a single bond (2.53 vs. 2.73 Å). Experimentally, in \textit{11}, the two distances are 2.411 and 3.417 Å, respectively. Since no experimental information is available on the aggregate of the organo-diphosphine with two diatomics, we also optimized the species 11:2I$_2$ and compared it with 9:2I$_2$. What it emerges is the definite cleavage of the first I$_2$ molecule (I$_{11}$-I$_{11}^*$ = 3.97 Å) and is lost collinearity with the P linearity with the P$_1$-I$_{11}$ vector. More remarkable are the free energy changes. While in Fig. 12a, the maximum free energy gain for 92I$_2$ is as usual not large (-2.25 kcal mol$^{-1}$), the addition of two diatomics to \textit{11} is -28.2 kcal mol$^{-1}$ (\textit{i.e.}, -19.6 kcal mol$^{-1}$ and -8.6 kcal mol$^{-1}$, in the order).
Fig. 12 a) Final I₂-promoted dissociation of P₂I₆ into two PỊ₅; b) different behavior of the organo-
diphosphine 10 with disfavoured P-P cleavage (Free energies in kcal mol⁻¹).

Also the terminal and asymmetric I₃⁻ in 11·2I₂ has almost monoanionic (charge = -0.93), the adduct is best formulated as ion pair [11I]⁺[I₃]⁻, whose cation closely recalls the well-known and stable
[P₂I₅]⁺ one, which is rather unreactive. It may be deduced at this point that the maximized electron transfer at the species in question is inconsistent with the till now proposed concerted mechanism in these processes. Nonetheless, we insisted with our strategy of relaxed scan and subsequent optimizations to evaluate the possible difficulties of the Cummins’s system in forming the new I₁₆-P₂ bond and the eventual P₁-P₂ cleavage. As a matter of fact, the profile b in Fig. 12 follows the trends already highlighted in a, although the energies are much different.

Thus, to reach (11·12)rs the energy cost is +21.0 kcal mol⁻¹ vs. the +3.0 kcal mol⁻¹ of (9·7)rs. While from the latter the generation of distinct PI₃ molecules is as smooth as in all of the previous
cases (the energy gains are -9.5 and -5.7 kcal mol\(^{-1}\) at 7-I2-7 and 2PI\(_3\), respectively), the structure of (11-12)\(_{TS}\) is highly questionable. In fact, this already features a broken P\(_1\)-P\(_2\) bonds with a separation as large as 3.53 Å, while after the high free energy cost to reach the point, the subsequent energy gains to obtain 12 or its immediate precursor 12-I\(_2\) are as small as -4.2 and -0.5 kcal mol\(^{-1}\), respectively. Likely, our computational strategy has forced the attainment of these minima, which are spontaneously attainable at least through the mechanism proposed in this paper. Incidentally, it is worth mentioning a compound of type 12 with halogen atoms other than iodine was spectroscopically detected after treating 11 with halogenating reactants other than diatomics, \(\text{e.g.}, \text{C}_2\text{Cl}_6\)\(^{18}\) or the Grignard species.\(^{18,52}\) In the lack of X-ray structure, we did not perform any computational analysis.

In closing this section, we mention a final intriguing problem about the reported method of preparation of the diphosphine P\(_2\)I\(_4\) upon the disproportionation of PI\(_3\).\(^{12,53}\) Without deepening any mechanistic aspect of this process, a reductive elimination of I\(_2\) seems unlikely for the same reasons illustrated for the reverse 2+2 direct addition implied by Eq. 3. Alternatively, the reverse process of Fig. 12a (from right to left) cannot be excluded \textit{a priori} in spite of the +15 kcal mol\(^{-1}\) barrier to be passed. On the other hand, such an event would not correspond to the actual PI\(_3\) disproportionation but its reaction with a I\(_2\) co-reactant, which is excluded from the environment if not specifically added. Perhaps, other factors may become important as for instance the role played by some specific solvent,\(^{53}\) which we have not explored at this time.

**Conclusions and Extensions**

The computational analysis of the P\(_4\) activation by I\(_2\) to generate the phosphine PI\(_3\) confirms the value of the \textit{in silico} approach in identifying unclear mechanisms with otherwise unknown intermediates. The overall process, which is exergonic by \(\sim -76\) kcal mol\(^{-1}\), occurs through a sequence of energetically favourable steps, except for an initial barrier of about +15 kcal mol\(^{-1}\). The latter seems due to the still low donor power of the unperturbed white phosphorus, which hardly transfers electron density from its compact and strained structure. After the barrier, a multi-step process is triggered
with a repeating concerted action, given the occurrence of 3+3 bond breakings/makings in each case.

The common feature is a dynamic electron transfer throughout six atoms, cyclically arranged. The process starts with a delocalization of some P electron density through the first formed P-I-I linear unit and continues at the subsequent tri-iodide XB adduct involving a second diatomic. Some electron density ends up into a P-P σ* level with cleavage of one of the original P₄ sides. The mechanism is evidently ter-molecular at any step with the peculiar reformation of a new di-iodine molecule.

Fig.1 has already been a useful reference throughout the paper, but provides no energy indication also relatively to the occurrence of alternative steps. For this, we present the conclusive Fig.13, outlining the most probable cascade of steps, with the significant barrier, (1-2)ₜₕ, appearing only at the very beginning.

![Diagram](image)

**Fig. 13** Favoured cascade of events in the P₄ demolition by I₂, except for the unique initial barrier (1-2)ₜₕ. Half amount of the PI₃ product forms in the earlier stages rather than at the very end.

The analysis indicates a fundamental role played in the attack to I₂ by the P atom donor power. The latter must not be large to trigger a concerted electron transfer without altering the oxidation states of the involved atoms. In fact, an excessive donor power, as in the case of organo-substituted P atoms, determines a major electron transfer and charge separation (ion pair formation), which does not allow concertedness. The point clearly emerged by comparing the P₂I₄ diphosphine with an organo-
substituted analogue of the type $P_2R_4$, which was reported by Cummins and co-workers as unable to induce P-P cleavage.\textsuperscript{18}

The present elucidation of the basic intermediates in the $P_4 + I_2$ process may be relevant for the widely investigated chemistry of phosphorus-based molecules. Moreover, it seems to have a direct impact on our ongoing studies on the functionalization of phosphorene 2D material.\textsuperscript{6} As in $P_4$, any P atom is pyramidal and directly linked to three equal ones, hence its coordination to an acidic metal center seems plausible, as found for some known $P_4$ complexes.\textsuperscript{2} As a matter of fact, we have gained some computational evidence, by using the solid state package CRYSTAL,\textsuperscript{54} that the P donor power is rather similar in the two cases, hence a number of metal fragments suitable for phosphorenes’s coordination in the $\eta^1$, $\eta^2$ and $\eta^3$ modes have been already individuated.\textsuperscript{55} By the same token, the reactivity of phosphorene toward di-iodine molecules could also follow a \textit{concerted} mechanism in place of a prompt charge separation. On the other hand, a number of disfavouring factors have emerged from our preliminary analyses, such as the reduced freedom of the initial P-I-I and I-I-I pendants of the XB-type to span over the 2D surface and attack a specific $\sigma^*$ level of a P-P to be broken. Possibly, some well tailored modelling is necessary on which we are working on.

**Conflict of interest**

There are no conflicts of interest to declare.

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Atomic Level Mechanism of the White Phosphorous Demolition by Di-iodine

The study describes the $\text{I}_2$-induced white phosphorus demolition into discrete $\text{PI}_3$ molecules. Dynamic halogen bonding supports reactivity based on a concerted mechanism. Each step involves $\text{P}_4$ or its derivatives and two I-I* diatomics, which overall undergo 3+3 bond breakings/makings, namely one P-P and two I-I cleavages plus two P-I and one I*-I* (in-situ) couplings, respectively. Organo in place of iodine substituents inhibit concertedness of the process but favor the formation of an unreactive ion pair.

**emblematic final step:**

$$
\text{P}_2\text{I}_4+2\text{I}^*-2\text{PI}_3 + \text{I}^*\text{-I}^*
$$

![Diagram of the atomic level mechanism of white phosphorus demolition by di-iodine](image)