

# Recent Advances in Transition metal-mediated transformations of white phosphorus

proposed initially: Functionalization of White and Red Phosphorus in the Coordination Sphere of Transition Metal Complexes)

*Franco Scalambra,<sup>[a]</sup> Maurizio Peruzzini,<sup>[b]</sup>\* Antonio Romerosa<sup>[a]</sup>\**

<sup>[a]</sup> *Área de Química Inorgánica-CIESOL, University of Almeria, 04120, Almeria, Spain*

<sup>[b]</sup> *Istituto di Chimica dei Composti Organometallici, Consiglio Nazionale delle Ricerche (ICCOM-CNR), Sesto Fiorentino (FI) 50019, Italy*

Corresponding/Contact Author Names : M. Peruzzini, A. Romerosa

Corresponding/Contact Author Phones: +39 3204317179, +34 950015305

Corresponding/Contact Author Email: [maurizio.peruzzini@iccom.cnr.it](mailto:maurizio.peruzzini@iccom.cnr.it), [romerosa@ual.es](mailto:romerosa@ual.es)

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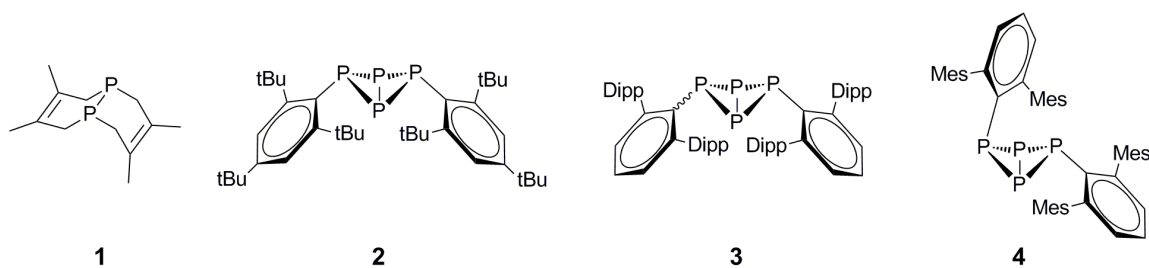
**Abstract:** Despite the large interest by both industrial and academic chemists to develop a safe and environmentally acceptable process to functionalize white phosphorus, only few but significant steps have been developed in the last years. New experimental results and theoretical studies provide indeed obust evidence that different metal complexes are really capable of mediating the formation of P-C bond starting from P<sub>4</sub> and organic reagents and that even catalytic processes accomplishing the direct phosphorylation of alcohols or other organic substrates may be achieved via the intermediacy of a suitable metal complex. Nevertheless and in spite of the relevant findings achieved so far and of the impressive variety of metal complexes containing P atoms and polyphosphorus, P<sub>x</sub>, units which have been synthesized and characterized up to now, the original target of the direct (catalytic) phosphorylation of elemental phosphorus remains still unsolved. In this chapter the more recent results paving the way to the direct functionalization of white phosphorus are presented and discussed.

## 1.1. Introduction

Since its discovery in the middle of the 17<sup>th</sup> century, elemental phosphorus has fascinated first alchemists and then chemists, but has also captivated general people. Among phosphorus allotropes, white phosphorus ( $P_4$ ) is the commercial product easily obtained from the reduction of phosphate minerals.[1] The industrial reduction of phosphate rocks (mostly apatites,  $Ca_{10}(PO_4)_6(X)_2$ ;  $X = OH, F, Cl, \text{ or } Br$ ) to white phosphorus as  $P_4$  still represents the major commercial P-atom source for the production of organophosphorus compounds which, in turn, are the standpoints to sustain the different industrial productions based on this element.[2,3] White phosphorus is indeed largely used as starting material for synthesizing a wide variety of phosphorus-containing inorganic and organic products, such as additives in fertilizers, detergents, food, fire-protection agents, drugs and semiconductors, among other applications. The most popular industrial process involves molecular phosphorus chlorination or oxychlorination to  $PCl_n$  ( $n = 3, 5$ ) and  $POCl_3$  before derivatization. For example, triphenylphosphine, that is largely used in organic and organometallic chemistry, is prepared by the high-temperature reaction of chlorobenzene with phosphorus trichloride in the presence of molten sodium.[4,5] Apart the rich chemistry based on the use of phosphorus chlorides and oxychlorides, there exist several specific methods which avoid the use of toxic and environmentally dangerous phosphorus chlorides to directly achieve the synthesis of specific organophosphorus compounds starting from elemental phosphorus. These methods have been recently reviewed [1] and will not be considered in the present summary. However, alternative strategies that lead to the direct functionalization of  $P_4$  under mild, eco-friendly and atom efficient conditions are still needed and highly desirable from an industrial view-point. For this reason  $P_4$  activation and functionalization have continued to interest chemists over the last 40 years.[6]

The ideal alternative for the actually employed synthesis of phosphorus-containing compounds would be the development of a true metal-mediated catalytic process that directly combines white phosphorus and organic molecules within the coordination sphere of the transition metal catalyst. The catalyst could be a transition metal complex able to bring about all the steps of the functionalization process in an efficient way with high turnovers. The necessary preliminary step for developing any suitable catalytic processes,

*i.e.* the interaction of a preformed transition metal complex with white phosphorus, has been extensively studied and a remarkable number of different activation pathways have been described.[3] To achieve a useful P<sub>4</sub>-functionalization process the metal coordination of the P<sub>4</sub> molecule should be selective and high-yielding, and may either result in P-P bond cleavage while simultaneously forming new P-C or P-X (X = N, O, S) bonds with organic molecules like alcohols, amines or thiols. Only few selective reactions involving the functionalization of P<sub>4</sub> were published.[6] Illustrative examples are collected in Scheme 1 and include the photolysis of P<sub>4</sub> in the presence of 1-3,dienes that leads to **1**.[7] Most reactions produce complex mixtures of organophosphorus species[2,6,8] or cause the fragmentation of the P<sub>4</sub> molecule with further possible reaggregation steps.[9–11] The cleavage of one P-P bond can give rise to the butterfly-like tetraphosphabicyclo[1.1.0]butane unit, which was observed as the first step of P<sub>4</sub> functionalization by metal complexes such as (TiAr<sup>Dipp</sup>)<sub>2</sub> (Ar<sup>Dipp</sup> = C<sub>6</sub>H<sub>3</sub>-2,6-(C<sub>6</sub>H<sub>2</sub>-2,6-iPr<sub>2</sub>)<sub>2</sub>) some time in very low yield.[12–14] Phosphines **2** and **3** were proposed to be assembled by a nucleophilic attack of RX (X = Cl, Br, I; R = 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>; 2,6-Dipp<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) to P<sub>4</sub> mediated by Ti(N[tBu]Ar)<sub>3</sub> (Ar = 3,5-C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>), while the synthesis of **4** was accomplished by the reaction with 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>X (X = Cl, Br, I) and was suggested to proceed by a radical reaction.[15] All these reactions involve sp<sup>2</sup>-hybridized carbon atoms as the reactive sites while no examples with sp<sup>3</sup>-hybridized carbon atoms have been reported so far.



**Scheme 1.** Examples of organophosphorus compounds obtained through different derivatization of P<sub>4</sub>.

Several excellent reviews have been already devoted to describe both the functionalization chemistry of white phosphorus by metal complexes and the properties and the reactivity of the intriguing compounds obtained by these reactions. This review, along with collecting and expanding the large amount of data reported so far on the coordination chemistry of elemental phosphorus, highlights the fact that this area represents nowadays a mature discipline.

In 2010, when the most recent reviews in this area appeared in the literature,[2,3,16] there were still few processes to directly convert  $P_4$  into organophosphorus molecules without using phosphorus chlorides as a necessary reagent as no catalytic method for the functionalization of  $P_4$  was documented and even today, and in spite of the huge amount of experimental information collected on the coordination and functionalization chemistry of white phosphorus, the entire research line is only in its preliminary stages of development and several experimental and theoretical efforts are still necessary. In particular, the mechanistic work to support the great body of synthetic information available is still rather modest although it would greatly enhance our ability to predict the outcomes and design of new metal-mediated transformations of  $P_4$  as many of the known reactions are mechanistically puzzling and the final products are often unpredictable. Moreover, a significant problem arises for the activation of the  $P_4$  molecule by transition metals because the formation of simple, stable coordination compounds may compete with the desired bond cleavage. Only with a highly nucleophilic reagent it is possible to overcome this problem.

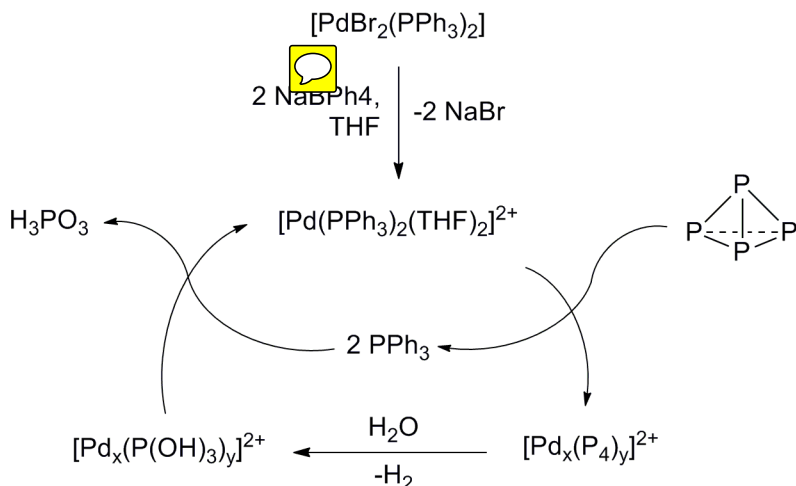
As great advances in the area of  $P_4$  activation and functionalization mediated by transition-metal complexes have been achieved in recent years, it seems timely to update in this review the comprehensive reviews already appeared in the literature and to highlight the wide array of contributions reported in the field of  $P_4$  activation and transformation since 2010. Although several new and sometime unexpected metal-promoted stoichiometric transformations of  $P_4$  have been described, only a few catalytic processes have been reported. Remarkably, although the latter are still far from reaching a reasonable efficiency, these results demonstrate that the possibility to carry out a genuine metal-mediated catalytic process for the phosphorylation of an organic substrate is a real opportunity well worth to attract further research efforts.

## 1.1 Functionalization of P<sub>4</sub> producing metal free new derivatives

### 1.1.1 Catalytic functionalization of P<sub>4</sub>

Two catalytic processes were described after 2010. The first one was published by the Russian team of D. G. Yakhvarov,[17] which reported on the catalytic synthesis of H<sub>3</sub>PO<sub>3</sub> from P<sub>4</sub> mediated by the palladium complex [Pd(PPh<sub>3</sub>)<sub>2</sub>Br<sub>2</sub>] (Scheme 2) in THF/water. Cationic palladium complexes were generated by a stoichiometric amount of NaBPh<sub>4</sub>, which favors the removal of the bromide ions from the coordination sphere of the palladium. The main product initially formed was phosphorous acid (<sup>31</sup>P NMR, 2.70 ppm, d, <sup>1</sup>J<sub>P,H</sub> = 667 Hz), being the minor products H<sub>3</sub>PO<sub>4</sub> (s, 0.00 ppm) and H<sub>4</sub>P<sub>2</sub>O<sub>7</sub> (s, 4.46 ppm). All the products were completely transformed into H<sub>3</sub>PO<sub>4</sub> upon addition of a small amount of 2 N aqueous HCl to the reaction mixture. The authors proposed that the formation of H<sub>3</sub>PO<sub>3</sub> results from hydrolysis of the coordinated white phosphorus molecule in the coordination sphere of palladium.

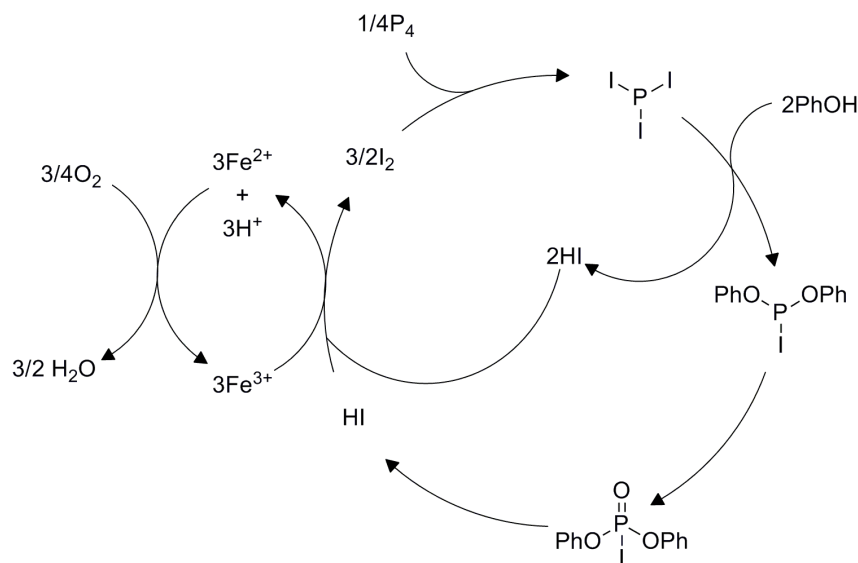
The mechanism of the reaction was proposed from a combination of NMR and MALDI-MAS spectrometries that support the presence of [Pd(PPh<sub>3</sub>)<sub>3</sub>]<sup>2+</sup> ions and [Pd<sup>0</sup>(PPh<sub>3</sub>)<sub>2</sub>]. Therefore, it was proposed that the reaction of the generated cationic palladium(II) starting complex with white phosphorus is followed by hydrolysis to phosphorous acid as the major product.



**Scheme 2.** Proposed mechanism of a Pd(II) catalysed hydrolysis of P<sub>4</sub>.

Although the reaction pathway has not been studied in detail, the proposed mechanism is supported by the assumption that the oxidation of white phosphorus to phosphorous acid is accompanied by the partial reduction Pd(II) → Pd(0), which is newly coordinated by the free PPh<sub>3</sub> in the reaction. For this reason the authors proposed that the formation of H<sub>3</sub>PO<sub>3</sub> from white phosphorus mediated by cationic palladium complexes is activated by PPh<sub>3</sub> molecules released from cationic complex [Pd(PPh<sub>3</sub>)<sub>2</sub>(THF)<sub>2</sub>]<sup>2+</sup> when coordinated to white phosphorus.

The second process was described by Armstrong and Kilian[18] who carried out the catalytic synthesis of triarylphosphates from white phosphorus and different phenols under aerobic conditions and in the presence of different Fe(III) catalysts and iodine, and without producing acid waste. The formation of PI<sub>3</sub> in the reaction mixture has been considered of pivotal importance for the sustainment of the catalytic reaction, being the vector for the synthesis of O=PI(OPh)<sub>2</sub> that gives rise finally the phosphate. The kinetic study of the reaction showed that reaction of phenol with O=PI(OPh)<sub>2</sub> to produce O=P(OPh)<sub>3</sub> is the rate-limiting step (Scheme 3). The water produced in the process that could hydrolyse the intermediate was found to be not a problem when a sufficient amount of catalyst was introduced in the reaction. Despite this reaction is not possible to be transferred into industrial production, it shows that it is possible to synthesize phosphates stoichiometrically from P<sub>4</sub> in a direct manner without implicate PCl<sub>3</sub> as intermediate.



Scheme 3. Proposed succession of steps involved in the reaction of  $P_4$  with phenol.

### 1.1.2 Stoichiometric functionalization of $P_4$

A very interesting finding was published in 2013: the reaction of  $P_4$  with  $[\{U(Ts^{Tol})\}_2(\mu-\eta^6:\eta^6-C_6H_5CH_3)]$  [19] (**5**,  $Ts^{Tol} = HC(SiMe_2NAr)_3$ ;  $Ar = 4-MeC_6H_4$ ) affords  $[\{U(Ts^{Tol})\}_3(\mu^3-\eta^2:\eta^2:\eta^2-P_7)]$  (**6**), the first example of an actinide- $P_7$  Zintl complex and the first example of fragmentation and catenation of  $P_4$  promoted by uranium.[20] This complex was showed to be the precursor of a range of derivatives that represent general methods for the preparation of hydrocarbon-, aromatic-, and silyl-functionalized  $P_7$  derivatives via Li-P, P-C ( $sp^2$ - and  $sp^3$ -hybridized carbon groups), and P-Si bond formation reactions. Additionally, it was showed that the developed synthetic method leads to the closure of synthetic cycles for the activation and functionalization of  $P_4$  under mild

conditions, which finally demonstrates the capacity of triamido uranium complexes to activate and liberate functionalized small molecules obtained from direct reaction with  $P_4$ . [21–23]

The reactivity of  $P_4$  with 5f metals could be considered as exceptionally rare: there is one report on thorium-mediated activation of  $P_4$  at elevated temperature or with co-reagents, [24] and two examples of uranium-mediated activation of  $P_4$ . [25] Significantly neither of both studies involving uranium complexes showed fragmentation or catenation of  $P_4$  providing access only to the cleavage of two P-P bonds in  $P_4$  to give  $(P_4)^{2-}$  rings. Remarkably, the conversion of  $P_4$  to  $(P_7)^{3-}$  mediated by early transition metal complexes has few precedents. [16,26,27]

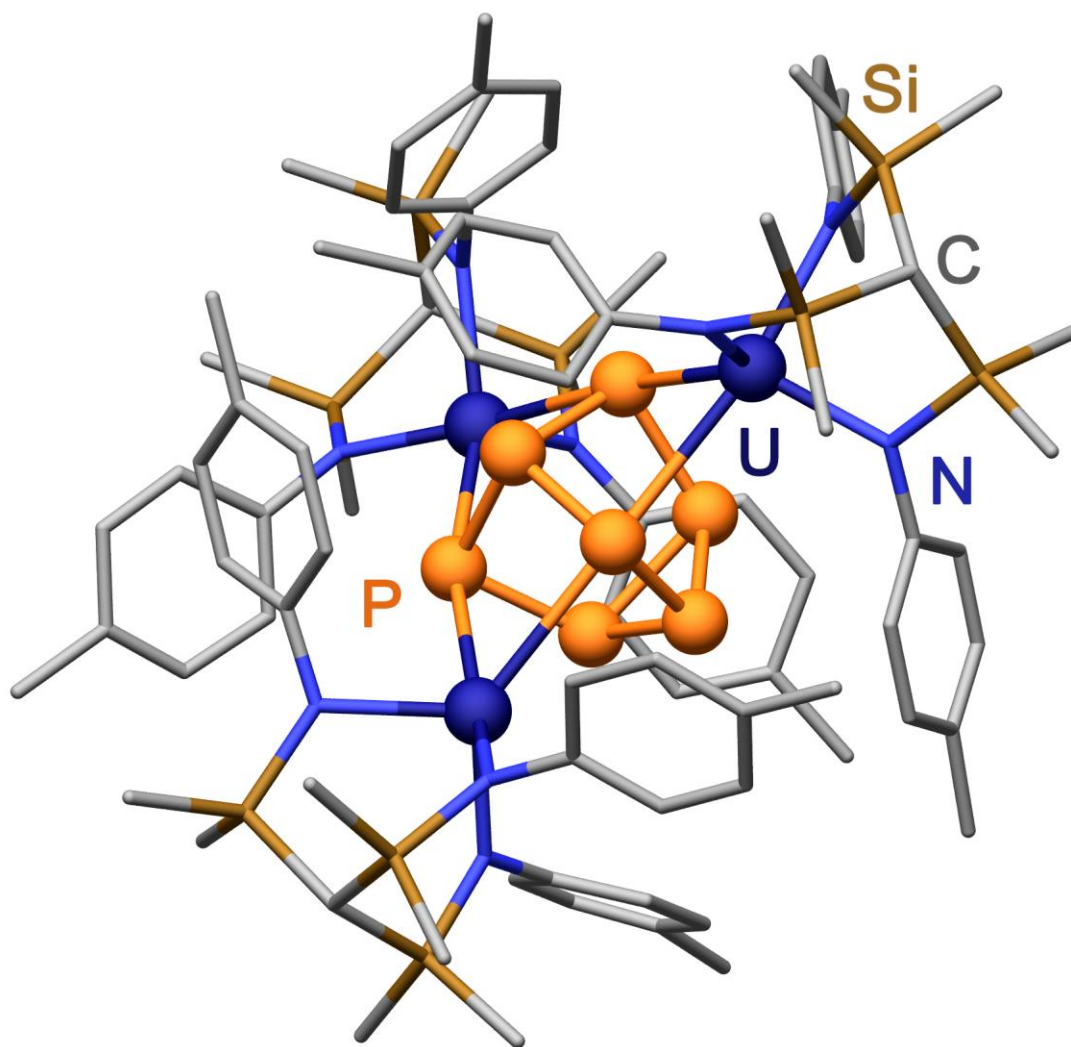
The reaction of **5** with  $P_4$  (1:1.1 of **5**: $P_4$ ) affords, after work-up and isolation, brown crystals of the Zintl complex  $[\{U(Ts^{Tol})\}_3(\mu^3-\eta^2:\eta^2:\eta^2-P_7)]$  (**6**) in 12% yield of crystalline product (Figure 1). NMR spectroscopy showed that the yield of **6** in the crude reaction mixture is 65% suggesting that the low yield obtained in solid state should reflect the surprisingly high solubility of **6**.

The  $(P_7)^{3-}$  trianion is well-known to undergo facile and very complicated Cope-type rearrangements in solution that are similar to what happens to bulvalene, [28] which was used by authors to justify the broad NMR resonances of the complex. Additionally, the magnetic moment of pure **6** in solution was found to be 4.67 mB at 298 K while, in reasonable agreement, the magnetic moment of the powdered complex was 4.20 mB at 298 K, which decreased slowly on cooling down to ca. 80 K before falling more drastically at lower temperatures, reaching 1.25 mB at 1.8 K and still decreasing. All these results along with electronic absorption spectrum of **6** supports the presence of uranium(IV) in this compound.

The structure of **6** was determined by single crystal X-ray diffraction (Figure 1). The most interesting feature of **6** is the  $(P_7)^{3-}$  trianion core of the complex, which bridges three  $[U(Ts^{Tol})]^+$  fragments. Each uranium center coordinates to two phosphorus centers on the upper rim of the  $(P_7)^{3-}$  trianion. The U-P bond lengths span within the range 2.9486(17)–3.0308(17) Å, which is comparable with the sum of the covalent radii of 2.81 Å for uranium and phosphorus, [29] and most likely reflects the sterically demanding nature of the  $\{U(Ts^{Tol})\}^+$  fragments and the bridging coordination mode. The most used parameter



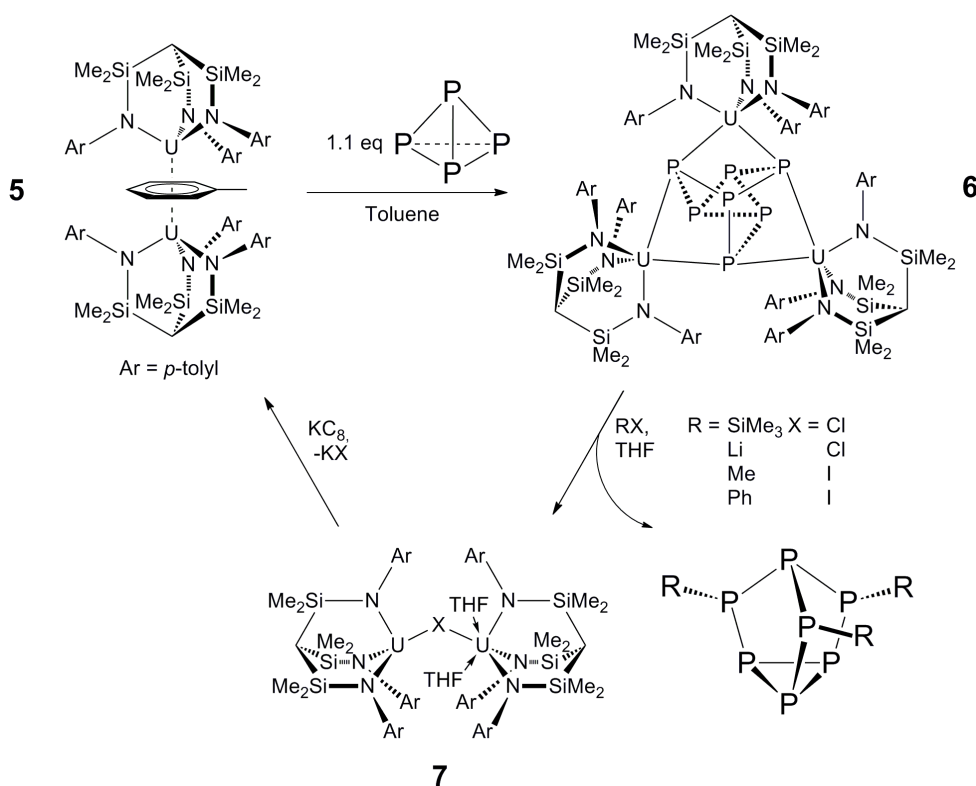
to assess the ionic character in  $(P_7)^{3-}$  trianions is the Q value,[30–32] ( $Q = h/a$ ;  $h$  = distance from the apical P-center to the center-point of the lower rim of three P centers;  $a$  = average P-P distance in the lower rim). The Q value for **6** is 1.39, which suggests that the U-P bonding is predominantly electrostatic, considering that the Q value is typically 1.3–1.4 for ionic systems. A preliminary single-point energy calculation on **6** revealed that the U-P interactions were in agreement with this finding as they were calculated to be essentially ionic and therefore in agreement with the structural and NMR spectroscopic data.



**Figure 1.** Ball and stick representation of the crystal structure of **6**. Hydrogen atoms omitted for clarity. Adapted from [20].

Under ambient conditions (Scheme 4) complex **6** reacts with three equivalents of  $\text{Me}_3\text{SiCl}$  to quantitatively afford  $\text{P}_7(\text{SiMe}_3)_3$  [33] and  $[(\text{Ts}^{\text{Tol}})\text{U}(\text{Cl})(\mu\text{-Cl})\text{U}(\text{THF})_2(\text{Ts}^{\text{Tol}})]$  [34] (**7**, after the addition of THF). Lithium chloride reacts quantitatively with **6** to afford **7** (after the addition of THF and tmeda) and  $\text{P}_7[\text{Li}(\text{tmeda})]_3$  [35] which is a very important alkali-metal derivative of  $(\text{P}_7)^{3-}$ , very difficult to prepare by conventional procedures.

When **6** was reacted with an excess of methyl iodide or phenyl iodide a clean and fast reaction takes place, which quantitatively affords  $\text{P}_7(\text{Me})_3$  [28] or  $\text{P}_7(\text{Ph})_3$  [36] respectively, with concomitant formation of **7** (after addition of THF). These phosphanotricyclanes were not previously straightforwardly prepared. These compounds obtained by these reactions show how both  $\text{sp}^3$  and  $\text{sp}^2$  (aromatic) carbon-based electrophiles can be substituted onto the  $\{\text{P}_7\}^{3-}$  framework via P-C bond forming reactions from **6**. Therefore, this uranium polyphosphido complex provides a reactive platform for subsequent functionalization of  $\text{P}_4$  and derivatization chemistry. As **7** is the direct precursor to **5**, the derivatization chemistry described herein presents the closure of synthetic cycles for the activation and functionalization of white phosphorus (Scheme 4).



**Scheme 4.** Synthetic cycle for the preparation of  $P_7(R)_3$  starting from **5**.

The performed reaction showed that only two turnovers could be achieved before the mixture of products rendered subsequent reactions unfeasible. From the first turnover the polyphosphide derivatives were generally obtained quantitatively. Unfortunately in the reaction conditions the yields dropped to ca. 40% in the second turnover. The reduction of the efficiency of the second run in comparison with the first one is due to the buildup of inorganic salts in the reaction. However, the diverse and straightforward nature of these reactions suggests that **6** is amenable to reactions with a wide range of functional electrophiles. Therefore, despite the developed synthetic processes are not catalytic, they are significantly important: the ability of **6** to mediate a large variety of possible reactions with different of nucleophiles provides a possible large number of compounds, most of them impossible to obtain by known procedures.

It is important to point out that the electronic absorption spectrum of **6** is constituted by charge-transfer bands from 25000 to 12000  $\text{cm}^{-1}$  along with a number of more than normal intense bands ( $\epsilon = 120\text{--}250 \text{ Lmol}^{-1}\text{cm}^{-1}$ ) from 12000 to 5000  $\text{cm}^{-1}$ , which are due

to f-f transitions and support the oxidation state of the uranium as IV. The  $^1\text{H}$  NMR spectrum of crystalline **6** is broad and the  $^{31}\text{P}$  NMR spectrum silent in the range from -1000 to 1000 ppm. This last fact was justified as the consequence of the reduction of the intensities of resonances produced by the extensive  $^nJ_{\text{PP}}$  couplings ( $n=1, 2, 3$ )[37–40] and line broadening, which is due to dynamic processes and fast relaxation produced by the uranium centers. Probably for this reasons, variable temperature NMR could not freeze out any dynamic processes or induce coalescence to one time-averaged species. As usually observed for U(IV) the observed moment for **2** that corresponds to  $2.42 \mu_{\text{B}}$  per uranium(IV) ion at room temperature is significantly lower than the value calculated for a free  $^3\text{H}_4$  term ( $3.58 \mu_{\text{B}}$ ).[41] The decreasing magnetic moment of **2** with decreasing temperature is commonly observed for uranium(IV) but in this case the decrease is lower than that expected, but not exceptional.[42]

New and selective one-step synthesis that allow the fast and clean synthesis of a large variety of new carbon substituted-phosphorus butterfly compounds in good yields were obtained by activation of white phosphorus by organic radicals generated in presence of metal complexes. The reactions of  $\text{NaCp}^{\text{R}}$  with  $\text{P}_4$  in the presence of  $\text{CuBr}$  or  $\text{FeBr}_3$  leads to the clean formation of organic substituted  $\text{P}_4$  butterfly compounds  $\text{Cp}^{\text{R}}_2\text{P}_4$  ( $\text{Cp}^{\text{R}}$ :  $\text{Cp}^{\text{BIG}} = \text{C}_5(4\text{-nBuC}_6\text{H}_4)_5$  (**8**),  $\text{Cp}^{\text{'''}}$  =  $\text{C}_5\text{H}_2\text{tBu}_3$  (**9**),  $\text{Cp}^*$  =  $\text{C}_5\text{Me}_5$  (**10**) and  $\text{Cp}^{4\text{iPr}} = \text{C}_5\text{HiPr}_4$  (**11**)).[43] Stable  $\{\text{Cp}^{\text{BIG}}\}$  radicals are suitable to selectively activate one P-P bond of the  $\text{P}_4$  tetrahedron to form the bicyclic butterfly compound **8**. Further attempts to transfer the procedure to other  $\text{Cp}^{\text{R}}$  derivatives, such as  $\text{Cp}^{\text{'''}}$ ,  $\text{Cp}^*$  or  $\text{Cp}^{4\text{iPr}}$ , failed. The generation of  $\{\text{Cp}^{\text{R}}\}$ ·radicals in the coordination sphere of Fe(III) complexes allows the transfer of carbon-centered radicals to the  $\text{P}_4$  tetrahedron, leading to a simple and selective synthesis of novel  $\text{Cp}^{\text{R}}_2\text{P}_4$  compounds (**8-11**) (Figure 2). The synthetic process takes place with a variety of  $\text{Cp}^{\text{R}}$  derivatives, providing a general access to this class of compounds.

Reaction of  $[\text{Cp}_{4\text{iPr}}\text{Cu}(\eta^2\text{-P}_4)]$  [44] with white phosphorus and column chromatographic work-up gives yellow cube-shaped crystals showing that the resulting product was the metal-free compound **8**, which exhibits two newly formed C-P bonds. Nevertheless checking the participation of  $[\text{Cp}^{\text{BIG}}\text{Cu}(\text{CO})]$  as potential intermediate, the reaction was repeated without the CO discharge step, again leading to **8** as the only product. Based on the EPR measurements, a radical mechanism including the formation of  $\{\text{Cp}^{\text{BIG}}\}$ ·

radicals together with elemental copper can be suggested. These radicals react with P<sub>4</sub> to afford the butterfly compound **8** in moderate isolated yields (Figure 2).

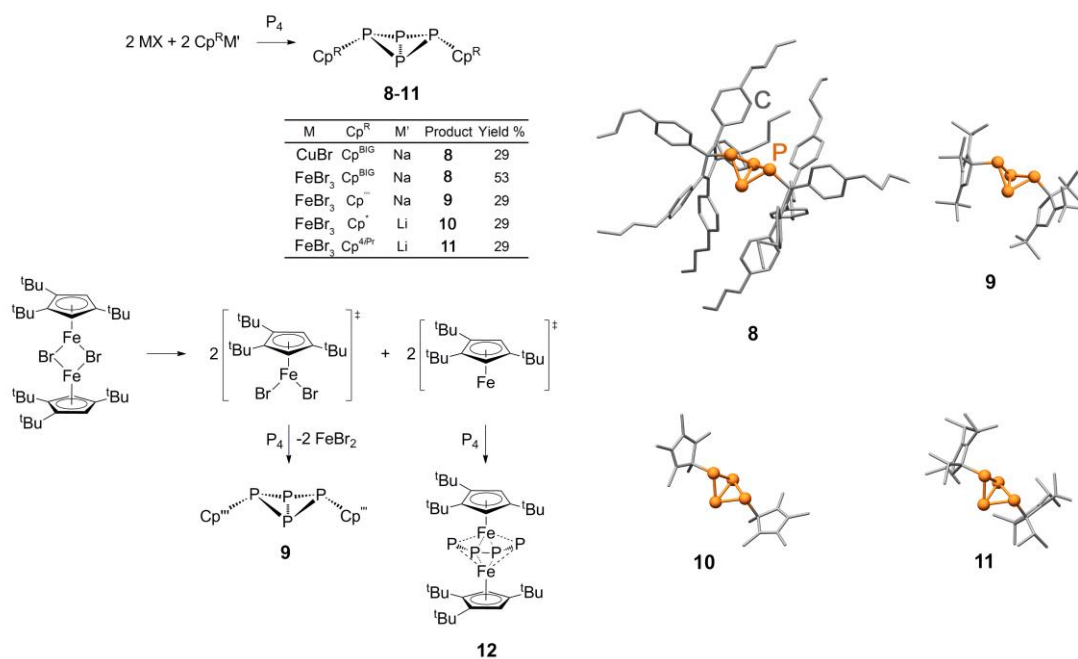
The X-ray molecular structure of **8** (Figure 2) shows how the organic substituents are in an exo-exo-configuration in the solid state. The P-P (2.1814(8)–2.2279(8) Å) and P-C (1.935(2)–1.954(2) Å) distances are in the range of similar P<sub>4</sub> butterfly compounds.[14,45,46]

Reaction in presence of Cu-halogen salts of P<sub>4</sub> with NaCp<sup>R</sup> such as NaCp, NaCp\*, NaCp''' and NaCp<sup>4iPr</sup> did not provide the expected CpR<sub>2</sub>P<sub>4</sub> products. This fact could be the result of the lower stability of {Cp<sup>R</sup>} radical compared to the aryl-substituted {Cp<sup>BIG</sup>}·radical. The aryl-radical combines a high steric demand and a possible mesomeric stabilization that produce less-reactive radical species and a hindered radical coupling, allowing the reaction with the P<sub>4</sub> molecule. The smaller and more reactive {Cp<sup>R</sup>}· derivatives lead to the radical decomposition, for example to Cp<sup>R</sup>H compounds, which could be faster than the reaction with white phosphorus, avoiding the formation of the P<sub>4</sub> butterfly molecules.

Nevertheless, using a more flexible redox system with a broader variety of oxidation states as Fe(II)/Fe(III) for the synthesis of a {Cp<sup>5iPr</sup>}C radical (Cp<sup>5iPr</sup> = C<sub>5</sub>iPr<sub>5</sub>) by the reaction with the corresponding sodium salt and FeCl<sub>2</sub>, the desired products were obtained, which was described by Sitzmann et al. [47] The reaction of [{Cp'''Fe(μ-Br)}<sub>2</sub>] with one equivalent of P<sub>4</sub> in toluene at room temperature leads to the formation of [{Cp'''Fe}<sub>2</sub>(μ,η<sup>4:4</sup>-P<sub>4</sub>)] [48] (**12**) (100 % row solution, 14 % after chromatography) as well as the carbon-substituted butterfly compound **9** (Figure 2) together with a brownish precipitate of FeBr<sub>2</sub>.

The proposed mechanism for this reaction involves radicals, as the formation of C-P bonds to secondary carbon atoms, which should be observed to a certain extent, was not detected. The resulting 1:1 ratio in the reaction crude for the two products **9** and **12** along with the formation of a brownish precipitate of FeBr<sub>2</sub> provides additional information to support the proposed reaction pathway (Figure 2). In solution, a disproportionation of [{Cp'''Fe(μ-Br)}<sub>2</sub>] into the two complex fragments {Cp'''Fe<sup>I</sup>} and {Cp'''Fe<sup>III</sup>Br<sub>2</sub>} is most probable. Two molecules of {Cp'''Fe<sup>I</sup>} react with one molecule of P<sub>4</sub> to form compound **12** that is constituted by a cisoid P<sub>4</sub><sup>2-</sup> ligand combed by the extreme phosphorus atoms to

$\text{Cp}^{\text{R}}$  groups. The remaining two  $\{\text{Cp}^{\text{'''}}\text{Fe}^{\text{III}}\text{Br}_2\}$  complex fragments are also able to interact with white phosphorus. The coordination of a  $\text{P}_4$  molecule to one iron atom enables the transfer of a radical  $\{\text{Cp}^{\text{'''}}\} \cdot$  onto the  $\text{P}_4$  tetrahedron to give **9** and the precipitation of the brownish  $\text{FeBr}_2$ . The presence of the  $[\text{Cp}^{\text{'''}}\text{FeBr}_2]$  in the reaction was checked by reaction of this complex, which was generated in situ from  $\text{Cp}^{\text{'''}}\text{Na}$  and  $\text{FeBr}_3$ , with white phosphorus (Figure 2). In fact, the  $\text{Cp}^{\text{'''}}$ -substituted compound **9** is obtained with an identical isomer distribution than that obtained by the reaction in presence of  $\text{FeBr}_2$ . An additional positive consequence of this reaction was that the intrinsic loss of 50% of the material due to the formation of **12** was also avoided and therefore workup by column chromatography is not necessary for purification, leading to significantly better yields of isolated product.



**Figure 2.** Top left: synthesis of **8-11**; bottom left: detail of the synthesis of **9**. Right: ball and stick representation of the crystal structure of **8-11**; hydrogen atoms removed for clarity. Structures adapted from [43].

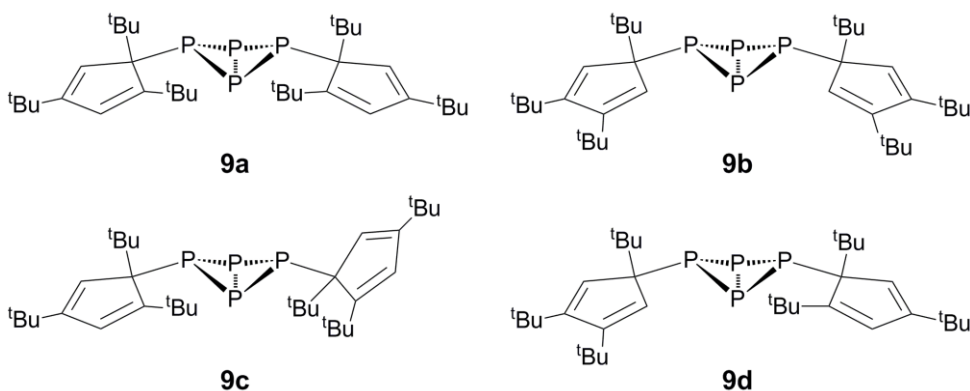
The P<sub>4</sub>-functionalization procedure was found to be general as compounds Cp<sup>BIG</sup><sub>2</sub>P<sub>4</sub> (**8**), Cp\*<sub>2</sub>P<sub>4</sub> (**10**), and Cp<sup>4iPr</sup><sub>2</sub>P<sub>4</sub> (**11**) were synthesized in good yields by using in the reaction Cp<sup>R</sup> ligands (Figure 2; Cp<sup>R</sup> = Cp, Cp<sup>BIG</sup>, Cp\*, Cp<sup>4iPr</sup>), but the parent compound Cp<sub>2</sub>P<sub>4</sub> was still not accessible. The reason for this might be the minimized stabilizing effects of the small Cp ring for the reaction intermediates as well as for the potential product.

The metal-mediated mechanism for the reaction in presence of FeBr<sub>2</sub> seems to be different to the above-mentioned formation of **8** by the “copper route”. The complex [Cp<sup>R</sup>Fe<sup>III</sup>Br<sub>2</sub>] should provide enough stability to transfer the {Cp<sup>R</sup>} radicals to P<sub>4</sub>, which were detected by EPR spectroscopy. The fact that the “copper route” is only suitable for Cp<sup>BIG</sup> while with iron halides also other Cp<sup>R</sup> moieties can be transferred to P<sub>4</sub> is an indication that in the presence of iron the process probably is metal-mediated. The radical formation proceeds via metal for the “copper route” as well, but the stability of the radical is much higher in the case of Cp<sup>BIG</sup>.

The molecular structures of **8-11** were obtained by single crystal X-ray diffraction structure analysis (Figure 2). For the three molecules a similar butterfly disposition with a exo-exo configuration of the phosphorus atoms were found. The structural parameters agree with those of known R<sub>2</sub>P<sub>4</sub> butterfly compounds.[14,45,46,49–51] The P-P bond lengths vary in the range of 2.178(6) and 2.244(7) Å, and the C-P bond lengths from 1.884(4) to 1.911(8) Å. Interestingly and in contrast to **8**, **9** and **10**, in **11**, the two Cp<sup>R</sup> substituents are pointing upwards probably as a consequence of packing effects.

The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of **8** is characterized by two coupled triplets of an A<sub>2</sub>M<sub>2</sub> spin system (δ = -181.0 ppm, “wing-tip” and δ = -308.2 ppm, bridgehead, <sup>1</sup>J<sub>PP</sub> = 192 Hz), characteristic for a P<sub>4</sub> butterfly structural motif. The nonequivalent 4-*n*BuC<sub>6</sub>H<sub>4</sub> moieties of the Cp<sup>BIG</sup> ligands in **8** leads to <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra showing several superimposed signals. Similarly to **8**, the <sup>31</sup>P{<sup>1</sup>H} NMR spectra of compounds **9-11** show two characteristic groups of signals at δ = -134 – -163 ppm (“wing-tip”) and δ = -307 – -367 ppm (bridgehead). For the pentasubstituted Cp\* moiety and isomers with high molecular symmetry such as **9b** and **9c** (Scheme 5), the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum is characterized by two triplets of an AM<sub>2</sub> spin system with <sup>1</sup>J<sub>PP</sub> coupling constants of 173–193 Hz. However, when Cp<sup>R</sup> = Cp''' and Cp<sup>4iPr</sup>, tri- or tetra-substituted, isomers with low

molecular symmetry are also formed due to non-equivalency of the CpR ligands, leading to more complex  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra, in which there are  $\text{A}_2\text{MN}$  or  $\text{ABMN}$  spin systems with patterns of signals in a 1:1 ratio. The chemical shifts and coupling constants of the two isomers of **11** are nearly identical to those published by Scherer and Akbayeva for the proposed copper complexes  $[\text{Cp}^{4\text{iPr}}\text{Cu}(\eta^2\text{-P}_4)]$  and  $[\{\text{Cp}^{4\text{iPr}}\text{rCu}\}_2(\mu,\eta^{2:1}\text{-P}_4)]$ .<sup>[44]</sup> Nevertheless, in the FD mass spectrum of the crude reaction mixture only the molecular ion peak of **11** (45%) was detected along with some phosphorus-free  $\{\text{Cp}^{4\text{iPr}}\text{Fe}\}$  complex moieties.



**Scheme 5.** Isomers of **9**.

## 1.2. Functionalization of $\text{P}_4$ producing new metal-containing phosphorus derivatives

### 1.2.1 Only Phosphorus derivative containing metal

A very interesting reaction of functionalization of phosphorus from  $\text{P}_4$  was presented by M. A. Ruiz et al. in 2011.<sup>[52]</sup> Starting from the knowledge that some reactions with group 11 metal(I) halides and cations are able to incorporate metal-based electrophiles at the P atoms of the  $\mu\text{-}\kappa^2\text{:}\kappa^2\text{-P}_2$  ligands, they investigate the reactivity of this ligand in a dimeric Mo complex.<sup>[53]</sup> They showed that the anionic complex  $[\text{Mo}_2\text{Cp}_2(\mu\text{-PCy}_2)(\mu\text{-CO})_2]^-$  (**13**;  $\text{Li}^+$  salt,  $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$ ),<sup>[54,55]</sup> reacts with  $\text{P}_4$  under mild conditions, in THF at 290 K, to give the anionic Mo complex  $[\text{Mo}_2\text{Cp}_2(\mu\text{-PCy}_2)(\text{CO})_2(\mu\text{-}\kappa^2\text{:}\kappa^2\text{-P}_2)]^-$  (**14**), which was the

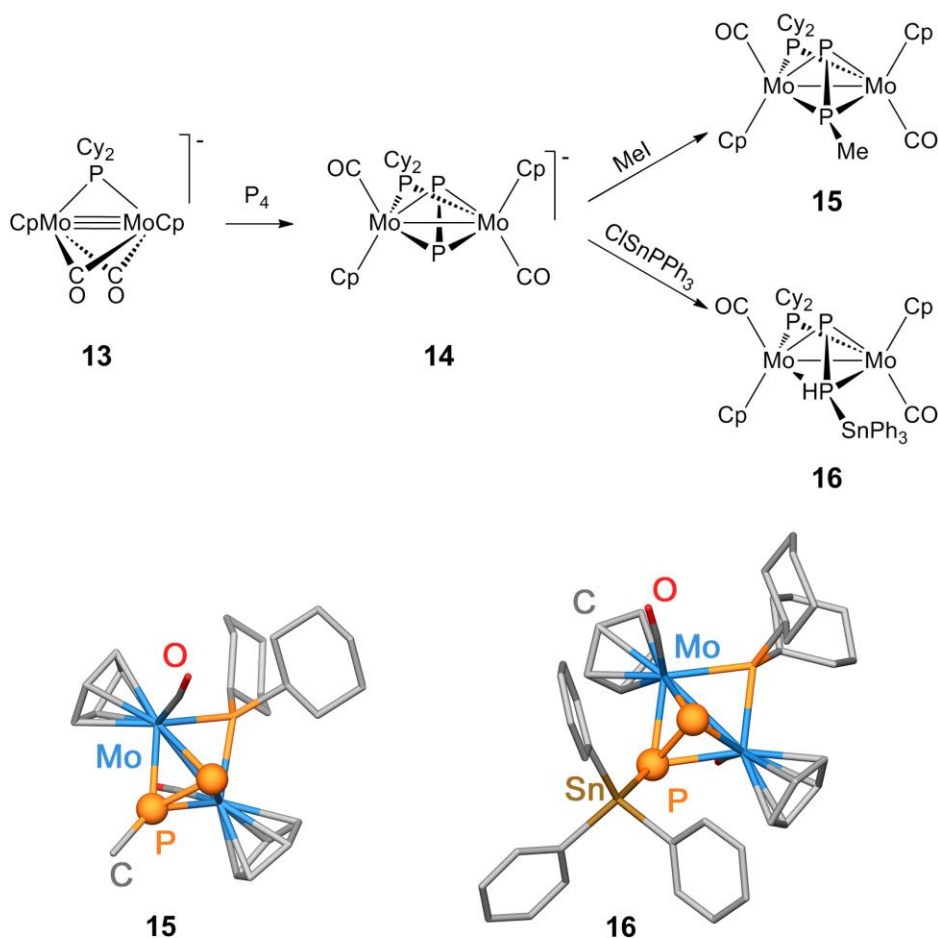


first anionic diphosphorus complex reported.

The complex **14** showed to be active for the functionalization of P atoms by reaction with simple electrophiles such as MeI and ClSnPh<sub>3</sub> (Figure 3). These reactions showed also that the  $\mu\text{-}\kappa^2\text{:}\kappa^2\text{-P}_2$  ligand has a unique donor behavior. The DFT calculations showed that this ligand displays a donor ability due to the presence in the anion of high-energy bonding orbitals with both  $\sigma(\text{Mo-P})$  and  $\pi(\text{P-P})$  character, which is additional to the traditional lone-pair-derived basicity of the P atoms. This particular property of the ligand in this complex produces that the binding of the electrophile also occurs in a terminal position but at nearly 90° angles with respect to the P-P edge, which is also a distinctive property, different to previously described  $\mu\text{-}\kappa^2\text{:}\kappa^2\text{-P}_2$  ligands.

The Li salt of **14** dissolved in tetrahydrofuran was obtained by reaction of **13** with one equivalent of P<sub>4</sub> at 290 K. The possible structure of **14** was calculated by DFT. The obtained results display a complex in which the metal atoms are symmetrically bonded by the P<sub>2</sub> atoms of the Mo<sub>2</sub>P<sub>2</sub> tetrahedral core, being the PCy<sub>2</sub> ligand placed in the plane defined by one of the Mo<sub>2</sub>P triangles. The coordination geometry of the metals are completed by Cp and CO ligands arranged in a slightly distorted transoid arrangement. The calculated P-P bond length was found to be 2.095 Å that is significantly shorter than the experimental value of 2.21 Å for the P<sub>4</sub> molecule, suggesting the presence of some  $\pi$  character in the P-P bond.

Complex **14** reacts rapidly with MeI at 290 K to give the diphosphenyl complex [Mo<sub>2</sub>Cp<sub>2</sub>( $\mu\text{-PCy}_2$ )(CO)<sub>2</sub>( $\mu\text{-}\kappa^2\text{:}\kappa^2\text{-P}_2\text{-Me}$ )] (**15**), which displays a crystal structure (Figure 3) similar to that of **14** but with the addition of a Me<sup>+</sup> group to the lone electron pair of the “basal” P<sub>4</sub> atom. The NMR data suggest that the solid state structure is retained in solution. The <sup>31</sup>P NMR spectrum of P<sub>2</sub>Me ligand displays signals at -84.3 ppm (PMe) and -293.2 ppm (P) ppm with a large mutual coupling of 503 Hz, chemical shifts and coupling constant are very close to those found for either free or  $\kappa^1$ -bound diphosphene complexes.[56] This fact is indicative of the presence of significant  $\pi(\text{P-P})$  bonding character in the P-P bond, similarly to complex **14**.



**Figure 3.** Top: Reactivity of **13** with  $P_4$  to give the diphosphenyl complex **14** and reactions of the latter with MeI and  $ClSnPPh_3$  leading to **15** and **16** respectively. Bottom: ball and stick representation of the crystal structure of **15** and **16**; hydrogen atoms and cocrystallized solvent were omitted for clarity. Structures adapted from [52].

The high activation of the  $\mu-\kappa^2:\kappa^2-P_2$  ligand in **14** was also ratified by reaction with  $ClSnPPh_3$ , which was accomplished rapidly at 290 K giving rise to the stannyl compound  $[Mo_2Cp_2(\mu-PCy_2)(CO)_2\{\mu-\kappa^2:\kappa^2-P_2(SnPh_3)\}]$  (**16**). The solid state structure of this complex is similar to that of **15** (Figure 3) except for the unexpected and unprecedented positioning angle (P-P-Sn:  $80.3(1)^\circ$ ) of the  $SnPh_3$  electrophile and some differences in bond distances.

Optimized geometries for **15** and **16** obtained by DFT calculations were in good agreement with the experimental structures although the P-P-Sn angle were different to the experimental value. When the structure for the SnH<sub>3</sub> analogue of **16** was calculated a shorter P-P-Sn angle was obtained, supporting that the differences observed among calculated and experimental angle values are not due to steric or crystal lattice effects but to distinct electronic interactions taking place between **14** and the respective electrophiles. The formation of **15** was attributed to the interaction of the incoming electrophile with the HOMO-2 orbital in **14** (-1.60 eV), which has little effect on the P-P bonding, in agreement with the structural data. Differently, the formation of **16** is produced through interaction with the HOMO-1 (-1.17 eV) and HOMO-7 (-3.40 eV) orbitals in the anion, these having significant  $\sigma(\text{Mo-P})$  and  $\pi(\text{P-P})$  bonding character. The unusual positioning of the SnPh<sub>3</sub> group in **16** was explained by the substantial increase in the P-P length and the dramatic decrease in the P-P coupling operated at the P<sub>2</sub> ligand. These results show that there is a peculiar  $\pi$ -donor-like ability of the P<sub>2</sub> ligand in complexes with M<sub>2</sub>P<sub>2</sub> cores. For the effectiveness of this interaction some of the frontier orbitals were characterized with a significant  $\pi(\text{P-P})$  bonding character, which for **14** was attributed to its anionic nature. Certainly, a large electron density at the dimetallic center should restrain the electron flow from the P<sub>2</sub> ligand to the dimetallic fragment, thus contributing to the development of a partial multiplicity in the P-P bond. Rather than a lone-electron-pair character the presence of P-P bonding character in the frontier orbitals is normal: the HOMO in P<sub>4</sub> is a  $\sigma(\text{P-P})$  bonding orbital,[57,58] and the HOMO in the diphosphene complex [AuCl( $\kappa^1$ -P<sub>2</sub>Me<sub>2</sub>)] is the  $\pi(\text{P-P})$  bonding orbital.[59]

The <sup>31</sup>P{<sup>1</sup>H}NMR spectrum of **14** at 298 K displays only a very broad resonance at -166.4 ppm for the P<sub>2</sub> ligand, which splits into two broad resonances at -80.0 and -273.0 ppm at 163 K, showing the chemical inequivalence of the P atoms. This fact also support the involvement of **14** in a fluxional process in solution that involves the movement of the P<sub>2</sub> unit around the Mo-Mo axis. Nevertheless, the IR spectrum showed that **14** in solution four C-O stretching bands, a consequence of more than one single species in solution rapidly exchanging in the NMR timescale. This is likely due to the presence of strong ion pairs in fast equilibrium with the solvent-separated ions.[54] In contrast, the spectroscopic data in solution for **15** suggest the retention of the structure found in the solid state, showing

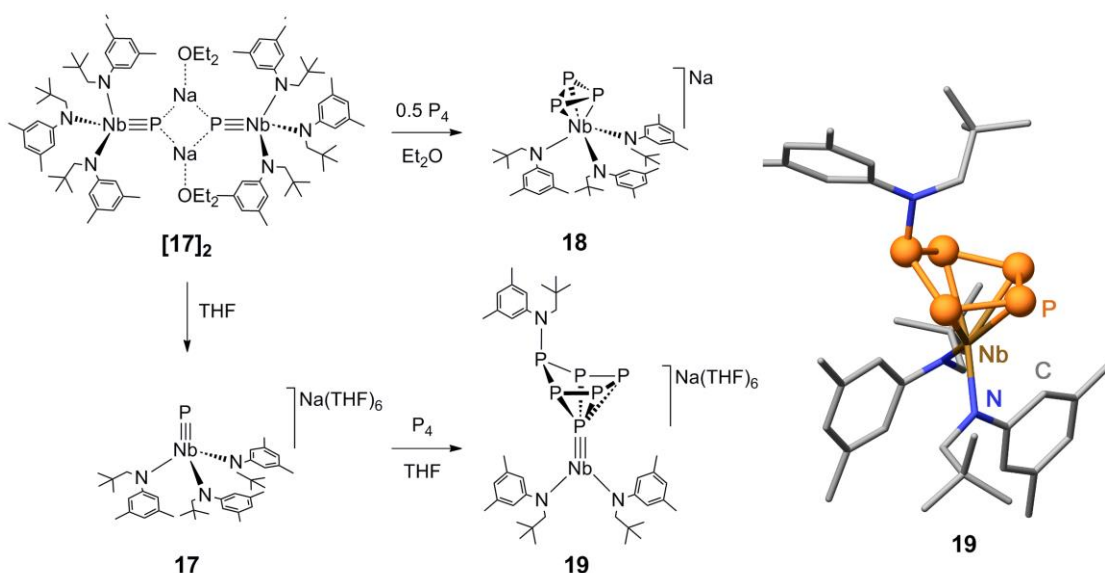
in its  $^{31}\text{P}$  NMR spectrum resonances at -84.3 (PMe) and -293.2 (P) ppm with a large mutual coupling of 503 Hz as expected for either free or  $\kappa^1$ -bound diphosphene complexes.[56] This large mutual coupling indicates the large  $\pi$  character of the P-P bonding as was also suggested for **14**. It is important to stress that complex **10** was the first example of a  $\mu$ - $\kappa^2$ : $\kappa^2$ -diphosphenyl complex in contrast with the known coordination modes of diphosphenyl ligands that involve terminal coordination of phosphorus ( $\kappa^1$  or  $\mu$ - $\kappa^1$ : $\kappa^1$  modes). The NMR spectra of **16**, however, reveal the presence of two isomers and dynamic effects in solution. The  $^{31}\text{P}$  NMR spectrum at 293 K shows a broad resonance at -148.0 ppm for the  $\text{P}_2$  group, which splits into two broad doublets at 38.8 ppm and -341.4 ppm with a  $^1J_{\text{PP}}$  of 185 Hz at 178 K. These signals were assigned to the isomer found in the crystal. A minor isomer (ca. 10% abundance) was also detected with  $\text{P}_2$  resonances at -92.5 ppm and -239.6 ppm, now with a  $^1J_{\text{PP}}$  of 475 Hz, comparable to that observed for **15**, which support that this isomer should be structurally similar to **15**.

Also in 2011 Cummins et al. showed for the first time how a metal-ligand multiple bond can be employed to activate  $\text{P}_4$  molecules and how the activation mechanism is dependent upon the solvent choice.[60] Reaction of phosphide  $[\text{Na}(\text{OEt}_2)_2[\text{P}\equiv\text{Nb}(\text{N}[\text{Np}]\text{Ar})_3]_2$  (**[17]2**) ( $\text{Ar}[\text{Np}]\text{N} = (\text{Np} = \text{CH}_2^t\text{Bu}$ ;  $\text{Ar} = 3,5\text{-Me}_2\text{C}_6\text{H}_3$ ) with  $\text{P}_4$  in benzene, toluene, diethyl ether, dimethoxyethane, fluorobenzene, benzonitrile, and pyridine at room temperature leads to a rapid color change from dark yellow to orange (Figure 4). The product can be isolated in 83% as an orange powder of  $[\text{Na}(12\text{-crown-4})_2][(\text{P}_3)\text{Nb}(\text{N}[\text{Np}]\text{Ar})_3]$  (**18**) after the addition of 2 equiv of 12-crown-4 and isolation of the orange powder from diethyl ether-pentane solutions. First described by Sacconi et al.,[61] cyclo- $\text{P}_3$  ligands have been of interest as products of white phosphorus activation by metal complexes.[3,16]

A pathway leading to the generation of a new activation product was observed when the  $\text{P}_4$  was reacted with anion **[17]2** in coordinating solvents such as THF. **Reaction of  $\text{P}_4$  and  $[\text{Na}(\text{THF})_6][\text{17}]$  independently of the amount of  $\text{P}_4$  used (from 0.25 to over 3 equiv) a different major product was formed.** The crystal structure of this product showed its composition as  $[\text{Na}(\text{THF})_6][(\text{Ar}[\text{Np}]\text{N})(\eta^4\text{-P}_5)\text{-Nb}(\text{N}[\text{Np}]\text{Ar})_2]$  ( $[\text{Na}(\text{THF})_6][\text{19}]$ ) (Figure 4). In THF the yield of this reaction was greater than 95 % as indicated by in situ  $^{31}\text{P}$  NMR studies. This product was isolated in 71% yield as a red-orange solid after recrystallization

from pentane/THF mixtures. The use of other coordinating solvents for the activation of  $P_4$  led to different yield for **19** and the complex  $[(P_3)Nb(N[Np]Ar)_3]_2^-$ . An interesting finding was that upon changing THF with a more sterically hindered derivative around the oxygen such as 2-methyltetrahydrofuran or 2,5-dimethyltetrahydrofuran, the ratio changed from 3:2 (10:1 in THF) to 9:1 and 6.4:1, respectively, while with 1,4-dioxane the ratio is 3.7:1 and with acetonitrile is 4.5:1. Small amounts of **19** can be also observed in diethyl ether upon the addition of stoichiometric amounts of THF. It is significant that in polar enough coordinating solvents such as dimethoxyethane, pyridine, fluorobenzene, benzonitrile, or dichloromethane the only product observed was the cyclo- $P_3$  anion **18**. In contrast, reaction of  $[Na(OEt_2)][(OC)_5WPNb(N[Np]Ar)_3]$  ( $[Na][\mathbf{17-W}]$ ) with  $P_4$  in nonpolar solvents produces similar products to those observed with **17**, but in THF complex **17-W** with  $P_4$  only provides **18-W**.

Complex **19** was fully characterized by single crystal X-ray diffraction. The asymmetric unit cell is constituted by two crystallographically distinct but chemically equivalent molecules of  $[Na(THF)_6][\mathbf{19}]$ . The complex is composed by a  $P_5$ -ring coordinated to the metal by four of the atoms and the fifth P atom is bonded to the N of the anilide group  $Ar(Np)N$ . The difference between the two conformers found in the crystal are the P-P bond distances of the five membered ring (Figure 4), being one of them in the range from 2.1550(18) to 2.1894(19) Å, similarly to the average value for P-P single bonds (2.21 Å).[62] Both conformers show the same  $^1H$  and  $^{13}C$  NMR spectra at room temperature consistent with the observed solid-state structure of the anion. The only previously reported early-transition-metal complex bearing a cyclopentaphosphane ligand is the  $[Ti(P_5)_2]_2^-$  anion.[16,63] The anion **19** is the first example of a sophisticated ligand accomplished by functionalization of  $P_4$  mediated by a metal complex. This ligand, the substituted cyclopentaphosphane  $\{RP_5\}$ , remains coordinated by a  $\eta^4$ -bond to the metal. It is important to stress that this finding underline that a metal complex is able to promote the synthesis of sophisticated ligands under mild reaction conditions.



**Figure 4.** Left: Solvent dependent reactivity of **[17]<sub>2</sub>** with  $P_4$  to give  $P_3$  or  $P_5$  rings. Right: ball and stick representation of the crystal structure of **19**; solvent molecules were removed for clarity. Crystal structure adapted from [60].

The reported approach is a simpler, synthetically useful methodology for the synthesis of salts of the cyclo- $P_3$  anion because the source of  $P_2$  units is elemental phosphorus, rather than the complicated niobium diphosphaazide complex used previously, which itself is the product of a multistep synthesis originating from  $P_4$ . In nonpolar solvents with either the uncapped phosphide anion **17** or **17-W** the activation of  $P_4$  molecules leads to complexes containing cyclo- $P_3$  ligands, which were produced by a formal addition of  $P_2$  units to the metal-phosphorus multiple bonds. Complexes  $[Na(12\text{-crown-}4)_2][\mathbf{18}]$  and  $[Na(12\text{-crown-}4)_2][\mathbf{18-W}]$  had been isolated previously in yields of 30% and 75%, by respective trapping of  $P_2$  and  $[(P_2)W(CO)_5]$  with **17**.<sup>[64]</sup> In addition, the method disclosed here also removes the requirement to sequester the cation with crown ethers for purposes of product separation.

This results suggested that the presence of the ionic charge may be a requirement for the activation of  $P_4$  molecules by metal-phosphorus multiple bonds. The related arsenide  $[Na][AsNb(N[Np]Ar)_3]$  in diethyl ether was reacted with  $P_4$  and the phosphide **17** with  $AsP_3$ . The obtained products display a cyclo- $As_xP_{3-x}$  distribution, which was similar to that

reported for a related niobium system.[58] When coordinating solvents were used for the reaction of  $P_4$  with **17** a different product distribution was observed. In particular, in THF the formation of the cyclo- $P_5$  occurs with over 90% and a whole molecule is consumed by a single phosphide instead of the  $P_4$  splitting in two phosphide anions, which was previously observed in non-polar solvents. The phosphide anion essentially undergoes a formal addition of an entire  $P_4$  molecule to form the novel cyclo- $P_5$  anion **19**. This result can be interpreted as the trapping of an intermediate pentaphosphacyclopentadienyl moiety through the migration of one of the anilide ligands from the metal center onto a phosphorus atom.

It was shown that the sodium salt of **17** exists as a dimer in diethyl ether, being its molecular formula  $[Na(OEt_2)]_2[17]_2$ , [3,65] but in THF it is broken apart as the cation is sequestered away by solvent molecules. This interpretation is corroborated by a significant downshift in the  $^{31}P$  NMR chemical shift of the phosphide  $^{31}P$  nucleus upon going from benzene to THF.[64] The formation of **19** is favored in solvents with large affinity for the sodium ion, the case of **18** being the opposite. Based on this, it was proposed that the appearance of  $P_5$  structures requires the cleavage of the dimer of phosphide  $[17]_2$ . ~~Additionally to some references in bibliography [64,65] reaction of  $[Na(12\text{-crown-}4)]_2[17]_2$ , in which the sodium cation is sequestered by crown ethers while the anion is in a "naked" monomeric form, [64] with  $P_4$  was preformed in different solvents.~~ In these reactions, even when diethyl ether was used, selective conversion to the  $\eta^4$ - $P_5$  anion **19** was observed. Therefore the authors proposed that in non-polar solvents a dimeric phosphide  $[Na(OEt_2)]_2[PtNb(N[Np]Ar)_3]_2$  reacts directly with  $P_4$  and breaks it to generate two niobium cyclo- $P_3$  anions. As the dimeric product was observed to be stable in solution it is possible that this pathway does not involve the breaking of the  $Na_2P_2$  diamond core at any point during the reaction. Nevertheless, another pathway could be possible. Taking into account that **17** is capable of trapping diphosphorus species to yield the cyclo- $P_3$  anions **18**, [64] it may react with a  $P_4$  molecule to form **18** and releasing  $P_2$ , which is trapped by a second phosphide molecule. This second possibility was checked by the study of the reaction of  $P_4$  with **17** in 1,3-cyclohexadiene and 2,3-dimethylbutadiene. In both solvents the anion **18** was observed and none of the expected trapping products could be detected in either of 1,3-cyclohexadiene or 2,3-dimethylbutadiene.[7] Nevertheless, the following

explanation could justify this fact: the dienes were unable to compete with the phosphide anion **17** for the trapping of the generated  $P_2$ .

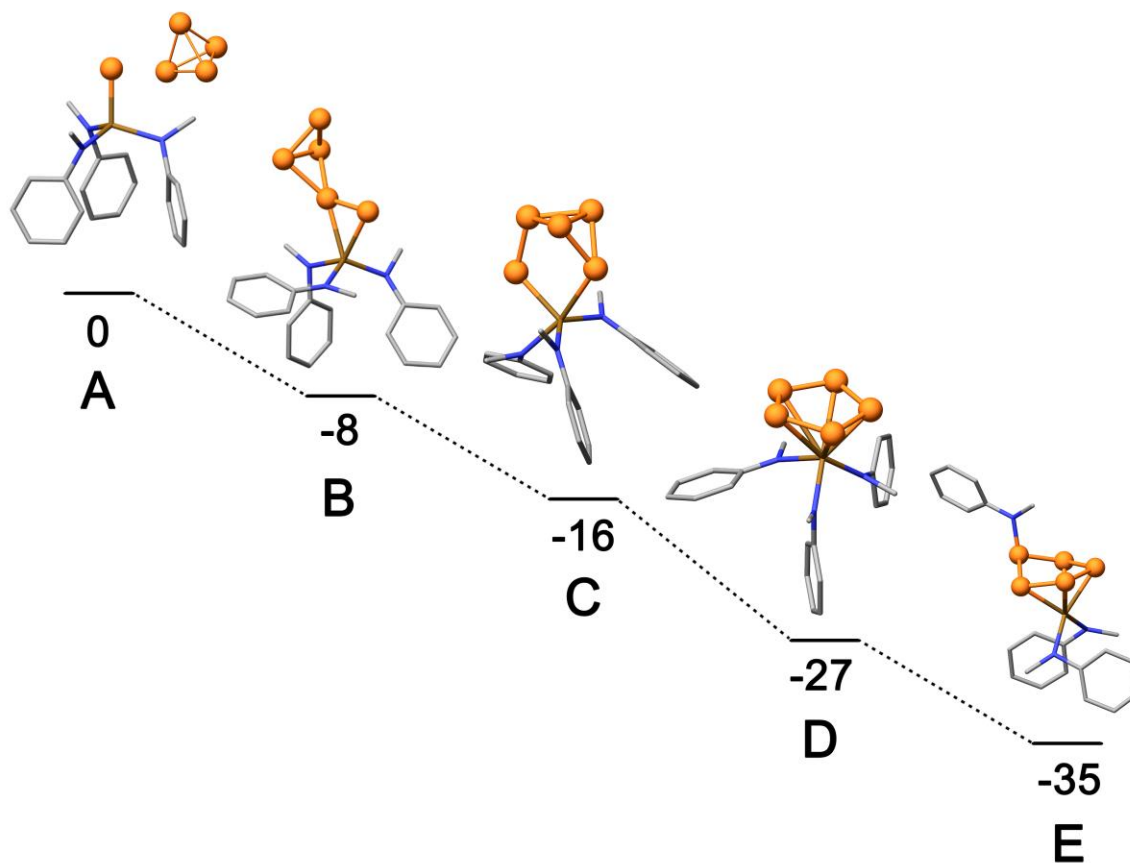
The possible mechanism of the reaction was studied in order to obtain information to generalize the reaction. The substituted-cyclo- $P_5$  anion formation was supposed to be the consequence of trapping during the reaction of an intermediate pentaphosphacyclopentadienyl through the migration of one of the anilide ligands from the metal center onto a phosphorus atom. That is in agreement with the fact that the conversion becomes less selective when the solvent is replaced with THF derivatives. This observation cannot be justified by the dielectric constants of the solvents as they do not change significantly (in the range of 7.5 to 6) and neither pyridine nor benzonitrile (dielectric constants of 12.26 and 25.9, respectively) show any selectivity for the cyclo- $P_5$  product when used as a solvent,[60] but the selectivity decreases in parallel with the steric hindrance increment around the oxygen atom of the solvent molecules. Based on this, the authors proposed that synthesis of **19** became disfavored with respect to that of **18** in solvents with lower sodium ion affinity, the formation of  $P_5$  ring requires the cleavage of the dimer of phosphide  $[17]_2$ , which was supported by alkalimetal salts literature.[66] By using  $[Na(12\text{-crown-}4)_2][17]$  as the phosphide source, for which it has been shown that the sodium cation is sequestered by crown ethers, while the anion is in a “naked”, monomeric form in all the checked solvents, including diethyl ether, selective formation of  $\eta^4\text{-}P_5$  anion **19** was observed.

The authors proposed that in nonpolar solvents the dimeric phosphide  $[Na(OEt_2)]_2[PtNb(N[Np]Ar)_3]_2$  breaks the  $P_4$  giving rise to two niobium cyclo- $P_3$  anions, which is, probably, dimeric in solution. This hypothesis suggests that the  $Na_2P_2$  diamond core is stable during the reaction and therefore leads to the final product. An alternative pathway is possible as phosphide anions **17** can trap diphosphorus species to yield the cyclo- $P_3$  anions **18**, releasing  $P_2$ , which further reacts with a second phosphide molecule. To prove this last possibility, the  $P_4$  activation reaction was performed in neat 1,3-cyclohexadiene and in neat 2,3-dimethylbutadiene. Anionic compound **18** was observed in both solvents but none of the expected trapping products were detected, which could mean that the dienes were unable to compete with the phosphide anion **17** for the trapping of any generated  $P_2$ . The structure of the phosphide **17-W** indicated a monomeric constitution,[64]



which suggest that one anion **17-W** could react with a molecule of  $P_4$  to produce the cyclo- $P_3$  anion **18** together with  $[(\eta^2-P_2)W(CO)]$ .<sup>[67,68]</sup> The reaction is completed by trapping of the latter species with another **17-W** anion and further  $[W(CO)_5]$  units would yield **18-W** as the final product. However, all the attempts to intercept  $[(\eta^2-P_2)W(CO)_5]$  species by carrying out the reaction in 2,3-dimethylbutadiene were unsuccessful as no in the NMR spectra for the reported diene-trapping product  $[(OC)_5WP_2C_{12}H_{20}]$  were found.<sup>[68]</sup>

The authors calculated, using density functional theory (DFT) the energetics of the reaction of the “naked” phosphide monomer with  $P_4$  using  $[PtNb(N[Me]Ph)_3]^-$  as the model (Figure 5). The  $\eta^2$ -bound phosphinophosphinidene complex (B), which is the product of the insertion of a vertex of  $P_4$  into the Nb-P triple bond, was found to be at lower energy (-8 kcal/mol) than the starting one (A). Reorganization of the P atoms leads to a  $\kappa^2$ - $P_5$  structure (C) that is 8 kcal/mol more stable than B, which can be interpreted as the consequence of the insertion of one edge of the  $P_4$  tetrahedron into the phosphide multiple bond. The next structure (D), which is characterized by a planar cyclopentaphosphane ring  $\eta^4$ -bound to niobium, was found to be quite stable (-27 kcal/mol referred to the starting compound). The phosphorus atom not bound to niobium is not allowed to undergo anilide transfer from the metal center to generate the observed final product.



**Figure 5.** Calculated energy diagram for the activation of  $P_4$  by anion **17**. Adapted from [60].

Finally, the formation of cyclo- $P_3$  anion **18** from the monomeric phosphide **17** is not evident. Probably, a  $P_2$  molecule is extracted from one of the intermediates but it is also possible that some intermediate structures are sufficiently long-lived to yield two cyclo- $P_3$  anions from a bimolecular reaction with another phosphide. This pathway should be preferred when excess of phosphide **17** is present. The overall reaction of two phosphide anions and one  $P_4$  molecule was predicted to be energetically downhill by 51 kcal/mol.

Remarkably, as indicated previously, several compounds have been isolated during the stepwise hydrolytic disassembly of coordinated  $P_4$  by tuning the relative amounts of the reagent complex and water. Thus, compounds containing one phosphorus atom ( $PH_3$ ,  $H_3PO/PH_2OH$ ,  $PH(OH)_2/H_3PO_2$ , and  $P(OH)_3/H_3PO_3$ )[69–72] as well as polyphosphorus

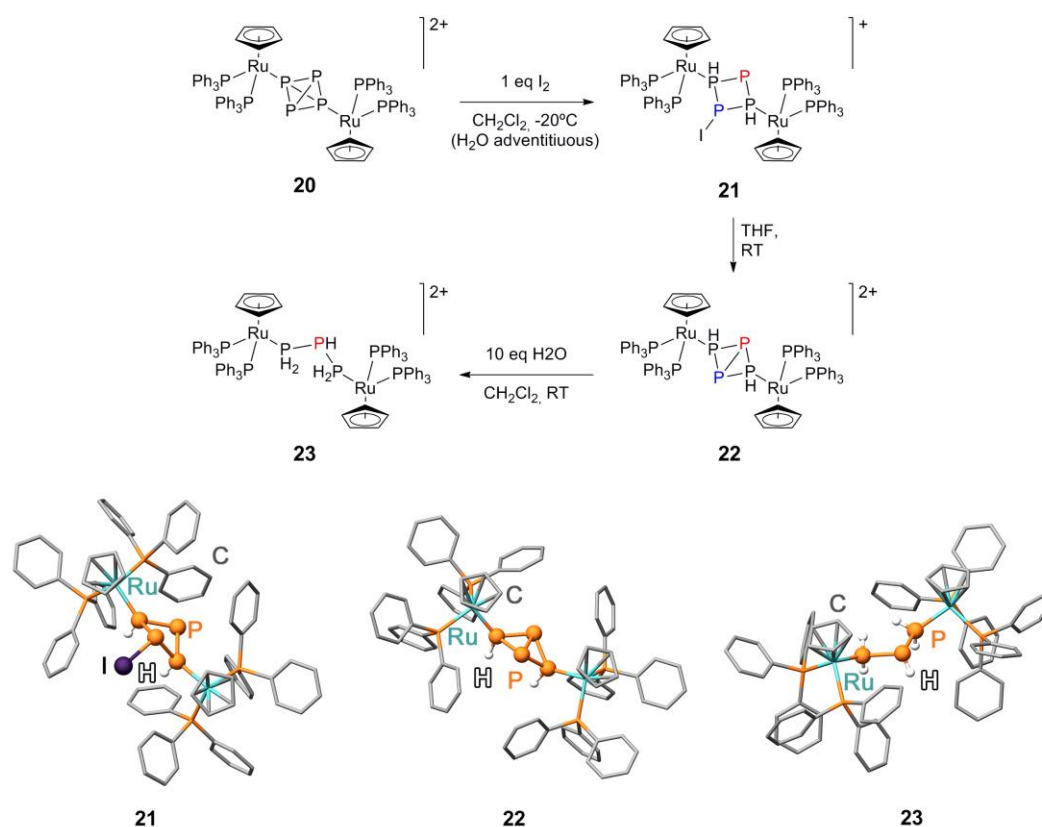
molecules ( $P_2H_4$ ,[73]  $P_3H_4OH$ ,[74] and  $P_4H_3(OH)_3$ [75]) were generated and characterized. Polyphosphorus products, which are usually stabilized through coordination to two metal fragments, are either extremely unstable or even unknown as free molecules.[38]

A very interesting way to functionalize  $P_4$  was found to be mediated by  $[RuCp(PPh_3)_2]$  by Peruzzini et al., providing as final product an interesting  $HP_3$ -Ru complex and  $H_3PO_3$ . [76] Reaction of  $P_4$  with  $[RuClCp(PPh_3)_2]$  provided complex  $[\{CpRu(PPh_3)_2\}_2(\mu^{1:1},\eta^{1:1}-P_4)](OTf)_2$  (**20**,  $OTf = CF_3SO_3$ ) that reacts with  $I_2$  in the presence of water giving the complex  $[\{CpRu(PPh_3)_2\}_2\{\mu^{1:3},\eta^{1:1}-PH_2PHPH_2\}](OTf)_2$  (**23**), through  $\{CpRu(PPh_3)_2\}_2(\mu^{1:3},\eta^{1:1}-P_4H_2I)^+$  (**21**, Figure 6), which contains the unprecedented 1,3-dihydride-2-iodidecyclo-tetraphosphane anion, and  $[\{CpRu(PPh_3)_2\}_2(\mu^{1:3},\eta^{1:1}-P_4H_2)](OTf)_2$  (**22**). The formation of **21** also takes place when the reaction is run in dry  $CD_2Cl_2$ , with added  $D_2O$  affording the perdeuterated analogue **21-[D<sub>2</sub>]**. Iodide is easily eliminated from compound **21** in polar solvents providing the so far elusive 1,3-dihydride-2,4-bicyclo-tetraphosphane[1,1,0] ( $P_4H_2$ ), which is stabilized by two ruthenium centers in complex **22**. Finally, the ligand  $P_4H_2$  in **22** reacts with three water molecules to form quantitatively the triphosphane ( $P_3H_5$ ) bridging the two  $\{RuCp(PPh_3)_2\}^+$  moieties atoms in complex **23** together with one molecule of phosphorous acid ( $H_3PO_3$ ). Inconsistent with the standard hydrolysis of **20**, the hydrolytic degradation of the  $P_4$  tetrahedron mediated by iodine does not include the formation of hydroxypolyphosphane species,[77] thus suggesting that the process might occur by a different hydrolytic mechanism.

The isolation of **21** from the starting material was very difficult. Nevertheless, purification including fractional crystallization gave single crystals of the compound useful for its characterization with single crystal X-ray diffraction. The crystal structure of **21** is characterized as the previously unknown  $P_4H_2I^-$  anion stabilized by coordination to two  $\{RuCp(PPh_3)_2\}^+$  moieties through the hydrogenated phosphorus atoms. The anion adopts a chair-type conformation with the iodine atom positioned trans to both ruthenium atoms and the naked P6 atom (Figure 6).

Complexes  $[\{CpRu(PPh_3)_2\}_2(\mu^{1:3},\eta^{1:1}-P_4H_2)](OTf)_2$  (**22**) and  $[\{CpRu(PPh_3)_2\}_2\{\mu^{1:3},\eta^{1:1}-PH_2PHPH_2\}](OTf)_2$  (**23**) crystallized in a molar ratio of 1:2 (Figure 6). The bidentate ligand tethering the metals fragments is the 1,3-dihydride-2,4-

cyclotetraphosphane[1,1,0] ( $P_4H_2$ ) in **22**, coordinated through the hydrogenated phosphorus atoms, and the triphosphane ( $P_3H_5$ ) in **23**. The coordination geometry in **22** is very similar to that of the parent  $[\{CpRu(PPh_3)_2\}_2(\mu^{1:3},\eta^{1:1}-P_4)]^{2+}$  cation,[73] with the cyclic  $P_4H_2$  molecule showing a butterfly arrangement: the angle between the P triangles being  $100.3(2)^\circ$  and a P-P separation between the uncoordinated P atoms of  $2.312(6)$  Å, which is longer than those reported for the few bicyclotetraphosphane species described until now.[77] Alkaline salts[78] and rhodium complexes[79,80] of the anion  $HP_4^-$  were described, but the neutral tetraphosphorus dihydride  $P_4H_2$  has only been observed by mass spectrometry.[38] Workup of the solution and crystallization from  $CHCl_3/C_6H_6$  provided **23** as pure yellow crystals, suitable for X-ray analysis, which shows how the fully hydrogenated triphosphane molecule ( $P_3H_5$ ) is bridging the two metal ends (Figure 6).



**Figure 6.** Top: reaction of **20** with  $I_2$  and traces of  $H_2O$  that gives the triphosphane-bridged **23** passing through the iodo-derivative **21**. Bottom: ball and stick representation of the

crystal structure of **21-23**; all hydrogen atoms were omitted for clarity but the ones bonded to phosphorus. Crystal structures adapted from [72-74].

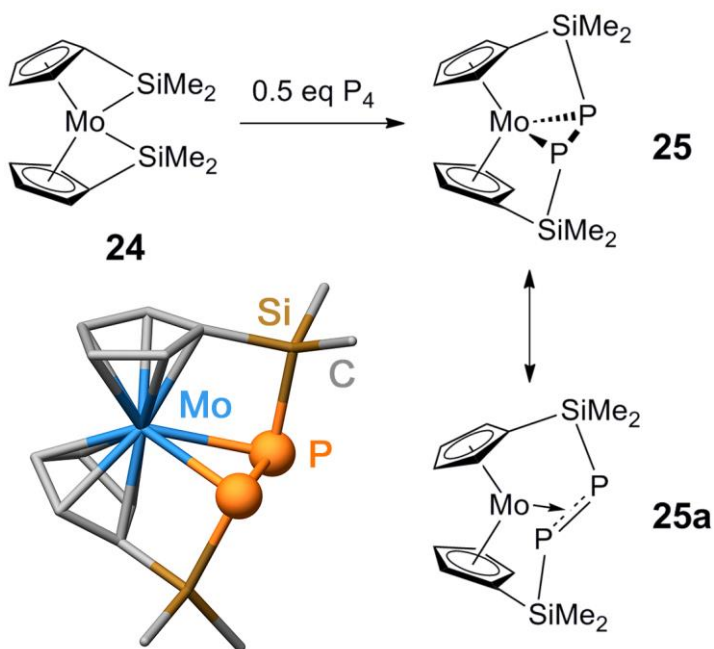
The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum showed that the solid-state structure of **21** is maintained in  $\text{CD}_2\text{Cl}_2$  solution. The spectrum is constituted by four broad resonances centred at  $\delta = 40.0, 16.3, -5.0$  and  $-49.5$  ppm in a 4:2:1:1 ratio, respectively. The signals were not resolved when the temperature was lowered to  $-90^\circ\text{C}$ . The observed signal at high-field is typical of  $\text{PPh}_3$  bonded to a  $\{\text{CpRu}\}$ . [69–75,81,82] The  $^{31}\text{P}$  NMR spectrum includes also three sets of resonances that are assigned to the tetraphosphorus  $\text{P}_4\text{H}_2\text{I}^-$  unit while the broad doublet of doublets of triplets at lower field may be readily assigned to the hydrogenated phosphorus atoms, which display a coupling constant system of 152 ( $^1J_{\text{P-P}}$ ), 160 ( $^1J_{\text{P-P}}$ ) and 45 Hz ( $^2J_{\text{P-P}}$ ) that are splitted in the  $^1\text{H}$ -coupled spectrum ( $^1J_{\text{P-H}} = 185$  Hz). Finally a sharp singlet and a broad triplet with coupling constant of 150 Hz ( $^1J_{\text{P-P}}$ ) are due to the substituted and the naked P-atoms of the  $\text{P}_4\text{H}_2\text{I}^-$  unit respectively. In contrast, complex **22**, which is obtained by reaction of **21** in polar solvents upon release of a iodide, shows a  $^{31}\text{P}\{^1\text{H}\}$  NMR splitting pattern that fully correlates with an  $\text{A}_2\text{A}'_2\text{FF}'\text{M}_2$  spin system, which was fitted by simulation. The two PH phosphorus atoms of the  $\text{P}_4\text{H}_2$  molecule resonate at 11.4 ppm ( $\delta_{\text{PF}}$ ) that is the region typical for coordinated PH groups of  $\text{PH}(\text{OH})\text{PHPHP}(\text{OH})_2$ , [75] while the two uncoordinated P atoms appear at high field at  $-297.3$  ppm ( $\delta_{\text{PM}}$ ). [10,14,83] Finally, the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **23** was fitted into an  $\text{ABA}'\text{B}'\text{FF}'\text{M}$  spin system, which is in agreement with its solid state structure, confirming that the complex is stable and only one isomer is present in solution.

Braunschweig's group investigated the potential of ansa-metallocene **24** for fragmentation and functionalization of  $\text{P}_4$ , finding an interesting way to generate P-Si bond. [84] Metallocenes were rarely exploited for  $\text{P}_4$  activation, with only few examples being known. [24,85–87] As a result of their research they showed an ansa-metallocene-mediated degradation of  $\text{P}_4$  into a  $\text{P}_2$  complex along with the formation of an unprecedented  $\text{Si}_2\text{P}_2$  bridging moiety. The reaction of  $\text{P}_4$  with **24** in toluene at  $80^\circ\text{C}$  resulted in the formation of compound **25** in 30% yield (Figure 7), which is an air- and moisture-sensitive red solid, which melts at  $291^\circ\text{C}$  and is stable up to  $500^\circ\text{C}$ .

Single crystals suitable for being studied by single crystal X-ray diffraction were

obtained by slow evaporation inside the glove box from a solution in toluene at ambient temperature. The molecular structure of **25** is constituted by a tricyclic compound in which the Mo atom is part of each ring (Figure 7). The Mo atom is four coordinated and displays a distorted tetrahedral geometry. The rings are constituted by the metal, Cp-carbon atoms, Si and P atoms. The P-P bond length (2.1721(5) Å) lies between P-P single (2.21 Å) and double bonds ((Me<sub>5</sub>C<sub>5</sub>)-P=P-(C<sub>5</sub>Me<sub>5</sub>): 2.031(3) Å; (tBu)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>-P=P-C<sub>6</sub>H<sub>2</sub>(tBu)<sub>3</sub>: 2.034(2) Å)[88,89] and it is longer than that previously published for [(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Mo(P<sub>2</sub>H<sub>2</sub>)] (2.15 Å),[86] which was presented by Green et al. in 1974 as the product of the reaction of P<sub>4</sub> with [(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>MoH<sub>2</sub>].[85] An important feature that is worth pointing out is the cleavage of two Si-Mo bonds and simultaneous formation of two Si-P bonds in the crystal. The Si-P bonds lengths are 2.2451(5) Å and 2.2418(5) Å, both of them in good agreement with the average Si-P single bond lengths (2.25 Å).[29,90]

The solid state structure shows that complex **25** exists in two possible resonance forms, **25a** and **25** (Figure 7). The bonding situation in the mesomeric form **25** is in agreement with somewhat long Mo-P bonds while quite large P-P separation can be described better by structure **25a**. The bonding in the complex was studied by quantum chemical calculations. The calculated Wiberg bond indices revealed that all bonds are single with the lone-pair electrons of each phosphorus atom clearly pointing away from the central MoP<sub>2</sub> core. The results indicate a bond order of unity for all bonds in the central {MoP<sub>2</sub>} core. However, there is some electronic delocalization in the three-membered ring and  $\pi$ - $\pi$  interaction between the phosphorus atoms. The final conclusion obtained from the calculation was that an overall bonding situation in which both mesomeric forms **25** and **25a** contribute to the structure of the molecule in solution.



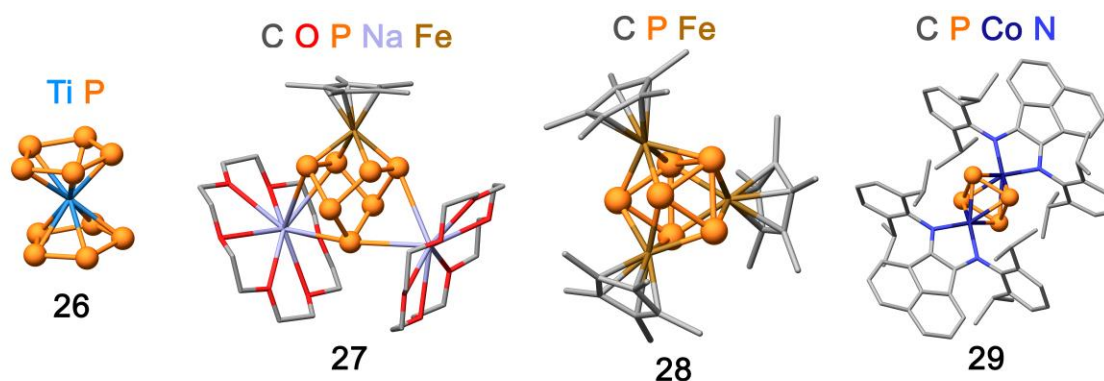
**Figure 7.** Synthesis and resonance formulae of **25** and ball and stick representation of its crystal structure. Crystal structure adapted from [84].

The  $^1\text{H}$  NMR spectrum of complex **25** is characterized by four signals: one for the  $\text{C}_5\text{H}_4$  rings at 5.17, 4.78, 4.75 and 3.59 ppm. For the  $\text{SiMe}_2$  groups a singlet at 0.27 ppm and a triplet at 0.34 ppm, are observed due to the hydrogen–phosphorus coupling constant of 5.9 Hz ( $J_{\text{PH}}$ ). The  $^{29}\text{Si}$  NMR spectrum exhibits one signal at -2.9 ppm, which is in good agreement with that observed for  $[\text{Cp}^*(\text{CO})_2\text{FeP}(\text{Ph})\text{SiMe}_2\text{Ph}]$ . [91] Both phosphorus nuclei are coupled with the silicon nucleus with different coupling constant ( $^1J_{\text{SiP}}$  and  $^2J_{\text{SiP}}$ ), producing a virtual triplet. This observation also hints at the formation of the Si-P bonds with concomitant cleavage of the parent Si-Mo bonds.

So far, the last published synthetic process based in the direct functionalization of  $\text{P}_4$  shows that is possible to obtain a selective synthesis by reacting  $\text{P}_4$  with a metal anion  $[\text{Cp}^*\text{Fe}(\text{CO})_2]^-$  ( $\text{Cp}^* = \text{C}_5(\text{CH}_3)_5$ ), which in the presence of bulky Lewis acids (LA) such as  $\text{B}(\text{C}_6\text{F}_5)_3$  or  $\text{BPh}_3$ , leads to a unique LA-stabilized bicyclo[1.1.0]tetraphosphabutanide anions  $[\text{Cp}^*\text{Fe}(\text{CO})_2(\eta^1\text{-P}_4\cdot\text{LA})]^-$ . Their P-nucleophilic site can be subsequently protonated to afford the transient LA-free neutral butterflies *exo,endo*- and *exo,exo*- $\{\text{Cp}^*\text{Fe}(\text{CO})_2(\eta^1\text{-P}_4\text{H})\}$ , allowing controllable stepwise metalate-mediated

functionalization of  $P_4$ . [92] The controlled and selective formation of these intriguing new anionic and neutral derivatives enables the selective functionalization of white phosphorus by anionic metalates.

In 2002, Ellis and co-workers provided the first insights by reacting  $P_4$  with a naphthalene-stabilized titanate that afforded the all-inorganic metallocene  $[(\eta^5-P_5)_2Ti]_2^-$  (**26**; Figure 8). [63]



**Figure 8.** Ball and stick representation of the crystal structure of **26-29**. Hydrogen atoms are omitted for clarity. Crystal structure adapted from [63,93,94].

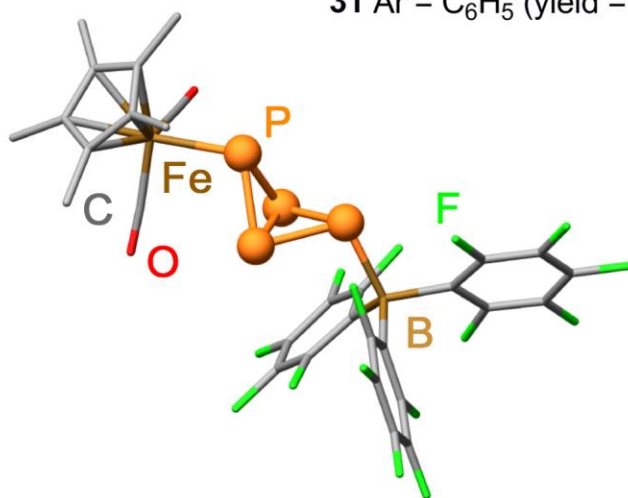
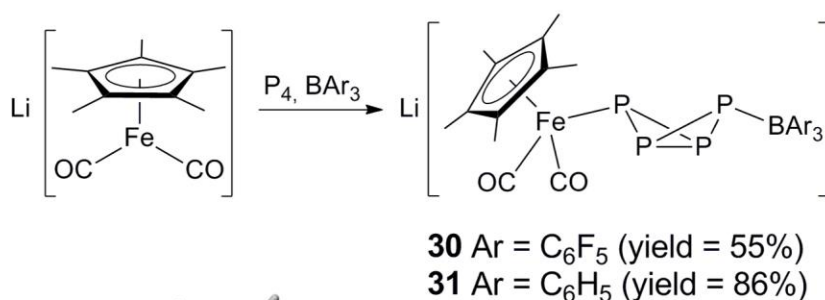
Some time later, Wolf et al. described the formation of iron polyphosphides **27** and **28** formed through  $P_4$ -aggregation mediated by  $[Cp^*Fe(\eta^4-C_{10}H_8)]^-$  ( $Cp^* = C_5(CH_3)_5$ ), [93] and some years after the dinuclear cobalt tetraphosphido complex **29** by reaction of  $P_4$  with  $[Co(BIAN)(cod)]^-$  (BIAN=1,2-bis(2,6-diisopropylphenylimino)-acenaphthene, cod = 1,5-cyclooctadiene). [94] Nevertheless, there is a significant unpredictability of the obtained product when using metal anions with the often uncontrolled reactions of  $P_4$  with carbanions. [8,95–97] This was tried to be eliminated by trapping the initial  $P_4$  adduct (using sterically bulky ArylLi) with Lewis acids (LA) to give stabilized bicyclo[1.1.0]tetraphosphabutane anions ( $[ArylP_4 \cdot LA]^-$ ; LA =  $B(C_6F_5)_3$  or  $BPh_3$ ) that can be substituted or fragmented to novel compounds containing  $P_4$ ,  $P_3$  and  $P_1$  units.

K. Lammertsma et al. in 2017 showed that this approach can lead to the functionalization of  $P_4$  by a controlled reaction with  $[Cp^*Fe(CO)_2]^-$ . Addition of a toluene solution of  $P_4$  into a mixture of  $Li[Cp^*Fe(CO)_2]$  and  $B(C_6F_5)_3$  (0 °C) produced instantaneously the novel LA-stabilized bicyclo[1.1.0]tetraphosphabutane **30** in 55%



yield as a dark yellow powder (Figure 9).

Single crystals of **30** obtained in Et<sub>2</sub>O by addition of 12-crown-4 were good enough for being determined by single crystal X-ray diffraction. The crystal structure revealed an unprecedented metalphosphido-borane (Figure 9) constituted by a bicyclic P<sub>4</sub> butterfly-type derivative. Compound **30** features a non-symmetric substitution pattern with the tetraphosphide unit being flanked by the {Cp\*Fe(CO)<sub>2</sub>} moiety and the {B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>} Lewis acid.

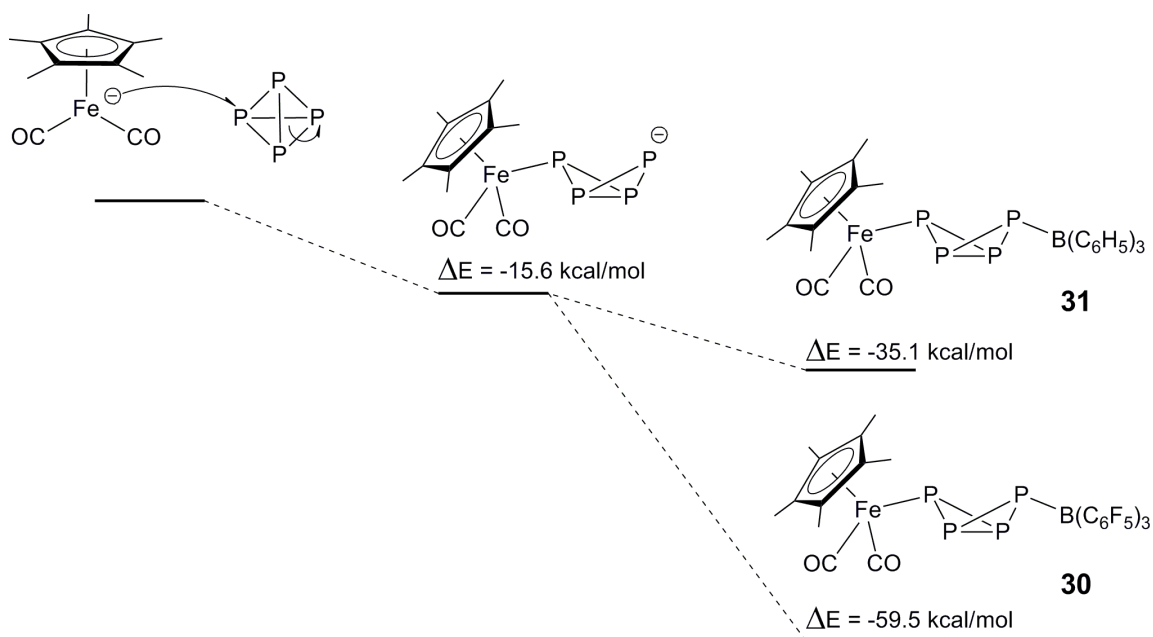


**Figure 9.** Top: synthesis of **30** and **31**. Bottom: ball and stick representation of the crystal structure of **30**; hydrogen atoms are omitted for clarity. Crystal structure adapted from [50].

Similar reaction but with Li[Cp\*Fe(CO)<sub>2</sub>] in a THF solution of P<sub>4</sub> and BPh<sub>3</sub> at 0 °C afforded **31**, which was isolated as a brown powder in 86% yield (Figure 9). Probably the better solubility of the anion in THF could be the responsible of the significant better yield

for  $\text{Li}[\text{Cp}^*\text{Fe}(\text{CO})_2]/\text{BPh}_3$  (86 %) than  $\text{Li}[\text{Cp}^*\text{Fe}(\text{CO})_2]/\text{B}(\text{C}_6\text{F}_5)_3$  in toluene (55%). The use of THF as a solvent for the synthesis of **30**, however, is precluded, owing to formation of the reactive  $\text{THF}\cdot\text{B}(\text{C}_6\text{F}_5)_3$  adduct. It is important to point out that phosphides **30** and **31** are the first examples of this kind of complexes.

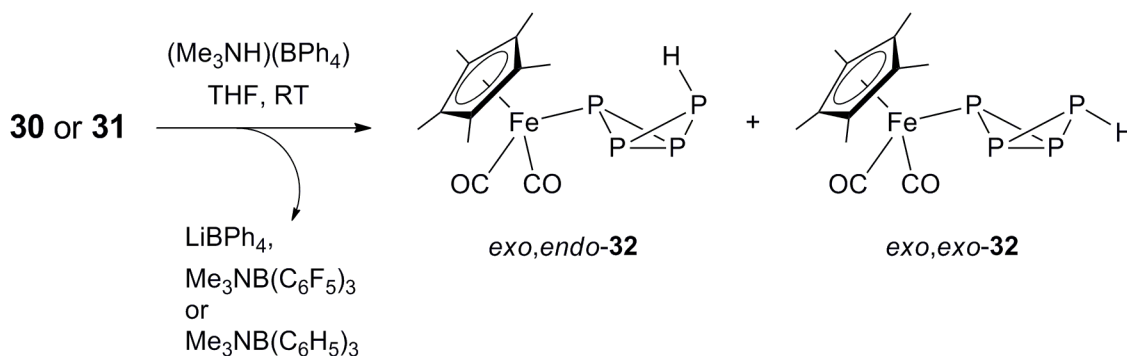
The mechanism of the reaction was studied by DFT calculations. The obtained results revealed (Scheme 6) that the nucleophilic addition of  $[\text{Cp}^*\text{Fe}(\text{CO})_2]^-$  to  $\text{P}_4$  causes the exothermic cleavage of one P-P bond. The resulting  $[\text{Cp}^*\text{Fe}(\text{CO})_2(\eta^1\text{-P}_4)]^-$  “butterfly” anion is then stabilized by the formation of the adduct with LA giving **30** and **31**. The latter, which is formed with the weaker Lewis acid  $\text{BPh}_3$ , is less stable than the former.



**Scheme 6.** Calculated mechanism of the reaction between  $[\text{Cp}^*\text{Fe}(\text{CO})_2]^-$ ,  $\text{P}_4$  and Lewis acids  $\text{BArF}$  and  $\text{BPh}_3$ . Adapted from [93].

To study the possible use of **30** and **31** as nucleophilic reagents their protonation was checked by using the mild acid  $[\text{Me}_3\text{NH}][\text{BPh}_4]$  in THF. Addition of the acid to the more reactive phosphide **26** (1:1 stoichiometry) showed the instantaneous formation of two new bicyclo[1.1.0]tetraphosphabutanes, which were identified as the neutral protonated LA-free exo,endo and exo,exo isomers of  $[\text{Cp}^*\text{Fe}(\text{CO})_2(\eta^1\text{-P}_4\text{H})]$  (**32**, 1:1.2 ratio; Scheme 7). The phosphanes decompose within 24 h, probably due to the lack of steric protection, which as indicated in other sections of this chapter is common for neutral bicyclic

tetraphosphanes bearing “small” substituents.



**Scheme 7.** Protonation of complexes **30** and **31**.

Similar protonation performed with the less reactive **30** gave a mixture of *exo,endo*-**32** and *exo,exo*-**32** (1:1.2 ratio) with Me<sub>3</sub>N·B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> as the sole byproduct. DFT calculations showed that protonation of the anions by Me<sub>3</sub>NH<sup>+</sup> are quite exothermic. Further cleavage of the *exo*-cyclic P-B bonds by the liberated NMe<sub>3</sub> is controlled by the formation of the amine–borane adduct producing the *exo,endo*-**32**. The calculated energies for these reactions indicated that this last reaction is more exothermic for BPh<sub>3</sub> than for B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>. The *exo,exo*-**32** isomer was found in the calculation to be almost equally stable and is likely formed experimentally through Lewis or Brønsted acid enhanced isomerization [98] in agreement with the high trigonal and turnstile inversion barriers.[99]

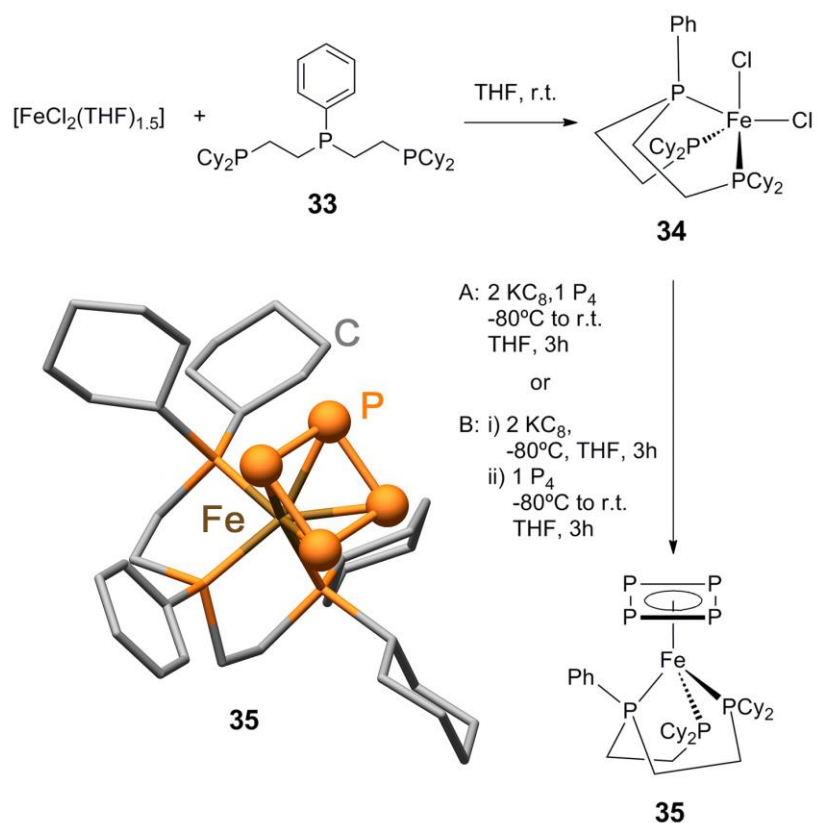
The selective protonation at the wing-tip P atoms of the complexed P<sub>4</sub> anions **30** and **31** confirms their P-nucleophilic character and provides a simple route to hitherto scarce nonsymmetrical neutral substituted-butterfly-P<sub>4</sub> derivatives. The reactivity is analogous to the organic-substituted congeners and should, therefore, be extendable to alkylations and possibly [3+1] fragmentations.[100] The controlled and selective formation of these intriguing new anionic and neutral derivatives enables the selective functionalization of white phosphorus by anionic metalates to be explored.

The <sup>31</sup>P NMR spectrum of **30** is characterized by signals at -65.0 (P1), -107.1 (P4), -340.7 ppm (P2/P3)) while that for **31** displays signals at -46.6 (P4), -84.3 (P1) and -337.0 ppm (P2/P3). As indicated previously, addition of acid to the most reactive phosphide **31**

provides two new bicyclo[1.1.0]tetraphosphabutanes, which were identified as the neutral protonated free *exo,endo* and *exo,exo* isomers of  $[\text{Cp}^*\text{Fe}(\text{CO})_2(\eta^1\text{-P}_4\text{H})]$  (**32**). Their  $^{31}\text{P}$  NMR spectra were solved by simulation, corroborating the observed  $\text{AMX}_2$  spin systems for *exo,endo*-**32** (70.6 (P<sub>A</sub>), -41.8 (P<sub>M</sub>), -335.5 (P<sub>X</sub>);  $^1J_{\text{P}_A,\text{P}_X} = -194.5$  Hz,  $^1J_{\text{P}_M,\text{P}_X} = -198.4$ ,  $^2J_{\text{P}_A,\text{P}_M} = 27.6$  Hz) and *exo,exo*-**27** (-19.8 (P<sub>A</sub>), -226.7 (P<sub>M</sub>), -355.2 (P<sub>X</sub>) ppm;  $^1J_{\text{P}_A,\text{P}_X} = -166.4$ ,  $^1J_{\text{P}_M,\text{P}_X} = -149.9$ ,  $^2J_{\text{P}_A,\text{P}_M} = 243.3$  Hz). It is important to point out that both isomers are distinguished through differences in the  $^2J_{\text{P}_A,\text{P}_M}$  ( $\Delta J = 215.7$  Hz) and  $^1J_{\text{P},\text{H}}$  (145.9 Hz *endo*-PH; 109.3 Hz *exo*-PH) coupling constants. The  $^1\text{H}$  NMR spectrum showed a resonance for only the *endo*-PH isomer (-1.14 ppm;  $^1J_{\text{H},\text{P}} = 152.9$  Hz). The  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum revealed two signals at 27.3 ppm and -8.4 ppm, due to the amine–borane adduct  $\text{Me}_3\text{N}\cdot\text{BPh}_3$  in equilibrium with its constituents and  $\text{Li}[\text{BPh}_4]$ .

Final lineal end-deck cyclo-P<sub>n</sub> complexes, which were commented previously, are rare but still interesting, presenting lone pairs at each P atom. The lone pairs could be available for further reactivity that could lead to new P<sub>4</sub> functionalization pathways. However, thus far, the only reactivity of cyclo-P<sub>n</sub> ligands was shown by Scheer and co-workers, who obtained spherical supramolecules by using stable  $[\text{Cp}^R\text{Fe}(\eta^5\text{-P}_5)]$  complexes, which are connected together to create a bigger structure constituted basically by P atoms.[101–108] Mézailles et al. reported in 2018 that the  $[(\text{PP}_2)\text{Fe}(0)]$  moiety, generated in situ, reacts with P<sub>4</sub> giving rise to the complex containing a cyclo-P<sub>4</sub> with a lone pair available to be reacted with metals and electrophiles.[109] These kind of complexes were only isolated with Group-V<sub>5</sub>-metals, but the low yields of their synthesis has limited the study of their chemistry.[110–113] The light purple complex  $[(^{\text{Ph}}\text{PP}_2^{\text{Cy}})\text{FeCl}_2]$  (**34**) can be prepared with 96% yield by simple reaction of  $^{\text{Ph}}\text{PP}_2^{\text{Cy}}$  (**33**) with  $[\text{FeCl}_2(\text{THF})_{1.5}]$  in THF (Figure 10). Due to the paramagnetism of this complex, its  $^1\text{H}$  NMR spectrum showed very broad, strongly paramagnetically shifted resonances from -10 to 150 ppm. The structure of the complex was evaluated by DFT calculations, which showed that distorted trigonal-bipyramidal geometry around the Fe ion is more favorable than a square-based pyramidal one in the quintuplet state. Reduction of **34** at -80°C with two equivalents of KC<sub>8</sub> in the presence of P<sub>4</sub> followed by warming up to room temperature for 3 h (Figure 10, pathway A) or by reaction with KC<sub>8</sub> at low temperature, followed after one hour by filtration and addition of the Fe<sub>0</sub>-containing solution to a solution of P<sub>4</sub> in THF (Figure 10, pathway B),

give rise to diamagnetic complex **35** quantitatively in both ways. Single crystals of **35** suitable for X-ray diffraction analysis were obtained in very good yield (75 %, Figure 10), confirming the structure of **35** as a monometallic iron cyclo-P<sub>4</sub> complex [(<sup>Ph</sup>PP<sub>2</sub>Cy)<sup>Fe</sup>(η<sup>4</sup>-P<sub>4</sub>)] with the P<sub>4</sub> moiety in a nearly perfect square-planar geometry (sum of the P-P-P bond angles equal to 359.99°). The P-P bonds (2.135(1)–2.166(1) Å) are shorter than a P-P single bond (2.21 Å) but longer than the known P=P bonds (ca. 2.0 Å).[114] These distances are moreover similar to the ones found in known end-deck cyclo-P<sub>4</sub> metal complexes featuring P<sub>4</sub><sup>2-</sup> moieties, and in cyclo-P<sub>5</sub> complexes (ca. 2.11 Å).

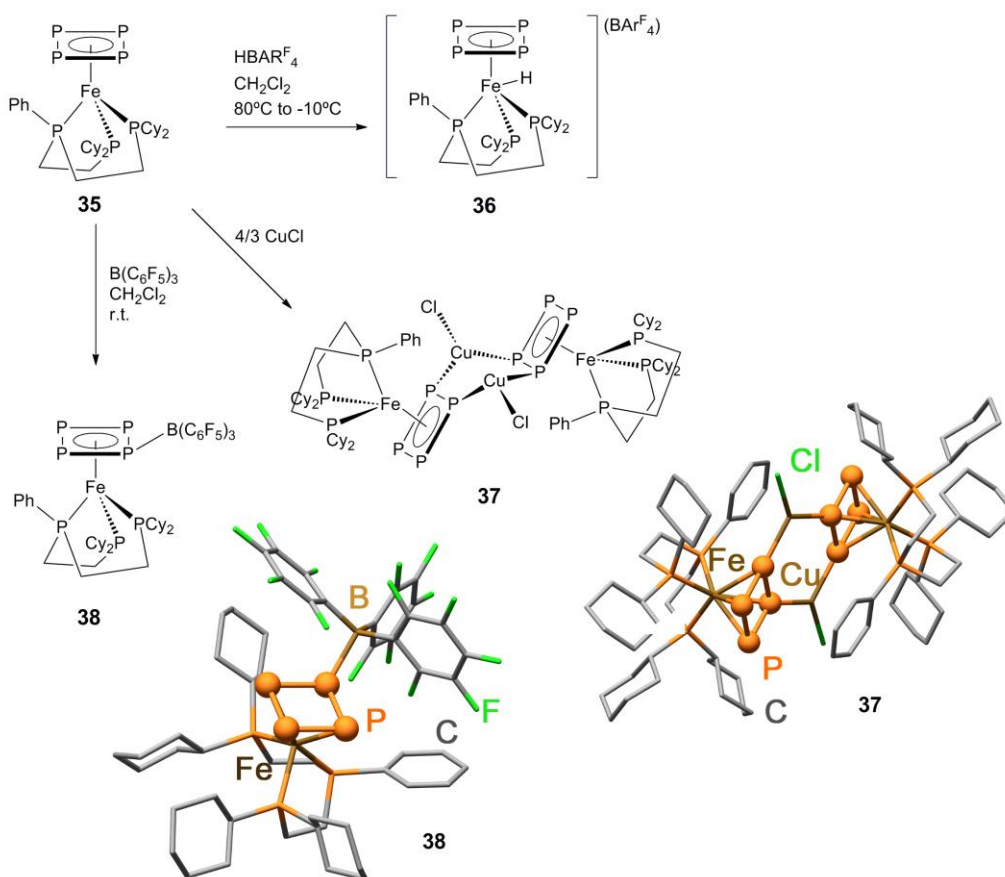


**Figure 10.** Synthesis and ball and stick representation of the crystal structure of **35**. Hydrogen atoms are omitted for clarity. Crystal structure adapted from [114].

Interestingly, the reaction of **35** with one equivalent of [H(Et<sub>2</sub>O)<sub>2</sub>][BAr<sup>F</sup><sub>4</sub>] (BAr<sup>F</sup><sub>4</sub> = tetrakis(3,5-bis(trifluoromethyl)phenyl)borate; Figure 11) at -80 °C led stoichiometrically to compound **36**. The P<sub>4</sub>-**36** chemical shift changes drastically upon protonation of the complex (53.6 ppm in **36** vs. 121.6 ppm in **35**). Complex **36** decomposes readily at room temperature by migration of the proton to the PP<sub>2</sub> ligand. The DFT study of this

protonation reaction corroborates the experimental results.

Remarkably complex **35** displays coordinative (Lewis basic) character, which led, by reaction with copper chloride in a slow-diffusion reaction (Figure 11), to a tetramer Fe-Cu<sub>2</sub>-Fe **32**.<sup>[113]</sup> Its crystal structure (Figure 11) is constituted by 1,2-coordination of the cyclo-P<sub>4</sub> to two CuCl moieties, therefore two molecules of **35** are linked via two bridging CuCl moieties.



**Figure 11.** Reactivity of **35** with Brønsted and Lewis acids and ball and stick representation of the crystal structure of **37** and **38**; hydrogen atoms removed for clarity. Crystal structures adapted from [49, 113].

The basicity of **35** was used to functionalize the P<sub>4</sub> ligand by reaction with the strong Lewis acid B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>. Direct addition of one equivalent of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> to a solution of **35** in dichloromethane (Figure 11) produced complex **38** in equilibrium with **35**, as

suggested by  $^{31}\text{P}$  and  $^{11}\text{B}$  NMR studies. To fully shift the equilibrium towards product formation, an additional equivalent of  $\text{B}(\text{C}_6\text{F}_5)_3$  is needed. The  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum showed, in addition to  $\text{B}(\text{C}_6\text{F}_5)_3$ , an upfield-shifted signal for a boron-containing product characteristic of a B–P bond, suggesting that a molecule of  $\text{B}(\text{C}_6\text{F}_5)_3$  is bonded by the B to a P atom of the cyclo- $\text{P}_4$ . Complex **38** was crystallized in 52% yield. Its crystal structure is constituted by a pair of enantiomers, in the unit cell, of the Lewis adduct  $[(^{\text{Ph}}\text{PP}_2^{\text{Cy}})\text{Fe}(\eta^4:\eta^1\text{-P}_4)\text{B}(\text{C}_6\text{F}_5)_3]$  (Figure 11). The  $\text{P}_4$  moiety is still planar and as expected less symmetric due to the coordination to the boron atom. The P–P bond lengths (2.129(2)–2.162(3) Å) are still in agreement with a  $\text{P}_4^{2-}$  moiety, indicating that only one P-lone pair is engaged in the interaction with BCF. The P–B bond length is 2.101(7) Å, which is similar to the one reported by Lammertsma and co-workers.[49]

The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of complex **35** shows three signals with intensity ratio of 1:2:4: a) a triplet of quintets at 115.4 ppm ( $^2J_{\text{PP}} = 38.0$  and 7.2 Hz) due to the central  $\text{P}^{\text{Ph}}$  atom of the tridentate ligand, which is coupled with two and four magnetically equivalent P atoms, respectively; b) a doublet at 95.4 ppm ( $^2J_{\text{PP}} = 38.0$  Hz) adscribable to the  $\text{P}^{\text{Cy}}$  atoms of the side arms that are coupled only to the central  $\text{P}^{\text{Ph}}$  atom; c) a broad singlet at 53.2 ppm, corresponding to the putative  $\text{P}_4$  unit, suggesting a dynamic process. When the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum was recorded at  $-60$  °C coalescence was reached, the central phosphorus atom giving rise to a broad triplet. The process could not be slowed down further at lower temperatures because of precipitation of the complex. In contrast, when the temperature was kept at  $60$  °C the signal at 53.2 ppm transformed into a broad doublet ( $^2J_{\text{PP}} = 7.2$  Hz), which is the consequence of the coupling of the  $\text{P}_4$  unit with the phosphorus  $\text{P}^{\text{Ph}}$  located in center of the ligand. The dynamic process is fully reversible, even after several cycles. This  $^{31}\text{P}\{^1\text{H}\}$  VT NMR study was very informative as it showed that the complex features a  $\text{P}_4$  moiety, with the four P atoms equilibrating in a low-energy process.

The  $^{31}\text{P}\{^1\text{H}\}$  NMR of compound **36** at  $-65$  °C shows two signals: a pseudo-triplet at 116.9 ppm and a doublet at 99.8 ppm ( $J_{\text{PP}} = 49.2$  Hz) for the “ $\text{PP}_2$ ” ligand coordinated to the Fe center. Increasing the temperature from  $-65$  °C to  $-10$  °C gave rise to the appearance of a broad singlet at 121.6 ppm. The three signals observed at  $-10$  °C, those at 116.9 and 99.8 ppm along with the new one at 121.6 ppm integrate respectively to 1:2:4. This indicates that the four magnetically equivalent P atoms for the  $\text{P}_4$  moiety are in a fast

dynamic exchange at this temperature. There is a drastic change in the chemical shift for the P<sub>4</sub> fragment upon protonation (53.6 ppm in **35** vs. 121.6 ppm in **36**), which is not common for these kind of complexes. In the <sup>1</sup>H NMR spectrum, one hydride moiety resonating as a broad triplet is observed at -7.26 ppm (<sup>2</sup>J<sub>HP</sub> = 78.3 Hz) for an apparent coupling with only two of the three P centers of the “PP<sub>2</sub>” ligand. The NMR data are thus consistent with the expected protonation of the Fe center.[115] Complex **36** decomposes readily at room temperature by migration of the proton to the PP<sub>2</sub> ligand and for this reason crystallization was not possible. The DFT calculation of the relative energies of the cationic complexes [(<sup>Ph</sup>PP<sub>2</sub><sup>Cy</sup>)Fe(η<sup>4</sup>-P<sub>4</sub>)(H)]<sup>+</sup> and [(<sup>Ph</sup>PP<sub>2</sub><sup>Cy</sup>)Fe(η<sup>4</sup>-P<sub>4</sub>H)]<sup>+</sup> (protonation at one P atom) showed that the protonation at the Fe center is favorable by 3.7 kcal mol<sup>-1</sup> (free energy), which corroborates the experimental results obtained by NMR.

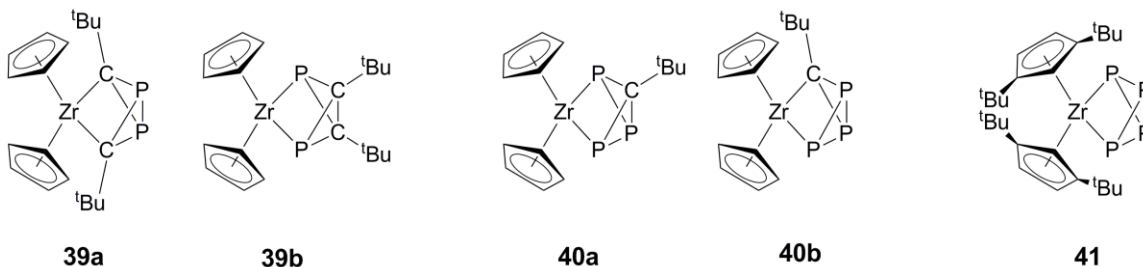
Pure complex **38** in solution is in equilibrium with complex **35**, and in solution both **38** and **35** are observed by <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy. DFT calculations showed that this equilibrium is possible as the difference in free energies (including solvent effects using the PCM method),[116] between both complexes is not very high. Formation of **35** was calculated to be favorable by only 1.6 kcalmol<sup>-1</sup> respecting to **38**, which fully rationalizes the coexistence of both compounds in solution. To support this fact, one equivalent of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> was reacted with **35** in dichloromethane (Figure 11) and studied by NMR. Immediately, after addition of the B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> the compound **38** was observed in 1:1 ratio with **35**. The <sup>11</sup>B{<sup>1</sup>H} NMR spectrum displays the signal for the B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> and an upfield-shifted signal for a boron-containing product at 2.9 ppm, in the range expected for a B–P interaction and suggesting a Lewis pair between the cyclo-P<sub>4</sub> and B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>. The <sup>19</sup>F NMR spectrum exhibits also one major compound characterized by two singlets at -164.1 ppm and -156.5 ppm and a broad singlet at -130.9 ppm. The NMR spectra indicate that there is an equilibrium between free B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> and B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> coordinated to complex **35**. To fully shift the equilibrium towards product formation, an additional equivalent of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> is needed.

### 1.3. Metal containing and metal-free products

One of the most exciting findings, published in 2011, was the activation of P<sub>4</sub> through the

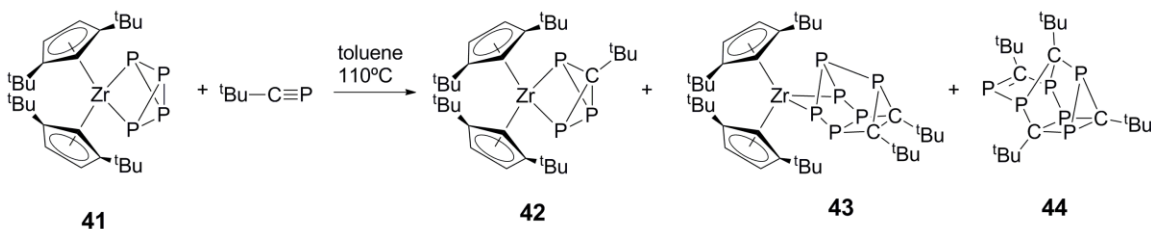


tetraphosphazirconocene derivative  $[\text{Cp}''_2\text{Zr}(\eta^2\text{-P}_4)]$  (**41**) by reaction with  $\text{tBuC}\equiv\text{P}$  that provides useful starting materials for the synthesis of novel phosphorus–carbon cage compounds. Based on this reaction, the novel complex  $[\text{Cp}''_2\text{Zr}(\eta^2\text{-P}_3\text{CtBu})]$  (**42**) as well as the cuneane-like complex  $[\text{Cp}''_2\text{Zr}\{\eta^2\text{-P}_6(\text{CtBu})_2\}]$  (**43**) were synthesized; the latter can be considered as an addition product of two  $\text{tBuC}\equiv\text{P}$  units at **41**. Compound **42** is the missing member **40** of the bicyclobutane zirconium complex family **39–41**. Moreover, synthetic evidence of another yet unknown isomer **39a** by using  $\{\text{Cp}''_2\text{Zr}\}$  moieties hints at the possibility to tune the steric influence of the ligands to form previously unknown isomers. In light of the known rich chemistry of **39**, the novel phosphorus-rich zirconium derivatives **42** (type **40**) and **43** will play a decisive role in the future of zirconium-mediated transfer reactions to obtain novel P-rich complexes and main-group-element cages (Scheme 8).[117]



**Scheme 8.** Triphosfabicyclobutane zirconium complexes **39–41**

Analysis of the reaction of **41** and tert-butylphosphaalkyne in boiling toluene for four days showed that complex bis(di-tert-butylcyclopentadienyl)-1,2,4-triphosfabicyclo[1.1.0]butane-2,4-diylzirconium ( $[\text{Cp}''_2\text{Zr}(\eta^2\text{-P}_3\text{CtBu})]$ ) (**37**) is the mayor product but also two other products, namely **43** and **44**, are also obtained (Scheme 9).



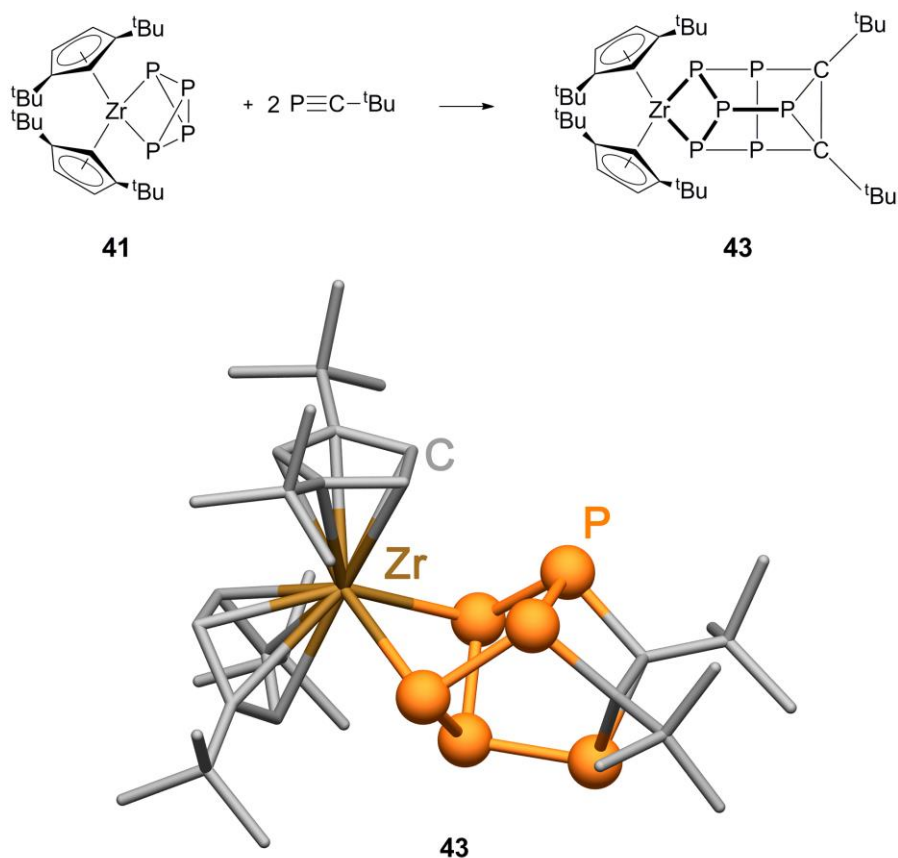
**Scheme 9.** Reactivity of **41** with tert-butylphosphaalkyne.

Brown crystals of **43** were obtained directly from the reaction mixture while **42** and **44** were isolated by column chromatography. Compound **44** crystallizes as single crystals and the residue contains almost pure **42**, characterized by NMR spectroscopy. From the NMR analysis it was concluded that the structure of **42** is similar to that of the isomer **40** (Scheme 9). Complex **42** is the first example of a metal complex containing triphoshabicyclo[1.1.0]butane ligand such as in isomer **40**. Only a few uncoordinated triphoshabicyclo[1.1.0]butanes with organic substituents  $RP_3CR'_2$  ( $R=tBu_3C_6H_2$ ,  $(Me_3Si)_2CH$ ,  $(Me_3Si)_2NN(SiMe_3)$ ;  $R'=Me_3Si$ ) are known.[118–120]

It was not possible to obtain valuable information on how **42** formed but authors proposed that **41** eliminates a  $P_2$  unit and the resulting unsaturated zirconium complex further reacts with  ${}^tBuC\equiv P$  leading to **42**. The released  $P_2$  units can react now with  ${}^tBuC\equiv P$  to provide carbon–phosphorus cages such as **44**: a tetramer of  ${}^tBuC\equiv P$  extended by one  $P_2$  moiety. Interestingly, all of the isolated products are present in an almost equimolar ratio in the crude reaction mixture. In addition, complex **43** can be interpreted as the addition product of two molecules of phosphoalkyne to the starting complex **41** (Scheme 9).

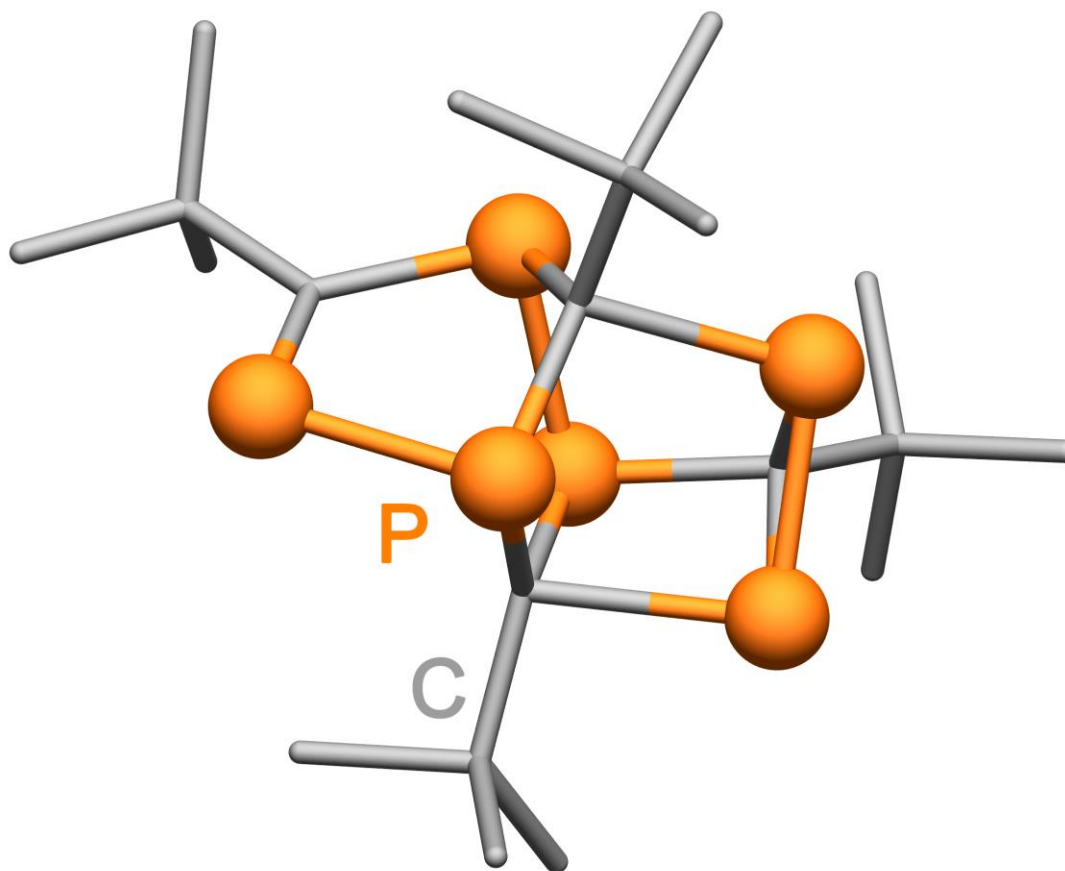
In order to obtain some useful information to understand the reaction mechanism, the reactivity of the parent arsenic complex  $[Cp''_2Zr(\eta^2-As_4)]$  with  ${}^tBuC\equiv P$  was investigated, providing a mixture of products. From the resulting raw solution brown crystals of the arsenic analogue of  $[Cp''_2Zr\{\eta^2-P_6(CtBu)_2\}]$  (**43**) were separated, which are soluble in common organic solvents such as n-hexane and toluene. The X-ray structure of **43** shows clearly as the phosphorus are in striking distance to the carbon atoms, showing that insertion of the phosphoalkyne occurs in one of the P-P and As-As bond, respectively, of the bridge-head atoms not bound to Zr. The most important structural features of **43** is that it is formed by a  $\{ZrP_6C_2\}$  core, which displays a cuneane-like structural motif (Figure 12)[121] constituted by six phosphorus atoms and two carbon atoms with the  $ZrCp''_2$  fragment inserted into one P-P bond of the cuneane core. The cuneate motif is sometimes found in polyphosphorus compounds, for example in Hittorf's phosphorus allotrope and

some polyphosphorus complexes and compounds,[122–125] being the most favorable structure calculated for a hypothetical P<sub>8</sub> molecule.[126,127]



**Figure 12.** Synthesis and ball and stick representation of the crystal structure of **43**. Hydrogen atoms are omitted for clarity. Crystal structure adapted from [117].

Compound **44** displays high solubility in all common organic solvents, showing a crystal structure (Figure 13) constituted by a framework that is similar to the carbon–phosphorus cage **43** with one tBuCP unit replacing the {Cp''<sub>2</sub>Zr} fragment, but containing four CtBu groups instead of only two as in **43**, with no vicinal CtBu groups. In the solid state structure of **44**, a certain disorder of the molecules is observed. The molecule possesses a crystallographic twofold axis through the P1-P1' bond. Therefore, the phosphorus atoms P2, P3, P4, P5, the carbon atom C2, and two tBu groups are disordered over two positions with occupation factors of 50%.

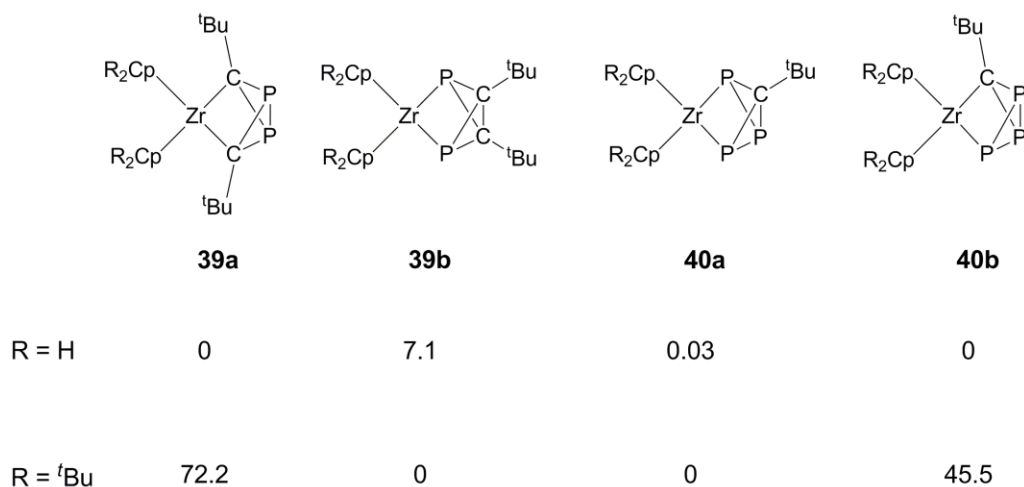


**Figure 13.** Ball and stick representation of the crystal structure of **44**. Hydrogen atoms are omitted for clarity. Adapted from [117].

The P-P and P-C bonds in **44** are single bonds but the P4-C2' bond corresponds to a P=C bond (1.713(5) Å). Seven isomers with composition  $P_6(CtBu)_4$  have been described,[128] being one of them closely related to **43** but differing in the position of the atoms P4 and C2' in the C=P bond,[129] the tBuC group and phosphorus atom in the tBuC=P unit are exchanged and, as a result, **43** contains three P-P units in contrast with only one P-P unit, one P-P-P chain, and an isolated P atom.

Nevertheless, it is important to point out that cages containing only phosphorus and C<sup>t</sup>Bu groups, such as the tetraphosphacubane (PC<sup>t</sup>Bu)<sub>4</sub>,[130] can also be obtained by oligomerization of neat <sup>t</sup>BuCP at higher temperatures[131] or by cyclooligomerization mediated by transition metal complexes[132] as well as by CuI.[133] Only isomer **39a** and not **39b** has so far been synthesized, the authors succeeding in synthesizing **40a** and not

**40b.** To shed light onto this problem, DFT calculations were carried out (Scheme 10).



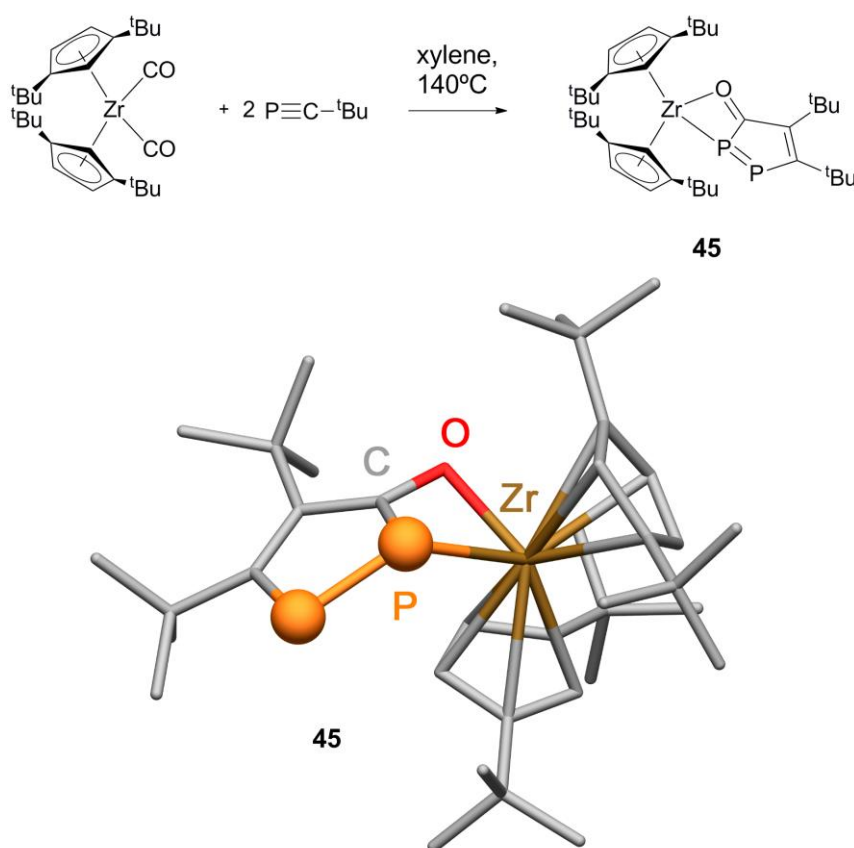
**Scheme 10.** Relative energies of the isomers of **39** and **40** calculated by DFT.

Calculations show that formation of **40a** and **40b** is almost energetically equivalent for Cp ligand (isomers energy difference = 0.03 kJmol<sup>-1</sup>), being the Cp'' isomer **40a** more stable by 45 kJmol<sup>-1</sup>. These results are in agreement with experimental isolation of **40a** respecting **40b**. Isomer **39a** is somewhat (7.1 kJmol<sup>-1</sup>) favored for the Cp ligand complex. In contrast, the Cp'' metal isomer **39b** is strongly favored over Cp isomer **39a** (by 72 kJmol<sup>-1</sup>). It was possible to detect the expected isomer **39a** by NMR spectroscopy by reaction of complex [Cp''<sub>2</sub>ZrCl<sub>2</sub>] with tBuC≡P after reducing the Zr complex. Nevertheless, complex **39a** could not to be isolated despite it was one of the major reaction products. The <sup>31</sup>P{<sup>1</sup>H} NMR chemical shift for this complex was 185.5 ppm, which is close to those of **36** (173.7 ppm) and **37** (179.1 ppm) for the Zr- P atoms.

Reaction of [Cp''<sub>2</sub>Zr(CO)<sub>2</sub>] with tBuC≡P (Figure 14) leads to new compounds that support the formation and structure of **39a**. The resulting blue-green product **45** is constituted by a diphosphacyclopentadienone ligand. In this complex a P and a O atoms are coordinated to the Zr moiety as a consequence of head-to-head coupling of the phosphalkyne. In this reaction a CO molecule is inserted into a P-C bond of the phosphalkyne. The zirconium-bound P atom shows a <sup>31</sup>P{<sup>1</sup>H} NMR chemical shift at 153.8 ppm, with a large P,P coupling constant of 430 Hz, which is in agreement with the

length of the P=P bond found in its X-ray crystal structure.

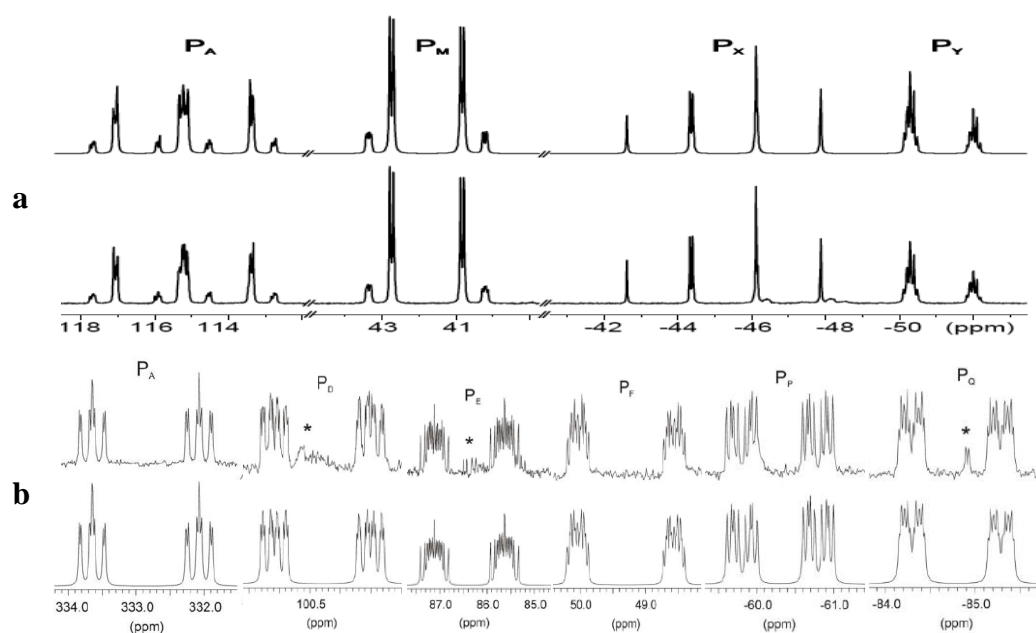
The crystal structure of **45** (Figure 14) is constituted by the new ligand obtained by the head-to-head coupling that is coordinated to the metal by a five membered ring with bonds in the usual range of P=P, C=P, and C=C double bonds. This fact indicates that over the five-membered ring a delocalized  $\pi$  system exists. The Zr atom is coordinated to the ligand by both the oxygen outside of the ring as well as the P1 atom, being the bond lengths within the expected range for similar compounds but probably due to the coordination of the O atom, the C=O double bond is slightly elongated.



**Figure 14.** Synthesis of **45** and ball and stick representation of its crystal structure; hydrogen atoms are omitted for clarity. Crystal structure adapted from [117].

The  $^1\text{H}$  NMR spectrum of **43** at room temperature shows four signals for the CH protons of the Cp'' ring and three signals for the  $^t\text{Bu}$  groups. This inequivalence of the signals, combined with large differences in the chemical shifts of the Cp'' ring protons,

5.50 ppm + 7.29 ppm, 5.32 + 7.95 ppm, lead to the assumption that Cp<sup>''</sup> ring rotation is hindered. A similar behavior with an inequivalence of the protons of the Cp<sup>R</sup> ring is observed in [ $\eta^5$ -P<sub>2</sub>(CtBu)<sub>3</sub>]CpZrCl<sub>2</sub>] as well as in [ $\eta^5$ -P<sub>3</sub>(CtBu)<sub>2</sub>]CpZrCl<sub>2</sub>].[121] The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of **43** shows a nice higher-order spectrum that was simulated as an AA'MM'XY spin system (indicated as P<sub>A</sub>, P<sub>M</sub>, P<sub>X</sub> and P<sub>Y</sub> in Figure 15a). Finally compound **44** is also highly soluble in all common organic solvents such as n-hexane and toluene. Also the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of **44** exhibits a ordered nice spectrum that was simulated as an ADEF PQ spin system (Figure 15b).



**Figure 15.** Simulated (top) and experimental (bottom) <sup>31</sup>P{<sup>1</sup>H} NMR spectra of **43** (a) and **44** (b). Adapted from SI [117].

### 1.5. Final comments

The functionalization of white phosphorus is one of the most important reactions to be tackled by chemical industry and its accomplishment in a sustainable and effective way is mandatory if the future society wants to enjoy the advantages of using phosphorus

compounds without the side effects accompanying their current production. To be really amenable this reaction should be catalytic and should avoid the use of noxious reagents. Some results appeared in the literature in recent years already show that a cost effective and ecobening catalytic production of phosphorus chemicals is possible. Now it seems clear that this reaction is feasible but more efforts are needed to achieve a truly useful and industrially practicable procedure for transforming white phosphorus into organophosphorus derivatives. Nevertheless the route toward that end is traced.

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