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Metal Free Phosphorus Butterfly Compounds

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Metal-free organophosphorus are demanded compounds due to their interesting properties in a variety of applications, spanning from fine to material chemistry. Unfortunately, their synthesis is very challenging, requiring a precise design of the reaction conditions to avoid the conspicuous formation of undesired products. The P-butterfly scaffold is considered the very first opening step of the white phosphorus tetrahedron upon selective cleavage of just one P–P bond. While the synthesis of metal-containing P-butterflies is nowadays reproducible with a variety of transition metal complexes, the metal-free analogues are still elusive and just a limited number of examples is described in the literature. The state of art on known metal-free phosphorus butterfly compounds is described herein.

1. Introduction

Elemental white phosphorus, P_4, is the main industrial source for the production of inorganic and organophosphorus compounds.[1,2] Despite of the intense research in this area, practically from the beginning of the modern chemistry, the selective functionalization of P_4 is still a growing discipline on the cutting edge of the research. From P_4 it is possible to synthesize a wide variety of P-containing inorganic and useful organic products fertilizers, detergents and food additives, fire-protection agents, drugs, semiconductors and popular chemicals such as PPh_3. The industrial production of phosphines implicates the chlorination or oxychlorination of phosphorus to PCl_n (n = 3, 5) and $POCl_3$ respectively, prior to further arylation by using halo-compounds and molten sodium under very harsh condition.[3,4] An intriguing new method for the direct, mild and – most important – catalytic arylation of P_4 to prepare arylphosphines and arylphosphonium salts was reported only in 2019.[5]

It is well known that functionalization of P_4 passes through a multistep decomposition of the P_4 core producing a plethora of different P_n (n = 1–4) products due to the difficult control of its reactivity. In the rational and selective synthesis of P_n organophosphorus compounds every stage of the P_4 degradation is very important and needs to be understood just starting from the simplest: the cleavage of just one of the six bonds of the P_4 core and substitution of the unsaturated phosphorus atoms. This process provides the 1,3-difunctionalized 1,2,3,4-tetraphospha-bicyclo[1.1.0]butanes, commonly known as phosphorus butterflies. The oxidation of P_4 by halogens to obtain PX_3 derivatives, which is the industrial procedure used to obtain PR_3 compounds, was investigated by Tattershall et al. The NMR studies showed that the butterfly halides with general formula $P_4X_nX'_{n-1}$ (X = Cl, X′ = Br) in their *exo-exo* and *endo-exo* geometries are intermediates of the reaction, corresponding to the very first step of the P_4 degradation.[6] Even if butterfly species containing iodine were not detected, calculations conducted by Peruzzini et al. strongly suggest the formation of $[I_2P_4]$ intermediates during the decomposition of P_4 to PI_3. Understanding and generalizing the formation of tetra-phosphabicyclo[1.1.0]butanes from P_4 could offer a great tool to finely control the synthesis of organophosphorus compounds from elemental phosphorus.[7]

The selective transformation of P_4 into P_4-butterflies usually is mediated by metal complexes, giving commonly rise to metal-containing products.[1,2] The rational synthesis of metal-free P_4-butterflies is accomplished by two main strategies: a) by assembly of P_n building blocks (n = 1–4), mainly by cyclization of phosphanes, [2 + 2] cycloaddition of diphosphenes and reduction of halophosphines; b) by direct P_4 activation. The latter strategy is the most intriguing synthetic procedure as a very high control of the reaction along with a fine choice of the reactants are required to cleave selectively a unique P–P bond. This last reaction is mostly achieved by bulky nucleophiles, radicals or frustrated Lewis pairs. Despite that the first metal-free P-butterfly compound was presented in 1982,[8] there are not many examples of such compounds, which will be the main subject discussed in this synopsis. For what concern metal complexes of P_4-butterflies and in general P_n compounds, extensive literature can be found elsewhere.[9–12]

2. Synthesis of P_4 butterfly compounds from P_n units

The first successful synthesis of one P_4-butterfly compound (Scheme 1) was reported by Niecke et al. in 1982. The reaction was not a direct P_4 activation but a base-mediated P–P coupling of the diaminophosphanes $R_2NHP\text{-}PClNR_2$ (**1**) and $R_2NHP\text{-}PH\text{-}NR_2$ (**2**) to give rise to the tetraphosphane **3**. Upon pyrolysis at 120 °C, **3** cyclized to **4** as a mixture of *exo-exo* (**4a**) and *endo-exo*

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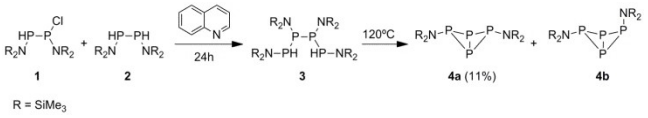


Scheme 1. Synthesis of **4b** and **4b**.[8]

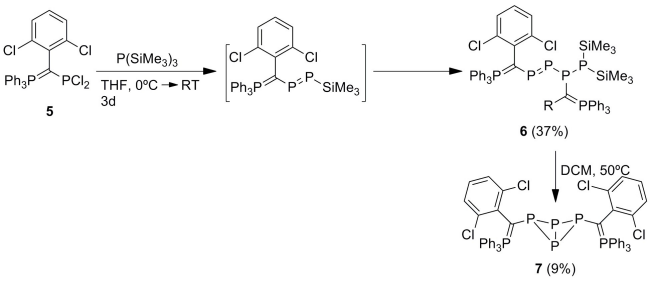
(**4b**) isomers (Scheme 1). From this mixture, isomer **4a** could be isolated by crystallization in a 11% yield.[8]

Reaction of **5** with $P(SiMe_3)_3$ produced a diphosphene that is not stable in solution and spontaneously dimerizes to **6**. Repeated crystallizations of **6** in dichloromethane led to the P-butterfly compound **7** (9% yield) by cyclization upon the loss of the trimethylsilyl substituents on the terminal P (Scheme 2). The large $^2J_{PP}$ coupling (140.6 Hz) observed in the ^{31}P NMR spectrum of **7** between the head-phosphorus atoms was justified by a strong interaction between both atoms and perhaps also a charge transfer from the yilidic carbon (Table S1).[13]

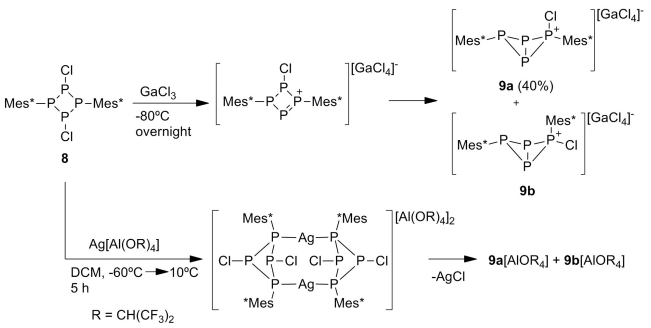
Abstraction of the chloride from $[ClP(\mu\text{-}PMes^*)]_2$ (**8**) by a Lewis acid, such as $GaCl_3$, leads to the cyclotetraphosphenium intermediate $[Mes^*P_4(Cl)Mes^*]^+$ that, at low temperatures, evolves into a *exo-exo* (**9a**) and *endo-exo* (**9b**) mixture of $[Mes^*P_4(Cl)Mes^*]^+$ within one day (Scheme 3).[14] The isomers ratio varies depending on the reaction temperature: at −80 °C it is almost similar (**9a**/**9b** = 3:4) while at −50 °C, an enrichment in **9b** is produced (**9a**/**9b** = 1:8). At room temperature, transformation of **9a** and **9b** into $[Mes^*P(H)(Cl)^tBu]^+$ occurs upon shift a ^{t}Bu group from a Mes* to a phosphorus atom, showing that the head-P display some Lewis acid behaviour.[15–19]

Attempts to trap the cyclotetraphosphenium intermediate $[Mes^*P_4(Cl)Mes^*]^+$ by using $Ag[Al\{OCH(CF_3)_2\}_4]$, led to the formation of a bimetallic silver complex, which above −30 °C thermally decomposes to a mixture of **9a** and **9b** through an intramolecular AgCl elimination (Scheme 3). The reaction also works if $Ag[B(C_6F_5)_4]$ is used as silver source but in this case, the formation of the di-silver complex was not observed.[20]

Complex **10** can be obtained in 40% yield by addition of P_4 into a solution of $(TlAr^{Dipp})_2$ in THF.[21] In this thallium complex, the central P_4 core is formally isolobal with the reported anions of functionalized 1,3-butadienes[22,23] and 1,2-bis(diphosphinyl) ethenes-Pt complexes.[24] Attempts to obtain a diaryl-1,3-phosphabutadiene by oxidation of **10** with I_2 resulted in the



Scheme 2. Synthesis of **7**.[13]



Scheme 3. Synthesis of **9a** and **9b** starting from $[ClP(\mu\text{-}PMes^*)]_2$ (**8**).[14,20]

formation of the butterfly compound **11** as a mixture of *exo-exo* (**11a**) and *endo-exo* (**11b**) isomers (Figure 1, Scheme 4). The reaction was proposed to proceed through a 1,3-phosphabutadiene intermediate that isomerizes to the bicyclic product, in a similar manner to that suggested for the isomerization of 1,3-butadiene into bicyclobutane. Interestingly, crystallization of the reaction crude in *n*-hexane gave rise to the less thermodynamically stable **11b** in a 53% yield. If benzene was used as crystallization media the compound **11a** was isolated.

A different synthetic route involves the [2 + 2] cycloaddition of diphosphenes, which may proceed thermally or photochemically. Photoactivation of diphosphenes was explored by Jutzi et al. studying by NMR the products resulting from the reaction of the diphosphenes Cp*P=PCp* (**12**) and Cp*P=PMes* (**14**) under UV irradiation. The authors proposed that an initial tetrasubstituted [2 + 2] cycloaddition product evolves to the

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Antonio Romerosa graduated in Chemistry in 1987 (U. of Granada) and received his PhD (U. Autonoma de Barcelona) in January 1992. The same year he undertook a postdoctoral research position at the ISSECC CNR (now ICCOM CNR) in Florence (Italy), before becoming Lecture Professor (1997) and finally Full Professor (2009) at the University of Almeria (Spain). His research interests range over homogeneous catalysis and organometallic chemistry in water, phosphorus chemistry, photo-inorganic-chemistry, bioinorganic chemistry and natural stones.

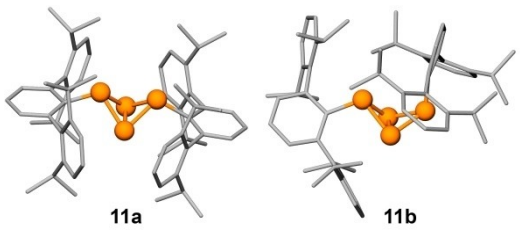
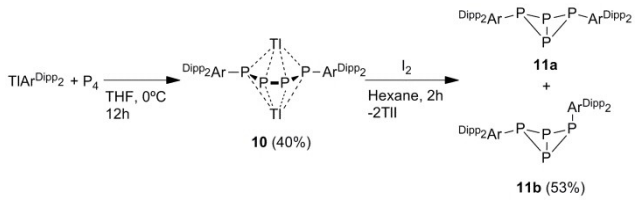


Figure 1. Molecular structure of **11a** and **11b**.[21] Hydrogen atoms have been omitted for clarity.



Scheme 4. Synthesis of **11a** and **11b**.[21]

reported butterfly compounds **13**, **15a** and **15b** after elimination of transannular substituents. In the case of **15a** and **15b** the leaving groups are the less hindered Cp* (Scheme 5).[25]

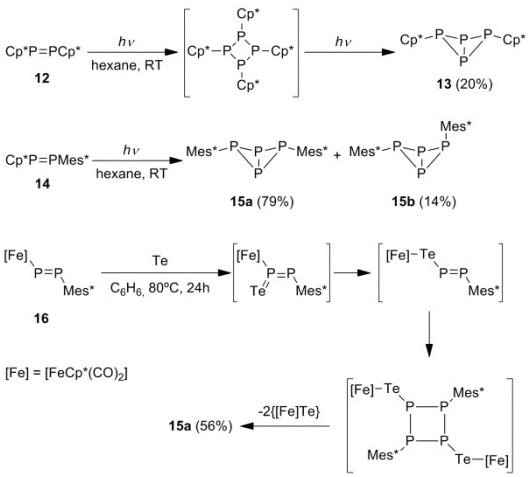
Complex **15a** can be obtained by [2+2] cycloaddition of diphosphenes by a thermal process, as shown by Weber et al. concurrently with Jutzi's photochemical approach, during an investigation concerning the reactivity of the iron diphosphenyl complex **16** against chalcogens. When this complex was treated with tellurium in refluxing benzene, compound **15a** was obtained with a 56% yield. The reaction seemed to proceed through insertion of a Te atom at the Fe–P bond, followed by cycloaddition and final elimination of an oxytelluride iron complex (Scheme 5).[26]

Another synthetic route employing the [2+2] cycloaddition of diphosphenes was reported years after by Cowley and coworkers, who obtained **18** marginally during an investigation conducted to determine the decomposition products of the silyl diphosphene $(Me_3Si)_3CP{=}PSiMe_3$ (**17**) at −20 °C in Et_2O (Scheme 6).[27] The authors suggest that the formation of **18** proceeds through a path similar to the previously reported photocycloaddition of diphosphenes **12** and **14**. Nevertheless, whether the reaction proceeded thermally or photochemically was not reported.

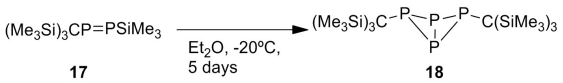
Upon warming to 20 °C the ammonium-diphosphenes **19–21** decomposes forming, among other products, the starting neutral aminodiphosphene and $[Mes^*PP]^+$ cations that suffer [2+2] cycloaddition. The resulting cyclotetraphosphane undergoes reductive elimination of the bridgehead amino substituents to give the bicyclotetraphosphanes **15a** and **22** in an approximately 1:1 ratio (Scheme 7). The reaction can be driven to the formation of **15a** upon acidification of a solution of [Ar*P=P-NHAr*] with CF_3SO_3H. The high tendency to the cycloaddition under the latter conditions leads to the formation of **15a** even at −78 °C.[28]

Although the spectral data for **15a** were unambiguous, the characterization of **22** was probably misinterpreted, as shown by Villinger et al. years later. When the authors tried to reproduce the previously mentioned reaction,[28] they obtained *endo-exo*-Mes*P_4Mes* (**15b**) instead of **22**, together with the *exo-exo* isomer **15a**.[29] In the same work, the selective synthesis of **15a** and **15b** were also set up, starting in both cases from the cyclotetraphosphane **23**. When this compound was reduced with Mg only **15a** was obtained in addition to a ca. 5% of impurities, yielding a 73% of **15a** after processing. On the other hand, reaction of **23** with 1,3,4,5-tetramethyl-imidazol-2-ylidene led to a 1:12 excess of **15b** with respect to the thermodynamically more stable **15a**. In the latter synthesis, along with **15a** and **15b**, also other side products formed, but **15b** could be isolated in a 14% yield (Figure 2, Scheme 8).

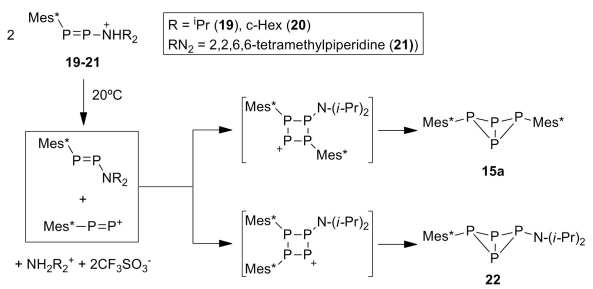
In 1985, Jutzi et al. explored the use of different halophosphines under reductive conditions to obtain P_4 butterflies. As a result of these studies, the previously described Cp* substituted



Scheme 5. Photochemical synthesis of **13**, **15a** and **15b** and thermal synthesis of **15a**.[25,26]



Scheme 6. Decomposition of **17** to **18**.[27]



Scheme 7. Proposed mechanism for the formation of **15a** and **22** involving the ammonium phosphenes **19–21**.[28] See also ref.[29]

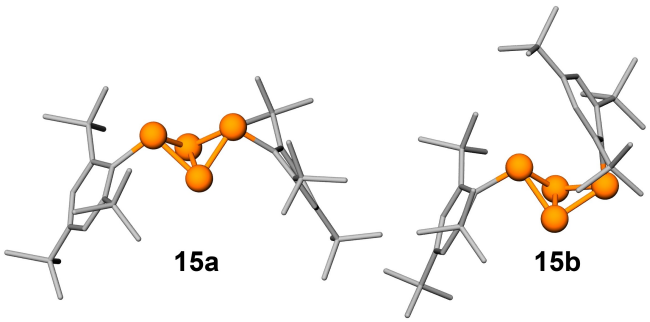
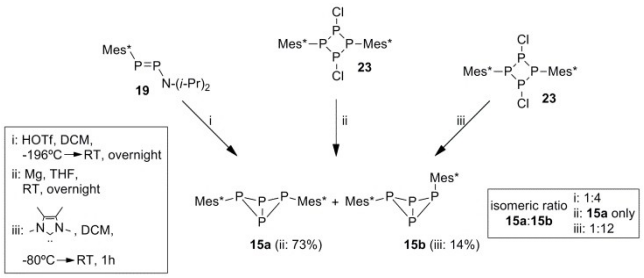


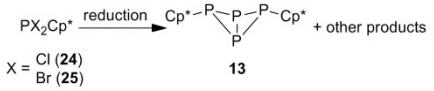
Figure 2. Molecular structure of **15a** and **15b**.[29] Hydrogen atoms have been omitted for clarity.



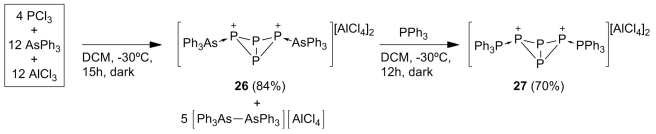
Scheme 8. Strategies developed by Villinger et al. for the synthesis of **15a** and **15b**.[29]

butterfly **13** was obtained upon reduction of the halophosphanes PX_2Cp^* (X = Cl (**24**), Br (**25**)) with Li, K, Mg or Li-naphthalenide in THF solution at −80 °C (Scheme 9). The reactions provided also unidentified P compounds, cyclic P_3 and monocyclic P_4, which could not be fully characterized.[30]

Dicationic P_4^{2+} butterfly compounds were elegantly synthesised by Weigand et al. upon reduction of PCl_3 by means of $AsPh_3$ as Lewis basic reducing agent and a halide abstractor (Scheme 10). The resulting compounds **26** and **27**, which are $AsPh_3$ and PPh_3 complexes of P_4^{2+} respectively, were obtained in good yields (**26**: 84%; **27**: 70%) (Figure 3, Scheme 10).[31] Compound **27** comes from the arsine-phosphine substitution in **26**. It is interesting to point out that the ^{31}P resonance of



Scheme 9. Reduction of **24** and **25** to give **13** and other products.[30]



Scheme 10. Synthesis of the butterfly dications **26** and **27**.[31]

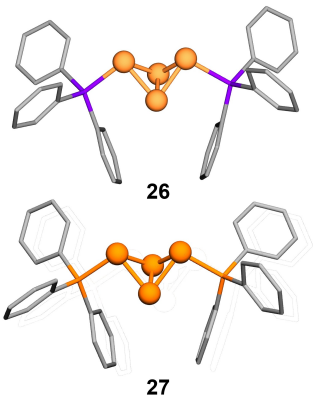
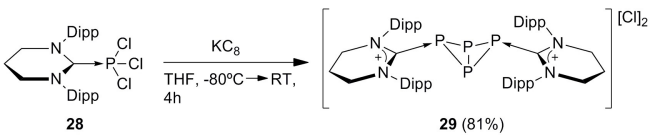


Figure 3. Molecular structure of **26** and **27**.[31] Hydrogen atoms have been omitted for clarity.

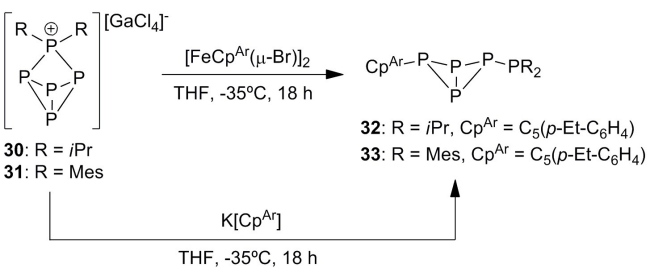
phosphonium heads in **26** and **27** is considerably shifted to higher field with respect to neutral P_4 butterflies (Table S1).

Following probably the same reaction pathway that leads to the formation of Weigand's P_4^{2+} cations, Jones et al. obtained NHC substituted phosphorus butterfly compounds starting from NHC-PCl_3 moieties: reduction of [(NHC)PCl_3] (**28**) with KC_8 in THF at −80 °C gave rise to the dicationic $[(NHC)_2(\mu\text{-}P_4)][Cl]_2$ (NHC = C{N(Dipp)CH_2}$_2$$CH_2$) (**29**) (Scheme 11)[32]

Finally, the synthesis of P_4-butterflies starting from P_n building blocks can also proceed by opening of P_5 cations. Reacting the bicyclopentaphosphorus cations $[P_5R_2][GaCl_4]$ (R = *i*Pr (**30**), Mes (**31**)) with the iron cyclopentadienyl dimer $[FeCp^{Ar}(\mu\text{-Br})]_2$ ($Cp^{Ar} = C_5(p\text{-Et-}C_6H_4)_5$) the unsymmetrical phosphacyclobutanes **32** and **33** were obtained (Scheme 12). Although the NMR analysis of the reaction mixtures indicated the formation of the products, their isolation was unsuccessful, so that a different and more convenient approach employing the cyclopentadienide $K[Cp^{Ar}]$ was set up. After reaction in toluene at −35 °C, the more hindered derivative **33** could be synthesized



Scheme 11. Synthesis of **29**.[32]



Scheme 12. Synthesis of **32** and **33**.[33]

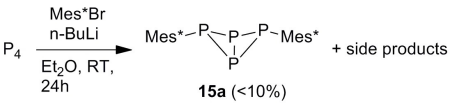
in 37% yield using K[Cp^{Ar}], while the *i*Pr substituted **32** was found unstable and was isolated only trapping it as a $GaCl_3$ adduct (Scheme 12).[33]

3. Direct activation of P_4

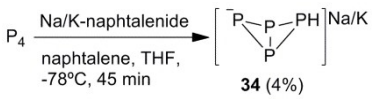
Early attempts to activate the P_4 tetrahedron were conducted in the 1960s by Rauhut et al. using strong nucleophiles such as Grignard or organolithiums. The poor reaction control resulted in the complete decomposition of P_4 to form a complex mixtures of primary, secondary and eventually tertiary phosphines.[34] In terms of selectivity and reaction control, more or less the same results were obtained when white phosphorus were reacted with alkynyls[35] or organolithium reagents in the presence of trimethylsilyl chloride.[36]

The first synthesis of a P_4 butterfly starting from white phosphorus was published in 1985 by Fluck et al., who reacted P_4 with Mes*Br in the presence of *n*-BuLi (Mes* = 2,4,6-^{t}Bu-(C_6H_2)). After workup, **15a** was obtained in low yield (< 10%) (Scheme 13).[37,38] This synthetic approach revealed that the selective cleavage of just one P–P bond of the P_4 core needs bulky reactants to prevent further and non-controlled reactions.

A different approach for the synthesis of P-butterflies compounds starting from P_4 consists in the radical-driven homolytic cleavage of one P–P bond in the molecule of white phosphorus. Following this route, Baudler and co-workers detected the anion $[HP_4]^-$ (**34**), which could be also accessed in



Scheme 13. Synthesis of **15a**.[37,38]



Scheme 14. Formation of **34** in solution.[39]

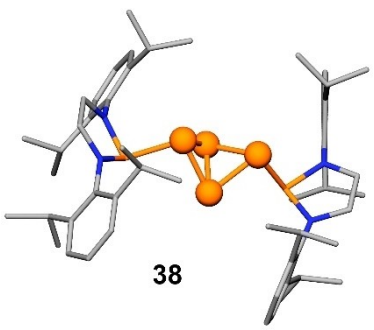


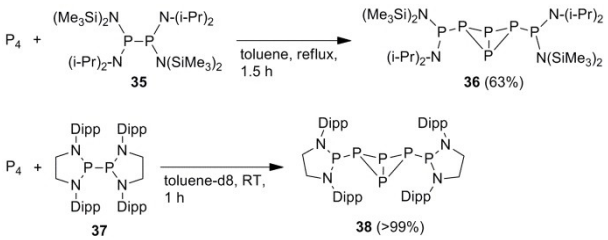
Figure 4. Molecular structure of **38**.[41] Hydrogen atoms have been omitted for clarity.

low yield (4%, based on NMR) by reduction of P_4 with Na/K-naphthalenide at low temperature. In DMF solution, compound **34** was stable at −78 °C up to 70 h and 1 h at room temperature (Scheme 14).[39] The ^{31}P NMR of **34** shows the resonance of the anionic P atom at 71.3 ppm (Table S1), while head-bridgehead shift of the hydrogen was not observed.

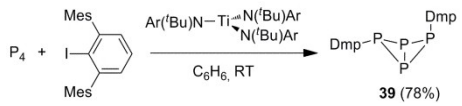
Persistent or stable P-centred radicals can be successfully used for the radical activation of P_4. For example, bis(amido) phosphido butterfly type compounds **36** and **38** can be obtained by reaction of P_4 respectively with the diphosphines **35** and **37** through the formation of P-centred radicals that promote the homolytic cleavage of a single P–P bond (Figure 4, Scheme 15). The $^{31}P\{^1H\}$ NMR spectra of these compounds show the expected AA'MM'X_2 pattern (Table S1 in supporting information).[40,41]

In 2010 Cummins et al. reported the synthesis of *endo-exo*-(Dmp-P_4-Dmp) **39** by treating P_4 with Dmp-I in the presence of the complex Ti(N[^{t}Bu]Ar)$_3$ (Dmp = 2,6-$Mes_2C_6H_3$; Ar = 3,5-dimethylphenyl). Reduction and homolytic abstraction of the ioide from the Dmp-I by the titanium complex produces the radical Dmp$^\bullet$, which further attacks the P_4 molecule. Due to the high steric demand of Dmp$^\bullet$, the degradation of P_4 stops after the cleavage of the first P–P bond, giving **39** as the exclusive product (Scheme 16).[42]

A different approach was employed by Scheer et al. through the in situ generation of Cp^R-radicals (Cp^R:Cp^{BIG} = C_5(4-(n-Bu)$C_6H_4)_5$ (**40**), Cp''' = $C_5H_2{}^tBu_3$ (**41**), Cp* = C_5Me_5 (**42**) and Cp^{4iPr} = C_5H(i-Pr)$_4$ (**43**)) (Figure 5) achieving the activation of white phosphorus to yield a series of fully organic Cp^R substituted butterfly compounds.[43] This was the first example of a P_4 direct functionalization headed by a sp^3 carbon. The oxidation of NaCp^{BIG} to Cp$^{BIG\bullet}$ by means of CuBr and further reaction with P_4 leads to the homolytic cleavage of one P–P bond and subsequent formation of the respective 1,3-disubstituted tetraphosphabicyclo[1.1.0]-butane. In the same work it was also shown that the reactions with smaller cyclopentadienyls such as Cp''', Cp* or Cp^{4iPr} does not afford the respective Cp$^R{}_2P_4$ compounds, which was justified considering the higher reac-



Scheme 15. Synthesis of **36** and **38**.[40,41]



Scheme 16. Synthesis of **39**.[42]

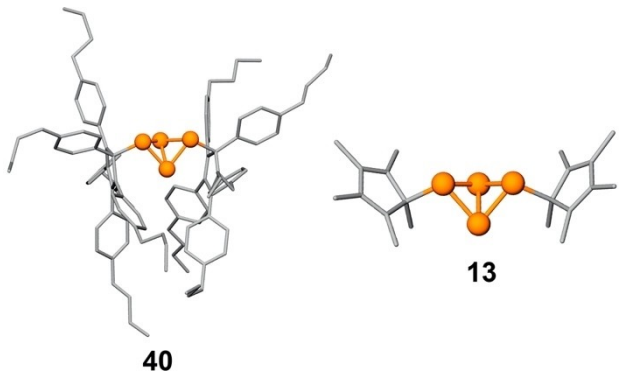
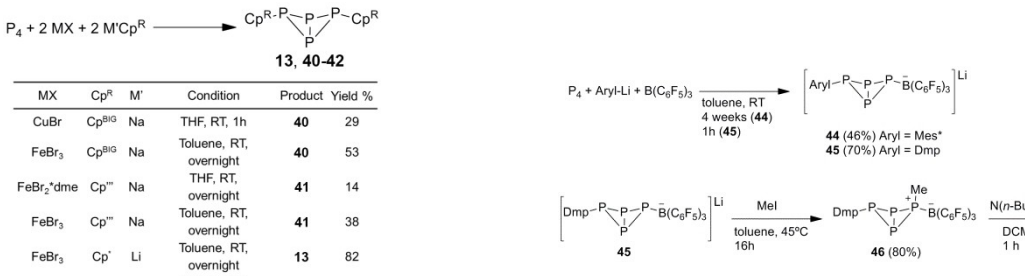


Figure 5. Molecular structure of **40** and **13**.[43] Hydrogen atoms have been omitted for clarity.

tivity of the smaller cyclopentadienyl radicals, caused by less mesomeric stabilisation and lower sterical hindrance. To bypass the problem, the Cp^R salt was reacted with $FeBr_3$ to form the respective $[\{Cp^RFe(\mu\text{-}Br)\}_2]$ prior to the addition of P_4. In these conditions, the Cp^R moiety was transferred from the iron to P_4, leading to the respective $Cp^R{}_2P_4$ in a 38%-82% yield (Scheme 17). The isomeric distributions obtained with Cp''' and Cp^{4iPr} suggested that the reaction occurs through a radical mechanism.

Recently P-butterfly compounds were synthesized from P_4 using frustrated Lewis pairs. This route was explored by Tamm et al. by reacting P_4 in benzene/toluene at room temperature with a mixture of 1,3-ditertbutyl-imidazol-2-ylidene and tris (pentafluorophenyl)borane. Under this condition, heterolytic cleavage of just an unique P–P bond of the P_4 molecule is achieved, obtaining **43** in 67% yield (Scheme 18). In this compound the imidazolyl group was found to be bonded to the P_4 scaffold through the C3 carbon. Based on spectroscopic evidences together with DFT calculations, the authors proposed that the mechanism beyond the formation of **43** should start from the phosphorus-borane adduct. Further, a nucleophilic attack of the carbene gives the P-butterfly intermediated that is substituted with the normal carbene (C1-bonded). Finally, an intramolecular 1–3 shift of the carbene ring gives compound **43**, which bears the abnormal carbene (C3-bonded), being more stable by 14.3 kcal/mol than the C1-bonded.[44]

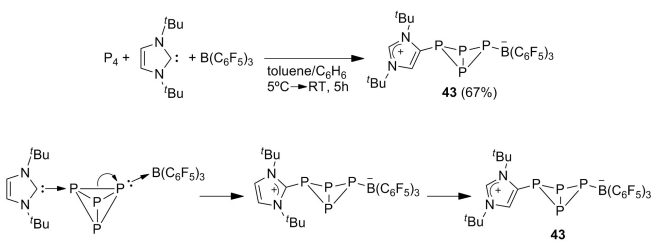
Substantial contributions about the direct activation of P_4 by means of frustrated Lewis pairs was given by Lammertsma et al., who also marked further steps to functionalize some of the obtained derivatives. In 2014 this group published the synthesis of the new and unprecedented asymmetric P_4 butterfly anions **44** and **45** (Scheme 19).[45] The synthesis involved a sterically demanding nucleophile and a Lewis acid to imitate a frustrated Lewis pair. Upon the addition of toluene to a stoichiometric mixture of P_4, $B(C_6F_5)_3$ and the nuclephiles Mes*Li or DmpLi. The anions $[(Ar)(\mu\text{-}P_4)(B(C_6F_5)_3)]^-$ formed over a period of 4 weeks by using Mes*Li while only 1 h was needed when DmpLi was used (Ar = **44** Mes*, **45**: Dmp) (Scheme 19). DFT calculations suggested that the reaction occurs in two steps: nucleophilic attack of the litiated Dmp onto P_4 with consequent cleavage of one P–P bond (-20.6 kcal mol^{-1}) and further trapping of the formed anion by $B(C_6F_5)_3$ (−23.8 kcal mol^{-1}). The next step implicates the methylation of **45** by means of MeI, giving rise to the neutral compound **46** (Figure 6), which upon deborylation finally afforded the asymmetric compound $[(Dmp)(\mu\text{-}P_4)(CH_3)]$ (**47**). Unfortunately, at-



MX	Cp^R	M'	Condition	Product	Yield %
CuBr	Cp^{BIG}	Na	THF, RT, 1h	**40**	29
$FeBr_3$	Cp^{BIG}	Na	Toluene, RT, overnight	**40**	53
$FeBr_2$*dme	Cp'''	Na	THF, RT, overnight	**41**	14
$FeBr_3$	Cp'''	Na	Toluene, RT, overnight	**41**	38
$FeBr_3$	Cp^*	Li	Toluene, RT, overnight	**13**	82
$FeBr_3$	Cp^{4iPr}	Li	Toluene, RT, overnight	**42**	62

Scheme 17. Synthesis of **13** and **40–42**.[43]

Scheme 19. Synthesis of **44–47**.[45]



Scheme 18. Synthesis (top) and proposed mechanism (bottom) for the formation of **43**.[44]

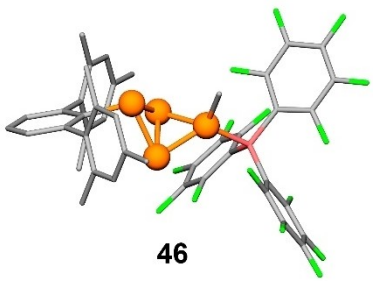


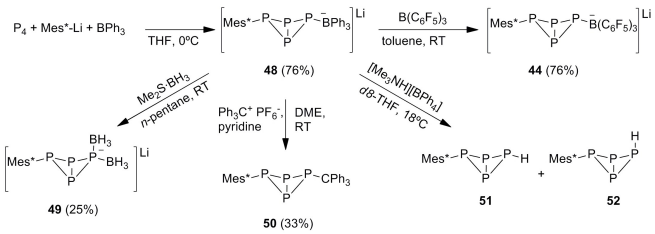
Figure 6. Molecular structure of **46**.[45] Hydrogen atoms have been omitted for clarity.

tempts to isolate **47** failed, but it was unambiguously characterized by NMR.

Further investigations, conducted to increase the reactivity of the borylated wingtip of **44**, used a Lewis acid less strong than $B(C_6F_5)_3$ to obtain more reactive $[RP_4]^-$ species (Scheme 20). Upon using BPh_3 as trapping agent in THF at 0 °C, product **48** (Figure 7) was conveniently obtained (76% yield). Functionalization of **48** by replacement of the Lewis acid could be achieved via substitution of BPh_3 with $B(C_6F_5)_3$ to give **44**. Treatment of **48** with an excess of $Me_2S{\cdot}BH_3$ led to the $[RP_4]^-$ transfer also to the smaller borane BH_3, leading to **49** as lithium or tetraphenylphosphonium salt after cation exchange (Figure 7). Additionally, the authors showed that **48** is also susceptible of deborylation and P–C bond formation, which can be achieved by using an all-hydrocarbon Lewis acid such as Ph_3C^+. This reaction finally provides the *exo-exo* Lewis-acid-free butterfly **50** (Scheme 20).[46] Nicely, compound **48** can be also the starting point to obtain neutral monosubstituted butterflies. This can be achieved by elimination of the Lewis acid upon protonation of **48**. Treatment of the latter compound with $[Me_3NH]Cl$ gave rise to its quantitative conversion (>99%) into *exo-exo* (**51**) and *exo-endo*-Mes*P_4H (**52**). Both isomers decompose at room temperature into Mes*PH_2 through a [3 + 1] fragmentation.[47]

4. Concluding Remarks

The state of the art regarding the synthesis of metal-free P-butterflies is summarized. These compounds represent a case study for the selective opening of the P_4 tetrahedron but also a possible starting point for the synthesis of new organophosphorus derivatives. Although these compounds were discovered in the early 1980s, just few examples have been described in literature and methods targeted to their selective functionalization were developed only recently starting from white phosphorus (P_4) and P_n building blocks. What emerges from the investigations is that the electronic and steric properties of the wingtip substituents are crucial in order to obtain stable P-butterflies. The use of P_2 building blocks as reactants for [2 + 2] cycloadditions of diphosphenes is one of the most reported synthetic methods but suffers of low control of the product isomeric distribution. Interestingly, simple and cheap P_1 reactants such as PCl_3 revealed to be an adequate starting point for one- or two-steps synthesis of remarkable cationic or neutral P_4-butterflies, guaranteeing certain stereo-control when the reaction conditions are properly chosen. For what concerns the intriguing direct activation of the P_4 tetrahedron to selectively form tetraphosphabicylobutanes, outstanding examples have been published, but quantitative procedures have been set up only in the last few years employing radicals or frustrated Lewis pairs. The relatively good stability and lower bulkiness of the unsymmetrical borylated derivatives obtained by the latter method permit to explore further functionalization of the wingtips.



Scheme 20. Synthesis and reactivity of **48**.[46,47]

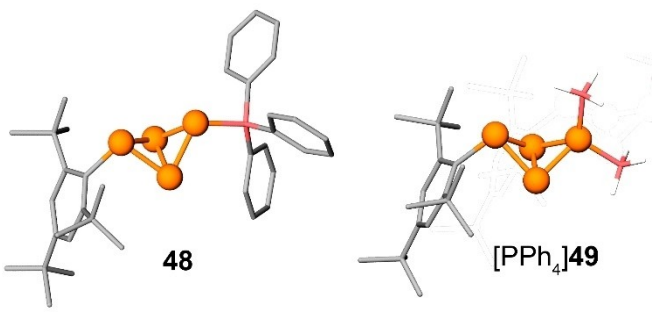


Figure 7. Molecular structure of **48** and $[PPh_4]$**49**.[46] Hydrogen atoms have been omitted for clarity.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: Butterfly compounds · Metal free compounds · Phosphorus · White phosphorous

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