From a $P_4$ butterfly scaffold to cyclo- and catena-$P_4$ units†

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The activation of small molecules is an active research topic. This research area focuses mainly on inert molecules such as $H_2$, $N_2$, $CO_2$, and $CH_4$ since their functionalisation might be important to solve e.g. energy problems. However, this research area also includes highly reactive compounds such as white phosphorus ($P_4$) where the focus is to control its reactivity. In industrial applications, $P_4$ is an important starting material for the synthesis of organophosphorus derivatives. However, their synthesis proceeds via multistep reactions with low atom economic efficiency. To increase the sustainability, a direct and selective functionalization is desired. Therefore, the degradation of tetrahedral $P_4$ in the presence of reactive main group compounds and transition metal complexes is investigated (Scheme 1, top). Typically, harsh reaction conditions are needed to generate these reactive metal species.7–12 In the field of $P_4$ conversion, work was done by the Scherer group, e.g. by showing that the photolysis of $[Cp''Fe(CO)_{2}]_n$ ($Cp'' = \eta^5-C_5H_5Bu_2$) in the presence of $P_4$ leads to $[Cp''Fe_3(CO)P_4]_n$ ($n$ = 3, 4 type A, $n$ = 2 type B, $n$ = 1 and $n$ = 0 type D) by successive decarbonylation (Scheme 1, top).6 Comparable results were obtained via thermolytic reactions of $P_4$ with $[Cp''Fe(CO)_{2}]_9$ ($Cp'' = \eta^5-C_5H_5Bu_2$), $[Cp^*Co(CO)]_{10}$ ($Cp^* = \eta^5-C_5Me_5$) and $[Cp^*Co(Pr_2Im)(\eta^5-C_5H_3Me)]^{10,14}$ ($Pr_2Im = 1,3$-di-isopropylimidazol-2-ylidine), respectively. The thermolysis of $[Cp^*Ni(CO)]_2$ leads to complexes of the type $E$.15 In molten GaCl$_3$, $P_4$ can also be converted by in situ generated Ph$_2$P$_2^{12}$ leading to the insertion of phosphonium cations into several P–P bonds to form cationic $P_4(PPh_2)_3$ (type A), $P_4(PPh_2)_2$ (type C) and $P_4(PPh_2)_3$ (type F) compounds.

Conversions of $P_4$ at mild conditions is an overall goal in this chemistry, which can be achieved with coordinative unsaturated complexes,16,17 like the triple-decker complex $[[Cp'/Co]_2[\mu-C_2H_4]]_{18}$ In solution it dissociates into the 14-valence-electron (VE) fragment $[Cp'/Co]$ and reacts readily with complexes bearing intact tetrahedral $P_4$ units to cyclo-$P_4$ (type B) containing derivatives.16 On the other hand we showed that the formation of the butterfly complex $[[Cp''/Fe(CO)]_2[\mu_1^{11-1}P_4]]$ (1) by the reaction of $[Cp''/Fe(CO)]_2$ with $P_4$ does not need thermal activation and already occurs quantitatively at room temperature.19 The reactivity of 1 is very versatile, since the reaction with PhC≡CPh or $P≡C$Bu gives access to triphospholyl- and tetraphospholyl-containing iron complexes.20 We could also show that 1 has the properties of a chelate ligand (Scheme 1, bottom, coordination type I).21,22 Here, the $P_4$ butterfly scaffold coordinates to various transition metal-based

Scheme 1 Top: Schematic overview of the first steps of the successive degradation of the $P_4$ tetrahedron. Charges and lone pairs of electrons are omitted for the sake of simplicity. Bottom: Donor capabilities of 1 and selected examples of the resulting complexes.
Lewis acids via the two “wing tip” phosphorus atoms. However, in the presence of a d⁶ metal Lewis acid like Fe(n) that bears ligands that can easily be substituted, an unusual isomerisation of the butterfly unit (σe⁻ donor, coordination type I) to an aromatic cyclo-
P₂R₂ unit (6σe⁻ donor, R = [Cp*’Fe(CO)₂]₃, coordination type II) is observed, giving access to the unique homoepic octaphosphorus sandwich complex [[(Cp*’Fe(CO)₂)₂(μ₃-n)₃:1:1-P₄]⁻Fe₂[P₆]₂].²²° To obtain deeper insight into the isomerisation reaction of 1, it was reacted with various 3d metal Lewis acids to give mainly coordination as a chelating ligand, but in one case an isomerisation via a redoxreacation to Co(n) occurred.²² Since the availability of 3d⁶ metal-based Lewis acids like Fe(n) and Co(n) is limited, the question to use 4d and 5d transition metal complexes, which typically yield products with a higher stability, came into mind. This might alter the reaction outcome in general. Herein, we report on the reactivity of 1 towards Ru(n), Rh(n), and Ir(n)-based Lewis acids, surprisingly leading exclusively to an isomerisation to form cyclo- and also catena-P₄ containing complexes.

A method to generate unsaturated transition metal fragments in solution is to treat the corresponding metal halide precursor with an excess of a thallium(s) salt that bears a weakly coordinating anion to eliminate poorly soluble thallium(s) halides. This was used to generate the solvent-stabilized [CH₃CN or CH₂Cl₂] species “[CymRu][PF₆]₂” (Cym = para-cymene) and “[Cp*M][PF₆]₃” ([M = Rh, Ir] in situ). These metal fragments react smoothly with 1 leading to [[(Cp*’Fe(CO)₂)₂(μ₃-n)₃:1:1-P₄][M][PF₆]] (2: LM = CymRu; 3: LM = Cp*Rh; 4: LM = Cp*Ir; Scheme 2). Complexes 2–4 feature all cyclo-P₂R₂ units that coordinate the central [LM]²⁻ fragments. This finding reveals that the isomerisation of the P₄ butterfly moiety (4σe⁻ donor, coordination type I) to a cyclo-P₂R₂ ligand (6σe⁻ donor, coordination type II) is a general feature, not only bound to 3d metals, if the 18 VE rule can be fulfilled and a d⁶ metal

![Scheme 2](https://example.com/scheme2.png)

**Scheme 2** Synthesis of the isomerisation products starting from 1. The yields in italics are based on the ³¹P NMR spectra of the crude reaction mixture, while the second value refers to the isolated yield.

The structural core of 3 exemplifies the one of 4 as well. Hydrogen atoms are omitted for clarity. A.d.p. are shown at 50% probability level.

**Fig. 1** Cationic parts of the molecular structures in solid state of 2 and 3. The P₄ ligands shown in italics are based on the ³¹P NMR spectra of the crude reaction mixture, while the second value refers to the isolated yield.
elimination, followed by the insertion of the [Cp’/’Fe(CO)] fragment into one of the adjacent P–P bonds, leads to 
\[\text{[(Cp’/’Fe(CO))]}_{2} \text{[(Cp’/’Fe(CO))]}_{2}(\mu_{1,2,3,4}) \text{[(Cp’Ru)]} \text{[PF}_{6}] \] (6) in moderate yield (22%, 70% according to \(^{31}\)P NMR spectroscopy). Complex 6 features a metallo-tetraphosphaene unit and represents a formally twofold activated P₄ butterfly complex 1. The formation of 6 also highlights the high diversity in different binding modes of the P₄ unit in 1. Furthermore, 6 should be handled with caution, as further treatment with UV light leads to subsequent transformations and finally to decomposition.

The insertion of Fe₁ into the P₁–P₄ bond leads to the formation of the 1S-2R-3R-4R-5S configuration (Fig. 2) while insertion into the P₃–P₄ bond leads to the formation of the 1R-2S-3S-4S-5R configuration (Fig. S5, ESI†). The two enantiomers form a racemate and are both present in the solid state structure. The central Fe₄ metallocycle reveals an envelope conformation with an almost planar catena-P₄ unit (dihedral angle P₁-P₂-P₃-P₄ of 7.73(3)°). The three Fe–P distances vary from 2.2413(6) to 2.2539(6) Å and are in the range of typical Fe-P single bonds. The P–P bond distances vary from 2.1335(8) to 2.1446(8) Å and are in a range between a P–P single and a P–P double bond. The [Cp’Ru] fragment is located over the center of the metallocycle with two shorter Ru–P distances (Ru₁–P₁: 2.3592(5); Ru₁–P₄: 2.3513(6) Å) and two longer Ru–P distances (Ru₁–P₂: 2.4454(5); Ru₁–P₃: 2.4469(6) Å). This results in a shift of the ruthenium fragment towards the [Cp’/’Fe(CO)] fragment and raises the question of a Ru–Fe interaction. While the Ru₁–Fe₁ distance of 2.9052(4) Å is longer than a predicted single bond (2.41 Å),\(^{23}\) the distance is still significantly smaller than the sum of the van der Waals radii (4.90 Å).\(^{26}\) A complex similar to 6 is for example the dirhodium complex \[\text{[(Cp’Rh(CO))]}_{2}(\mu_{1,2,3,4}) \text{[(Cp’Rh)]} \] (III, Cp’ = \(\eta^{5}\)-C₅Me₅Et).\(^{11}\) Although, III has two electrons more than 6, the P–P bond lengths (2.150(3)–2.160(3) Å) are comparable. However, in III, no metal–metal interaction was observed since the \(\eta^{5}\)-coordinated [Cp’Rh] fragment is located over the center of the P₄ chain. The complex [K(dme)]\(_{2}\)([Me₆BIAN]Co \(\mu_{1,2,3,4}) \text{[Ga(nacnac)]} \] (IV, dme = dimethylolethylen, Me₆BIAN = 1,2-bis[2,4,6-dimethylphenylimino]acenaphthene, nacnac = CH(CMeN(2,6-iPr₂C₆H₃))₂) exhibits a similar, however main group-based, heteroatomic core, but without significant metal–metal interaction. The bond lengths (2.1198(7)–2.1286(7) Å) are comparable to the ones in 6. A similar carbon-based complex is \[\text{[(CpFe(CO))]}_{2}(\mu_{1,2,3,4}) \text{(CR–(CH)₂–CR}) \text{[(Cp’Ru)]} \] (R = CMe₂OH) where the [Cp’Ru] fragment is \(\eta^{5}\)-coordinated to the cyclopentadiene ring of iron.\(^{28}\) The reported Ru–Fe distances of 2.6688(7)–2.6743(7) Å are shorter compared to the one in 6 and are described as Ru–Fe single bonds.

The \(^{1}H\) NMR as well as the \(^{31}P\)\(^{1}H\) NMR spectrum (CD₂Cl₂) of a crystalline sample of 6 points to the presence of two conformers in solution which are formed in a ratio of 1:1.7. At room temperature, both conformers are involved in dynamic processes leading to signal broadening. This is most likely caused by the rotation of either one of the Cp’/’ ligands or the whole [Cp’/’Fe(CO)]₂ fragment. At lower temperatures, the rotation is slowed down resulting in sharp signals.\(^{‡}\) The \(^{31}P\)\(^{1}H\) NMR spectrum shows an AMXY spin system for both isomers which resonate at similar chemical shifts so that they mainly overlap. The signals at \(\delta = 501.1, 465.5, 144.1\) and 126.0 ppm can be assigned to the main species while the signals at \(\delta = 500.9, 457.0, 145.2\) and 126.5 ppm correspond to the minor species. With chemical shifts and coupling constants (Table S7, ESI†) being almost identical, the structure of the two species must be very similar.\(^{‡}\) However, these findings compare well to \[\text{[(Cp’Fe)}_{2}(\mu_{1,2,3,4}) \text{[(Cp’Fe(CO)]} \] (δ = 567.2 and 169.1 ppm) and \[\text{IV} \] (δ = 74.0 and −125.4 ppm) showing both an AA’XX’ spin system for the catena-P₄ unit. The dirhodium complex III (δ = 201.4 and 150.8 ppm) reveals an AA’NMXX’ spin system (N and M correspond to Rh).

To obtain deeper insight into the electronic structure of 6, DFT calculations at the BP86/def2-TZVP level were performed which show the absence of a direct Ru₁–Fe₁ bond. Instead, a multi-center bond with bond contributions of Ru₁ = 40%, Fe₁ = 25% and P₁ = P₄ = 17.5% is present. The Wiberg Bond Index of the Ru₁–Fe₁ bond of only 0.32 in good agreement with the multi-center bond description. The corresponding localised molecular orbital, which contains 41% Ru, 24% Fe and 35% P atomic orbital contribution, is depicted in Fig. 3 (left). We could not locate a bond-critical point between Ru and

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**Table 2**

<table>
<thead>
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<th>Bond Length (Å)</th>
<th>Value</th>
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<tr>
<td>Ru₁–P₁</td>
<td>2.3592(5)</td>
</tr>
<tr>
<td>Ru₁–P₄</td>
<td>2.3513(6)</td>
</tr>
<tr>
<td>Ru₁–P₂</td>
<td>2.4454(5)</td>
</tr>
<tr>
<td>Ru₁–P₃</td>
<td>2.4469(6)</td>
</tr>
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**Fig. 3**

Left: The localised molecular orbital of 6 showing the interaction between Ru, Fe and P. Right: Frontier orbitals in 6 at the BP86/def2-TZVP level.
Fe1 by the analysis of the topology of the electron density of 6 by means of the Atoms in Molecules (AIM) approach. However, a ring-critical point could be detected, situated in the plane spanned by Ru, Fe1, P1 and P4. The frontier orbitals in 6 are depicted on the right hand side in Fig. 3. The highest occupied molecular orbital (HOMO) shows mainly the lone pairs of the phosphorus atoms while both HOMO−1 and HOMO−2 show mainly bonding interaction within the P4Fe unit. The lowest unoccupied molecular orbital (LUMO) shows mainly nonbonding orbitals at the phosphorus as well as the metal atoms.

Furthermore, we were interested in why 5 transforms into 6, while the transformation from 2 to the hypothetical complex [(Cp’/Fe(CO))2(Cp’/Fe(CO))(μ3-P4)(CymRu)]2+ (7) is not observed under the same conditions. Therefore, we determined the natural charge distribution of the four complexes. According to this, the [CymRu]2+ fragments act as weak electron acceptors, while [Cp*Ru]+ act as strong electron acceptors. In contrast, the cyclo-P4R2 (R = Cp/Fe(CO)) units in 2 and 5 act as strong electron donors. During the transformation from cyclo-P4R2 units to catena-P4 units, this effect is even enhanced. Therefore, it is suggested that the further transformation is dependent on the nature of the ligands that are attached to the central Lewis acid. The disfavored formation of 7 in comparison to 6 is also highlighted by the calculated reaction energies at the B3LYP level (solvation effects incorporated by the COSMO model). The calculations showed that the formation of 6 starting from 5 is endothermic by 95.87 kJ mol−1. However, these calculations do not take into account the terms of entropy which should have a mayor impact due to the release of CO gas during this process. The formation of 7 starting from 2 would be endothermic by 150.87 kJ mol−1 which shows that, in principle, the formation of 6 in comparison to 7 would be energetically less disfavored.

In summary, we could show that the P4 butterfly complex 1 can easily be activated by a vast variety of different d6 metal-based Lewis acids, leading to the formation of 2-5 bearing cyclo-P3R2 units. However, by using [Cp*Ru(NCCH3)]2+PF6 the in the presence of light 6 is formed. Complex 6 exhibits an iron-tetrathiaphiene unit which is formed via CO elimination and the subsequent insertion of the iron fragment into a P-P bond. However, this second activation step is not observed for complexes 2-4 under the same reaction conditions. DFT calculations confirmed that the transformation is strongly dependent on the nature of the ligand at the Lewis acid. The formation of different complexes under mild conditions highlights the high diversity of binding modes of the P4 unit in 1.

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Conflicts of interest

There are no conflicts to declare.

Notes and references

† See ESI† for further information.