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

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The reactivity of $\{\text{Cp}''/\text{Fe}(\text{CO})_2\}_{1-a} \cdot \text{P}_4$ (1) towards half-sandwich complexes of Ru(μ), Rh(μ), and Ir(μ) is studied. The coordination of these Lewis acids leads to a rearrangement of the $P_4$ butterfly unit to form complexes with either an aromatic cyclo-$P_4R_2$ unit ($R = \text{Cp}''/\text{Fe}(\text{CO})_2$) or a catena-tetraphosphaene entity.

The activation of small molecules is an active research topic. This research area focuses mainly on inert molecules such as $\text{H}_2$, $\text{N}_2$, $\text{CO}_2$, and $\text{CH}_4$ 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 $\{\text{Cp}'/\text{Fe}(\text{CO})_2\}_{1-a} \cdot \text{P}_4$ in the presence of $P_4$ leads to $[\text{Cp}''/\text{Fe}(\text{CO})_2]_2P_4$ ($n = 3$, 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 $[\text{Cp}'/\text{Fe}(\text{CO})_2]_3$ (Cp’’ = $\eta^5$-C$_5$H$_5$Bu$_3$), $[\text{Cp}'/\text{Co}(\text{CO})_2]_2$ (Cp’’ = $\eta^5$-C$_5$H$_5$Me$_3$), and $[\text{Cp}'/\text{Co}(\text{Pr}_2\text{Im})_2]$ ($\eta^5$-C$_5$H$_5$Bu$_3$)10,14 ($\text{Pr}_2\text{Im} = 1,3$-diisopropylimidoazoline-2-ylidine), respectively. The thermolysis of $[\text{Cp}'\text{Ni}(\text{CO})_2]_2$ leads to complexes of the type E.15 In molten GaCl$_3$, $P_4$ can also be converted by in situ generated Ph$_2P^-$, leading to the insertion of phosphonium cations into several P–P bonds to form cationic $P_4(\text{PPh}_2)_6$ (type A), $P_4(\text{PPh}_2)_3$ (type C) and $P_4(\text{PPh}_2)_2$ (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 $[\text{Cp}'/\text{Co}(\mu-\text{C}_5\text{H}_5\text{Bu}_3)]_2$.18 In solution it dissociates into the 14-valence-electron (VE) fragment $[\text{Cp}'/\text{Co}]$ 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 $[\text{Cp}'/\text{Fe}(\text{CO})_2]_2P_4$ (type F) by the reaction of $[\text{Cp}'/\text{Fe}(\text{CO})_2]_2$ 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≡CCBu gives access to triphosphol- and tetraphosphol-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...
Lewis acids via the two “wing tip” phosphorus atoms. However, in the presence of a d⁶ metal Lewis acid like Fe(II) that bears ligands that can easily be substituted, an unusual isomerisation of the butterfly unit (ση ν-donor, coordination type I) to an aromatic cyclo-P₄R₂ unit (6η ν-donor, R = [Cp*′′Fe(CO)₂]2, coordination type II) is observed, giving access to the unique homoletic octaphosphorus sandwich complex [[(Cp*′′Fe(CO)₂)₂μ₃-P₄]Fe₂PF₆]₂. To obtain deeper insight into the isomerisation reaction of 1, it was reacted with various 3d metal Lewis acids to give mainly coordination to a chelating ligand, but in one case an isomerisation via a redoxreaction to Co(II) occurred. The C-P bond lengths of 1.8890(2) Å in 3 and 1.8915(2) Å in 12.28 Since the availability of d⁶ 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(I) salt that bears a weakly coordinating anion to eliminate poorly soluble thallium(I) halides. This was used to obtain deeper insight into the isomerisation reaction of 3, i.e., twowhile the P₄ core isomerises to a cyclic P₄ unit. Despite the molecular structures of 2–4 shows that the central metal atom is coordinated in a η¹ fashion by the cyclo-P₄R₂ unit (Fig. 1). The similar covalent radii of Ru (r_Ru = 1.25 Å), Rh (r_Rh = 1.25 Å), and Ir (r_Ir = 1.22 Å) lead to similar M–P₄ distances of 1.8990(2) Å in 2, 1.8939(3) Å in 3 and 1.8915(2) Å in 4. Compared to [[(Cp*′′Fe(CO)₂)₂μ₃-P₄]Fe₂PF₆] the distances are approx. 0.13 Å longer (1.7609(5) Å) which is attributed to the smaller covalent radius of Fe (r_Fe = 1.16 Å). The P–P bond lengths are with 2.1356(7)–2.1481(7) Å (2), 2.1433(8)–2.1459(8) Å (3), and 2.1488(6)–2.1518(6) Å (4) in the range between a P–P single bond (2.20–2.25 Å) and a P–P double bond (2.00–2.05 Å). These bond lengths are in good agreement with the determined P–P distances in the isolated cyclo-P₄, anion (2.146(1) and 2.148(9) Å) in C₈P₄S₂Cl₃, as well as in other complexes with formal P₄²⁻ ligands. The cyclo-P₄ units exhibit similar diamond-shaped geometries in all three complexes, which was also found in the other complexes derived from 3.²²

The ¹H NMR spectrum of 2 in CD₂Cl₂ shows two singlets at δ = 1.33 and 1.45 ppm and a multiplet at δ = 5.66 ppm with an integral ratio of 18 : 36 : 4 for the two Cp*⁻ ligands. The signals at δ = 1.35, 2.59, and 6.71 ppm can be assigned to the Cym ligand. The ¹H NMR spectra of 3 and 4 show similar signals for the Cp⁺⁻ ligands while the singlet of the Cp⁺ signal can be detected at δ = 2.46 (3, CD₂Cl₂) and 2.64 ppm (4, CD₂CN), respectively. The ³¹P{¹H} NMR spectra of 2 and 4 show each an AA’XX’ spin system for the cation (2 in CD₂Cl₂: δ = 148.9 and 102.9 ppm; 4 in CD₂CN: δ = 102.3 and 62.7 ppm). The cation of 3 shows two signals at δ = 169.8 and 121.1 ppm that are part of an AA’MM’X spin system (X corresponds to Rh) caused by the NMR-active ¹⁰³Rh nuclei (I = 1/2, 100% natural abundance). However, the ³¹P{¹H} NMR spectrum of the reaction solution of 3 reveals an additional set of signals at δ = 201.7, 157.7 and 125.7 ppm corresponding to a byproduct (AA’MNX spin system, X corresponds to Rh), in a ratio of 3 to the byproduct of approximately 2 : 1. Despite several attempts, the exact structure of the byproduct could not be clarified yet, but, according to the NMR features, the presence of a cyclo-P₄ unit bound to a ¹⁰³Rh core is very likely.

The reaction of 1 with [Cp*Ru(NCCH₃)₃][PF₆] in the absence of light yields [[(Cp*′′′Fe(CO)₂)₂μ₃-P₄]Fe₂PF₆] (5). During this reaction, all acetonitrile ligands are substituted by 1, while the P₄ core isomerises to a cyclic P₄ unit. Despite numerous attempts, it was not possible to isolate 5 in crystalline form. However, the ³¹P{¹H} NMR spectrum of 5 in CD₂Cl₂ shows an AA’XX’ spin system at δ = 82.0 and 51.6 ppm unambiguously confirms its identity. The chemical shift values as well as the spin system compare well to that found for 2–4 and [[(Cp*′′′Fe(CO)₂)₂μ₃-P₄]Fe₂PF₆] (δ = 78.9, 56.8 and 45.6 ppm).
elimination, followed by the insertion of the \([\text{Cp}^{\prime\prime}\text{Fe(CO)}]\) fragment into one of the adjacent P–P bonds, leads to \([[\text{Cp}^{\prime\prime}\text{Fe(CO)}]_2[\text{Cp}^{\prime\prime}\text{Fe(CO)}][\mu_1,\eta^1:2:1:3-\text{P}_4](\text{Cp}^{\prime}\text{Ru})][\text{PF}_6]]\) (6) in moderate yield (22%, 70% according to \(^{31}\text{P}\) NMR spectroscopy).

Complex 6 features a metallo-tetraphenene unit and represents a formally twofold activated \(\text{P}_4\) butterfly complex 1. The formation of 6 also highlights the high diversity in different binding modes of the \(\text{P}_4\) 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 \(\text{Fe}^+\) into the \(\text{P}_1–\text{P}_4\) bond leads to the formation of the 1S-2R-3R-4R-5S configuration (Fig. 2) while insertion into the \(\text{P}_3–\text{P}_4\) 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 \(\text{FeP}_4\) metallacycle reveals an envelope structure. The central \(\text{FeP}_4\) 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 \(^1\text{H}\) NMR as well as the \(^{31}\text{P}\{^1\text{H}\}\) NMR spectrum (CD\(_2\)Cl\(_2\)) 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 \(\text{Cp}^{\prime\prime}\) ligands or the whole \([\text{Cp}^{\prime}\text{Ru}](\text{Cp}^{\prime\prime}\text{Fe(CO)})_2]\) fragment. At lower temperatures, the rotation is slowed down resulting in sharp signals.‡ The \(^{31}\text{P}\{^1\text{H}\}\) NMR spectrum shows an AA′XX′ spin system for both isomers which resonate at similar chemical shifts so that they mainly overlap. The signals at \(\delta = 500.9, 457.0, 145.2\) and 126.5 ppm can be assigned to the main species while the signals at \(\delta = 501.1, 465.5, 144.1\) and 126.0 ppm are assigned 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}^{\prime}\text{Fe}][\mu_1,\eta^1:2:1:3-\text{P}_4](\text{Cp}^{\prime}\text{Fe(CO)})]_2] (\(\delta = 567.2\) and 169.1 ppm) and \(\text{IV}^{\text{‡}}\) (\(\delta = 74.0\) and –125.4 ppm) showing both an AA′XX′ spin system for the catena-P\(_4\) unit. The dirhodium complex \(\text{III}^{\text{†}}\) (\(\delta = 201.4\) and 150.8 ppm) reveals an AA′NNMX′ 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 is 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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**Fig. 2** Cationic part of the 1S-2R-3R-4R-5S enantiomer of 6 in the solid state. Hydrogen atoms are omitted for clarity. A.d.p. are shown at 50% probability level.

**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-P)]{42:1-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]2+ act as strong electron acceptors. In contrast, the cyclo-P4R2 (R = Cp′′/′′Fe(CO)2) 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 d⁸ metal-based Lewis acids, leading to the formation of 2–5 bearing cyclo-P4R2 units. However, by using [Cp∗Ru(NCCH3)]2[PF6] in the presence of light 6 is formed. Complex 6 exhibits an iron-tetraphosphaene 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 ESf for further information.