From a P₄ butterfly scaffold to cyclo- and catena-P₄ units†

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The reactivity of \([\text{Cp}^\text{III} \text{Fe} \text{(CO)}_2]_2(\mu_{1,1,1}-\text{P}_4)\) (I) towards half-sandwich complexes of Ru(u), Rh(u), and Ir(u) is studied. The coordination of these Lewis acids leads to a rearrangement of the P₄ butterfly unit to form complexes with either an aromatic cyclo-P₄R₂ unit (R = \text{Cp}^\text{III} \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 H₂, N₂, CO₂, and CH₄ 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 (P₄) where the focus is to control its reactivity. In industrial applications, P₄ 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 P₄ 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 P₄ conversion, work was done by the Scherer group, e.g. by showing that the photolysis of \([\text{Cp}^\text{III} \text{Fe} \text{(CO)}_2]_2(\eta^2-\text{C}_5\text{H}_5\text{Bu}_3)\) in the presence of P₄ leads to \([\text{Cp}^\text{III} \text{Fe} \text{(CO)}_2 \text{P}_4]\) (n = 3, 4 type A, n = 2 type B, n = 1 and n = 0 type D) by successive decarbonylation (Scheme 1, top).⁸ Comparable results were obtained via thermolytic reactions of P₄ with \([\text{Cp}^\text{IV} \text{Fe} \text{(CO)}_2]_2\) (\text{Cp}^\text{IV} = \eta^2-\text{C}_5\text{H}_5\text{Bu}_3), \([\text{Cp}^\text{IV} \text{Co} \text{(CO)}_2]_2\), \([\text{Cp}^\text{IV} \text{Co} \text{(Cp)}_2]_2\) \([\text{Cp}^\text{IV} = \eta^2-\text{C}_5\text{Me}_2\text{Me}_2] \) and \([\text{Cp}^\text{IV} \text{Co} \text{(Pr}_2\text{Im)}(\eta^2-\text{C}_5\text{H}_4)]\).³⁰,³¹ \(\text{Pr}_2\text{Im} = 1,3\text{-di-isopropylimidazol-2-ylidene}\), respectively. The thermolysis of \([\text{Cp}^\text{IV} \text{Ni} \text{(CO)}_2]_2\) leads to complexes of the type E.⁹ In molten GaCl₃, P₄ can also be converted by \textit{in situ} generated Ph₂P⁺, which can be used as a synthetic precursor for the preparation of di- and tetraphosphaene structures. In the presence of P₄ conversion, work was done by the Scherer group, e.g. by showing that the photolysis of \([\text{Cp}^\text{IV} \text{Fe} \text{(CO)}_2]_2(\mu_{1,1,1}-\text{P}_4)\) by successive decarbonylation (Scheme 1, top).⁸ Comparable results were obtained via thermolytic reactions of P₄ with \([\text{Cp}^\text{IV} \text{Fe} \text{(CO)}_2]_2\) (\text{Cp}^\text{IV} = \eta^2-\text{C}_5\text{H}_5\text{Bu}_3), \([\text{Cp}^\text{IV} \text{Co} \text{(CO)}_2]_2\), \([\text{Cp}^\text{IV} \text{Co} \text{(Cp)}_2]_2\) \([\text{Cp}^\text{IV} = \eta^2-\text{C}_5\text{Me}_2\text{Me}_2] \) and \([\text{Cp}^\text{IV} \text{Co} \text{(Pr}_2\text{Im)}(\eta^2-\text{C}_5\text{H}_4)]\).³⁰,³¹ \(\text{Pr}_2\text{Im} = 1,3\text{-di-isopropylimidazol-2-ylidene}\), respectively. The thermolysis of \([\text{Cp}^\text{IV} \text{Ni} \text{(CO)}_2]_2\) leads to complexes of the type E.⁹ In molten GaCl₃, P₄ can also be converted by \textit{in situ} generated Ph₂P⁺, which can be used as a synthetic precursor for the preparation of di- and tetraphosphaene structures. In the presence of
Lewis acids via the two “wing tip” phosphorus atoms. However, in the presence of a d0 metal Lewis acid like Fe(n) that bears ligands that can easily be substituted, an unusual isomerisation of the butterfly unit ($\sigma$-e- donor, coordination type I) to an aromatic cyclo-P4R2 unit (6e- donor, $R = [\text{Cp}^*\text{Fe}(%CO)\text{]}_2$, coordination type II) is observed, giving access to the unique homoleptic octaphosphorus sandwich complex $[[\text{Cp}^*\text{Fe}(%CO)\text{]}_2][\text{Ru(n)}(1^{1:1}:1^-\text{P}_4)][\text{Fe3PF}_6]_{2.22}$. 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 redoxreaction to Co(n) occurred.228 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(i) salt that bears a weakly coordinating anion to eliminate poorly soluble thallium(i) halides. This was used to generate the solvent-stabilized [CH3CN or CH2Cl2] species “[CymRu[PF6]2]” (Cym = para-cymene) and “[Cp*M[PF6]2]” ($M = \text{Rh}, \text{Ir}$) in situ. These metal fragments react smoothly with 1 leading to $[[\text{Cp}^*\text{Fe}(\text{CO})_2][\text{Ru(n)}(1^{1:1}:1^-\text{P}_4)][\text{LM}][\text{PF}_6]_{2.22}$ (2: $\text{LM} = \text{CymRu}$; 3: $\text{LM} = \text{Cp}*\text{Rh}$; 4: $\text{LM} = \text{Cp}*\text{Ir}$, Scheme 2). Complexes 2–4 feature all cyclo-P4R2 units that coordinate the central [LM]2+ fragments. This finding reveals that the isomerisation of the P3 butterfly moiety (4e- donor, coordination type I) to a cyclo-P4R2 ligand (6e- donor, coordination type II) is a general feature, not only bound to 3d metals, if the 18 VE rule can be fulfilled and a d0 metal is present. The molecular structures of 2–4 shows, that the central metal atom is coordinated in an η4 fashion by the cyclo-P4R2 unit (Fig. 1). The similar covalent radii of Ru (rRu = 1.25 Å), Rh (rRh = 1.25 Å), and Ir (rIr = 1.22 Å) lead to similar M–P4 core distances of 1.8990(2) Å in 2, 1.8939(3) Å in 3 and 1.8915(2) Å in 4.23 Compared to $[[\text{Cp}^*\text{Fe}(\text{CO})_2][\text{Ru(n)}(1^{1:1}:1^-\text{P}_4)][\text{Cp}^*\text{Fe}][\text{PF}_6]_{2.22}$, the distances are approx. 0.13 Å longer (1.7609(5) Å) which is attributed to the smaller covalent radius of Fe (rFe = 1.16 Å).228 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 Cs2P4·2NH3.23 as well as in other complexes with formal P4− ligands.16,22,23 The cyclo-P4 units exhibit similar diamond-shaped geometries in all three complexes, which was also found in the other complexes derived from 1.22

The $^1H$ NMR spectrum of 2 in CD2Cl2 shows two singlets at $\delta = 1.33$ and 1.45 ppm and a multiplet at $\delta = 5.66$ ppm with an integral ratio of 18:36:4 for the two Cp* signals. The signals at $\delta = 1.35, 2.59,$ 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 $\delta = 2.46$ (3, CD2Cl2) and 2.64 ppm (4, CD2CN), respectively. The $^{31}P(^1H)$ NMR spectra of 2 and 4 show each an AA’XX’ spin system for the cation (2 in CD2Cl2: $\delta = 148.9$ and 102.9 ppm; 4 in CD2CN: $\delta = 102.3$ and 62.7 ppm). The cation of 3 shows two signals at $\delta = 169.8$ and 121.1 ppm that are part of an AA’MM’X spin system (X corresponds to Rh) caused by the NMR-active $^{103}$Rh nuclei ($I = 1/2, 100%$ natural abundance).24 However, the $^{31}P(^1H)$ NMR spectrum of the reaction solution of 3 reveals an additional set of signals at $\delta = 201.7, 157.7$ 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 $^{103}$Rh core is very likely.

The reaction of 1 and [Cp*Ru(NCCH3)3][PF6] in the absence of light yields $[[\text{Cp}^*\text{Fe}(\text{CO})_2][\text{Ru(n)}(1^{1:1}:1^-\text{P}_4)][\text{Cp}^*\text{Ru}][\text{PF}_6]_{2.22}$ (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 $^{31}P(^1H)$ NMR spectrum of 5 in CD2Cl2 shows an AA’XX’ spin system at $\delta = 82.0$ and 51.6 ppm unambiguously confirms its identity.25 The chemical shift values as well as the spin system compare well to that found for 2–4 and $[[\text{Cp}^*\text{Fe}(\text{CO})_2][\text{Ru(n)}(1^{1:1}:1^-\text{P}_4)][\text{Cp}^*\text{Fe}][\text{PF}_6]_{2.22}$ ($\delta = 78.9, 56.8$ and 45.6 ppm).

Performing the reaction of 1 with [Cp*Ru(NCCH3)3][PF6] in the presence of light, a different reaction outcome is observed. Surprisingly, the main product is not 5, but a subsequent CO

![Scheme 2](https://example.com/scheme2.png)
elimination, followed by the insertion of the [Cp"^7/Fe(CO)] fragment into one of the adjacent P–P bonds, leads to \( [(\text{Cp}^\text{Fe}(\text{CO}))_2][\text{Cp}^\text{Fe}(\text{CO})] \left[ \mu_1, \mu_2(1:1:1:1-P4) \right] (\text{Cp}^*\text{Ru}) \] [PF_6] \) (6) in moderate yield (22%, 70% according to \( ^{31}\text{P} \) NMR spectroscopy). Complex \( 6 \) features a metallo-tetraphosphaene 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 \( \text{Fe}^1 \) 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 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 \( \text{FeP}_4 \) metallacycle reveals an envelope conformation with an almost planar catena-P_4 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.\(^{21-23}\) The P–P bond distances vary from 2.1335(8) to 2.2146(8) Å and are in a range between a P–P single and a P–P double bond. The \( [\text{Cp}^*\text{Ru}] \) fragment is located over the center of the metallacycle 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 \( [\text{Cp}^\text{Fe}(\text{CO})] \) 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),\(^{24}\) 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 \( [\text{Cp}^\text{Rh}(\text{CO})] \left[ \mu_1, \mu_2(1:1:1:1-P4) \right] (\text{Cp}^*\text{Rh}) \) (\( \text{III} \), \( \text{Cp}^* = \eta^5-\text{C}_5\text{Me}_5\text{Et} \)).\(^{11}\) Although, \( \text{III} \) has two electrons more than \( 6 \), the P–P bond lengths (2.150(3)–2.160(3) Å) are comparable. However, in \( \text{III} \), no metal–metal interaction was observed since the \( \eta^4 \)-coordinated \( [\text{Cp}^\text{Rh}] \) fragment is located over the center of the \( \text{P}_4 \) chain. The complex \( [\text{K}(\text{dme})_2][\text{MesBIAN})\text{Co} \left[ \mu_1, \mu_2(1:2)-\text{P}_4\text{Ga}](\text{nacnac}) \) \(^{27} \) (IV, dme = dimethoxyethane, \( \text{McBIAN} = 1,2\text{-bis}(2,4,6\text{-dimethylphenyl})\text{acenaphthene}, \text{nacnac} = \text{CH}[\text{CMeN}(2,6\text{-iPr}_2\text{C}_6\text{H}_3)]_2 \) 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 \( [\text{Cp}^\text{Fe}(\text{CO})] \left[ \mu_1, \mu_2(1:2)-\text{CR}-(\text{CH}_2)_2-\text{CR} \right] \left[ \text{Cp}^*\text{Ru} \right] \) (R = \( \text{CMe}_2\text{OH} \)) where the \( [\text{Cp}^*\text{Ru}] \) fragment is \( \eta^5 \)-coordinated by 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 \( ^1\text{H} \) NMR as well as the \( ^{31}\text{P}[^1\text{H}] \) NMR spectrum (CD_2Cl_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 \( \text{Cp}^\text{"} \) ligands or the whole \( [\text{Cp}^\text{"}\text{Fe}(\text{CO})]_2 \) fragment. At lower temperatures, the rotation is slowed down resulting in sharp signals.\(^{‡}\) The \( ^{31}\text{P}[^1\text{H}] \) NMR spectrum shows an AXMY 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 \( [\text{Cp}^\text{Fe}(\mu_1, \mu_2(1:1:1:1-P4))[\text{Cp}^\text{Fe}(\text{CO})]]^8 (\delta = 567.2 \) 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 \( \text{III} \) (\( \delta = 201.4 \) 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.
FeI by the analysis of the topology of the electron density of Fe by means of the Atoms in Molecules (AIM) approach. However, a ring-critical point could be detected, situated in the plane spanned by Ru, FeI, P1 and P4. The frontier orbitals in Fe 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 P3Fe 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 Fe transforms into 6, while the transformation from 2 to the hypothetical complex [(Cp′/Fe(CO))₃(Cp′/Fe(CO))(μ₃-P₄)]²⁺-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)) 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 major 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)₃][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 ES† for further information.