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

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The reactivity of $[\text{Cp''Fe(CO)_2}]_2(\mu,P_4)$ (1) towards half-sandwich complexes of Ru(II), Rh(III), and Ir(III) 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 ($R = \text{Cp''Fe(CO)_2}$) 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 $H_2$, $N_2$, $CO$, 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. In the field of $P_4$ conversion, work was done by the Scherer group, e.g. by showing that the photolysis of $[\text{Cp''Fe(CO)_2}]_2(\mu,P_4)$ in the presence of $P_4$ leads to $[\text{Cp''}_2\text{Fe}_2(P_4)P_4]$ ($n = 3, 4$ type A, $n = 2$ type B, $n = 1$ and $n = 0$ type D) by successive decarbonylation (Scheme 1, top). Comparable results were obtained via thermolytic reactions of $P_4$ with $[\text{Cp''''Fe(CO)_2}]_2$ ($\mu,P_4'' = \eta^3$-$C_5H_4$Bu$_2$), $[\text{Cp''Co(CO)}_2]_2$ ($\mu,P_4''' = \eta^3$-$C_5Me_3$), and $[\text{Cp''Co(Pr_3Im)}_2(\eta^3$-$C_5H_4)](10,14 (Pr$_3$Im = 1,3-diisopropylimidazoline-2-ylidene), respectively. The thermolysis of $[\text{Cp''Ni(CO)_2}]_2$ leads to complexes of the type E. In molten GaCl$_3$, $P_4$ can also be converted by in situ generated Ph$_3P$, leading to the insertion of phosphonium cations into several $P$-$P$ bonds to form cationic $P_4(PPh_2)$ (type A), $P_4(PPh_3)$ (type C) and $P_4(PPh_3)$ (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, like the triple-decker complex $[\text{Cp''Co}](\mu,P_4)$ containing derivatives. In solution it dissociates into the 14-valence-electron (VE) fragment $[\text{Cp''Co}]$ and reacts readily with complexes bearing intact tetrahedral $P_4$ units to cyclo-$P_4$ (type B) containing derivatives. On the other hand we showed that the formation of the butterfly complex $[\text{Cp''''Fe(CO)_2}]_2(\mu,P_4''')$ (1) by the reaction of $[\text{Cp''''Fe(CO)_2}]_2$ with $P_4$ does not need thermal activation and already occurs quantitatively at room temperature. The reactivity of 1 is very versatile, since the reaction with PhC≡CPh or $P≡C$Bu gives access to triphospholy- and tetraphospholy-containing iron complexes. We could also show that 1 has the properties of a chelate ligand (Scheme 1, bottom, coordination type I). 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 d^6 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-

P,R_2 unit (6e – donor, R = [Cp''/Fe(CO)]_2, coordination type II) is observed, giving access to the unique homolectic octaphosphorus sandwich complex [[(Cp''/Fe(CO)]_2][Z_4(P_4)[P_4]]_2(PF_6)]_2(PF_6). 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 redox reaction to Co(n) occurred. Since the availability of 3d transition 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 3 towards Ru(n), Rh(n), and Ir(n)-based Lewis acids, surprisingly leading exclusively to an isomerisation to form cycl- and also catena-P_4 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 [CH_3CN or CH_2Cl_2] species “[CymRu][PF_6]_2” (Cym = para-xylylene) and “[Cp*M][PF_6]_2” (M = Rh, Ir) in situ. These metal fragments react smoothly with 1 leading to [[Cp''/Fe(CO)]_2][Z_4(P_4)[P_4]]_2(LM)[PF_6]_2 (2: LM = CymRu; 3: LM = Cp*Rh; 4: LM = Cp*Ir, Scheme 2). Complexes 2-4 feature all cyclo-P,R_2 units that coordinate the central [L]_2^+ fragments. This finding reveals that the isomerisation of the P_4 butterfly moiety (4σe – donor, coordination type I) to a cyclo-P,R_2 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 d^6 metal is present. The molecular structures of to 

Fig. 1 Cationic parts of the molecular structures in solid state of 2 and 3. 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.

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-P,R_2 anion (2.146(1) and 2.148(9) Å) in Cs,P_2-2NH_2, as well as in other complexes with formal P_4^2– ligands. The cyclo-P_4 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 CD_2Cl_2 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, CD_2Cl_2) and 2.64 ppm (4, CD_3CN), respectively. The 31P{1H} NMR spectra of 2 and 4 show each an AA’XX’ spin system for the cation (2 in CD_2Cl_2: δ = 143.9 and 102.9 ppm; 4 in CD_3CN: 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’XX 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-P_4 unit bound to a 103Rh core is very likely.

The reaction of 1 and [Cp*Ru(NCCH_3)]_2[PF_6] in the presence of light yields [[Cp''/Fe(CO)]_2][Z_4(P_4)[P_4]]_2(Cp*Ru)[PF_6]_2 (5). During this reaction, all acetonitrile ligands are substituted by 1, while the P_4 core isomerises to a cyclic P_4 unit. Despite numerous attempts, it was not possible to isolate 5 in crystalline form. However, the 31P{1H} NMR spectrum of 5 in CD_2Cl_2 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][Z_4(P_4)[P_4]]_2(Cp''/Fe)[PF_6]_2 (δ = 78.9, 56.8 and 45.6 ppm).

Performing the reaction of 1 with [Cp*Ru(NCCH_3)]_2[PF_6] in the presence of light, a different reaction outcome is observed. Surprisingly, the main product is not 5, but a subsequent CO
The binding modes of the P₄ unit in moderate yield (22%, 70% according to 3¹P NMR spectroscopy).

The Ru₁–Fe₁ distance of 2.9052(4) Å is longer than a predicted fragment and raises the question of a Ru–Fe interaction. While 6 electrons more than 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 bond and a P–P double bond. The [Cp*Ru] fragment is located over the center of the metallacycle with a multi-center bond description. The corresponding group-based, heteroatomic core, but without significant metal–metal interaction. The bond lengths (2.1198(7)–2.1286(7) Å) are comparable to [(Cp[Rh(CO)]₄)₂]⁺(C₅Me₅)⁻(Cp[Rh(CO)]₄)⁻(C₅Me₅)⁻. The 1H NMR as well as the 3¹P{¹H} 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.

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 3¹P{¹H} NMR spectrum shows an AMXY spin system for both isomers which resonate at similar chemical shifts so that they mainly overlap. The signals at δ = 501.1, 463.5, 144.1 and 126.0 ppm can be assigned to the main species while the signals at δ = 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 [(Cp⁺Fe)[μ,η²-P₄](Cp⁺Fe(CO))²]⁺ δ = 567.2 and 169.1 ppm) and 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 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 Fe.
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—I and HOMO—2 show mainly bonding interaction within the P2Fe 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′/3′Fe(CO))2(Cp′/3′Fe(CO)][μ3,S]4:2:1—P4](CymRu)2+ (7) is not observed under the same conditions. Therefore, we determined the natural charge distribution of the four complexes.² 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′/3′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 2 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 5.

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Conflicts of interest

There are no conflicts to declare.

Notes and references

² See ESI for further information.