Abstract: A comparison of \( \text{P}_4 \) activations mediated by low-valent \( \beta \)-diketiminato (L) cobalt complexes is presented. The formal Co(II) source \( [K(\text{L}^3\text{Co})_2(\mu_3-\text{η}^1-N_2)] \) (1) reacts with \( \text{P}_4 \) to form a mixture of the monoanionic complexes \([\text{K}(\text{thf})_4][(\text{L}^3\text{Co})_2(\mu_3-\text{η}^1-\text{η}^1-P_3)] \) (2) and \([\text{K}(\text{thf})_4][(\text{L}^3\text{Co})_2(\mu_3-\text{η}^1-\text{η}^1-P_3)] \) (3). The analogue Co(I) precursor \( [\text{L}^3\text{Co}(\text{tol})] \) (4a), however, selectively yields the corresponding neutral derivative \([[(\text{L}^3\text{Co})_2(\mu_3-\text{η}^1-\text{η}^1-P_3)] \) (5a). Compound 5a undergoes thermal P atom loss to form the unprecedented complex \([[(\text{L}^3\text{Co})_2(\mu_3-\text{η}^1-\text{η}^1-P_3)] \) (6). The products 2 and 3 can be obtained selectively by an one-electron reduction of their neutral precursors 5a and 6, respectively. The electrochemical behaviour of 2, 3, 5a, and 6 is monitored by cyclic voltammetry and their magnetism is examined by SQUID measurements and the Evans method. The initial Co(II)-mediated \( \text{P}_4 \) activation is not influenced by applying the structurally different ligands \( \text{L}^1 \) and \( \text{L}^2 \), which is proven by the formation of the isostuctural products \([[(\text{L}^3\text{Co})_2(\mu_3-\text{η}^1-\text{η}^1-P_3)] \) \( [\text{L} = \text{L}^1 \text{ (5a)}, \text{L}^1 \text{ (5b)}, \text{L}^2 \text{ (5c)}] \).

Introduction

The activation of white phosphorus (\( \text{P}_4 \)) with transition metal (TM) complexes with the objective of generating organophosphorus compounds has been an ongoing research topic.\(^{[1]}\) For this purpose, an understanding of the \( \text{P}_4 \) transformation pathway in the coordination sphere of transition metals is necessary. Thus, a variety of \( \text{P}_4 \) ligand moieties were stabilized to give insight into the stepwise \( \text{P}_4 \) degradation and aggregation processes using well-established ligand systems such as the \( \text{Cp}^8 \) family (\( \text{Cp} = \text{cyclopentadienyl} \)).\(^{[11]}\) However, over the last years, \( \beta \)-diketiminato (nacnac = L) ligand systems have gained increasing attention in mild \( \text{P}_4 \) activations using M\(^{II} \) precursors: The initial \( \text{P}_4 \) fixation step of an intact \( \text{P}_4 \) tetrahedron at a metal center was achieved at an electron-rich Cu(I) nacnac compound.\(^{[2]}\) In reactions with transition metal complexes of Groups 5\(^{[5]}\) and 8–10,\(^{[6]}\) products with modified \( [\text{P}_4]\), \( [\text{P}_4]^2^- \), \( [\text{P}_4]^2 \), and \( [\text{P}_4]^3^- \) ligands, respectively, were obtained. So far, for nacnac systems, a \( [\text{P}_4]^3^- \) ligand was found solely in compound \([[(\text{L}^3\text{Co})_2(\mu_3-\text{η}^1-\text{η}^1-P_3)] \) \( [\text{R} = \text{N}(\text{tolyl})_2 \text{, } n = 0.1; \text{R} = \text{O}(\text{dipp}), n = 0) \) and \([[(\text{L}^3\text{Co})_2(\mu_3-\text{η}^1-\text{η}^1-P_3)] \) \( [\text{A, Scheme } 1]^{[a]} \).

However, cyclo-P\(_4\) complexes of the type \([[(\text{L}^3\text{Co})_2(\mu_3-\text{η}^1-\text{η}^1-P_3)] \) \( [\text{M,L}]^{\pm n} \) have been structurally characterized using neutral, tridentate triphos (1,1,1-tris(diphenylphosphinomethyl)ethane) groups 5\(^{[5]}\) and 8–10,\(^{[6]}\) products with modified \( [\text{P}_4]^2^- \), \( [\text{P}_4]^2 \), \( [\text{P}_4]^2^- \), and \( [\text{P}_4]^3^- \) ligands, respectively, were obtained. So far, for nacnac systems, a \( [\text{P}_4]^3^- \) ligand was found solely in compound \([[(\text{L}^3\text{Co})_2(\mu_3-\text{η}^1-\text{η}^1-P_3)] \) \( [\text{R} = \text{N}(\text{tolyl})_2 \text{, } n = 0.1; \text{R} = \text{O}(\text{dipp}), n = 0) \) and \([[(\text{L}^3\text{Co})_2(\mu_3-\text{η}^1-\text{η}^1-P_3)] \) \( [\text{A, Scheme } 1]^{[a]} \).

However, cyclo-P\(_4\) complexes of the type \([[(\text{L}^3\text{Co})_2(\mu_3-\text{η}^1-\text{η}^1-P_3)] \) \( [\text{M,L}]^{\pm n} \) have been structurally characterized using neutral, tridentate triphos (1,1,1-tris(diphenylphosphinomethyl)ethane)
and etriphos (1,1,1-tris(diethylphosphinoethyl)ethane) ligands in different combinations with 3d metals (Fe, Co, Ni) and 4d metals (Rh, Pd).[9] The influence of the ligand substituents in Fe²⁺-mediated P₃ transformations has recently been illustrated by a comparative study using a set of ligands L¹⁻L¹ (Scheme 1). [9]

Despite the application of the same reaction conditions, different products were obtained, which are sensitively dependent on small changes of the ligand substituents. 2,6-Disopropylphosphinophenyl (dipp) substituents as the ligands' aromatic flanking groups support the formation of the dinuclear complexes ([L²Fe]₂[(µ₂-η¹-η¹-N₃-P₃)] (B) [7] and [L²Fe]₂[(µ₂-η¹-η¹-P₃)] (C). [4,6] The latter was synthesized by the Driess group. [4,6] The ligands L₀ and L₁ only differ in their backbone substituents. However, for sterically less demanding 2,6-dimethylphosphinophenyl (dmp) substituents, the formation of the tetranuclear complexes [(LFe)₂[(µ₂-η¹-η¹-η¹-N₃-P₃)] [L = L⁰ (D1), L¹ (D2)] with dimerized P₃ units was observed. [7] These results demonstrate that the product formation is affected by both the aromatic flanking groups and the ligand backbone substituents. Simultaneously, we investigated the [L²Co]⁻-mediated transformations of white phosphorus, which resulted in novel P₃- and P₄-containing complexes (vide infra). In the meantime, Driess and co-workers reported P₃ activation by [LCo] fragments leading to the neutral complexes [(LCo)₂[(µ₂-η¹-η¹-P₃)] [L = L⁰ (E₁), L¹ (E₂)] (Scheme 1). [4,6] One-electron reduction led to the mononuclear products [K(dme)₂] [[(LCo)₂[(µ₂-η¹-η¹-P₃)] [L = L⁰ (F₁), L¹ (F₂)] and transformed the [P₄]²⁻ middle deck into a [P₄]²⁻ ligand. Recently, Wolf and co-workers have reported on [[BIVN]⁻]-mediated P₃ activations with a nacnac-related bidentate redox non-innocent BIAN (1,2-bis(2,6-diisopropylphenylimino)acacaphosphate) ligand system yielding compounds containing [P₄]⁺⁺ moieties. [5]

Motivated by our first results with [L⁰Co] complexes, we speculated that the P₃ activation outcome should be sensitive to the oxidation state of the precursor (Co⁰ versus Co¹). Additionally, we wanted to address the question of the ligands' influence (L⁻¹⁻L⁻¹) in Co⁻¹-mediated P₃ activations and we were intrigued by the observed P-atom exisituation from the initially obtained P₃ middle deck to form P₃ compounds. The latter ones are still quite rare in comparison to P₄ ligand complexes.

Here, we report on the P₃ activation by a formal Co⁰ precursor yielding the mononuclear [K(thf)₁][[(L⁰Co)₂[(µ₂-η¹-η¹-P₃)] (2) and [K(thf)₁][[(L⁰Co)₂[(µ₂-η¹-η¹-P₃)] (3). Through a Co⁰-mediated P₃ transformation at room temperature or under thermolytic conditions, the corresponding neutral relatives are obtained, which generate 2 and 3 selectively after subsequent one-electron reduction. The redox chemistry of the products was investigated by cyclic voltammetry (CV), and their magnetic behavior was examined both in solution (Evans method) and in the solid state (SQUID).

**Results and Discussion**

The formal Co⁰ precursor [K₆[(L⁰Co)₂[(µ₂-η¹-η¹-N₃)]] (1) was synthesized by a one-pot reaction and was isolated as two different solvomorphs, 1-solv (solv = n-hexane) [9] or OEt₄. [10] The X-ray structures of 1-solv consist of two [L⁰Co] fragments bridged by a N₃ unit. Two potassium atoms cover the N₃ moiety and are coordinated in the phenyl pockets of the dipp substituents. [11] The N–N distance in 1-n-hexane/OEt₄ is 1.215(3) and 1.220(4) Å, respectively, which is in line with the that (1.220(2) Å) of the previously reported [K₆[(L⁰Co)₂[(µ₂-η¹-η¹-N₃)] [L² = CH((Bu)N(2,6-iPr,C₆H₃))] [12] The presence of a [N₃]²⁻ moiety in 1-n-hexane is supported by Raman spectroscopy (ν₉P₃ = 1568 cm⁻¹). [9] The reaction of 1 with P₃ proceeds by N₃ evolution, showing that the formal [N₃]²⁻ species is re-oxidized and revealing 1 as a formal dicobalt(0) starting material.

Conducting the reaction in 1:1 stoichiometry leads to the complete consumption of P₃ and the formation of a mixture of the mononionic complexes [K(thf)₆][[(L⁰Co)₂[(µ₂-η¹-η¹-P₃)] (2) and [K(thf)₆][[(L⁰Co)₂[(µ₂-η¹-η¹-P₃)] (3), which were detected by ¹H NMR spectroscopy. [13] The appearance of a cyclo-P₃ moiety in product 3 indicates that an extrusion of one P atom from the cyclo-P₄ moiety in 2 is possible. However, if the reaction is conducted with two equivalents of P₃ compound 2 is the only product found in the ¹H NMR spectrum.

The solid state structure of 2-2thf reveals a salt consisting of two [K(thf)₆]⁺⁺ cations and two crystallographically distinguishable [L⁰Co]₂[(µ₂-η¹-η¹-P₃)] monoanions (Figure 1). [15] Each anion is a centrosymmetric dicobalt complex that consists of two [L⁰Co] fragments bridged by a planar cyclo-P₃ ligand. The P–P distances amount to 2.1913(10)–2.1951(10) Å in anion 1 and 2.1897(10)–2.2004(10) Å in anion 2, respectively. These values correspond well with the cyclo-[P₄]²⁻ moiety (2.178(1) and 2.207(1) Å) of the reported compound [K₂[Fe(CN)₃]₂][[L⁰Fe]₂[(µ₂-η¹-η¹-P₃)] (B) [7]. The central P₃ ligands in 2 are almost square planar with interior angles of 86.07(3) and 93.92(3)° in anion 1 and 86.38(3)° and 93.62(3)° in anion 2. The Co–P distances range from 2.3362(7)–2.4149(7) Å in anion 1 and 2.3441(7)–2.4190(7) Å in anion 2. Selected atomic distances of compound 2 are summarized in Table 1. Minor deviations within the atomic parameters of compound 2-2thf and the related compounds [K(dme)₆][[(L⁰Co)₂[(µ₂-η¹-η¹-P₃)] [L = L⁰ (F₁), L¹ (F₂)] can be explained by small changes in the organic environment of the counter ion and the nacnac ligands of the complex monoanions. They may affect the Co–Co’ distances and their coordination geometry (torsion angle θ between the Co–Co’ axis and the plane formed by the nitrogen atoms and the methine carbon in the ligand backbone; Figure 1 for graphical presentation of θ). [14] The mononionic [L⁰Co]₂[(µ₂-η¹-η¹-P₃)] was obtained in two different solvomorphs [K(dme)₆][[(L⁰Co)₂[(µ₂-η¹-η¹-P₃)]-dme (3a)] as white crystals, which resulted in novel P₄ ligands. No conclusions were drawn at 50% probability level. The torsion angle θ is depicted spanning between the Co–Co’ axis and the plane formed by the nitrogen atoms and the methine carbon in the ligand backbone.

![Figure 1. Anionic part of the molecular structure of 2. Hydrogen atoms and aromatic flanking groups are omitted for clarity; thermal ellipsoids are drawn at 50% probability level. The torsion angle θ is depicted spanning between the Co–Co’ axis and the plane formed by the nitrogen atoms and the methine carbon in the ligand backbone.](image-url)
and (K(thf)][(L’Co)₂(μ₃-η⁵-P₃)]·2thf (3b). Both compounds are ionic and consist of solvent (DME or THF) molecules, one solvent-saturated potassium counter ion, and the [(L’Co)₂(μ₃-η⁵-P₃)]⁻ monoanion (Figures 2 and 3). In both X-ray structures, the complex anions are built from two [L’Co] fragments bridged by a P₂ triangle. In 3a, the L¹ ligand planes are almost parallel to each other with an dihedral angle of 2.00° (N₁-N₂ versus N₃-N₄). However, in 3b, the ligand planes are in a twisted conformation with a dihedral angle of 74.2° (N₁-N₂ versus N₃-N₄, Figure 2).

The different complex anion conformations may originate from packing effects directed by the unequally shaped counter cations. The cyclo-P₃ middle deck is disordered over two positions in 3a (occupancy 81:19). The middle deck in 3b, however, is localized at one distinct position. As can be seen in Table 2, the P–P distances in 3a are similar to the ones in the

| Complex | 2: anion 1 | 2: anion 2 | F₂⁻[4c] | F₂⁻[4d] |
|---------|-----------|-----------|---------|---------|
| d(P–P) [Å] | 2.1913(10) | 2.1897(10) | 2.1739(7) | 2.1541[4c] |
| d(Co–Co) [Å] | 2.1951(10) | 2.2004(10) | 2.1976(7) | 2.1631[4c] |
| θ (°) | 13.87(6) | 15.87(6) | 15.33(4) | 6.608[4c] |
| θ² [°] | 14.97(7) | 8.15 | 2.2301[4c] | 2.2301[4c] |

Table 1. Comparison of P–P and Co–Co’ atomic distances and torsion angles θ in anions of [(K(solvol)][(L’Co)₂(μ₃-η⁵-P₃)] (L = L¹ [2]¹⁰, L² (F₁)⁴, L’ (F₂)⁴).

Figure 3. Anionic part of the molecular structure of 3b. Hydrogen atoms are omitted for clarity; thermal ellipsoids are drawn at 50% probability level.

| Complex | 3a | 3b | A[4c] | G[4d] |
|---------|----|----|------|------|
| d(P–P–P) [Å] | 2.1674(13) | 2.217(4) | 2.1658(10) | 2.226(8) |
| θ (P–P–P) [°] | 57.34(5) | 59.59(13) | 59.03(3) | – |
| θ (P–P–P) [°] | 58.82(5) | 59.93(14) | 59.68(3) | – |
| d(M–M–M) [Å] | 3.7359(5) | 3.7124(2) | 4.460 | 3.80 |
| θ [°] | 9.43(7) | 8.7(3) | – | – |
| θ² [°] | 12.22(7) | 13.5(6) | – | – |

Table 2. Comparison of selected atomic distances and angles in the [(L¹Co)₂(μ₃-η⁵-P₃)]⁻ anion in 3a (major component of disordered) and 3b, and the dication in [(tri-phos)Co(μ₃-η⁵-P₃)cyclo-P₃]Fe(etriphos)][PF₆]₃ (G)[4d].

Figure 2. Comparison of the anions in the molecular structures of 3a (left) and 3b (right). Hydrogen atoms and aromatic flanking groups are omitted for clarity; thermal ellipsoids of Co and P atoms are drawn at 50% probability level; major component of disordered cyclo-P₃ ligand is drawn in 3a.
As mentioned above, starting from the formal Co\(^0\) precursor 1, we obtained the compounds 2 and 3 as a mixture of products, the ratio of which is sensitively dependent on stoichiometry and reaction conditions. To discover an alternative approach, we targeted the use of the Co\(^0\) starting material [L\(^2\)Co(tol)] (4a), which was speculated to yield the neutral analogues of 2 and 3. After their one-electron reduction, the compounds 2 and 3 should be accessible.

Therefore, the Co\(^0\) compound [L\(^2\)Co(tol)] (4a) was reacted with P\(_n\) and [L\(^2\)Co\(_n\)](μ\(_n\)η\(_n\)η\(_n\)-P\(_n\))] (5a) was selectively formed. Metric parameters and the characterization of compound 5a are discussed in detail below.

Refluxing 5a for three hours (110 °C, toluene) gives rise to the loss of one phosphorus atom and the formation of [(L\(^2\)Co)\(_n\)](μ\(_n\)η\(_n\)η\(_n\)-P\(_n\))] (6),\(^{[16]}\) which was clearly characterized by mass spectrometry\(^{[20]}\) and \(^{1}\)H NMR spectroscopy.\(^{[21]}\) The dinuclear compound contains two [L\(^2\)Co] fragments, and the bridging middle deck exhibits a savage disorder within its cyclo-P\(_3\) moiety. We emphasize that the P–P distances cannot be precisely described. However, the initially localized electron density unambiguously displays triangle-shaped cyclo-P\(_3\) constitution and enables an estimation of the P–P distances in 6 (approx. d(P–P): 2.147(3), 2.223(2), 2.235(2) Å). These values are comparable with the ones found in 3a (2.1674(13), 2.1790(16), 2.3303(17) Å) and 3b (2.217(4), 2.224(4) and 2.237(4) Å) and are elongated compared to the ones in A (2.1658(10), 2.1804(9) and 2.21559(9) Å).\(^{[22]}\) The Co–Co distance in 6 is 3.747 Å and therefore comparable to the ones in 3a (3.7359(5) Å) and 3b (3.724(2) Å), but elongated compared to its precursor complex 5a (3.610 Å, vide infra).

The \(^{1}\)H NMR spectrum of 6 reveals signals between 20.06 and –12.68 ppm. No signal is detected in the \(^{31}P\)\(^{1}\)H NMR spectrum. The magnetic moment (μ\(_{\text{eff}}\)) of 6 in C\(_{0}\)D\(_{8}\) is 2.97 μ\(_{\text{B}}\) at room temperature (Evans method).\(^{[22]}\) This value is confirmed in the solid state by a SQUID measurement. A successive decrease from 2.7 to 2.0 μ\(_{\text{B}}\) was measured in the temperature range from 300 to 2 K (see the Supporting Information). The values are in agreement with antiferromagnetically coupled Co\(^0\) and Co\(^5\) metal centers.

**Electrochemistry**

The electrochemical properties of the complexes 5a and 6 were probed by cyclic voltammetry (CV) in THF solution containing Bu\(_4\)NPF\(_6\) electrolyte (0.1 mol L\(^{-1}\), 295 K, see Supporting Information for further details).\(^{[20]}\) An irreversible oxidation was detected at \(E_{\text{pa}} = –0.34\) V for 5a and \(E_{\text{pa}} = –0.11\) V for 6 (vs. Cp\(_2\)Fe/Cp\(_2\)Fe\(^+\)). The compounds 5a and 6 each reveal one reversible reduction at \(E_{\text{pc}} = –1.62\) V (vs. Cp\(_2\)Fe/Cp\(_2\)Fe\(^+\)). The complexes 2\(^{[9]}\) and 3 confirm these values by the corresponding electrochemical behavior. For 3, an additional reduction event was monitored at –2.52 V (vs. Cp\(_2\)Fe/Cp\(_2\)Fe\(^+\)).

We experimentally performed the reduction of 5a and 6, respectively, with one equivalent of potassium graphite in THF at room temperature. The corresponding anionic compounds [(K\(_{\text{thf}}\)](L\(^2\)Co\(_n\))(μ\(_n\)η\(_n\)η\(_n\)-P\(_n\))] (2) and [(K\(_{\text{thf}}\)](L\(^2\)Co\(_n\))(μ\(_n\)η\(_n\)η\(_n\)-P\(_n\))] (3), respectively, are selectively quantitatively formed, which was proven by \(^{1}\)H NMR spectroscopy of the crude reaction solution. On a preparative scale, the isolated yields obtained as single crystals are 41% for 2 and 62% for 3. Consequently, regarding selectivity, this synthetic route is superior to the Co\(^{0}\)-mediated P\(_n\) activation, which, in contrast, yielded a mixture of products.

**Impact of ligand design**

Three β-diketimines (L\(^1\)H, L\(^2\)H, L\(^3\)H) were synthesized to provide a comparable hybrid ligand set L\(^1\)-L\(^3\) with backbone (R = H, Me) and aromatic (Ph\(^+_\) = dmp or dipp) substituents (Scheme 1 and Scheme 2), and to investigate the influence of the ligand design on the Co\(^0\)-mediated P\(_n\) transformation. The [LCo(tol)] \([L = L\(^1\) \ (4a), L\(^1\) \ (4b), L\(^2\) \ (4c)]\) starting materials were prepared in one-pot reactions (see the Supporting Information). All conducted P\(_n\) activation reactions were performed under the same conditions ([LCo(tol)]\(\times\)P\(_n\) = 2:1, toluene, 2–3 h, RT) and yielded similar isolated products \([L\text{Co}](\mu\(_n\)η\(_n\)η\(_n\)-P\(_n\))] \([L = L\(^1\) \ (5a), L\(^1\) \ (5b), L\(^2\) \ (5c)]\). The crystals of all the new compounds 5a–c were grown from saturated toluene solutions, and single crystal X-ray diffraction was performed. The molecular structures of 5a–c are shown in Figure S5 in the Supporting Information. As a representative, compound 5a is presented in Figure 4a. Its P\(_n\) moiety is rectangularly shaped, consequently spanned by two shorter and two longer P–P atom distances. Together with two coordinating Co atoms, the [P\(_2\)Co\(_n\)] complex core builds a distorted octahedron. In 5a–c, the shorter P–P atom distances are between 2.1256(8) and 2.1301(7) Å and the longer P–P distances are between 2.2513(10) and 2.2980(7) Å. Compared with a phosphorus single bond in the tetrahedral P\(_n\), the planar rectangular-shaped P\(_n\) moieties in 5a–c contain a pair of shorter and a pair of elongated P–P bonds. The Co–Co distances in 5a–c are between 3.502 and 3.610 Å and, therefore, any bonding interaction can be ruled out. Due to the centrosymmetric molecular structure (P2\(\text{I}_{\text{I}}\) in 5a–c), the ligands are parallel to each other. In 5a–c, the torsion angles θ

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**Scheme 2.** Performed Co\(^0\)- and Co\(^{0}\)-mediated P\(_n\) transformations.
The \(^1\)H NMR spectra of the compounds 5a–c display signals between 11.99 and \(-28.61\) ppm and reveal their paramagnetic nature in solution. Therefore, no signals are detected in their \(^{31}\)P\(^{1}\)H NMR spectra. Their magnetic moment (\(\mu_{\text{BH}}\)) in solution (RT) was determined by the Evans method: 3.02 \(\mu_\text{B} \) (5a\(^{2}\)) in \(\text{C}_\text{D}_\text{O}\), 2.42 \(\mu_\text{B} \) (5b in \(\text{C}_\text{D}_\text{O}\)), 1.84 \(\mu_\text{B} \) (5c in \(\text{D}_\text{2}\text{THF}\)). In the solid state, however, the SQUID measurements of 5a and 5b display diamagnetic behavior in the temperature range of 2–300 K. Their electronic structure in the solid state is best described as two antiferromagnetically coupled Co\(^{3}\) centers bridged by a \([\text{P}_\text{4}]^+\) ligand similar to the previously reported compounds E1,2\(^{0}\) in solution, exclusively one signal set for the ligand is observed in the \(^1\)H NMR spectrum of 5a–c, respectively, suggesting the integrity of each dinuclear compound in solution on the NMR time scale (Figure S15).

**Conclusion**

We reported different \([\text{LCo}]\)-mediated \(\text{P}_\text{2}\) activations yielding neutral complexes \([\text{[LCo]}_2(\mu_\text{4}-\eta_\text{5}^\text{1}-\eta_\text{5}^\text{2}-\eta_\text{2}^\text{1}-\text{P}_\text{3}] \right\}{\text{L}=\text{L}^1, \text{L}^2, \text{L}^3, \text{L}^4}\), each containing a similar rectangular-shaped \([\text{P}_\text{2}]^2\) moiety. In contrast to the \(\text{P}_\text{2}\) activation by \(\text{LFe}^\text{2}\) compounds, for the Co system, the ligand substituents (L\(^1\)–L\(^3\)) do not alter the reaction outcome. For the ligand system L\(^1\), we demonstrate that one P atom can be extruded thermally to generate an unprecedented neutral cyclo-[\(\text{P}_\text{2}]^2\)-containing compound \([\text{[LCo]}_2(\mu_\text{4}-\eta_\text{5}^\text{1}-\eta_\text{5}^\text{2}-\eta_\text{2}^\text{1}-\text{P}_\text{3}]\) ].

As a novel approach, we present the \(\text{P}_\text{2}\) transformation with a formal \([\text{LCo}]^2\) precursor, which generates corresponding mononanoins with cyclo-[\(\text{P}_\text{2}]^2\) and cyclo-[\(\text{P}_\text{3}]^2\) ligands as a mixture of products. Each product was selectively accessed through the one-electron reduction of its neutral precursor.

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**Keywords:** cyclic voltammetry · paramagnetic NMR · small molecule activation · white phosphorus · \(\beta\)-diketimines

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[10] After lithiation of L3H and subsequent transmetalation with CoBr2, its reduction was performed with an excess of potassium graphite under N2 atmosphere.

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[15] Due to the disorder of the cyclo-p3 moiety, only the geometric parameters of the major component are discussed. Furthermore, it has to be noted that the positions of the disordered P3 and P3A atoms are close to each other and hence, the involved bond lengths might not be determined with high accuracy.

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[21] During the thermolysis, a black, pyrophoric precipitate is formed. The CHN analysis of the washed and dried precipitate suggests only some organic content (C%: &35, H%: &5, N%: &3). Exclusively, compound 6 and 1H were detected in the 1H NMR spectrum (reaction control) as the only soluble products formed during the thermolysis reaction.

[22] For initial investigations see reference [20]. For further information see the Supporting Information.