▋ Phosphorus Chemistry

Nacnac-Cobalt-Mediated P$_4$ Transformations

Fabian Spitzer,[a] Christian Graßl,[a] Gábor Balázs,[a] Eric Mädl,[a] Martin Keilwerth,[b] Eva M. Zolnhofer,[b] Karsten Meyer,[b] and Manfred Scheer*[a]

Dedicated to Professor Walter Frank on the occasion of his 60th birthday

Abstract: A comparison of P$_4$ activations mediated by low-valent β-diketiminato (L) cobalt complexes is presented. The formal Co^0 source [K$_2$(L^{3}Co)$_2$(μ$_2$:η^1,η^1-N$_2$)] (**1**) reacts with P$_4$ to form a mixture of the monoanionic complexes [K(thf)$_6$][(L^{3}Co)$_2$(μ$_2$:η^4,η^4-P$_4$)] (**2**) and [K(thf)$_6$][(L^{3}Co)$_2$(μ$_2$:η^3,η^3-P$_3$)] (**3**). The analogue Co^I precursor [L^{3}Co(tol)] (**4a**), however, selectively yields the corresponding neutral derivative [(L^{3}Co)$_2$(μ$_2$:η^4,η^4-P$_4$)] (**5a**). Compound **5a** undergoes thermal P atom loss to form the unprecedented complex [(L^{3}Co)$_2$(μ$_2$:η^3,η^3-P$_3$)] (**6**). The products **2** and **3** can be ob-

tained 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^I-mediated P$_4$ activation is not influenced by applying the structurally different ligands L^1 and L^2, which is proven by the formation of the isostructural products [(LCo)$_2$(μ$_2$:η^4,η^4-P$_4$)] [L=L^3 (**5a**), L^1 (**5b**), L^2 (**5c**)].

Introduction

The activation of white phosphorus (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 P$_4$ transformation pathway in the coordination sphere of transition metals is necessary. Thus, a variety of P$_n$ ligand moieties were stabilized to give insight into the stepwise P$_4$ degradation and aggregation processes using well-established ligand systems such as the Cp^R family (Cp=cyclopentadienyl).[1] However, over the last years, β-diketiminato (nacnac=L) ligand systems have gained increasing attention in mild P$_4$ activations using M^I precursors: The initial P$_4$ fixation step of an intact 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[3] and 8–10,[4] products with modified [P$_2$]$^{2-}$, [P$_4$]^0, [P$_4$]$^{2-}$ and [P$_8$]$^{4-}$ ligands, respectively, were obtained. So far, for nacnac systems, a [P$_3$]$^{3-}$ ligand was found solely in compound [(L^{3}VR)$_2$(*cyclo*-P$_3$)]$^{n-}$ (R=N(tolyl)$_2$, n=0,1; R=O(dipp), n=0) and [{L^{3}V(N(tolyl)$_2$)}$_2$(μ$_2$:η^3,η^2-*cyclo*-P$_3$)] (**A**, Scheme 1).[3c]

However, *cyclo*-P$_3$ complexes of the type [LM(μ$_2$:η^3,η^3-P$_3$)M′L′]$^{\pm n}$ have been structurally characterized using neutral, tridentate triphos (1,1,1-tris(diphenylphosphinomethyl)ethane)

[a] F. Spitzer, Dr. C. Graßl, Dr. G. Balázs, Dr. E. Mädl, Prof. Dr. M. Scheer
Institut für Anorganische Chemie, Universität Regensburg
Universitätsstrasse 31, 93040 Regensburg (Germany)
E-mail: manfred.scheer@chemie.uni-regensburg.de
Homepage: http://www.uni-regensburg.de/chemie-pharmazie/anorgani-
sche-chemie-scheer/

[b] M. Keilwerth, E. M. Zolnhofer, Prof. Dr. K. Meyer
Department of Chemistry and Pharmacy, Inorganic Chemistry
Friedrich-Alexander University Erlangen-Nürnberg (FAU)
Egerlandstrasse 1, 91058 Erlangen (Germany)

⊞ Supporting information and the ORCID number(s) for the author(s) of this
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Scheme 1. Selected examples of P$_n$-TM complexes containing ligands **L^0–L^4** (**L^0**=CH[CHN(2,6-iPr$_2$C$_6$H$_3$)]$_2$, **L^1**=CH[C(Me)N(2,6-Me$_2$C$_6$H$_3$)]$_2$, **L^2**=CH[CHN(2,6-Me$_2$C$_6$H$_3$)]$_2$, **L^3**=CH[C(Me)N(2,6-iPr$_2$C$_6$H$_3$)]$_2$, **L^4**=CH[C(Me)N(2,6-Et$_2$C$_6$H$_3$)]$_2$). Bottom: Comparison of the nacnac ligands used in this study, **L^1**, **L^2** and **L^3**.[5]

and etriphos (1,1,1-tris(diethylphosphinomethyl)ethane) ligands in different combinations with 3d metals (Fe, Co, Ni) and 4d metals (Rh, Pd).[6] The influence of the ligand substituents in Fe^{I}-mediated P$_4$ transformation has recently been illustrated by a comparative study using a set of ligands L^1-L^3 (Scheme 1).[7] 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-Diisopropylphenyl (dipp) substituents as the ligands' aromatic flanking groups support the formation of the dinuclear complexes [(L^{3}Fe)$_2$(μ_2:η^4,η^4-P$_4$)] (**B**)[7] and [(L^{0}Fe)$_2$(μ_2:η^2,η^2-P$_2$)$_2$] (**C**).[4c] The latter was synthesized by the Driess group.[4c] The ligands L^0 and L^3 only differ in their backbone substituents. However, for sterically less demanding 2,6-dimethylphenyl (dmp) substituents, the formation of the tetranuclear complexes [(LFe)$_4$(μ_4:η^2,η^2,η^2,η^2-P$_8$)] [L=L^1 (**D1**), L^2 (**D2**)] with dimerized P$_4$ 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 [L^{3}Co]-mediated transformations of white phosphorus, which resulted in novel P$_4$- and P$_3$-containing complexes (vide infra). In the meantime, Driess and co-workers reported P$_4$ activation by [LCo] fragments leading to the neutral complexes [(LCo)$_2$(μ_2:η^4,η^4-P$_4$)] [L=L^0 (**E1**), L^4 (**E2**)] (Scheme 1).[4b] One-electron reduction led to the monoanionic products [K(dme)$_4$][(LCo)$_2$(μ_2:η^4,η^4-P$_4$)] [L=L^0 (**F1**), L^4 (**F2**)] and transformed the [P$_4$]^0 middle deck into a [P$_4$]$^{2-}$ ligand. Recently, Wolf and co-workers have reported on [(BIAN)Co]$^-$-mediated P$_4$ activations with a nacnac-related bidentate redox non-innocent BIAN (1,2-bis(2,6-diisopropylphenylimino)acenaphthene) ligand system yielding compounds containing [P$_4$]$^{4-}$ moieties.[8]

Motivated by our first results with [L^{3}Co] compounds, we speculated that the P$_4$ activation outcome should be sensitive to the oxidation state of the precursor (Co^0 versus Co^I). Additionally, we wanted to address the question of the ligands' influence (L^1–L^3) in Co^I-mediated P$_4$ activations and we were intrigued by the observed P-atom extrusion from the initially obtained P$_4$ middle deck to form P$_3$ compounds. The latter ones are still quite rare in comparison to P$_4$ ligand complexes.

Here, we report on the P$_4$ activation by a formal Co^0 precursor yielding the monoanionic [K(thf)$_6$][(L^{3}Co)$_2$(μ_2:η^4,η^4-P$_4$)] (**2**) and [K(thf)$_6$][(L^{3}Co)$_2$(μ_2:η^3,η^3-P$_3$)] (**3**). Through a Co^I-mediated P$_4$ 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 Co^0 precursor [K$_2$(L^{3}Co)$_2$(μ_2:η^1,η^1-N$_2$)] (**1**) was synthesized by a one-pot reaction and was isolated as two different solvomorphs, **1**·solv (solv=n-hexane[9] or OEt$_2$).[10] The X-ray structures of **1**·solv consist of two [L^{3}Co] fragments bridged by a N$_2$ unit. Two potassium atoms cover the N$_2$ moiety and are

coordinated in the phenyl pockets of the dipp substituents.[11] The N—N distance in **1**·n-hexane/OEt$_2$ 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 [K$_2$(L^{5}Co)$_2$(μ_2:η^1,η^1-N$_2$)] [L^5=CH[C(tBu)N(2,6-iPr$_2$C$_6$H$_3$)]$_2$].[12] The presence of a [N$_2$]$^{2-}$ moiety in **1**·n-hexane is supported by Raman spectroscopy (ν_{NN} = 1568 cm^{-1}).[9] The reaction of **1** with P$_4$ proceeds by N$_2$ evolution, showing that the formal [N$_2$]$^{2-}$ 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 P$_4$ and the formation of a mixture of the monoanionic complexes [K(thf)$_6$][(L^{3}Co)$_2$(μ_2:η^4,η^4-P$_4$)] (**2**) and [K(thf)$_6$][(L^{3}Co)$_2$(μ_2:η^3,η^3-P$_3$)] (**3**), which were detected by ^{1}H NMR spectroscopy.[13] The appearance of a *cyclo*-P$_3$ moiety in product **3** indicates that an extrusion of one P atom from the *cyclo*-P$_4$ moiety in **2** is possible. However, if the reaction is conducted with two equivalents of P$_4$, compound **2** is the only product found in the ^{1}H NMR spectrum.

The solid state structure of **2**·2 thf reveals a salt consisting of two [K(thf)$_6$]$^+$ cations and two crystallographically distinguishable [(L^{3}Co)$_2$(μ_2:η^4,η^4-P$_4$)]$^-$ monoanions (Figure 1).[9] Each anion is a centrosymmetric dicobalt complex that consists of two [L^{3}Co] fragments bridged by a planar *cyclo*-P$_4$ ligand. The P—P
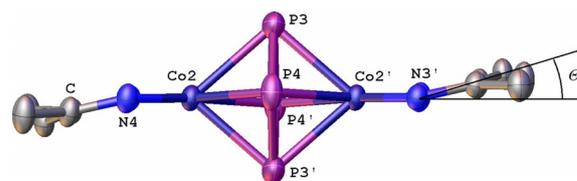
Figure 1. Anionic part of the molecular structure of **2**. Hydrogen atoms and aromatic flanking groups are omitted for clarity; thermal ellipsoids are drawn at 50% probability level. The torsion angle Θ is depicted spanning between the Co···Co′ axis and the plane formed by the nitrogen atoms and the methine carbon in the ligand backbone.

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*-[P$_4$]$^{2-}$ moiety (2.178(1) and 2.207(1) Å) of the reported compound [(L^{3}Fe)$_2$(μ_2:η^4,η^4-P$_4$)] (**B**).[7] The central P$_4$ 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**·2 thf and the related compounds [K(dme)$_4$][(LCo)$_2$(μ_2:η^4,η^4-P$_4$)] [L=L^0 (**F1**), L^4 (**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 monoanionic [(L^{3}Co)$_2$(μ_2:η^3,η^3-P$_3$)]$^-$ was obtained in two different solvomorphs [K(dme)$_4$][(L^{3}Co)$_2$(μ_2:η^3,η^3-P$_3$)]·dme (**3a**)

Table 1. Comparison of P—P and Co···Co' atomic distances and torsion angles Θ in anions of [K(solv)$_x$][(LCo)$_2$(μ_2:η^4,η^4-P$_4$)] (L = L^3 (**2**)[9], L^0 (**F1**)[4b], L^4 (**F2**)[4b]).

Complex	2:anion 1	2:anion 2	F1[4b]	F2[4b,a]
d(P—P) [Å]	2.1913(10)	2.1897(10)	2.1739(7)	2.154(1)[a]
	2.1951(10)	2.2004(10)	2.1976(7)	2.163(1)[a]
				2.225(1)[a]
				2.230(1)[a]
d(Co···Co') [Å]	3.603	3.625	3.626	3.603
Θ [°]	13.87(6)	15.87(6)	15.33(4)	6.60(8)[a]
				14.97(7) [a]

[a] Anion of **F2** is not centrosymmetric. Therefore, four individual d(P—P) and two Θ values are given.

and [K(thf)$_6$][(L^{3}Co)$_2$(μ_2:η^3,η^3-P$_3$)]·2 thf (**3 b**). Both compounds are ionic and consist of solvent (DME or THF) molecules, one solvent-saturated potassium counter ion, and the [(L^{3}Co)$_2$(μ_2:η^3,η^3-P$_3$)]$^-$ monoanion (Figures 2 and 3). In both X-ray structures, the complex anions are built from two [L^{3}Co] fragments bridged by a P$_3$ triangle. In **3 a**, the L^3 ligand planes are almost parallel to each other with an dihedral angle of 2.00(7)° (N1-N2 versus N3-N4). However, in **3 b**, the ligand planes are in a twisted conformation with a dihedral angel of 74.2(4)° (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*-P$_3$ middle deck is disordered over two positions in **3 a** (occupancy 81:19).[15] The middle deck in **3 b**, however, is localized at one distinct position. As can be seen in Table 2, the P—P distances in **3 a** are similar to the ones in the

Table 2. Comparison of selected atomic distances and angles in the [(L^{3}Co)$_2$(μ_2:η^3,η^3-P$_3$)]$^-$ anion in **3 a** (major component) and **3 b**, [{L^{3}V(N(tolyl)$_2$)}$_2$(μ_2:η^3,η^2-*cyclo*-P$_3$)] (**A**)[3c] and the dication in [(triphos)Co(μ_2:η^3,η^3-*cyclo*-P$_3$)Fe(etriphos)](PF$_6$)$_2$ (**G**).[6b]

Complex	3 a	3 b	A[3c]	G[6b]
d(P—P) [Å]	2.1674(13)	2.217(4)	2.1658(10)	2.226(8)
	2.1790(16)	2.224(4)	2.1804(9)	2.229(8)
	2.3303(17)	2.237(4)	2.2155(9)	2.234(8)
∢ (P-P-P) [°]	57.34(5)	59.59(13)	59.03(3)	
	57.82(5)	59.93(14)	59.68(3)	–
	64.84(5)	60.48(13)	61.29(3)	
d(M···M') [Å]	3.7359(5)	3.724(2)	4.460	3.80
Θ [°]	9.43(7)	8.7(3)	–	–
	12.22(7)	13.5(6)		

Figure 2. Comparison of the anions in the molecular structures of **3 a** (left) and **3 b** (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*-P$_3$ ligand is drawn in **3 a**.

nacnac containing compound [{L^{3}V(N(tolyl)$_2$)}$_2$(μ_2:η^3,η^2-*cyclo*-P$_3$)] (**A**),[3c] displaying a *cyclo*-[P$_3$]$^{3-}$ moiety. In **3 b**, they compare better with the ones in [(triphos)Co(μ_2:η^3,η^3-*cyclo*-P$_3$)Fe(etriphos)](PF$_6$)$_2$ (**G**).[6b] Overall, they are in line with P—P single bonds [for comparison: P—P single bond in white phosphorus determined by X-ray diffraction: 2.209(5) Å,[16] electron diffraction: 2.1994(3) Å,[17] Raman spectroscopy: 2.2228(5) Å,[18] and DFT calculations: 2.1994(3) Å[17]]. The Co—P distances in **3 a** are between 2.2046(17) and 2.3684(8) Å and for **3 b** in the range of 2.248(3) and 2.277(3) Å. The Co···Co' distance in **3 a** is 3.7359(5) and amounts to 3.724(2) Å in **3 b**, which is slightly elongated compared to **2** (3.603 and 3.625 Å, Table 1).

The ^{1}H NMR spectra in [D$_8$]THF display signals between 11.42 and −35.29 ppm for **2**[9] and 8.15 and −12.85 ppm for **3**, respectively. Except for the THF and DME signals, respectively, the ^{1}H NMR spectra of **3 a,b** do not deviate from each other. No signals are detected in the ^{31}P{^{1}H} NMR spectra for **2** and **3** due to their paramagnetic nature. Their magnetic moment (μ_{eff}) in [D$_8$]THF solution (RT) was determined by the Evans method: 3.90 μ_B (**2**) and 3.51 μ_B (**3**). In the solid state, these values are confirmed by SQUID measurements displaying a gradual decrease of the magnetic moment in the temperature range from 300 to 2 K of 3.80 to 3.30 μ_B in **2** and 3.58 to 1.70 μ_B in **3 a**. Therefore, the electronic structure of **2** is best described as containing a [P$_4$]$^{2-}$ moiety bridging mixed valence Co^I and Co^{II} centers. This is in agreement with the previously reported compounds **F1** and **F2**.[4b] Compound **3**, however, contains a [P$_3$]$^{3-}$ ligand, which is bridged by two Co^{II} metal centers.

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

As mentioned above, starting from the formal Co⁰ 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^I starting material [L^{3}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^I compound [L^{3}Co(tol)] (**4a**) was reacted with P$_4$, and [(L^{3}Co)$_2$(μ$_2$:η^4,η^4-P$_4$)] (**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^{3}Co)$_2$(μ$_2$:η^3,η^3-P$_3$)] (**6**),[19] which was clearly characterized by mass spectrometry[20] and ¹H NMR spectroscopy.[21] The dinuclear compound contains two [L^{3}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 2.2155(9) Å).[3c] 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 ¹H NMR spectrum of **6** reveals signals between 20.06 and −12.68 ppm. No signal is detected in the ³¹P{¹H} NMR spectrum. The magnetic moment (μ$_{eff}$) of **6** in C$_6$D$_6$ solution is 2.97 μ$_B$ 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$_B$ was measured in the temperature range from 300 to 2 K (see the Supporting Information). The values are in agreement with antiferromagnetically coupled Co^{II} and Co^{III} 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 $E_{1/2}$ = −0.34 V for **5a** and $E_{1/2}$ = −0.11 V for **6** (vs. Cp$_2$Fe/Cp$_2$Fe$^+$). The compounds **5a** and **6** each reveal one reversible reduction at $E_{1/2}$ = −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(thf)$_6$][(L^{3}Co)$_2$(μ$_2$:η^4,η^4-P$_4$)] (**2**) and [K(thf)$_6$][(L^{3}Co)$_2$(μ$_2$:η^3,η^3-P$_3$)] (**3**), respectively, are selectively and quantitatively formed,

which was proven by ¹H 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 Co⁰-mediated P$_4$ 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
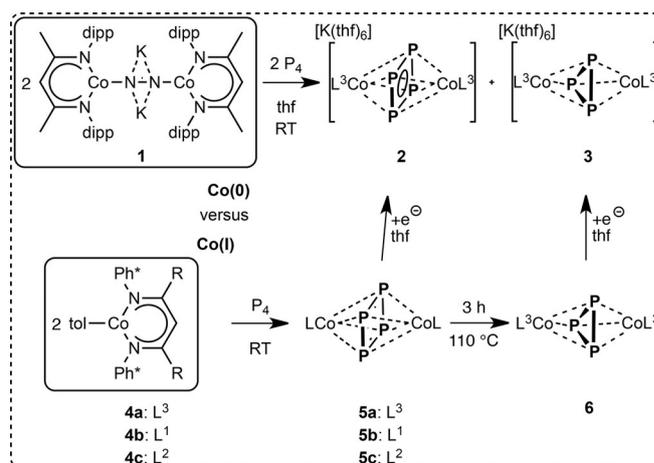
Scheme 2. Performed Co⁰- and Co^I-mediated P$_4$ transformations.

design on the Co^I-mediated P$_4$ transformation. The [LCo(tol)] [L=L^3 (**4a**), L^1 (**4b**), L^2 (**4c**)] starting materials were prepared in one-pot reactions (see the Supporting Information). All conducted P$_4$ activation reactions were performed under the same conditions ([LCo(tol)]:P$_4$ = 2:1, toluene, 2–3 h, RT) and yielded similar isolated products [(LCo)$_2$(μ$_2$:η^4,η^4-P$_4$)] [L=L^3 (**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$_4$ moiety is rectangularly shaped, consequently spanned by two shorter and two longer P–P atom distances. Together with two coordinating Co atoms, the [P$_4$Co$_2$] complex core builds a distorted octahedron. In **5a–c**, the shorter P–P atom distances are between 2.1256(6) 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$_4$, the planar rectangular-shaped P$_4$ 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$_1$/n in **5a–c**), the ligands are parallel to each other. In **5a–c**, the torsion angles Θ
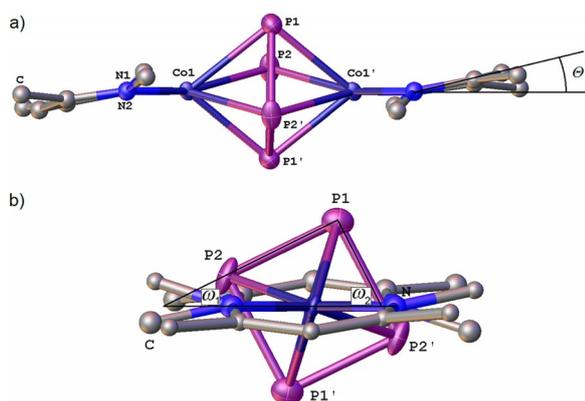
Figure 4. a) Molecular structure of the compound **5a**. Hydrogen atoms and aromatic flanking groups are omitted for clarity; thermal ellipsoids are drawn at 50% probability level. The torsion angle Θ is depicted, which spans between the Co···Co′ axis and the plane formed by the nitrogen atoms and the methine carbon in the ligand backbone; b) view along Co1···Co1′ axis, revealing the angles ω_1 and ω_2, which span between the N—N axis of coordinating nitrogen atoms and the edges of the cyclo-P_4 unit.

(between the Co···Co′ axis and the plane formed by the nitrogen atoms and the methine carbon in the ligand backbone) are between 3.40(6) and 12.32(6)°. In **5b,c** (and **E1,2**[4b]), the P—P edges of the cyclo-P_4 unit are nearly parallel or rectangular, respectively, compared to the N—N axis of coordinating nitrogen atoms (compare ∡(NN-PP$_{short}$) = ω_1 and ∡(NN-PP$_{long}$) = ω_2, see Figure 4b). The structural parameters of **5a–c** and **E1,2** are summarized in Table 3.

Table 3. Comparison of P—P and Co···Co′ atomic distances in neutral [(LCo)$_2$(μ_2:η^4,η^4-P$_4$)] [L=L^3 (**5a**), L^1 (**5b**), L^2 (**5c**), L^0 (**E1**), L^4 (**E2**)].

Complex	5a	5b	5c	E1[4b]	E2[4b]
d(P—P) short [Å]	2.1295(10)	2.1256(6)	2.1301(7)	2.1237(13)	2.1298(14)
d(P—P) long [Å]	2.2513(10)	2.2972(6)	2.2980(7)	2.2984(13)	2.2889(15)
d(Co···Co′) [Å]	3.610	3.502	3.503	3.491	3.533
Θ [°]	12.22(8)	12.32(6)	3.40(6)	14.88(9)	7.0(1)
ω_1 [°]	26.34(6)	2.18(4)	1.97(4)	1.96(7)	2.58(8)
ω_2 [°]	62.36(6)	87.87(4)	87.95(4)	88.02(7)	87.43(8)

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 (μ_{eff}) in solution (RT) was determined by the Evans method: 3.02 μ_B (**5a**[22] in C$_6$D$_6$), 2.42 μ_B (**5b** in C$_6$D$_6$), 1.84 μ_B (**5c** in [D$_8$]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^I centers bridged by a [P$_4$]^0 ligand similar to the previously reported compounds **E1,2**.[4b] In solution, exclusively one signal set for the ligand is observed in the ^{1}H NMR spectrum of **5a–c**, respectively, sug-

gesting the integrity of each dinuclear compound in solution on the NMR time scale (Figure S15).

Conclusion

We reported different [LCo^I]-mediated P$_4$ activations yielding neutral complexes [(LCo)$_2$(μ_2:η^4,η^4-P$_4$)] (L=L^1, L^2, L^3), each containing a similar rectangular-shaped [P$_4$]^0 moiety. In contrast to the P$_4$ activation by LFe^I compounds, for the Co system, the ligand substituents (L^1–L^3) do not alter the reaction outcome. For the ligand system L^3, we demonstrate that one P atom can be extruded thermolytically to generate an unprecedented neutral cyclo-[P$_3$]$^{3-}$-containing compound [(L^{3}Co)$_2$(μ_2:η^3,η^3-P$_3$)]. As a novel approach, we present the P$_4$ transformation with a formal [L^{3}Co^0] precursor, which generates corresponding monoanions with cyclo-[P$_4$]$^{2-}$ and cyclo-[P$_3$]$^{3-}$ ligands as a mixture of products. Each product was selectively accessed through the one-electron reduction of its neutral precursor.

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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.

[11] In **1**·*n*-hexane the NCCCN ligand planes are orientated parallel to each other. However, in **1**·OEt₂, they are twisted (dihedral angel of coordinating N atoms: 32.38(9)°). Further analytical data (X-ray, ¹H NMR, Evans method, EA, Raman spectrum) and pictures of **1**·solv are presented in the Supporting Information.

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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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[19] The crystal structures of **6** and **5a** were initially reported in reference [20]. However, to present improved structural values, crystals of **6** and **5a** were re-measured.

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