

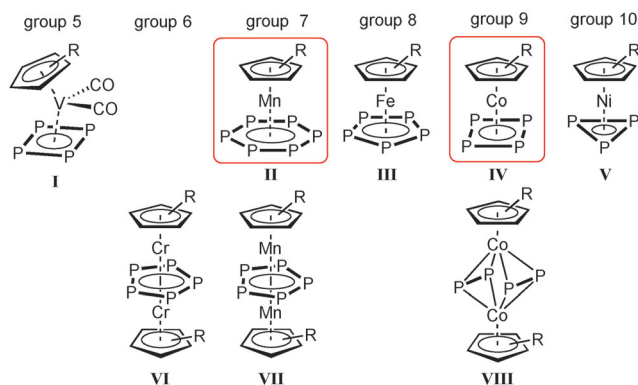
cyclo-P₄ ComplexesInternational Edition: DOI: 10.1002/anie.201610967
German Edition: DOI: 10.1002/ange.201610967The Cobalt cyclo-P₄ Sandwich Complex and Its Role in the Formation of Polyphosphorus Compounds

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Dedicated to Professor Evamarie Hey-Hawkins on the occasion of her 60th birthday

Abstract: A synthetic approach to the sandwich complex $[\text{Cp}^{\text{R}}\text{Co}(\eta^4\text{-P}_4)]$ (**2**) containing a cyclo-P₄ ligand as an end-deck was developed. Complex **2** is the missing homologue in the series of first-row cyclo-P_n sandwich complexes, and shows a unique tendency to dimerize in solution to form two isomeric P₈ complexes $[(\text{Cp}^{\text{R}}\text{Co})_2(\mu, \eta^4:\eta^2:\eta^1\text{-P}_8)]$ (**3** and **4**). Reactivity studies indicate that **2** and **3** react with further $[\text{Cp}^{\text{R}}\text{Co}]$ fragments to give $[(\text{Cp}^{\text{R}}\text{Co})_2(\mu, \eta^2:\eta^2\text{-P}_2)_2]$ (**5**) and $[(\text{Cp}^{\text{R}}\text{Co})_3\text{P}_8]$ (**6**), respectively. Furthermore, complexes **2**, **3**, and **4** thermally decompose forming **5**, **6**, and the P₁₂ complex $[(\text{Cp}^{\text{R}}\text{Co})_3\text{P}_{12}]$ (**7**). DFT calculations on the P₄ activation process suggest a $\eta^3\text{-P}_4$ Co complex as the key intermediate in the synthesis of **2** as well as in the formation of larger polyphosphorus complexes via a unique oligomerization pathway.

Among the many examples of transition metal complexes with polyphosphorus ligands resulting from the activation and transformation of white phosphorus, the classes of compounds containing a cyclo-P_n ligand as an end-deck are limited to only a few examples (Scheme 1).^[1] This is surprising considering the extensive research activity and the many isolobal relatives among the carbon-based arenes, a well-established class of compounds in organometallic chemistry including catalysis.^[2] However, in contrast to the carbon aromatic ligands, the phosphorus atoms possess coordinatively active lone pairs enabling their reactivity. The resulting associated reactivity is valuable for the formation of e.g.,



Scheme 1. Selected classes of polyphosphorus ligand complexes, exemplified for 3d elements. The compounds in red frames are still unknown.

novel heterocycles and P-rich compounds.^[3] Moreover, their coordination behavior regarding the formation of unique organometallic-organic hybrid compounds^[4] and spherical supramolecules attracts increasing interest. In contrast, triple-decker complexes with a P_n ligand as a middle-deck are not able to form spherical supramolecules and their coordination properties result in oligomeric and polymeric assemblies.^[5] This underlines the importance of complexes containing a cyclo-P_n ligand as an end-deck for building blocks in aggregation chemistry. By using the cyclo-P₅ complex $[\text{Cp}^*\text{Fe}(\eta^5\text{-P}_5)]$ ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$) in the reactions with Cu^I halides, spherical and capsule-like supramolecules were obtained.^[6] These inorganic cage compounds serve as containers for small guest molecules such as carboranes and ferrocene and can even stabilize $[\text{CpCr}(\eta^5\text{-As}_5)]$ ($\text{Cp} = \text{cyclopentadienyl}$), which is not known to exist as a free molecule.^[6b] Moreover, we could demonstrate that, by using the cyclo-P₄ complex $[\text{Cp}^{\text{R}}\text{Ta}(\text{CO})_2(\eta^4\text{-P}_4)]$ in the reaction with CuCl, the smallest spherical molecule $[(\text{Cp}^{\text{R}}\text{Ta}(\text{CO})_2(\mu, \eta^4:\eta^1:\eta^1:\eta^1\text{-P}_4))_6\{\text{CuCl}\}_8]$ ($\text{Cp}^{\text{R}} = \eta^5\text{-C}_5\text{H}_3\text{tBu}_2$) containing 32 non-carbon atoms could be obtained. This sphere is composed of four- and six-membered rings and is therefore unique in the family of fullerenes and fullerene-like molecules.^[7]

It is astonishing that mononuclear cyclo-P₄ complexes are only known for Group 5 metal complexes $[\text{Cp}^{\text{R}}\text{M}(\text{CO})_2(\eta^4\text{-P}_4)]$ (type I: $\text{M} = \text{V},^{[8]}$ $\text{Nb},^{[9]}$ $\text{Ta},^{[10]}$ $\text{Cp}^{\text{R}} = \text{C}_5\text{Me}_5, \text{C}_5\text{H}_3\text{tBu}_2$), which were synthesized by co-photolysis of P₄ with metal carbonyl complexes (Scheme 1). Iron cyclo-P₅ sandwich complexes $[\text{Cp}^{\text{R}}\text{Fe}(\eta^5\text{-P}_5)]$ (type III: $\text{Cp}^{\text{R}} = \text{C}_5\text{Me}_5,^{[11]}$ $\text{C}_5\text{Me}_4\text{Et},^{[12]}$ $\text{C}_5\text{H}_2\text{tBu}_3,^{[13]}$ $\text{C}_5(\text{CH}_2\text{Ph})_5,^{[14]}$ and nickel cyclo-P₃ sandwich complexes $[\text{Cp}^{\text{R}}\text{Ni}(\eta^3\text{-P}_3)]$ (type V: $\text{Cp}^{\text{R}} = \text{C}_5\text{Me}_5,^{[15]}$

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$C_5H_3tBu_2$,^[16] $C_5H_2tBu_3$ ^[17] can be easily prepared by co-thermolysis of P_4 with metal carbonyl complexes. They are thermally stable compounds and can even be handled in air without decomposition. Moreover, to date, there is no known hexaphosphabenzene derivative of manganese (type **II**) and its heavier homologues. The most phosphorus-rich complex of manganese is $[Cp^{BIG}Mn(CO)_2(\eta^1-P_4)]$ ($Cp^{BIG} = C_5(4-nBuC_6H_4)_5$),^[18] and, recently, we have been able to synthesize the *cyclo*- P_5 -containing triple-decker complex (type **VII**).^[19]

Considering the thermal stability of the *cyclo*- P_3 and *cyclo*- P_5 sandwich complexes, it is surprising that cobalt *cyclo*- P_4 sandwich complexes **IV**, the missing homologues of this series, are not accessible under similar conditions. For instance, thermolysis of $[Cp^{III}Co(CO)_2]$ ($Cp^{III} = \eta^5-C_5H_2tBu_3$) in the presence of P_4 leads to the formation of the double P_2 ligand complex $[(Cp^{III}Co)_2(P_2)_2]$ (**5**) as the major product, along with traces of the larger polyphosphorus complexes $[(Cp^{III}Co)_3P_8]$ (**6**), $[(Cp^{III}Co)_3P_{12}]$ (**7**), and $[(Cp^{III}Co)_4P_{10}]$.^[20] In fact, the P_4 activation chemistry of cobalt half-sandwich precursors is tremendously rich, involving the degradation of the P_4 molecule into P_1 , P_2 , and P_4 units^[21] as well as the aggregation into extended polyphosphorus P_8 , P_{10} , P_{12} , P_{16} , and P_{24} cages (cf. Scheme S1 in SI).^[20,21b,22] Among these, *cyclo*- P_4 -containing complexes were accessible in polymetallic assemblies only.^[21g] In particular the aggregation behavior of P_4 moieties in studies in which the 14-valence-electron (VE) complex source $[(Cp^{III}Co)_2(\mu, \eta^4:\eta^4-C_7H_8)]$ (**1**) provided the largest known polyphosphorus ligands raised the question of whether the initial formed key intermediate was either the missing *cyclo*- P_4 complex **IV** or a different transient species. As this intermediate is a neutral and sterically unprotected compound (with standard Cp^R ligands), its stability might not be high, since the lattice energy in charged compounds is a decisive factor for stabilization as well as the steric bulk of large Cp ligands such as Cp^{BIG} .

Herein, we present the synthesis and single-crystal X-ray diffraction study of the cobalt *cyclo*- P_4 sandwich complex $[Cp^{III}Co(\eta^4-P_4)]$ (**2**), which is stable in the solid state, although a rather usual and sterically not encumbered Cp ligand is used, but shows an unprecedented tendency to dimerize in solution. Moreover, **2** is the first sandwich complex in which the metal is coordinated only by the Cp and the *cyclo*- P_4 ligand and represents the missing example of a Group 9 metal complex of type **IV**. Furthermore, the pathways of the formation of **2** as well as of polyphosphorus complexes were explored.

We reasoned that the *cyclo*- P_4 sandwich complex $[Cp^{III}Co(\eta^4-P_4)]$ (**2**) should be the direct product of the reaction of a 14-valence-electron $Cp^{III}Co$ metal fragment with P_4 , and performed a variable-temperature NMR study of a 1:2 mixture of $[(Cp^{III}Co)_2(\mu, \eta^4:\eta^4-C_7H_8)]$ (**1**) and P_4 in CD_2Cl_2 (Figure 1). When the frozen mixture was warmed to $-80^\circ C$ in the NMR spectrometer, a singlet appeared in the ^{31}P NMR spectrum at 165 ppm. Upon further warming to above $-55^\circ C$, this signal disappeared and the signals of complexes **5** and **6** arose. Considering the poor solubility of P_4 at low temperatures, this experiment indicates that a *cyclo*- P_4 species is initially formed in the reaction of **1** with P_4 , but reacts with excess **1** to form **5** and **6**.

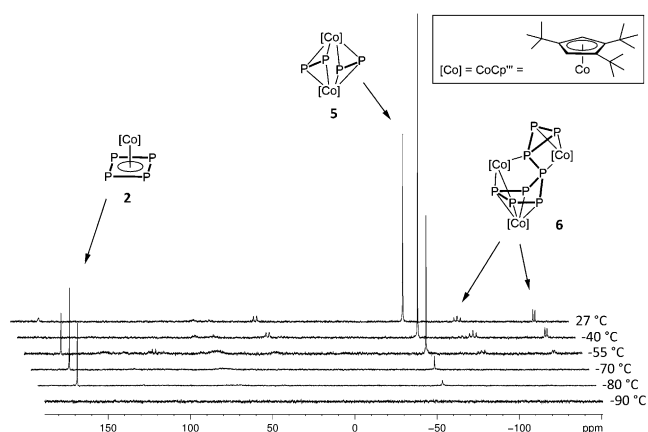
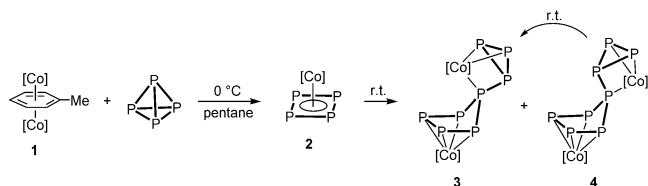


Figure 1. Variable-temperature ^{31}P NMR spectra of a 2:1 mixture of P_4 and **1** in CD_2Cl_2 starting at $-90^\circ C$.

Encouraged by these observations, we optimized the reaction conditions for the synthesis of **2** at different temperatures and solvents. A mixture of complexes with various polyphosphorus ligands was formed,^[22] and only traces of **2** were detected when toluene or THF were used as solvents. However, complex **2** appeared as the major product when hydrocarbons served as solvents.^[23] The highest yields for **2** were obtained by performing the reaction in *n*-pentane at $0^\circ C$ (Scheme 2).



Scheme 2. Synthesis and reactivity of *cyclo*- P_4 complex **2**. $[Co] = Cp^{III}Co$.

The column chromatographic separation of the reaction mixture afforded a red fraction of complex **2** which was followed closely by a brown fraction containing the two isomeric P_8 complexes $[(Cp^{III}Co)_2(\mu, \eta^4:\eta^2:\eta^1-P_8)]$ (**3**) and $[(Cp^{III}Co)_2(\mu, \eta^4:\eta^2:\eta^1-P_8)]$ (**4**) as well as traces of the P_{12} complex $[(Cp^{III}Co)_3P_{12}]$ (**7**). This indicates that **2** oligomerizes during the column chromatography, in particular because the fractions containing **5–7** and larger P_n complexes are eluted subsequently with toluene. Collection of the first part of the red fraction afforded **2** in 25% yield. The following red-to-brown fraction contained monomer **2** and the oligomerization products **3**, **4**, and **7** in the ratio of 84:11:4:1, respectively (cf. Figure S6). When a solution of **2**, **3**, and **4** in toluene was stored at room temperature for 5 hours, compound **3** crystallized exclusively while the amounts of **2**, **3**, and **4** in solution decreased (Figure S7). Similarly, **3** crystallized in 27% yield from a concentrated solution of pure **2** in *n*-hexane after 4 hours at room temperature (Figure S8). Both experiments clearly show the dimerization of **2** in solution and the isomerization of **4** to **3**, indicating the greater stability of the latter.

The *cyclo*-P₄ complex **2** gives a singlet at 175.2 ppm in the ³¹P NMR spectrum and one set of signals in the ¹H NMR spectrum for the Cp''' ligand. The ³¹P NMR spectra of **3** and **4** show the five multiplets of an AA'BCC'DX₂ and an AA'BCDD'XX' spin system, respectively (Figure 2). The simulation of the experimental ³¹P{¹H} NMR spectra reveals similar J_{PP} coupling constants for the P₈ ligands, indicating the isomeric nature of **3** and **4** (Table S1).

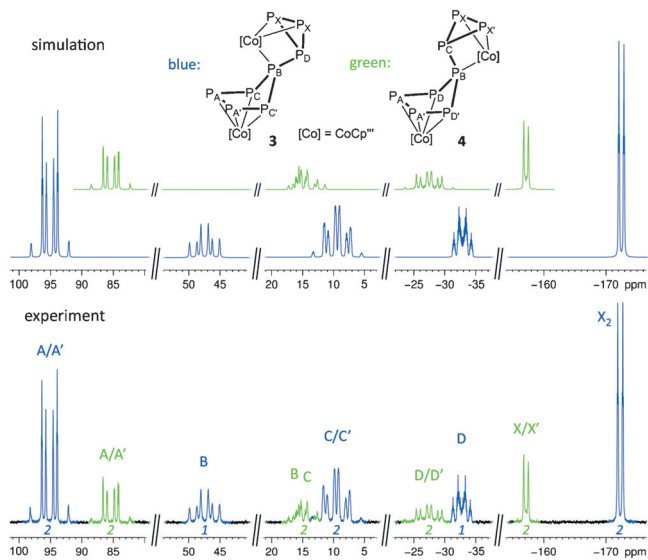


Figure 2. Section of the ³¹P{¹H} NMR spectrum (C₆D₆, 162.0 MHz, 300 K) of a solution containing **2**, **3**, and **4**. Experimental (below) and simulated (above) signals of **3** (blue) and **4** (green). Only the signals corresponding to **3** and **4** are shown.

Single crystals of **2** were obtained by the fast evaporation of *n*-pentane from a freshly prepared solution of **2**. A single-crystal X-ray diffraction study confirmed the identity of **2** as a *cyclo*-P₄ sandwich complex (Figure 3A) comprising an almost perfectly square-planar P₄ ligand. The P–P–P bond angles differ by less than 1° with an angular sum of 360.0°. The Cp''' ring and the P₄ ring are tilted away from each other by 1°. The P–P bonds (2.1557(18)–2.1699(14) Å) are significantly shorter than typical P–P single bonds (2.21 Å) and compare well with those in the dicesium salt of P₄²⁻ (2.147(1) Å).^[24] The molecular structure of **3** (Figure 3B) reveals a P₈ ligand containing a P₅–P₃ ring topology that acts as an eight-electron-donor ligand towards two CoCp''' metal fragments. The Co2–P5 bond (2.1574(12) Å) is significantly shorter than the Co–P bonds with π-character (2.3215(13)–2.2834(13) Å). The P–P bonds with double-bond character (P1–P3: 2.1356(16) Å, P2–P4: 2.1307(15) Å, P7–P8: 2.1359(17) Å) are shorter than the single bonds.

The reactivity of the *cyclo*-P₄ complex **2** towards CoCp''' fragments was investigated by adding 0.5 equivalents of **1** to a solution of **2** in toluene which led to the quantitative formation of **5** (Scheme 3). This is in agreement with the results of the low-temperature NMR study and provides an approach to dinuclear cobalt complexes of type **VIII** with different cyclopentadienyl ligands. Similarly, the transforma-

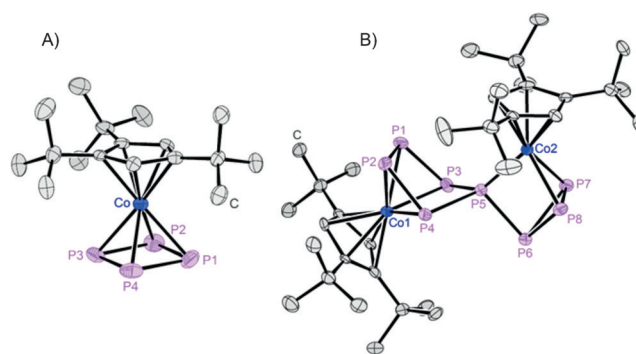
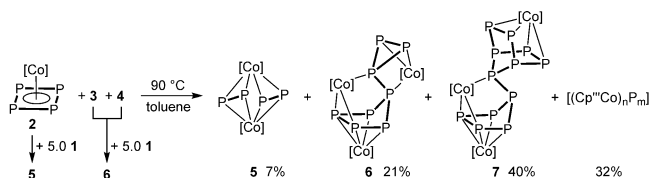


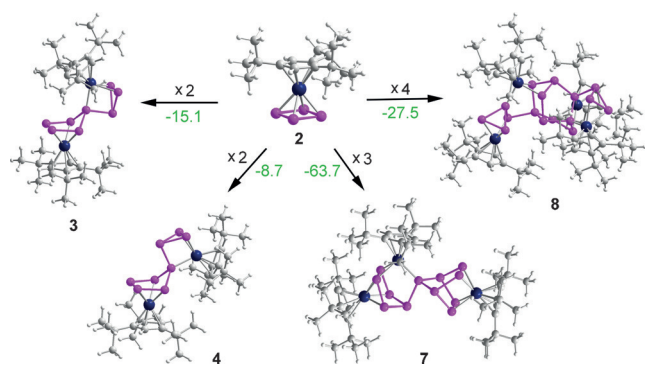
Figure 3. Molecular structure of A) **2** and B) **3**.^[27] Hydrogen atoms are omitted for clarity; thermal ellipsoids are drawn with 50% probability. Selected bond lengths [Å] and angles [°]: **2**: P1–P2 2.1557(18), P2–P3 2.1699(14), P3–P4 2.1659(16), P1–P4 2.1611(14), Co–P1 2.3273(13), Co–P2 2.3147(12), Co–P3 2.3050(12), Co–P4 2.3051(12), P1–P2–P3 89.70(6), P2–P3–P4 90.06(6), P3–P4–P1 89.67(6), P4–P1–P2 90.56(6), Co–P₄ 1.7350(5), Co–Cp_{cent} 1.6671(5). **3**: P1–P2 2.1573(17), P1–P3 2.1356(16), P2–P4 2.1307(15), P3–P5 2.2027(14), P4–P5 2.2019(15), P5–P6 2.1914(15), P6–P7 2.2390(17), P6–P8 2.2321(18), P7–P8 2.1359(17), Co1–P1 2.3206(15), Co1–P2 2.3074(13), Co1–P3 2.3215(13), Co1–P4 2.3124(13), Co2–P5 2.1574(12), Co2–P7 2.2912(13), Co2–P8 2.2834(13).



Scheme 3. Reactivity of complexes **2**, **3**, and **4**. [Co] = CoCp'''.

tion of complex **3** into complex **6** upon addition of 0.5 equiv of **1** proceeded cleanly. Furthermore, the thermal stability of complexes **2**, **3**, and **4** was studied by NMR spectroscopy (Figure S10). Before the mixture in toluene was heated, **2** was the major component; after the solution had been warmed to 90 °C, the amount of complexes **2**, **3** and **4** decreased continuously and complexes **5**, **6**, and **7** were formed. This clearly indicates the greater thermal stability of the complexes **5–7** and explains why **2–4** were not observed in the thermolytic reaction of [Cp'''Co(CO)₂] with P₄ in decalin at 190 °C.^[20]

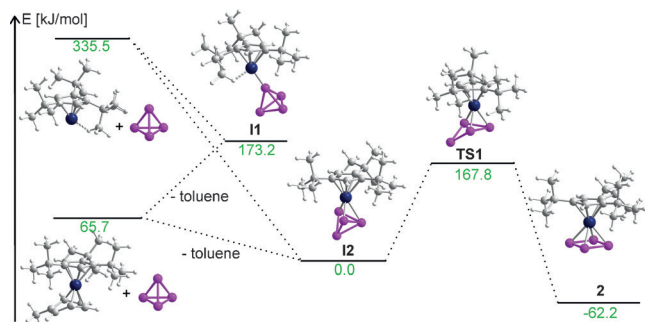
The relative energies of the complexes [Cp'''CoP₄]_n (n = 1–4) were further probed by DFT calculations on the B3LYP/6-31G(d) level (Scheme 4). All oligomerization processes turned out to be energetically favored. The formation of the dimer **3** is favored by 6.4 kJ mol⁻¹ over the formation of dimer **4**, which explains the isomerization of **4** into **3** at room temperature if one considers the possible “rotation” around the exocyclic P–P bond that has been identified for complex **7** to be a low-barrier process.^[20] The trimerization of **2** to give **7** is energetically the most favored process. This is in agreement with the formation of **7** as the major product upon thermal decomposition of **2**. The tetramer **8** was not detected in the NMR spectrum of the red-to-brown fraction and its formation is disfavored, indicating that **8** is formed from a more reactive species.



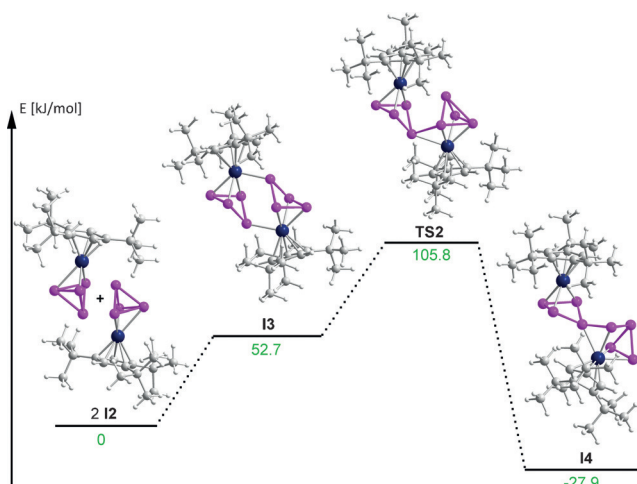
Scheme 4. Optimized geometries of complexes **2**, **3**, **4**, **7**, and **8**. Green: reaction enthalpies in kJ mol^{-1} .

Hence, we decided to study the interaction of P_4 with a CoCp^{R} metal fragment. The slipped triple-decker complex **1** was shown to partly dissociate in solution into a $[\text{Cp}^{\text{R}}\text{Co}(\text{C}_7\text{H}_8)]$ sandwich complex and solvated $[\text{Cp}^{\text{R}}\text{Co}]$ fragments.^[25] Our calculations show that the unsolvated 14 VE $[\text{CoCp}^{\text{R}}]$ fragment is very high in energy and, hence, the dissociation of **1** in the gas phase is strongly endothermic. However, the dissociation becomes almost thermoneutral if the $[\text{CoCp}^{\text{R}}]$ fragment is stabilized by a toluene molecule (cf. Table S4). This indicates that **1** dissociates to a minor degree in aliphatic solvents such as *n*-pentane, which would explain the strong influence of the solvent on the formation of **2**.

Two minimum structures **I1** and **I2** were located for the interaction of a $[\text{Cp}^{\text{R}}\text{Co}]$ fragment with P_4 (Scheme 5). The apical P_4 complex **I1** is $173.2 \text{ kJ mol}^{-1}$ higher in energy than the $\eta^3\text{-P}_4$ complex **I2**. The energy barrier for the transformation of **I2** into the *cyclo*- P_4 complex **2** was evaluated by locating the transition state **TS1**. With an energy barrier of $167.8 \text{ kJ mol}^{-1}$, complex **I2** is expected to be a kinetically inert intermediate in the reaction mixture at lower temperatures. The dimerization process of **I2** leading to polyphosphorus complexes proceeds via intermediate **I3** and transition-state structure **TS2** (Scheme 6). Complex **I4** is $-27.9 \text{ kJ mol}^{-1}$ more stable than two molecules of **I2**, but $117.2 \text{ kJ mol}^{-1}$ higher in energy than the isomeric complex **3**. This suggests **I4** to be the key intermediate in the formation of larger polyphosphorus complexes. Remarkably, the formation of the P_{16} complex **8**, which is the main product in the kinetically controlled reaction of **1** with P_4 at -60°C ,^[22] can be



Scheme 5. Relative energies [kJ mol^{-1}] of complexes **I1**, **I2**, **2**, and the transition state **TS1**.



Scheme 6. Relative energies [kJ mol^{-1}] of complexes **I3**, **I4**, and the transition state **TS2** illustrating a possible dimerization pathway for two **I2** molecules.

rationalized by the dimerization of two **I4** complexes based on their particular structural analogy (Scheme S2).

In summary, we have shown that the Cp^{R} -containing complex **2**, containing an unprecedented *cyclo*- P_4 end-deck, can be synthesized by the reaction of **1** with P_4 if the reaction is performed at 0°C in *n*-pentane. The polarity of the solvent has a decisive influence on the reaction outcome, which originates from the degree of the dissociation of **1** into $\text{Cp}^{\text{R}}\text{Co}$ fragments. Performing the reaction in solvents such as toluene or THF leads to the formation of the two isomeric Co_2P_8 complexes **3** and **4**. At room temperature, **4** isomerizes to **3**. The metastability of the *cyclo*- P_4 complex **2** and the Co_2P_8 complexes **3** and **4** in solution has been studied in the subsequent reaction with the $[\text{Cp}^{\text{R}}\text{Co}]$ source **1** and the thermolytically promoted rearrangement to P-rich polyphosphorus complexes. Based on DFT calculations, the key intermediate of the reaction of **1** with P_4 to give **2** was found to be the intermediate $\eta^3\text{-P}_4$ complex **I2**. The Co_2P_8 complex **I4**, which forms in the dimerization of **I2**, points the way to the formation of phosphorus-rich complexes such as the Co_4P_{16} complex **8** and even larger polyphosphorus complexes, which remains an ongoing research topic.^[26]

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Conflict of interest

The authors declare no conflict of interest.

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