Check for updates

Chemistry–A European Journal

Research Article
doi.org/10.1002/chem.202301930

Chemistry
Europe
European Chemical
Societies Publishing

www.chemeurj.org

Hot Paper

Special Collection

Formation of a Hexaphosphido Cobalt Complex through P−P Condensation

Christian M. Hoidn+,[a] Karolina Trabitsch+,[a] Kai Schwedtmann,[b] Clemens Taube,[b] Jan J. Weigand,*[b] and Robert Wolf*[a]

Dedicated to Dietrich Gudat, Evamarie Hey-Hawkins, Manfred Scheer, Rainer Streubel, Werner Uhl, and Hansjörg Grützmacher on the occasion of their retirement.

The reaction between diphosphorus derivatives [(^{Cl}Im^{Dipp})P$_2$(Dipp)]OTf (1[OTf]) and [(^{Cl}Im^{Dipp})P$_2$(Dipp)Cl] (1[Cl]) with the cyclotetraphosphido cobalt complex [K(18c-6)][(PHDI)Co(η^4-cyclo-P$_4$)] (2) leads to the formation of complex [(PHDI)Co{η^4-cyclo-P$_6$(Dipp)(^{Cl}Im^{Dipp})}] (3), which features an unusual hexaphosphido ligand [^{Cl}Im^{Dipp} = 4,5-dichloro-1,3-bis(2,6-diisopropylphenyl)imidazol-2-yl, Dipp = 2,6-diisopropylphenyl, 18c-6 = 18-crown-6, PHDI = bis(2,6-diisopropylphenyl)phenan-threne-9,10-diimine]. Complex 3 was obtained as a crystalline material with a moderate yield at low temperature. Upon exposure to ambient temperature, compound 3 slowly transforms into two other compounds, [K(18c-6)][(PHDI)Co(η^4-P$_7$Dipp)] (4) and [(PHDI)Co{cyclo-P$_5$(^{Cl}Im^{Dipp})}] (5). The novel complexes 3–5 were characterized using multinuclear NMR spectroscopy and single-crystal X-ray diffraction. To shed light on the formation of these compounds, a proposed mechanism based on ^{31}P NMR monitoring studies is presented.

Introduction

In recent years, the synthesis of early and late transition metal polyphosphido complexes has garnered significant interest due to their potential of developing novel phosphorus-containing functionalities.[1] However, the construction of extended poly-phosphorus frameworks through the condensation of suitable cationic and anionic building blocks remains a key challenge. Currently, electrophilic functionalization reactions forming P−P bonds are limited to the use of reactive organo-substituted phosphenium cations [R$_2$P]$^+$, restricting the extension of the phosphorus frameworks to tetra- and pentaphosphido moieties.[2]

[a] Dr. C. M. Hoidn,+ K. Trabitsch,+ Prof. Dr. R. Wolf
University of Regensburg
Institute of Inorganic Chemistry
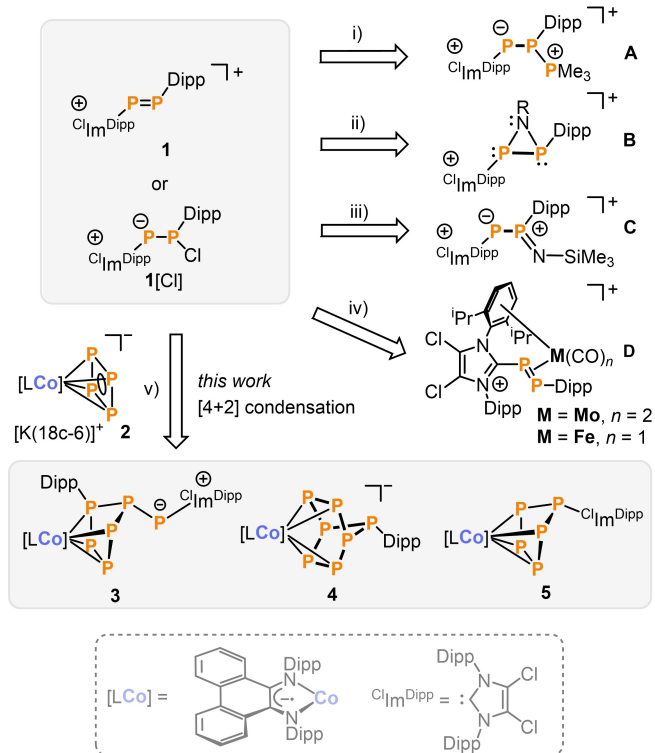93040 Regensburg (Germany)
E-mail: robert.wolf@ur.de

[b] Dr. K. Schwedtmann, Dr. C. Taube, Prof. Dr. J. J. Weigand0000-0001-7323-7816
TU Dresden
Department of Chemistry and Food Chemistry
01062 Dresden (Germany)
E-mail: jan.weigand@tu-dresden.de
Homepage: 0000-0001-7323-7816

[+] These authors contributed equally to this manuscript.

Supporting information for this article is available on the WWW under https://doi.org/10.1002/chem.202301930

Special Collection Part of a Special Collection on the p-block elements.

Nucleophilic N-heterocyclic carbene (NHC)-stabilized poly-phosphorus cations have emerged as promising precursors for P−P bond formation.[3] Recently, the synthesis of the cationic diphosphene [(^{Cl}Im^{Dipp})P$_2$(Dipp)]$^+$ (1) (^{Cl}Im^{Dipp} = 4,5-dichloro-1,3-bis(2,6-diisopropylphenyl)imidazol-2-yl, Dipp = 2,6-diisopropyl-phenyl) was reported,[4,5] accessible as the triflate salt [(^{Cl}Im^{Dipp})P$_2$(Dipp)]OTf (1[OTf]) and tetrachlorogallate [(^{Cl}Im^{Dipp})P$_2$(Dipp)]GaCl$_4$ (1[GaCl$_4$]), obtained by chloride abstraction from the corresponding neutral diphosphanide [(^{Cl}Im^{Dipp})P$_2$(Dipp)Cl] (1[Cl]).[6,7]

The polarized P=P double bond in 1 allows for versatile transformations, including reactions with nucleophiles such as PMe$_3$ (A, Scheme 1i),[6] and reactions with azides RN$_3$ (R = Dmp, Dipp; Dmp = 2,5-dimethylphenyl) to afford azadiphosphiridine cations B (Scheme 1ii),[7] or diphosphenimine C (R = SiMe$_3$, Scheme 1iii).[7] Additionally, compounds 1 and 1[Cl] have proven to be excellent precursors for the preparation of transition metal carbonyl η^2-diphosphene complexes (D, Scheme 1iv), which undergo light-induced haptotropic rearrangement to η^1-complexes upon irradiation with blue light (λ = 470 nm).[8] These results highlight the potential of compounds 1 and 1[Cl] as precursors for various new phosphorus species.

In this work, we demonstrate the applicability of these diphosphorus species in P−P condensation reactions with the cyclotetraphosphido complex [K(18c-6)][(PHDI)Co(η^4-cyclo-P$_4$)] (2, 18c-6 = 18-crown-6, PHDI = bis(2,6-diisopropylphenyl)phenanthrene-9,10-diimine)[2b] for the synthesis of novel polyphosphorus complexes. Specifically, we describe the synthesis and characterization of the hexaphosphido complex [(PHDI)Co{η^4-cyclo-P$_6$(Dipp)(^{Cl}Im^{Dipp})}] (3) and its subsequent transformation at ambient temperature into the bicyclo[2.2.1]heptaphosphide [K(18c-6)][(PHDI)Co(η^4-P$_7$Dipp)] (4)

Chem. Eur. J. 2023, e202301930 (1 of 8)

© 2023 The Authors. Chemistry - A European Journal published by Wiley-VCH GmbH

Chemistry–A European Journal

Research Article
doi.org/10.1002/chem.202301930

Chemistry Europe
European Chemical
Societies Publishing

Scheme 1. Utilizing inversely polarized diphosphene **1** and diphosphanide **1**[Cl] as acceptors for nucleophiles and electrophiles; reagents and by-products: (i) **1**[GaCl₄], +PMe₃; (ii) **1**[OTf], +RN₃/−N₂; R = Dmp, Dipp; Dmp = 2,5-dimethylphenyl, Dipp = 2,6-diisopropylphenyl; (iii) **1**[OTf] or **1**[GaCl₄], +Me₃SiN₃/−N₂; (iv) **1**[OTf], M = Mo: +[Mo(CO)₃(CH₃CN)₃]/−CO, −3 CH₃CN; M=Fe, blue LED (470 nm): +[Fe₂(CO)₉]/−[Fe(CO)₅], −3 CO; (v) formation of novel P₆ (**3**), P₇ (**4**) and P₅ (**5**) complexes by P–P condensation of cyclotetraphosphido cobalt complex **3** with **1**[OTf] or **1**[Cl]; [LCo] = (PHDI)Co, PHDI = bis(2,6-diisopropylphenyl)phenanthrene-9,10-diimine.

and the pentaphosphido derivative [(PHDI)Co{*cyclo*-P₅(^{Cl}Im^{Dipp})}] (**5**, Scheme 1v). Furthermore, through detailed ³¹P NMR spectroscopic investigations, we propose a mechanism of formation for complexes **3**–**5**. These results provide important new insight into the formation of polyphosphorus transition metal complexes via the condensation of cationic and anionic phosphorus fragments, as well as the subsequent disproportionation tendencies of such products.

Results and Discussion

The synthesis of a novel hexaphosphido cobalt complex was targeted by reacting cationic diphosphene [(^{Cl}Im^{Dipp})P₂(Dipp)][OTf] (**1**[OTf]) with [K(18c-6)][(PHDI)Co(η⁴-*cyclo*-P₄)] (**2**) in fluorobenzene at −35 °C. ³¹P NMR spectroscopy confirmed the predominant formation of complex **3** (Scheme 2).[7] Subsequent work-up at −15 °C yielded dark blue crystals of **3**, which were isolated with a yield of 20% following crystallization from a concentrated *n*-pentane:Et₂O (1:2, *v:v*) mixture and characterized by single-crystal X-ray diffraction (XRD).
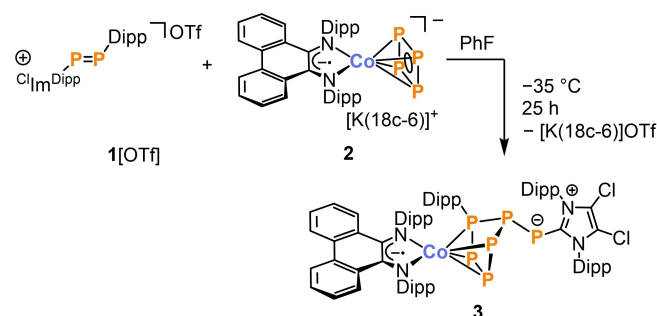
Scheme 2. Synthesis of [(PHDI)Co{η⁴-*cyclo*-P₆(Dipp)(^{Cl}Im^{Dipp})}] (**3**) by the reaction of [(^{Cl}Im^{Dipp})P₂(Dipp)]OTf (**1**[OTf]) with [K(18c-6)][(PHDI)Co(η⁴-*cyclo*-P₄)] (**2**) in fluorobenzene (PhF) at −35 °C for 25 h.

The solid-state molecular structure of compound **3** (Figure 1a) presents a cobalt atom coordinated by a hexaphosphido ligand in an η⁴-fashion. A formally radical anionic PHDI•⁻ ligand is also observed, as indicated by the C–N (1.338(2), 1.344(2) Å) and C–C (1.446(2) Å) distances within its α-diimine backbone.[9]
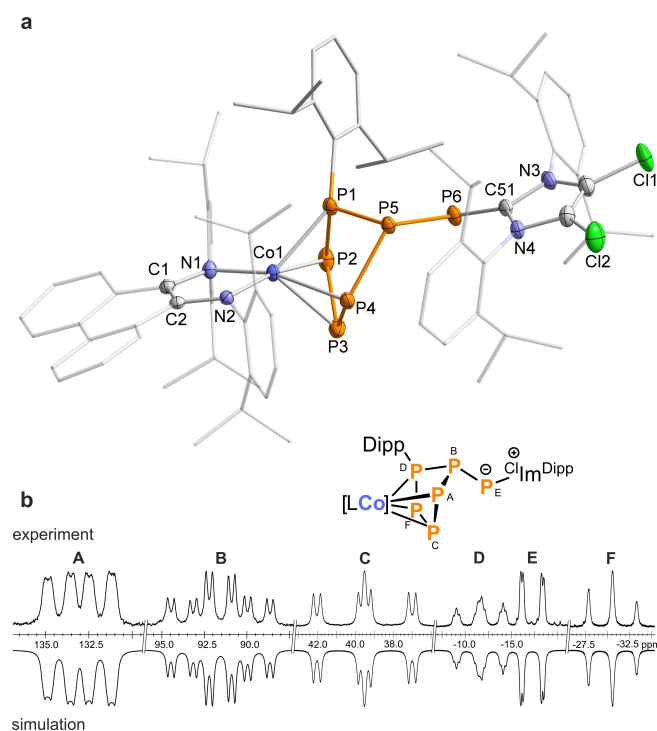

Figure 1. a) Solid-state molecular structure of compound **3**; hydrogen atoms are omitted for clarity and thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and angles [°]: Co1–N1 1.931(2), Co1–N2 1.903(2), Co1–P1 2.3021(5), Co1–P2 2.3766(5), Co1–P3 2.3488(6), Co1–P4 2.3861(5), P1–P2 2.1510(7), P1–P5 2.1483(6), P2–P3 2.1160(8), P3–P4 2.1348(7), P4–P5 2.2410(6), P5–P6 2.1632(6), P6–C51 1.777(2) C1–N1 1.338(2), C2–N2 1.344(2), C1–C2 1.446(2), C51–N3 1.379(2), C51–N4 1.375(2), P1–P2–P3 98.14(3), P1–P5–P4 82.15(2), P1–P5–P6 97.68(2), P2–P3–P4 102.53(3), P3–P4–P5 110.50(3), P4–P5–P6 118.94(2), C51–P6–P5 102.92(6); b) section of the ³¹P{¹H} NMR spectrum of compound **3** with nuclei assigned to an ABCDEF spin system; experimental (top); simulation (bottom): δ(P_A) = 133.0 ppm, δ(P_B) = 91.5 ppm, δ(P_C) = 39.5 ppm, δ(P_D) = −11.7 ppm, δ(P_E) = −17.3 ppm, δ(P_F) = −30.5 ppm; ¹J_AB = −213.5 Hz, ¹J_AC = −383.7 Hz, ¹J_BD = −370.6 Hz, ¹J_BE = −362.7 Hz, ¹J_CF = −433.2 Hz, ¹J_DF = −449.2 Hz, ²J_AD = 58.6 Hz, ²J_AE = 18.1 Hz, ²J_AF = 24.7 Hz, ²J_BC = 60.9 Hz, ²J_BF = 6.4 Hz, ²J_CD = 9.9 Hz, ²J_DE = 47.1 Hz; [LCo] = (PHDI)Co.

Chemistry–A European Journal

Research Article
doi.org/10.1002/chem.202301930

Chemistry Europe
European Chemical
Societies Publishing

The hexaphosphido ligand features an aryl-substituted *cyclo*-P_5Dipp moiety bound to cobalt via its DippP1–P2–P3–P4 subunit. The P5 atom at the apex of the P_5 envelope is positioned away from the metal center and is further connected to the two-coordinate phosphorus atom, P6. This atom is stabilized by the NHC $^{Cl}Im^{Dipp}$. The P6–C51 distance (1.777(2) Å) lies between the values calculated for P–C single (1.86 Å) and P=C double bonds (1.69 Å).[10] Moreover, this NHC-stabilized phosphorus atom is assigned to a high field shifted $^{31}P\{^1H\}$ NMR signal ($\delta(P_E) = -17.3$ ppm). Both these observations are comparable to other NHC-stabilized, low coordinate phosphorus species, such as Arduengo's (IMes)PPh (P–C 1.763(6) Å, $\delta(P) = -23$ ppm, IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene),[11] Robinson's (IPr)P_2(IPr) (P–C 1.7504(2) Å, $\delta(P) = -52.4$ ppm, IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene),[12] Grützmacher's (IPr)P$_2$(Cl)(R) (R = Ph: P–C 1.8017(18), $\delta(P) = -17.3$ ppm; R = NiPr: P–C 1.7835(16), $\delta(P) = -18.4$ ppm),[13,14] as well as C-amino-functionalized phosphaalkenes RPC(NMe$_2$)$_2$ (R = H: P–C 1.740(1) Å, $\delta(P) = -52.4$ ppm; R = SiMe$_3$, $\delta(P) = -47.1$ ppm).[15,16] Analogously, the bonding at P6–$^{Cl}Im^{Dipp}$ can be described by either a zwitterionic imidazolium-2-yl phosphanide (resonance structure **I**, Figure 2a) or a phosphaalkene resonance structure (resonance structure **II**).

The doubly-substituted *cyclo*-P_5 ligand in compound **3** bears resemblance to the associated heterobimetallic species [(^{Mes}BIAN)Co(μ-η^4:η^1-P$_5t$Bu)GaCl(nacnac)] (**E**, Figure 2b, ^{Mes}BIAN = 1,2-bis(2,4,6-trimethylphenylimino)acenaphthene, nacnac = CH-(CMeNDipp)$_2$). This species is obtained from the reaction of [K(dme)$_2${(^{Mes}BIAN)Co(μ-η^4:η^2-P$_4$)Ga(nacnac)}] with tBuPCl$_2$.[2a] Similar to compound **E**, all P–P distances of compound **3** fall within a very close range (2.1160(8) to 2.1632(6) Å), with the exception of the P4–P5 bond (2.2410(6) Å). The contraction of the bonds between the phosphorus atoms coordinating to the cobalt, compared to a typical P–P single bond (2.22 Å),[10] implies the presence of some delocalized multiple bond characteristics.

In line with the six non-equivalent phosphorus atoms observed in the solid-state structure, the $^{31}P\{^1H\}$ NMR spectrum of compound **3**, recorded in THF-d_8 at $-40\,°C$ (Figure 1b and Figure S3, Supporting Information), reveals an ABCDEF spin system. This spin system was simulated using an iterative fitting procedure. A ^{31}P–^{31}P COSY experiment supports the assignment of the resonances for P_E and P_B (Figure S4). The resonance for P_D was determined based on its large $^1J_{PP}$ couplings [$^1J_{BD} = -370.6$ Hz and $^1J_{DF} = -449.2$ Hz], which are comparable to the coupling constants observed in compound **E** (Figure 2).[2a]

Similar to the reaction of **1**[OTf] with **2**, hexaphosphido complex **3** also forms when diphosphanide **1**[Cl] reacts with **2** in THF-d_8. Monitoring using variable temperature $^{31}P\{^1H\}$ NMR (Figure S14) suggests that **3** disproportionates into the thermally stable species [K(18c-6)][(PHDI)Co(η^4-P$_7$Dipp)] (**4**) and [(PHDI)Co{*cyclo*-P$_5$($^{Cl}Im^{Dipp}$)}] (**5**) when the reaction mixture is kept at ambient temperature. This disproportionation is also observed for the reaction of **1**[OTf] with **2**. Even though products **4** and **5** were not directly isolated from this mixture, subsequent investigations revealed that the bicyclo[2.2.1]heptaphosphide compound **4** can be obtained by conducting the reaction of **1**[Cl] with **2** in diethyl ether (Et$_2$O) at room temperature (Scheme 3). Crystallization from THF/methyl-*tert*-butylether (MTBE) afforded crystals of **4** suitable for single-crystal XRD, with a combined yield of 16%.

The solid-state molecular structure of compound **4** shows a [K(18c-6)(Et$_2$O)]$^+$ cation separated from a [(PHDI)Co(η^4-P$_7$Dipp)]$^-$ anion (Figure 3a). The central cobalt atom is coordinated by the bidentate PHDI ligand and an η^4-coordinated Dipp-functionalized heptaphosphido ligand, exhibiting P–P distances ranging from 2.115(3) to 2.224(3) Å. The P–P distances between the metal-coordinating phosphorus atoms (P3–P4 2.140(3) Å, P6–P7 2.115(3) Å) are slightly shortened, indicating a partial double bond character.[10] Meanwhile, the P–P distances between the bridging atoms P2 and P5 and the cobalt-coordinated phosphorus atoms (P2–P3 2.211(3), P2–P7 2.209(3), P4–P5 2.193(4), P5–P6 2.224(3)) align with a typical P–P single bond (2.22 Å).[10] Conversely, the bond lengths of the apical phosphorus atom P1 are somewhat reduced (P1–P2 2.159(3), P1–P5 2.154(3)). The C–C (1.433(8) Å) and C–N (1.358(8), 1.368(8) Å) bond distances of the PHDI moiety suggest it is present in its radical anionic form.[9]

Although compound **4** appears to be the first cobalt complex featuring a substituted RP$_7^{2-}$ ligand, the observed heptaphosphanorborna-2,5-diene motif is well-established, for instance in [K(2,2,2-crypt)]$_2$[Fe(HP$_7$)$_2$] (**F**, 2,2,2-crypt = 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane),[17] in [K(2,2,2-crypt)][(RP$_7$)W(CO)$_3$] (**G**, R = H, Me, Et, nBu),[18,19] and in [{K(18c-6)}$_2$(Cp*FeP$_7$)] (**H**).[20] While compounds **F** and **G** originate from P$_7^{3-}$ Zintl anions, complex **H** was formed through aggregation of white phosphorus with a polyarene ferrate
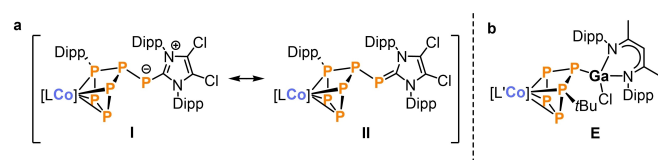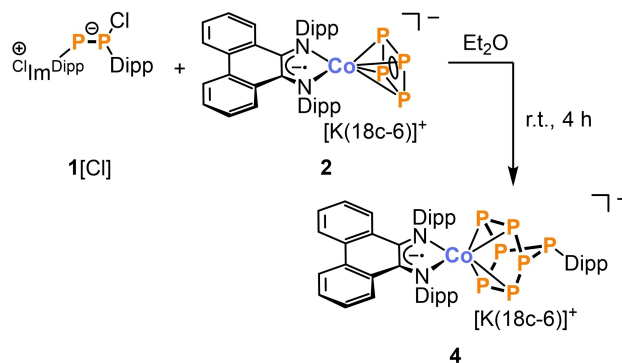

Figure 2. a) Conceivable resonance structures describing the bonding within the hexaphosphido ligand in compound **3**; [LCo] = (PHDI)Co; b) related disubstituted *cyclo*-P$_5$ complex **E**;[2a] [L'Co] = (^{Mes}BIAN)Co, ^{Mes}BIAN = 1,2-bis(2,4,6-dimethylphenylimino)acenaphthene.

Scheme 3. Synthesis of [K(18c-6)][(PHDI)Co(η^4-P$_7$Dipp)] (**4**) by reaction of [($^{Cl}Im^{Dipp}$)P$_2$(Dipp)Cl] (**1**[Cl]) with [K(18c-6)][(PHDI)Co(η^4-*cyclo*-P$_4$)] (**2**) in Et$_2$O at room temperature for 4 h.
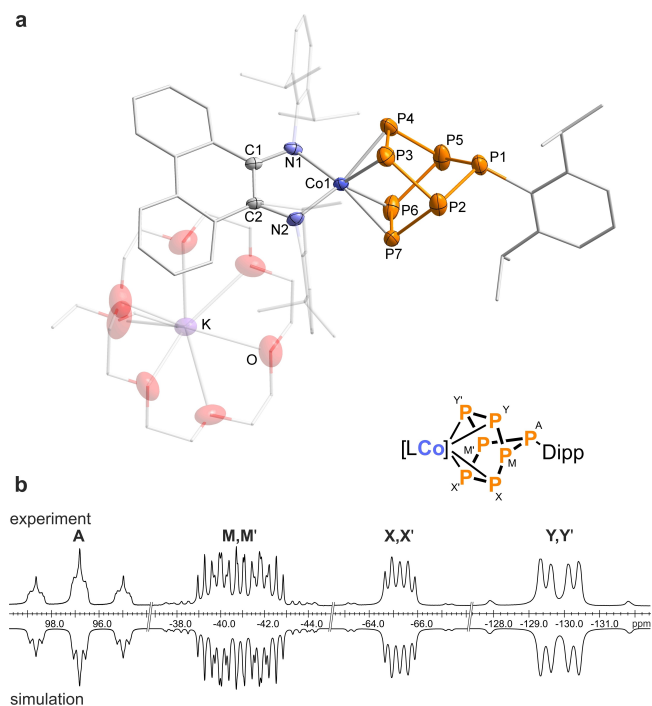
Figure 3. a) Solid-state molecular structure of compound **4**; hydrogen atoms are omitted for clarity and thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å]: Co1–N1 1.922(5), Co1–N2 1.910(5), Co1–P3 2.330(2), Co1–P4 2.337(2), Co1–P6 2.328(2), Co1–P7 2.335(2), P1–P2 2.159(3), P1–P5 2.154(3), P2–P3 2.211(3), P2–P7 2.209(3), P3–P4 2.140(3), P4–P5 2.193(4), P5–P6 2.224(3), P6–P7 2.115(3), C1–N1 1.358(8), C2–N2 1.362(8), C1–C2 1.433(8); b) section of the $^{31}P\{^1H\}$ NMR spectrum of compound **4** with nuclei assigned to an AMM'XX'YY' spin system; experimental (top); simulation (bottom): $\delta(P_A) = 96.8$ ppm, $\delta(P_{MM'}) = -40.9$ ppm, $\delta(P_{XX'}) = -65.3$ ppm, $\delta(P_{YY'}) = -129.9$ ppm, $^1J_{AM} = ^1J_{AM'} = -370.5$ Hz, $^1J_{MX} = ^1J_{M'X'} = -216.9$ Hz, $^1J_{MY} = ^1J_{M'Y'} = -249.8$ Hz, $^1J_{YY'} = -351.7$ Hz, $^1J_{XX'} = -373.8$ Hz, $^2J_{AX} = ^2J_{AX'} = 51.3$ Hz, $^2J_{MX'} = ^2J_{M'X} = 18.7$ Hz, $^2J_{MY'} = ^2J_{M'Y} = 29.3$ Hz, $^2J_{XY} = ^2J_{X'Y'} = 14.4$ Hz, $^3J_{X'Y} = ^3J_{XY'} = -4.6$ Hz; [LCo] = (PHDI)Co.

anion precursor. In contrast, compound **4** is synthesized through a completely different "bottom up" approach.

The $^{31}P\{^1H\}$ NMR spectrum of **4** in THF-d_8 features an AMM'XX'YY' spin system (Figure 3b), which corresponds well with the solid-state molecular structure. It presents resonances at $\delta = 96.8$, -40.9, -65.3 and -129.9 ppm, maintaining a 1:2:2:2 integral ratio. The resonance at $\delta = 96.8$ ppm (P_A) can be assigned to the apical phosphorus atom P1, while the resonance at $\delta = -40.9$ ppm ($P_{MM'}$) corresponds to the bridging atoms P2 and P5. The multiplets at low frequencies [$\delta = -65.3$ ppm ($P_{XX'}$) and $\delta = -129.9$ ppm ($P_{YY'}$)] can be associated with the P atoms that are coordinated to the cobalt atom.

Alongside the AMM'XX'YY' spin system, a second set of higher order multiplets at $\delta = 77.5$, 66.9 and 24.8 ppm, with a 2:1:2 integral ratio, can be observed in the $^{31}P\{^1H\}$ NMR spectrum of the isolated crystals of **4** (Figure S8). These resonances are assigned to an AA'BMM' spin system, suggesting the presence of a pentaphosphido compound. Indeed, such a species was identified by a single-crystal X-ray diffraction experiment using dark brown crystals, which were obtained from the n-hexane fraction of the reaction mixture of **1**[OTf] with **2** (Scheme 2). The single-crystal XRD analysis revealed the

formation of [(PHDI)Co{η^4-cyclo-P$_5$(^{Cl}Im^{Dipp})}] (**5**, Figure 4). Formally, this compound results from the insertion of an [(^{Cl}Im^{Dipp})P]$^+$ fragment into the cyclo-P$_4$ ring of compound **2**.[21]

The structure of this compound closely resembles those of disubstituted cyclo-P$_5$R$_2$ cobalt complexes [(^{Mes}BIAN)Co(η^4-P$_5$R$_2$)] (**I**, R = iPr, tBu, Cy) and [(PHDI)Co(η^4-P$_5$R$_2$)] (**J**, R = Cy, tBu, Ph, Mes, N(iPr)$_2$).[2a,b] It also bears similarities to recently reported Fe complexes [Cp*Fe(η^4-P$_5$(NHC))] [**K**, NHC = IMe (1,3,4,5-tetramethylimidazol-2-yl), IDipp (1,3-bis(Dipp)-imidazol-2-yl)] and [Cp*Fe-(η^4-P$_5$R)]$^-$ (**L**, R = CH$_2$SiMe$_3$, NMe$_2$).[22,23] The η^4-coordinated cyclo-P$_5$(^{Cl}Im^{Dipp}) ligand adopts an envelope conformation, wherein the four unsubstituted P atoms are coordinated to cobalt. Similar to the structures of compounds **3** and **4**, the metric parameters of the α-diimine backbone suggest the presence of a radical anionic PHDI$^{\bullet-}$ ligand (see also Table S5, Supporting Information).[9] The P–P bond lengths within the cyclo-P$_5$(^{Cl}Im^{Dipp}) ligand are closely spaced (2.1134(1) to 2.1648(8) Å), and are comparable to those of compounds **I**–**L**. The P1–C39 distance corresponds to a single bond.[10] While the low intensity of the signals from compound **5** made simulation of the $^{31}P\{^1H\}$ NMR resonances using an iterative fitting procedure unattainable, the integral ratio of 2:1:2 and the splitting pattern are fully consistent with the molecular structure of compound **5**.[22]

Based on the $^{31}P\{^1H\}$ NMR reaction monitoring experiments (Figure S14) and existing literature, we propose a mechanism for the formation of compounds **3**–**5** (Scheme 4). Initially, the reaction of compound **1**[Cl] with **2** gives the intermediate **3'**, which is formed via the formal insertion of the diphosphene cation [(Dipp)P=P(^{Cl}Im^{Dipp})]$^+$ into the nucleophilic cyclo-P$_4$ unit of compound **2** (Scheme 4a). A subsequent 1,2-shift of the Dipp moiety gives rise to the isolable complex **3**. At temperatures above $-50\,°C$, compound **3** transforms into multiple polyphosphorus compounds, with compound **4** being the primary isolable product after the transformation is complete (Scheme 4b). Pentaphosphido species **5** is initially formed in con-
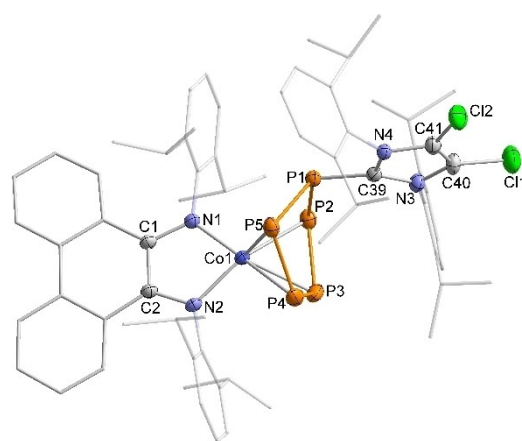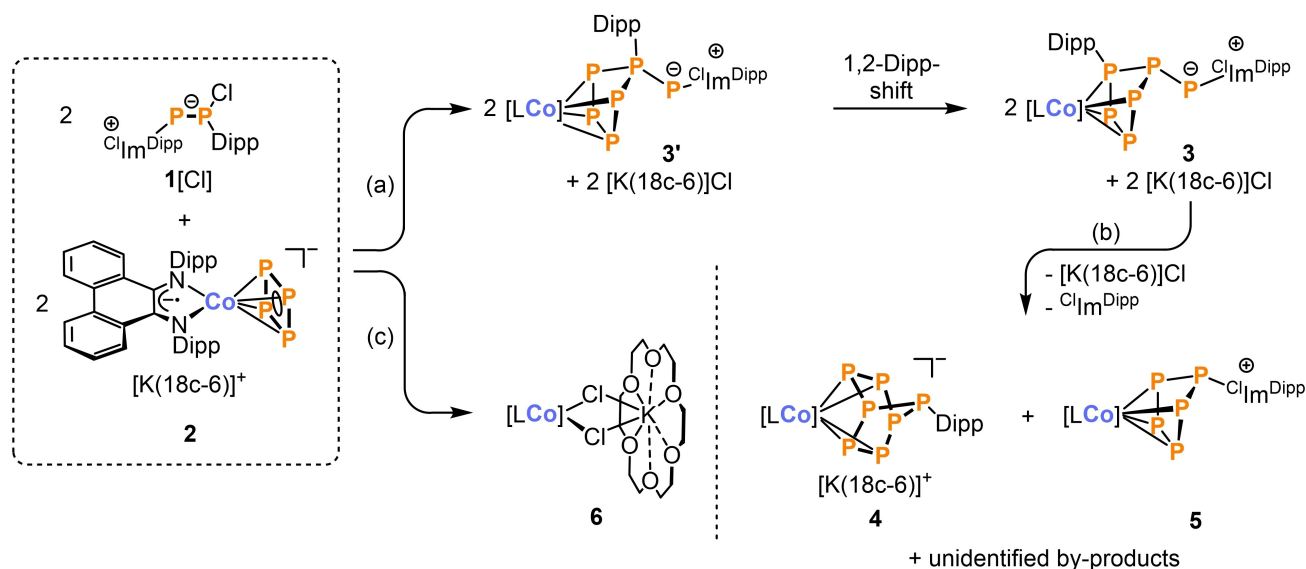

Figure 4. Solid-state molecular structure of compound **5**; hydrogen atoms are omitted for clarity and thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å]: Co1–N1 1.874(2), Co1–P2 2.3601(6), Co1–P3 2.3301(7), Co1–P4 2.3859(6), Co1–P5 2.3394(7), P1–P2 2.1590(8), P1–P5 2.1648(7), P2–P3 2.1274(8), P3–P4 2.1131(9), P4–P5 2.1258(9), P1–C39 1.855(2), C1–N1 1.360(3), C2–N2 1.355(3), C1–C2 1.436(3).[21]

Chemistry–A European Journal

Research Article
doi.org/10.1002/chem.202301930

Chemistry Europe
European Chemical
Societies Publishing

Scheme 4. Propose sequence of the reaction of diphosphanide **1**[Cl] with complex **2**; (a) P–P condensation forms complex **3'**, a subsequent 1,2-Dipp shift forms isolable CoP$_6$ complex **3**; (b) at ambient temperature, complex **3** undergoes disproportionation into the CoP$_7$ complex **4** and the CoP$_5$ complex **5**; (c) formation of paramagnetic dichloride cobaltate **6** by chloride abstraction in an independent pathway. [LCo] = (PHDI)Co.

junction with compound **4** at a 1:1 ratio by the disproportionation of compound **3**, but it decomposes over time (Figures S14 and S18). A second, unidentified pentaphosphido species is formed at room temperature (see Supporting Information, Figures S14 and S18). We propose that this species is [(PHDI)Co{η^4-*cyclo*-P$_5$(Dipp)(Cl)}], the formal product of the insertion of a [P(Dipp)(Cl)]$^+$ fragment into the *cyclo*-P$_4$ ring of compound **2**. As of now, isolation of this species remains elusive due to its formation in minor quantities, and as its signals vanish during work-up. A more comprehensive discussion regarding the NMR spectroscopic details can be found in the Supporting Information Further by-products are evident in the variable temperature ^{1}H NMR spectra of the reaction mixture of **1**[Cl] and **2**. These spectra indicate the release of the free carbene ^{Cl}Im^{Dipp} during the decomposition of compound **3** at 280 K (Figure S15) and the paramagnetic dichlorido cobaltate, [{K(18c-6)}(μ-Cl)$_2${Co-(PHDI)}] (**6**, Figure S16).[24,25] Compound **6** was identified by comparing its characteristic and distinct ^{1}H NMR signals at δ = −25.6, −25.3, −15.7, −13.9, −4.8, 0.4, 2.4, 7.7, 79.0 and 83.6 ppm to those of an authentic sample, which was prepared by oxidizing [K(18c-6)(THF)$_2$][(PHDI)Co(η^4-1,5-cod)] (**7**) with C$_2$Cl$_6$ (see the Supporting Information for further details).[2b]

Conclusions

The CoP$_6$ complex **3** is formed through an unprecedented [4+2] condensation reaction of the P$_2$ species **1**[OTf] or **1**[Cl] with the CoP$_4$ complex **2**. The molecular structure of **3** exhibits an unusual P$_6$ ligand composed of a *cyclo*-P$_5$ ring and an exocyclic (^{Cl}Im^{Dipp})P moiety. Owing to this unique structural arrangement, complex **3** is thermally unstable and undergoes disproportionation into the more stable complexes **4** and **5**, which feature P$_7$ and P$_5$ frameworks, respectively. Comprehen-

sive understanding of the formation mechanism of compound **3** and its subsequent disproportionation has been obtained through ^{31}P NMR spectroscopic studies. Although the resulting CoP$_6$ complex **3** readily transforms into comparatively stable CoP$_7$ and CoP$_5$ complexes, it is plausible that similar structures could be stabilized with appropriate metal fragments and ancillary substituents.

This research shows that the condensation of diphosphorus cations with transition metal polyphosphides offers a promising strategy for generating novel polyphosphorus transition metal complexes with unprecedented structural motifs. Given the growing diversity of polyphosphorus anions[26] and cations[3] available in the literature, it is anticipated that this approach could be exploited to access further unknown polyphosphorus frameworks in the future.

Experimental Section

spectrometer equipped with a BBO Prodigy Cryo probe. Qualitative $^{31}P\{^1H\}$ NMR reaction monitoring experiments were recorded on a Bruker Avance 600 spectrometer. ^1H and $^{13}C\{^1H\}$ spectra were referenced internally to residual solvent resonances. $^{31}P\{^1H\}$ NMR spectra were referenced externally to 85% H_3PO_4(aq.). The assignment of the ^1H and ^{13}C NMR signals was confirmed by two-dimensional (COSY, HSQC and HMBC) experiments. Chemical shifts (δ) are reported in ppm. Coupling constants (J) are reported in Hz.

UV/vis spectra were recorded on an Ocean Optics Flame Spectrometer. Elemental analyses were determined by the analytical department of the University of Regensburg.

The starting materials $[(^{Cl}Im^{Dipp})P_2(Dipp)Cl]$ (**1[Cl]**),[5] $[(^{Cl}Im^{Dipp})P_2(Dipp)][OTf]$ (**1[OTf]**),[7] $[K(18c-6)(thf)_2][(PHDI)Co(\eta^4\text{-}1,5\text{-}cod)]$,[2b] and $[K(18c-6)][(PHDI)Co(\eta^4\text{-}cyclo\text{-}P_4)]$ (**2**),[2b] were prepared according to literature procedures. C_2Cl_6 was purchased from Sigma Aldrich.

Experimental Procedures

$[(PHDI)Co\{\eta^4\text{-}cyclo\text{-}P_5Dipp(P(^{Cl}Im^{Dipp}))\}]$ (3): A double-walled Schlenk flask was charged with $[K(18c-6)][(PHDI)Co(\eta^4\text{-}cyclo\text{-}P_4)]$ (**2**) (86.5 mg, 0.084 mmol, 1.0 equiv) and $[(^{Cl}Im^{Dipp})P_2(Dipp)][OTf]$ (**1[OTf]**) (70 mg, 0.084 mmol, 1.0 equiv). The flask was connected to a cryostat and cooled to $-45\,°C$. Subsequently, fluorobenzene (12 mL) was added. The dark blue mixture was stirred at $-35\,°C$ for 25 h. The cooling was stopped, and the solvent was removed *in vacuo*. In order to remove residual amounts of PhF, the blue residue was triturated with *n*-pentane (5 mL) while cooling to $-15\,°C$. The dark blue residue was dried *in vacuo* for 30 min at $-15\,°C$. The procedure was repeated one more time using *n*-pentane (20 mL). Subsequently, the dark blue residue was extracted at $0\,°C$ with a mixture of *n*-pentane and Et_2O (1:2, *v:v*) in four portions (55 mL in total, Whatman filter). The dark blue filtrate was collected in a flask cooled in an ice bath. The volume was reduced to ca. one eighth of the original volume until a dark blue solid began to precipitate. Storage of the concentrated dark blue solution at $-30\,°C$ for five days gave dark blue crystals of **3**. The crystals were isolated at $-40\,°C$ by decantation of the supernatant and subsequently washed quickly with cold *n*-pentane ($-100\,°C$, 10 mL). The crystals were dried for 1 h *in vacuo* at $-30\,°C$. Yield: 24 mg (20%). A UV/Vis spectrum was not recorded due to the high temperature sensitivity of the product. A satisfactory elemental analysis could not be obtained due to the high thermal sensitivity of the complex.
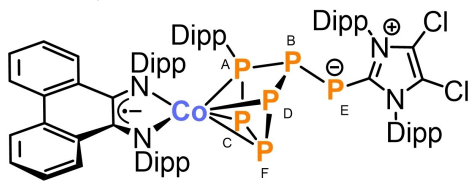

^1H NMR (400.30 MHz, 223 K, THF-d_8): δ/ppm = −0.13 (d, $^3J_{HH}$ = 6.2 Hz, 6H, −CH(CH$_3$)$_2$ of Dipp), 0.15 (d, $^3J_{HH}$ = 6.0 Hz, 3H, −CH(CH$_3$)$_2$ of Dipp), 0.53–0.65 (m, 6H, −CH(CH$_3$)$_2$ of Dipp), 0.80 (d, $^3J_{HH}$ = 6.5 Hz, 3H, −CH(CH$_3$)$_2$ of Dipp), 0.87–0.91 (m, 5H, −CH(CH$_3$)$_2$ of Dipp overlapping with −CH$_3$ of *n*-pentane), 1.09–

1.16 (m, 21H, −CH(CH$_3$)$_2$ of Dipp overlapping with −CH$_2$ of Et$_2$O), 1.23–1.28 (m, 11H, −CH(CH$_3$)$_2$ of Dipp overlapping with −CH$_2$ of *n*-pentane), 1.34–1.35 (m, 8H, −CH(CH$_3$)$_2$ of Dipp), 1.64 (d, $^3J_{HH}$ = 6.9 Hz, 3H, −CH(CH$_3$)$_2$ of Dipp), 2.39 (m, 2H, −CH(CH$_3$)$_2$ of Dipp), 2.54 (m, 2H, −CH(CH$_3$)$_2$ of Dipp), 3.32–3.39 (m, 4H, −CH(CH$_3$)$_2$ of Dipp overlapping with −CH of Et$_2$O), 4.01 (m, 1H, −CH(CH$_3$)$_2$ of Dipp), 4.24–4.26 (m, 1H, −CH(CH$_3$)$_2$ of Dipp), 5.20–5.23 (m, 1H, −CH(CH$_3$)$_2$ of Dipp), 6.57–6.61 (m, 1H, Ar−H), 6.73–6.81 (m, 2H, Ar−H), 6.95 (d, $^3J_{HH}$ = 7.3 Hz, 1H, Ar−H), 7.00 (d, $^3J_{HH}$ = 7.7 Hz, 1H, Ar−H), 7.05 (d, $^3J_{HH}$ = 7.6 Hz, 1H, Ar−H), 7.18–7.22 (m, 1H, Ar−H), 7.24–7.28 (m, 1H, Ar−H), 7.32 (d, $^3J_{HH}$ = 7.5 Hz, 1H, Ar−H), 7.36 (d, $^3J_{HH}$ = 8.1 Hz, 1H, Ar−H), 7.39–7.50 (m, 6H, Ar−H), 7.56–7.58 (m, 2H, Ar−H), 8.27 (d, $^3J_{HH}$ = 8.5 Hz, 2H, Ar−H). $^{13}C\{^1H\}$ NMR (100.61 MHz, 223 K, THF-d_8): δ/ppm = 20.9 (s, −CH(CH$_3$)$_2$ of Dipp), 23.1 (s, −CH(CH$_3$)$_2$ of Dipp), 23.6 (s, −CH(CH$_3$)$_2$ of Dipp), 23.7 (s, −CH(CH$_3$)$_2$ of Dipp), 24.4 (s, −CH(CH$_3$)$_2$ of Dipp), 24.7 (s, −CH(CH$_3$)$_2$ of Dipp), 25.6 (s, −CH(CH$_3$)$_2$ of Dipp overlapping with THF-d_8 solvent signal), 25.8 (s, −CH(CH$_3$)$_2$ of Dipp), 26.1 (s, −CH(CH$_3$)$_2$ of Dipp), 26.3 (s, −CH(CH$_3$)$_2$ of Dipp), 26.4 (s, −CH(CH$_3$)$_2$ of Dipp), 26.9 (s, −CH(CH$_3$)$_2$ of Dipp), 28.1 (s, −CH(CH$_3$)$_2$ of Dipp), 28.5, 29.6 (s, −CH(CH$_3$)$_2$ of Dipp), 29.9 (s, −CH(CH$_3$)$_2$ of Dipp), 30.4 (s, −CH(CH$_3$)$_2$ of Dipp), 34.9 (s, −CH(CH$_3$)$_2$ of Dipp overlapping with −CH$_2$ of *n*-pentane), 35.3 (s, −CH(CH$_3$)$_2$ of Dipp), 35.5, 116.9 (br s, C^1−P of Dipp), 123.5 (s, Ar−CH), 124.4 (s, Ar−CH), 124.7, 124.9 (s, Ar−CH), 125.0, 125.5 (s, Ar-CH), 125.7, 126.0 (s, Ar−CH), 126.3 (s, Ar−CH), 126.5 (s, Ar−CH), 126.8 (s, Ar−CH), 127.0 (s, Ar−CH), 128.0 (s, Ar−CH), 128.3 (s, Ar−CH), 130.2 (s, Ar−CH), 130.4 (s, Ar−CH), 130.6 (s, Ar−CH), 130.7 (s, Ar−CH), 131.4 (s, Ar−CH), 135.4 (s, Ar−C), 136.3 (s, Ar−C), 137.3 (s, Ar−C), 137.6 (s, Ar−C), 140.0 (s, Ar−C), 147.0 (s, Ar−C), 150.3 (s, Ar−C), 151.3 (s, Ar−C), 155.3 (s, Ar−C), 160.9 (s, Ar−C), 163.3. $^{31}P\{^1H\}$ NMR (162.04 MHz, 233 K, THF-d_8, ABCDEF spin system): δ/ppm = −33.3 – −27.9 (m, 1P, P$_F$), −18.5 – −16.1 (m, 1P, P$_E$), −14.1 – −9.1 (m, 1P, P$_D$), 36.8–42.2 (m, 1P, P$_C$), 88.4–94.6 (m, 1P, P$_B$), 131.3–135.0 (m, 1P, P$_A$), coupling constants are given in Table S1, Supporting Information **Elemental analysis** calcd. for $C_{77}H_{93}Cl_2CoN_4P_6$ (Mw = 1390.29 g·mol^{-1}) C 66.52, H 6.74, N 4.03; found C 65.02, H 6.71, N 3.63.

$[K(18c-6)][(PHDI)Co(\eta^4\text{-}P_7Dipp)]$ (4): A deep yellow suspension of $[(^{Cl}Im^{Dipp})P_2(Dipp)Cl]$ (**1[Cl]**) (140 mg, 0.195 mmol, 1.0 equiv.) in Et$_2$O (15 mL) was added dropwise to a dark turquoise suspension of **2** (201 mg, 0.195 mmol, 1.0 equiv.) in Et$_2$O (15 mL) at room temperature. The mixture slowly turned dark green upon stirring for 4 h at room temperature. The volume was reduced to ca. 3 mL and the green mixture was filtered through a Whatman filter. The dark green residue was washed with Et$_2$O (8×1 mL) and then with MTBE (3×1 mL) until the washings were only slightly colored. The dark green residue was extracted into THF (4×0.5 mL) and filtered. The dark green filtrate was reduced to two thirds of the original volume. Diffusion of MTBE into the concentrated THF solution gave **4** as a dark green oil. The mother liquor was decanted and the oil was dried *in vacuo* (fraction 1, 31.9 mg, 11%). The ^1H NMR spectrum of the oil contained 1.3 MTBE solvate molecules per formula unit. To obtain a solid for elemental analysis, 6.2 mg of the oil were dissolved in C$_6$H$_6$ and freeze-dried. The ^1H NMR spectrum of the freeze-dried solid contained no more MTBE but

Chemistry–A European Journal

Research Article
doi.org/10.1002/chem.202301930

Chemistry Europe
European Chemical
Societies Publishing

0.2 *n*-hexane solvate molecules, attributable to contaminated glovebox atmosphere, and 0.1 molecules of [(PHDI)Co{η⁴-*cyclo*-P₅(^{Cl}Im^{Dipp})}] (**5**) per formula unit. After two weeks, dark green shimmering crystals of **4** were isolated from the mother liquor and were dried in *vacuo* (fraction 2, 13.9 mg, 5%). This sample was used for further characterization. Fraction 2 contained 0.04 molecules of [(PHDI)Co{η⁴-*cyclo*-P₅(^{Cl}Im^{Dipp})}] (**5**) per formula unit and 0.1 *n*-hexane solvate molecules according to the ¹H NMR spectrum.
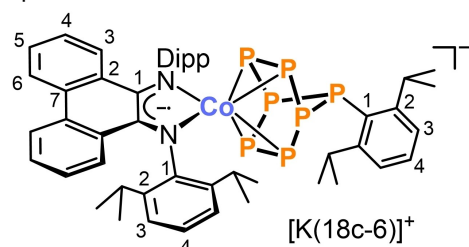

UV/vis (THF, λ_{max}/nm, ε_{max}/L·mol⁻¹·cm⁻¹): 400 (30000), 720 (36000). **¹H NMR** (500.13 MHz, 300 K, THF-d_8): δ/ppm = 0.53 (d, ³J_{HH} = 6.8 Hz, 12H, −CH(CH_3)₂ of N−Dipp), 0.94 (d, ³J_{HH} = 6.8 Hz, 12H, −CH(CH_3)₂ of P−Dipp), 1.53 (d, ³J_{HH} = 6.8 Hz, 12H, −CH(CH_3)₂ of N−Dipp), 2.51–2.57 (m, 2H, −CH(CH₃)₂ of P−Dipp), 3.60 (br s, 24H, 18c-6 overlapping with THF-d_8 solvent signal), 3.72 (sept, ³J_{HH} = 6.8 Hz, 4H, −CH(CH₃)₂ of N−Dipp overlapping with 18c-6), 6.58–6.61 (m, 2H, C⁴−H of PHDI), 6.80 (d, ³J_{HH} = 7.7 Hz, 2H, C³−H of P−Dipp), 6.97 (t, ³J_{HH} = 7.6 Hz, 1H, C⁴−H of P−Dipp), 7.02 (d, ³J_{HH} = 8.9 Hz, 2H, C³−H of PHDI), 7.13–7.16 (m, 2H, C⁵−H of PHDI), 7.25–7.27 (m, 4H, C³−H of N−Dipp), 7.30–7.33 (m, 2H, C⁴−H of N−Dipp), 8.16 (d, ³J_{HH} = 8.1 Hz, 2H, C⁶−H of PHDI). **¹³C{¹H} NMR** (125.76 MHz, 300 K, THF-d_8): δ/ppm = 25.1 (s, −CH(CH₃)₂ of N−Dipp overlapping with THF-d_8 solvent signal), 26.3 (s, −CH-(CH₃)₂ of N−Dipp), 29.4 (−CH(CH₃)₂ of N−Dipp), 33.4 (d, ³J_{CP} = 15.4 Hz, −CH(CH₃)₂ of P−Dipp), 71.4 (s, 18c-6), 122.3 (s, C^5 of PHDI), 123.1 (s, C^3 of P−Dipp), 123.6 (s, C^6 of PHDI), 124.2 (s, C^3 of N−Dipp), 125.1 (s, C^4 of N−Dipp), 125.3 (s, C^4 of PHDI), 127.5 (s, C^3 of PHDI), 128.8 (s, C^7 of PHDI), 129.4 (s, C^4 of P−Dipp), 130.3 (s, C^2 of PHDI), 135.5 (d, ¹J_{CP} = −55.4 Hz, C^1 of P−Dipp), 140.6 (s, C^2 of N−Dipp), 143.5 (s, C^1 of PHDI), 155.0 (d, ²J_{CP} = 11.5 Hz, C^2 of P−Dipp), 162.6 (s, C^1 of N−Dipp). **³¹P{¹H} NMR** (202.46 MHz, 300 K, THF-d_8, AMM′XX′YY′ spin system): δ/ppm = −131.8 − −127.9 (m, 2P, P$_{YY'}$), −67.4 − −63.2 (m, 2P, P$_{XX'}$), −44.3 − −37.5 (m, 2P, P$_{MM'}$), 95.0–98.6 (m, 1P, P$_A$), coupling constants are given in Table S2, Supporting Information. **Elemental analysis** calcd. for fraction 1, C₆₂H₈₃CoKN₂O₆P₇(C₆₅H₇₆Cl₂CoN₄P₅)₀.₁(C₆H₁₄)₀.₂ (Mw = 1404.2 g·mol⁻¹) C 59.62, H 6.70, N 2.39; found C 59.80, H 6.73, N 2.04. **Elemental analysis** calcd. for fraction 2, C₆₂H₈₃CoKN₂O₆P₇(C₆₅H₇₆Cl₂CoN₄P₅)₀.₀₄(C₆H₁₄)₀.₁ (Mw = 1323.7 g·mol⁻¹) C 59.16, H 6.66, N 2.29; found. C 59.96, H 6.79, N 2.05.

[{K(18 c-6)}(μ-Cl)₂{Co(PHDI)}] (6): Solid C₂Cl₆ (22 mg, 0.09 mmol, 1.0 equiv.) was added to a dark green solution of [K(18c-6)(THF)₂][(PHDI)Co(η⁴−1,5-cod)] (**7**) (100 mg, 0.09 mmol, 1.0 equiv.) in THF (10 mL) at room temperature. An immediate colour change to dark brown occurred, and the mixture was stirred for 20 min. The solvent was removed *in vacuo* and the

dark brown residue was washed with *n*-hexane (2×1 mL) and extracted into benzene (5×1 mL). The dark brown extracts were filtered, and the volume was reduced to ca. 2 mL. After addition of 1,4-dioxane (0.05 mL) the solution was layered with *n*-hexane (15 mL). Small dark brown crystals formed over ten days, which were isolated by decanting the mother liquor and drying the crystals in *vacuo*. Yield: 65 mg (72%).

Note: Cobaltate **6** can be detected in the ¹H NMR spectra of the fractions obtained by extraction with non-polar solvents (e.g. *n*-pentane, *n*-hexane, Et₂O; Figure S13, Supporting Information top).
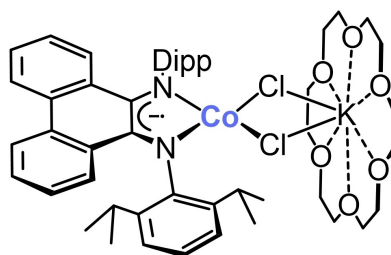
UV/vis (THF, λ_{max}/nm, ε_{max}/L·mol⁻¹·cm⁻¹): 340sh (8000), 410 (12000), 470 (12000), 510sh (8000), 615 (2000), 675 (1200). **¹H NMR** (400.30 MHz, 300 K, C₆D₆): δ/ppm = −25.6 (br s, 4 H) overlapping with −25.3 (s, 2H), −15.7 (br s, 12H, −CH(CH₃)₂ of Dipp), −13.9 (s, 4H), −4.8 (s, 2H), 0.4 (br s, 12H, −CH(CH₃)₂ of Dipp), 2.4 (s, 2H), 7.7 (br s, 24H, 18c-6), 79.0 (br s, 2H), 83.6 (s, 2H). **¹³C{¹H} NMR** (100.66 MHz, 300 K, C₆D₆): δ/ppm = 69.8 (s, −CH(CH₃)₂ of Dipp), 85.5 (s, 18c-6). **Elemental analysis** calcd. for C₅₀H₆₆Cl₂CoKN₂O₆ (Mw = 960.02 g·mol⁻¹): C 62.56, H 6.93, N 2.92; found C 62.25, H 6.70, N 2.77. **HRMS** (ESI, DME): m/z(%) calculated for C₅₀H₆₆Cl₂CoKN₂O₆: 958.33; found: 958.3208 and calculated for C₃₈H₄₂Cl₂CoN₂⁻ [M⁻]: 655.21; found: 655.2013.

Supporting Information

The authors have cited additional references within the Supporting Information.[32–45]

Acknowledgements

## Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Chemistry–A European Journal

Research Article
doi.org/10.1002/chem.202301930

Chemistry
Europe
European Chemical
Societies Publishing

[1] a) B. M. Cossairt, N. A. Piro, C. C. Cummins, *Chem. Rev.* **2010**, *110*, 4164–4177; b) M. Caporali, L. Gonsalvi, A. Rossin, M. Peruzzini, *Chem. Rev.* **2010**, *110*, 4178–4235; c) M. Scheer, G. Balázs, A. Seitz, *Chem. Rev.* **2010**, *110*, 4236–4256; d) L. Giusti, V. R. Landaeta, M. Vanni, J. A. Kelly, R. Wolf, M. Caporali, *Coord. Chem. Rev.* **2021**, *441*, 213927; e) C. M. Hoidn, D. J. Scott, R. Wolf, *Chem. Eur. J.* **2021**, *27*, 1886–1902.

[2] a) C. G. P. Ziegler, T. M. Maier, S. Pelties, C. Taube, F. Hennersdorf, A. W. Ehlers, J. J. Weigand, R. Wolf, *Chem. Sci.* **2019**, *10*, 1302–1308; b) C. M. Hoidn, T. M. Maier, K. Trabitsch, J. J. Weigand, R. Wolf, *Angew. Chem. Int. Ed.* **2019**, *58*, 18931–18936; c) C. Riesinger, L. Dütsch, G. Balázs, M. Bodensteiner, M. Scheer, *Chem. Eur. J.* **2020**, *26*, 17165–17170; d) M. Piesch, S. Reichl, M. Seidl, G. Balázs, M. Scheer, *Angew. Chem. Int. Ed.* **2021**, *60*, 15101–15108; e) C. Riesinger, M. Erhard, M. Scheer, *Chem. Commun.* **2023**, *59*, 10117–10120.

[3] a) J. J. Weigand, K.-O. Feldmann, F. D. Henne, *J. Am. Chem. Soc.* **2010**, *132*, 16321–16323; b) F. D. Henne, A. T. Dickschat, F. Hennersdorf, K.-O. Feldmann, J. J. Weigand, *Inorg. Chem.* **2015**, *54*, 6849–6861; c) C. Taube, K. Schwedtmann, M. Noikham, E. Somsook, F. Hennersdorf, R. Wolf, J. J. Weigand, *Angew. Chem. Int. Ed.* **2020**, *59*, 3585–3591; d) K. Schwedtmann, J. Haberstroh, S. Roediger, A. Bauzá, A. Frontera, F. Hennersdorf, J. J. Weigand, *Chem. Sci.* **2019**, *10*, 6868–6875; e) P. Royla, K. Schwedtmann, Z. Han, J. Fidelius, D. P. Gates, R. M. Gomila, A. Frontera, J. J. Weigand, *J. Am. Chem. Soc.* **2023**, *145*, 10364–10375.

[4] M. H. Holthausen, K.-O. Feldmann, S. Schulz, A. Hepp, J. J. Weigand, *Inorg. Chem.* **2012**, *51*, 3374–3387.

[5] M. H. Holthausen, S. K. Surmiak, P. Jerabek, G. Frenking, J. J. Weigand, *Angew. Chem. Int. Ed.* **2013**, *52*, 11078–11082.

[6] K. Schwedtmann, M. H. Holthausen, C. H. Sala, F. Hennersdorf, R. Fröhlich, J. J. Weigand, *Chem. Commun.* **2016**, *52*, 1409–1412.

[7] K. Schwedtmann, F. Hennersdorf, A. Bauzá, A. Frontera, R. Fischer, J. J. Weigand, *Angew. Chem. Int. Ed.* **2017**, *56*, 6218–6222.

[8] C. Taube, K. Schwedtmann, J. Fidelius, C. Ziegler, F. Kreuter, R. Tonner-Zech, R. Wolf, J. J. Weigand, *submitted manuscript.*

[9] B. Gao, X. Luo, W. Gao, L. Huang, S. Gao, X. Liu, Q. Wu, Y. Mu, *Dalton Trans.* **2012**, *41*, 2755–2763.

[10] For calculated single- and double-bond lengths, see P. Pyykkö, M. Atsumi, *Chem. Eur. J.* **2009**, *15*, 12770–12779.

[11] A. J. Arduengo, J. C. Calabrese, A. H. Cowley, H. V. R. Dias, J. R. Goerlich, W. J. Marshall, B. Riegel, *Inorg. Chem.* **1997**, *36*, 2151–2158.

[12] Y. Wang, Y. Xie, P. Wei, R. B. King, H. F. Schaefer, P. von Ragué Schleyer, G. H. Robinson, *J. Am. Chem. Soc.* **2008**, *130*, 14970–14971; Schleyer, G. H. Robinson, *J. Am. Chem. Soc.* **2008**, *130*, 14970–14971.

[13] A. Beil, R. J. Gilliard, H. Grützmacher, *Dalton Trans.* **2016**, *45*, 2044–2052.

[14] For a review on N-heterocyclic carbene-phosphinidene adducts, see: T. Krachko, J. C. Slootweg, *Eur. J. Inorg. Chem.* **2018**, 2734–2754.

[15] For a review on inversely polarized phosphaalkenes, see: L. Weber, *Eur. J. Inorg. Chem.* **2000**, 2425–2441.

[16] A. N. Chernega, A. V. Ruban, V. D. Romanenko, L. N. Markovski, A. A. Korkin, M. Y. Antipin, Y. T. Struchkov, *Heteroat. Chem.* **1991**, *2*, 229–241.

[17] C. M. Knapp, J. S. Large, N. H. Rees, J. M. Goicoechea, *Chem. Commun.* **2011**, *47*, 4111–4113.

[18] S. Charles, J. C. Fettinger, B. W. Eichhorn, *J. Am. Chem. Soc.* **1995**, *117*, 5303–5311.

[19] S. Charles, J. A. Danis, S. P. Mattamana, J. C. Fettinger, B. W. Eichhorn, *Z. Anorg. Allg. Chem.* **1998**, *624*, 823–829.

[20] E.-M. Schnöckelborg, J. J. Weigand, R. Wolf, *Angew. Chem. Int. Ed.* **2011**, *50*, 6657–6660.

[21] The substituent at C40 in the molecular structure of **5** was disordered. This substituent was refined with a split model, which gave a Cl and an H atom at this position with 50% occupancy each. This indicates partial chloride substitution of Cl atoms on the ^{Cl}Im^{Dipp} imidazolyl substituent. Similar observations were previously made by Weigand and co-workers in related complexes, for this see: K. Schwedtmann, R. Schoemaker, F. Hennersdorf, A. Bauzá, A. Frontera, R. Weiss, J. J. Weigand, *Dalton Trans.* **2016**, *45*, 11384–11396.

[22] F. Riedlberger, S. Todisco, P. Mastrorilli, A. Y. Timoshkin, M. Seidl, M. Scheer, *Chem. Eur. J.* **2020**, *26*, 16251–16255.

[23] E. Mädl, M. V. Butovskii, G. Balázs, E. V. Peresypkina, A. V. Virovets, M. Seidl, M. Scheer, *Angew. Chem. Int. Ed.* **2014**, *53*, 7643–7646.

[24] A. J. Arduengo, R. Krafczyk, R. Schmutzler, H. A. Craig, J. R. Goerlich, W. J. Marshall, M. Unverzagt, *Tetrahedron* **1999**, *55*, 14523–14534.

[25] Structurally related β-diketiminato complexes [{K(18c-6)}(μ-Cl)$_2${Fe-(nacnac)}] (nacnac = CMe[CMeN(2,6-Me$_2$C$_6$H$_3$)]$_2$)[27] and [{Li(L$_2$)}(μ-Cl)$_2${Co-(nacnac)}] (L=THF, Et$_2$O); nacnac = CH[CMeN(2,6-Me$_2$C$_6$H$_3$)]$_2$, CH-[CMeN(Mes)]$_2$, CH[CMeN(Dipp)]$_2$, CH[CtBuN(Dipp)]$_2$) have been reported by Holland,[28,29] Power[30] and Hannedouche.[31] In addition, it is noteworthy that **6** is also formed during the reaction of **1**[OTf] with **2** (Scheme), which suggests the abstraction of chloride atoms of the ^{Cl}Im^{Dipp} ligand and the formation of **6** as a thermodynamic sink.

[26] For selected polyphosphorus complexes, see a) N. A. Piro, C. C. Cummins, *J. Am. Chem. Soc.* **2008**, *130*, 9524–9535; b) E. Mädl, G. Balázs, E. V. Peresypkina, M. Scheer, *Angew. Chem. Int. Ed.* **2016**, *55*, 7702–7707; c) F. Dielmann, A. Timoshkin, M. Piesch, G. Balázs, M. Scheer, *Angew. Chem. Int. Ed.* **2017**, *56*, 1671–1675; d) A. Cavaillé, N. Saffon-Merceron, N. Nebra, M. Fustier-Boutignon, N. Mézailles, *Angew. Chem. Int. Ed.* **2018**, *57*, 1874–1878; e) K. A. Mandla, C. E. Moore, A. L. Rheingold, J. S. Figueroa, *Angew. Chem. Int. Ed.* **2019**, *58*, 1779–1783.

[27] M. M. Rodriguez, E. Bill, W. W. Brennessel, P. L. Holland, *Science* **2011**, *334*, 780–783.

[28] P. L. Holland, T. R. Cundari, L. L. Perez, N. A. Eckert, R. J. Lachicotte, *J. Am. Chem. Soc.* **2002**, *124*, 14416–14424.

[29] C. Chen, M. B. Hecht, A. Kavara, W. W. Brennessel, B. Q. Mercado, D. J. Weix, P. L. Holland, *J. Am. Chem. Soc.* **2015**, *137*, 13244–13247.

[30] A. Panda, M. Stender, R. J. Wright, M. M. Olmstead, P. Klavins, P. P. Power, *Inorg. Chem.* **2002**, *41*, 3909–3916.

[31] C. Lepori, P. Gómez-Orellana, A. Ouharzoune, R. Guillot, A. Lledós, G. Ujaque, J. Hannedouche, *ACS Catal.* **2018**, *8*, 4446–4451.

[32] P. H. M. Budzelaar, *IvorySoft: G NMR for Windows, NMR Simulation Program*, **2006**.

[33] S. Aime, M. Fild, E. M. McVicker, M. Fild, *J. Chem. Soc. Dalton Trans.* **1976**, 2144–2153.

[34] J. P. Albrand, H. Faucher, D. Gagnaire, J. B. Robert, *Chem. Phys. Lett.* **1976**, *38*, 521–523.

[35] J. E. Del Bene, J. Elguero, I. Alkorta, *J. Phys. Chem. A* **2004**, *108*, 3662–3667.

[36] E. G. Finer, R. K. Harris, *Mol. Phys.* **1967**, *28*, 65–75.

[37] M. A. M. Forgeron, M. Gee, R. E. Wasylishen, *J. Phys. Chem. A* **2004**, *108*, 4895–4908.

[38] H. C. E. McFarlane, W. McFarlane, J. A. Nash, *J. Chem. Soc. Dalton Trans.* **1980**, 240–244.

[39] S. Pelties, T. Maier, D. Herrmann, B. de Bruin, C. Rebreyend, S. Gärtner, I. G. Shenderovich, R. Wolf, *Chem. Eur. J.* **2017**, *23*, 6094–6102.

[40] SCALE3ABS, CrysAlisPro, Aglient Technologies Inc., Oxford, GB, **2012**.

[41] G. M. Sheldrick, SADABS, Bruker AXS, Madison, USA, **2007**.

[42] R. C. Clark, J. S. Reid, *Acta Crystallogr. Sect. A* **1995**, *51*, 887–897.

[43] G. M. Sheldrick, *Acta Crystallogr. Sect. A* **2015**, *A71*, 3–8.

[44] G. M. Sheldrick, *Acta Crystallogr. Sect. C* **2015**, *C71*, 3–8.

[45] K. Schwedtmann, R. Schoemaker, F. Hennersdorf, A. Bauzá, A. Frontera, R. Weiss, J. J. Weigand, *Dalton Trans.* **2016**, *45*, 11384–11396.

[46] Deposition Numbers 2269912 (for **3**), 2269920 (for **4**), and 2269908 (for **5**) contains the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

RESEARCH ARTICLE

P–P condensation **disproportionation**

$P_2 + P_4$ P_6 P_7 P_5
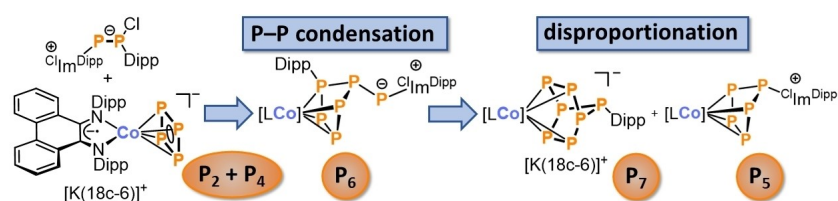
[4+2] condensation reaction of diphosphene [$(^{Cl}Im^{Dipp})P_2(Dipp)$]OTf and diphosphanide [$(^{Cl}Im^{Dipp})P_2(Dipp)Cl$] with the *cyclo*-$P_4$ cobalt complex [K(18c-6)][(PHDI)Co(η^4-*cyclo*-P_4)] forms a CoP$_6$ complex, featuring an unusual hexaphosphido ligand composed of a *cyclo*-P_5 ring and an exocyclic ($^{Cl}Im^{Dipp}$)P moiety. ^{31}P NMR spectroscopic studies reveal that at ambient temperature, this CoP$_6$ complex undergoes disproportionation into more stable CoP$_7$ and CoP$_5$ complexes.

Dr. C. M. Hoidn, K. Trabitsch, Dr. K. Schwedtmann, Dr. C. Taube, Prof. Dr. J. J. Weigand*, Prof. Dr. R. Wolf*

Formation of a Hexaphosphido Cobalt Complex through P–P Condensation