Showcasing research from the laboratories of Prof. Robert Wolf (University of Regensburg, Germany) and Prof. Jan J. Weigand (Technical University of Dresden, Germany).

Construction of alkyl-substituted pentaphosphido ligands in the coordination sphere of cobalt

P-P condensations afford unusual diorganopentaphosphido ligands in cobalt complexes. These new species were obtained by reacting a tetraphosphido cobalt-gallium compound (accessible in two steps from white phosphorus) with chlorophosphanes. This work presents a proof-of-principle for the use of heterobimetallic complexes as precursors for the targeted construction of novel substituted polyphosphorus frameworks.

As featured in:
See Jan J. Weigand, Robert Wolf et al., Chem. Sci., 2019, 10, 1302.
Construction of alkyl-substituted pentaphosphido ligands in the coordination sphere of cobalt†‡

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Rare mono- and diorganopentaphosphido cobalt complexes are accessible by P–P condensation using the unprecedented, reactive cobalt–gallium tetraphosphido complex [K(dme)\(_2\)\((\text{MesBIAN})\text{Co}((\mu-\eta^4:1,5-P_3)\text{Ga}(nacnac))\)] (2). Compound 2 was prepared in good yield by reaction of [K(Et\(_2\)O)]\((\text{MesBIAN})\text{Co}(\eta^4:1,5-cod))\] [1, BIAN = bis(mesitylimino)acenaphthene diimine, cod = 1,5-cyclooctadiene] with [Ga(nacnac)(\(\eta^2\)–P\(_2\))\_2] (nacnac = CH[CMen\(\{2,6-iPr_2C_6H_3\}\])\_2). Reactions with \(R_i\text{PCl}\) (\(R_i = iPr, tBu,\) and Cy) selectively afford [\(\text{MesBIAN}\)\text{Co}(cyclo\(-P_3R_2)\)] \(3a\) and \(3c\), which feature \(\eta^3\)-coordinated 1,1-dianorganophosphido ligands. The formation of metalate anions (Scheme 1a). Cummins and co-workers also devised a synthetic cycle to yield useful phoshaalkynes, and they have been using their niobium phosphido complexes to access several further unprecedented \(P\) compounds, including the previously unknown \(\text{AsP}_5\) molecule obtained by reacting \(A\) with arsenic trichloride. The \([\text{Nb(OAr)}(\eta^3\text{-}P_3)]^-\) anion \((A, \text{Ar} = 2,6-iPr_2C_6H_3)\) was used for generating a coordinated diphosphorus molecule in situ under mild conditions to access diphosphanes (Scheme 1a). Cummins and co-workers also devised a synthetic cycle to yield useful phoshaalkynes, and they have been using their niobium phosphido complexes to access several further unprecedented \(P\) compounds, including the previously unknown \(\text{AsP}_5\) molecule obtained by reacting \(A\) with arsenic trichloride.

While these results indicate that anionic phosphido complexes are attractive precursors for functionalisation reactions, there have only been scattered examples with other metals. Peruzzini and Stopponi reported the alklylation and hydrolysis of group 8 and 9 complexes, for example using ruthenium phosphido compounds (Scheme 1b). Moreover, Scheer described the functionalization of \(cyclo\,-\text{P}_3\) and \(cyclo\,-\text{P}_4\) units in iron and nickel complexes by main group element nucleophiles such as amides, phosphinides, and hydrocarbyl anions (Scheme 1c). The same group recently reported the synthesis of the first triarsa- and the triphosphatrisilabenzenes by a successful metathesis reaction of a tetraphosphido zirconium complex with a chlorosilylene.

Here, we describe a new strategy for the synthesis of unprecedented polyphosphido complexes, which uses heterobimetallic complexes derived from \(\text{P}_4\) as a tool for the construction of more extended \(P_n\) units. As a proof of principle, we have synthesised the new \(\text{CoGaP}_4\) complex [K(dme)\((\text{MesBIAN})\text{Co}(\mu-\eta^4:1,5-P_3)\text{Ga}(nacnac))\] (2, \(\text{MesBIAN} = 1,2\)-...
we report the synthesis of \([\text{MesBIAN}]\text{Co} (\text{nacnac})\] (4) isolated in 59% yield by crystallization from DME/\(\text{C}_0\text{NaCl}\), as the sole P-containing product. A noteworthy that the 2,6-diisopropylphenyl-substituted complex \([\text{MesBIAN}]\text{Co} (\text{nacnac})\] contains a disubstituted P5 ligand with a single terminal P atom (P1 – P4) and a gallium-substituted GaCl(nacnac) moiety suggests that it is present in its radical anionic form. The coordination sphere of the potassium cation (K1 – K4) hydrogen atoms are omitted for clarity

Fig. 1 Solid-state molecular structure of \([\text{K(dme)}]_2[\text{(MesBIAN}]\text{Co} (\mu - \eta^4 : \eta^2 - P_4)\text{Ga(nacnac)}]] (2) hydrogen atoms are omitted for clarity and thermal ellipsoids are drawn at the 40% probability level; selected bond lengths [\(\AA\)] and angles [\(^\circ\)]: P1 – P2 2.1198(7) \(\AA\), P3 – P4 = 2.1286(7) \(\AA\) are shorter than the internal P–P bond (P2 – P3 = 2.1755(8) \(\AA\) and the distance between the terminal P atoms (P1 – P4 = 3.3073(6) \(\AA\) is large. The dihedral angle P1, P2, P3, P4 with a value of 1.3\(^\circ\) indicates that the P4 chain is nearly planar. The C–C and C–N bond distances of the BIAN moiety suggests that it is present in its radical anionic form. The coordination sphere of the potassium cation contains two DME molecules and two P atoms of the P4 chain

synthesized and isolated in an analogous manner in 53% yield by recrystallization from THF/\(n\)-hexane. The dihedral angle P1, P2, P3, P4 with a value of 1.3\(^\circ\) indicates that the P4 chain is nearly planar. The C–C and C–N bond distances of the BIAN moiety suggests that it is present in its radical anionic form. The coordination sphere of the potassium cation contains two DME molecules and two P atoms of the P4 chain.

bis[2,4,6-dimethylphenylimino]acenaphthene, nacnac = CH \([\text{CMEN}(2,6-\text{iPr}_2\text{C}_6\text{H}_3])_2\)]. This complex is a useful precursor for the targeted synthesis of the first diorganopentaphosphido complexes \([\text{[MesBIAN}]\text{Co}(\text{cyclo-P}_2\text{R}_2)]\] (3a, R = iPr; 3b, R = tBu; 3c, R = Cy). \(^{31}\text{P}\) NMR monitoring and the structural characterization of a presumed intermediate \([\text{[MesBIAN}]\text{Co}(\mu - \eta^4 : \eta^2 - P_2;i\text{Pr}_2)\text{Ga(nacnac)}]\) (4) shed light on the reaction mechanism. Moreover, we report the synthesis of \([\text{[MesBIAN}]\text{Co}(\mu - \eta^4 : \eta^1 - P_2;\text{tBu})\text{GaCl(nacnac)}]\) (5). The molecular structure of 5 is unusual in that it contains a disubstituted P2 ligand with a single tBu moiety and a gallly-substituent GaCl(nacnac).

Results

Reaction of \([\text{K(Et}_2\text{O)](\text{MesBIAN}]\text{Co}(\mu - \eta^4 : 1,5-\text{cod})}] (1)\) with \([\text{nacnac}]\text{Ga(n}_2\text{P}_4]\), obtained from white phosphorus and \([\text{Ga(nacnac)}]\) according to a literature procedure, in THF affords the heterodinuclear complex 2 (Scheme 2). \(^{31}\text{P}\)\(^{1}H\) NMR monitoring indicates that the reaction is very selective and affords 2 as the sole P-containing product. After work-up, 2 was isolated in 59% yield by crystallization from DME/\(n\)-hexane. It is noteworthy that the 2,6-diisopropylphenyl-substituted complex \([\text{K(thf)}]_2[\text{(DippBIAN}]\text{Co}(\mu - \eta^4 : \eta^2 - P_4)\text{Ga(nacnac)}]\) (2') can be

Scheme 1 Functionalization of activated phosphorus units; reagents and products: (i) +Ph_2SnCl/\(-\text{NaCl}\); (ii) +Mo[N(\text{Bu})\text{Ar}]_2/\(-\text{NaI}\); (iii) +1,3-cyclohexadiene, +\text{C}_2\text{H}_5\text{NO/} -\text{C}_2\text{H}_5\text{HN}; (iv) +\text{ECl}_2/-\text{NaCl}; (v) +\text{NB} = \text{O}; (vi) +\text{H}_2\text{O}; (vii) +\text{H}_2\text{O}; (viii) +\text{LiCH}_2\text{SiMe}_3; (ix) +\text{LiNMe}_2; (x) +\text{LiPH}_2; (xi) +\text{NaNH}_2; (xii) +\text{LiPH}_2. (top).

Scheme 2 Synthesis of \([\text{K(dme)}]_2[\text{(MesBIAN}]\text{Co}(\mu - \eta^4 : \eta^2 - P_4)\text{Ga(nacnac)}]\) (2).

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Chem. Sci., 2019, 10, 1302-1308 | 1303
A very similar motif with a P4 chain (P–P = 2.150(3) Å – 2.160(3) Å) coordinating to two rhodium centers in an η² and an η¹ fashion, respectively.16 [L3Si(μ-η¹:η³-P₄)Ni(nacac)] (L = CH[(C≡CH₂)₂CMe][N(2,6-iPr₂C₆H₃)]) reported by Driess and co-workers, is also similar, but this complex features a more weakly activated, “butterfly”-P₄ ligand (P1–P₄ = 2.335(4) Å).17 Roesky, Konchenko, Scheer, and co-workers synthesized [[(Cp*)Co₂(μ-η¹:η³-P₄)SmCP₂] (Cp* = η⁵-C₅Me₅, Cp*″ = η⁵-1,2,4-iPr₃C₆H₃)] via an unusual intramolecular P–P coupling process.18 The P₄ chain observed in this trimetalllic complex shows even somewhat longer P–P bonds (2.154(4) Å – 2.251(4) Å) than 2. Further examples of transition metal complexes with bridging catena-P₄ units are diiron species reported by Scherer,19 Miluykov,20 and Walter,21 as well as a dizirconium complex described by Fryzuk.22

In agreement with the solid-state structure, the 31P{1H} NMR spectrum of 2 in THF-d₈ (Fig. 2 and S6, ESI†) shows an AA′XX′ spin system.11 DFT calculations indicate that the multiplet at low frequency (−125.4 ppm) can be assigned to the terminal P atoms (P_X'), while the multiplet at high frequency can be assigned to the internal P atoms (P_A′, see the ESI† for details).13 Iterative fitting of the 31P{1H} NMR spectrum revealed a JAA′ coupling constant of −450.5 Hz, which is 70 Hz larger in magnitude than the JX′X coupling constant (−380.5 Hz). The JX′X (6.6 Hz) and JXX′ (−7.2 Hz) couplings are rather small which is in line with the constrained alignment of the P atoms in the P₄ chain observed in the solid-state structure, causing an antiparallel orientation of the lone pairs.23

Initial reactivity studies of 2 focused on reactions with dialkylchlorophosphines. 31P{1H} NMR monitoring of the reactions of 2 with R₂PCl (R = iPr, tBu, and Cy) suggests the formation of pentaphosphido complexes [[(Mes⁵BIAN)Co(η⁵-P₅R₂)] (3a, R = iPr; 3b, R = tBu; 3c, R = Cy, Scheme 3).

Fig. 2 31P{1H} NMR spectrum of compound 2 with nuclei assigned to an AA′XX′ spin system; insets: extended signals (upwards) and simulations (downwards); δ(P_X′) = 74.0 ppm, δ(P_A′) = −125.4 ppm, 1JAA′ = 1JX′X = −380.5 Hz, 1JXX′ = 1JXX′ = −450.5 Hz, 2JXX′ = 2JXX′ = 6.6 Hz, 2JX′X = 2JX′X = −7.2 Hz; the spectrum of 2’ is very similar (see Fig. S11 and S12, ESI†).13 [Co] = (Mes⁵BIAN)Co, [Ga] = (nacac)Ga.

Chromatographic work-up is necessary to remove the by-product [Ga(nacac)]. Recrystallization from n-hexane (3a and b) or n-hexane/toluene (3c) gave analytically pure, cyan-colored crystals of the products 3a–c in moderate yields (26% to 31%). According to single-crystal XRD studies, compounds 3a–c are isostructural and feature an unprecedented η¹-coordinated cyclo-P₅R₂ ligand in an envelope conformation. Interestingly, 3a–c may be regarded as transition metal complexes of the corresponding [P₅R₂]⁺ cage cations,24 but in fact they show structural isomers of these cations previously prepared by phosphonium ion insertion into P₄. The molecular structure of 3a is shown in Fig. 3, while those of 3b and 3c are presented in the ESI (Fig. S40 and S41†). The structural parameters of the BIAN ligand are similar to those of 2 (vide supra). The coordinating phosphorus atoms P1, P2, P3, and P4 form an almost planar arrangement (Co–P = 2.3442(1) Å – 2.3720(1) Å for 3a). The coordinated P–P bonds show a short-long-short pattern (3a: P1–P2 2.12969(2) Å, P2–P3 2.1576(2) Å, P3–P4 2.1297(2) Å, which indicates a diene-like arrangement. Scheer’s salts [Li[(EtO)₂][CP*Fe(η⁵-P₅C₆H₃)]], [Na(dme)₄][CP*Fe(η⁵-P₅)];N] and [Li(dme)₄][CP*Fe(η⁵-P₅)]₂PH (vide supra, Scheme 1c).

Fig. 3 Solid-state molecular structure of [(Mes⁵BIAN)Co(η⁵-P₅R₂)] (3a); hydrogen atoms are omitted for clarity and thermal ellipsoids are drawn at the 40% probability level; selected bond lengths [Å] and angles [°]: P1–P2 2.12969(2), P2–P3 2.1576(2), P3–P4 2.1297(2), P4–P5 2.1347(2), P5–P1 2.1506(1), P5–C1 1.8423(1), P5–C2 1.8458(1), Co1–P1 2.3720(1), Co1–P2 2.3442(1), Co1–P3 2.3447(2), Co1–P4 2.3595(2), Co1–N1 1.9104(1), Co1–N2 1.9408(1), N1–C3 1.32559(8), N2–C4 1.32069(8), C3–C4 1.43661(6), P1–P2–P3 103.926(5), P2–P3–P4 107.049(5), P3–P4–P5 98.104(6), P4–P5–P1 99.966(5), P5–P1–P2 100.689(5), C1–P5–C2 113.0644(5); bond distances and angles of derivatives 3b and c are presented in the ESI (see Fig. S40 and S41, ESI†).
display a similar envelope conformation of the monosubstituted
cyclo-P₅R units.¹⁰

The ³¹P[¹H] NMR spectra of 3a–c in C₆D₆ (Fig. 4 and S16, S21, and S26, ESI†)¹¹ show very similar AMM’XX’ spin systems that are consistent with molecular structures observed in the solid state. The spectrum of 3a will be discussed in more detail here. The tetracoordinate, diorgano-substituted phosphorus nucleus (P₄) resonates at higher frequency (161.0 ppm for 3a) compared to the resonances of the metal-coordinated P atoms (88.6 ppm and 111.4 ppm, respectively, for 3a). The Jₚᵥ coupling constants for the derivatives 3a–c were obtained by the iterative simulation of the ³¹P[¹H] NMR spectra.¹³ The one-bond P–P coupling constants of the coordinated P atoms (Jₚₓ = −380.6 Hz and Jₚ₦ = −414.2 Hz for 3a) are comparable to those reported for [Li(ET₃)][Cp⁺Fe(η¹-P₅CH₂SiMe₃)] (Jₚₓ = −409.7 Hz, Jₚ₦ = −382.6 Hz), but the Jₚₓ₦ coupling constant (−392.9 Hz) is substantially larger (−275.3 Hz for [Li(ET₃)][Cp⁺Fe(η¹-P₅CH₂SiMe₃)]).¹⁰ The values of the Jₚₓ (Jₚₓ = 39.9 Hz, Jₚ₦ = 10.4 Hz, and Jₚₓ₦ = 9.2 Hz for 3a) are in the usual range.

In order to gain more insight in the mechanism of formation of the diorganopentaphosphido ligands in 3a–c, we studied the reactions of 2 with R₂PCl (R = tBu and iPr) by ³¹P[¹H] NMR spectroscopy. While we did not detect any intermediate in the reaction with tBuPCl, we observed two intermediate species in case of iPr₂PCl (Fig. 5). The starting materials are consumed within ten minutes, while two similar ABCDE spin systems arise that are presumably assigned to the two intermediates Int-A and Int-B. Monitoring the reaction by ³¹P[¹H] VT NMR spectroscopy initially shows the exclusive formation of intermediate Int-A at −30 ºC. Upon warming the reaction mixture above 0 ºC, the signals of Int-B arise in the ³¹P[¹H] NMR spectra. According to ³¹P[¹H] NMR integration, Int-A and Int-B are present in a 4 : 1 ratio at room temperature independent of the reaction time (see Fig. S36, ESI†).¹² Given the fairly similar ³¹P NMR patterns, it seems probable that Int-A and Int-B are constitutional isomers.

It is difficult to determine the precise molecular structures of Int-A and Int-B only from ³¹P NMR investigation, but fortunately one of the intermediates crystallized from the reaction mixture and was characterized as [[(MesBIAN)Co(η¹-P₅CH₂SiMe₃)] (4, Fig. 6). The ³¹P[¹H] NMR spectrum of crystalline 4 in C₆D₆ recorded at room temperature after 10 min showed two sets of resonances which were identified as Int-A and Int-B in the same ratio as observed in the reaction mixture. Based on our calculated ³¹P NMR chemical shiftings of 4, it seems plausible that intermediate Int-A can be assigned to 4 (see the ESI‡ for details).¹³ Solid 4, when stored under an inert atmosphere, is stable for several weeks without decomposition, but it irreversibly converts to 3a when dissolved in C₆D₆ at ambient temperature over the course of five days as indicated by ³¹P[¹H] NMR monitoring.

Based on these data, a mechanism of formation can be proposed for 3a (Scheme 4), which involves a pre-equilibrium between Int-A and Int-B. The latter species slowly converts into 3a by dissociation of [Ga(nacnac)], this process appears to be irreversible.

The molecular structure of 4 confirms that P–P bond formation has already occurred in this intermediate (Fig. 6). The structure is in line with the ³¹P[¹H] NMR data (ABCDE spin system, vide infra) and shows an almost planar P₅ unit which coordinates to cobalt via the four unsubstituted P atoms (P₁–P₂ = 2.122(1) Å, P₂–P₃ = 2.139(1) Å, and P₃–P₄ = 2.164(1) Å). The Pt₂P₂ unit adopts the terminal position (P₄–P₅ = 2.239(1) Å) and does not show close contacts to cobalt or gallium. The [Ga(nacnac)] moiety is η¹-coordinated to the 1,4-positions of the
in its radical monoanionic form.

t a pentaphosphido framework, however, mono- and comparable to Co(m-

Solid-state molecular structure of [(MesBIAN)Co(η4-η1-P5(Bu)Cl(nacnac)] (4).

Proposed mechanism of the condensation of iPr2PCl with 2 leading to product 3a. NMR monitoring revealed two intermediates Int-A and Int-B in a 4 : 1 integral ratio at room temperature.

P5 chain (P1–Ga1 = 2.3320(9) Å, P4–Ga1 = 2.418(1) Å) and the C–N and C–C bond lengths of the BIAN moiety are again comparable to 2 and 3a–c, suggesting that the ligand is present in its radical monoanionic form.

Dialkylchlorophosphanes smoothly reacted with 2 to form a pentaphosphido framework, however, mono- and diarylchlorophosphanes gave intractable products. By contrast, tBuPCl3 (Scheme 5) readily affords tBu-substituted [(MesBIAN) Co(η4-η1-P5tBu)Cl(nacnac)] (5) as the sole P-containing species detected by 31P(1H) NMR. An unidentified paramagnetic by-product was detected in the 1H NMR spectrum of the crude reaction mixture. This undesired species can be completely removed by several recrystallization steps from toluene. This work-up procedure is the reason for the relatively low yield (6%) for the spectroscopically and analytically pure isolated compound 5. The synthesis of 5 nevertheless is remarkable because it shows that P–P condensations also occur with monoalkyl dichlorophanes. The molecular structure of 5 determined by single-crystal XRD (Fig. 7) features an η4:η1-coordinated cyclo-P5Bu ligand similar to the dialkyl-substituted ligands in 3a–c. The phosphorus atoms P2, P3, P4, and P5 coordinated to cobalt form an almost planar arrangement (Co–P = 2.33156(7) Å – 2.37439(6) Å). Notably, the P atom at the tip of the cyclo-P5 envelope is coordinated to the gallium atom of GaCl(nacnac) (P1–Ga1–P5 82.28(3)°, Ga1–P1–P5 115.834(2)°, and Ga1–P1–P2 112.634(2)°). The structural parameters of the BIAN ligand are close to 2 and 3a–c (vide supra). The P–P bond distances (P1–P5 = 2.14146(8) Å, P2–P3 = 2.13102(7) Å, and P4–P5 = 2.13310(5) Å) are in a very close range except for the P1–P2 bond (2.19903(6) Å).

Compound 5 gives rise to an ABEMX spin system in the 31P(1H) NMR spectrum, which was simulated using an iterative

Fig. 6  

Fig. 7  

Scheme 4 

Scheme 5
The reaction properties of intermediate 4 have been characterized by NMR and single-crystal XRD experiments. It was revealed that halophosphanes are a potentially powerful synthetic approach towards the condensation reactions of anionic polyphosphido complexes and related species. Remarkably, related metal-free \([\text{P}_5\text{R}_2]^+\), \([\text{P}_6\text{R}_4]^2+\), and \([\text{P}_7\text{R}_6]^2+\) cations have readily formed. Anionic cobalt-gallium tetraphosphido complex \(\text{P}^\text{catena-P}_4\) is readily accessed by reaction of nucleophiles, e.g. alkali metal alkyls, amides and phosphides, on pentaphosphaferrocene and related complexes. Notwithstanding these previous examples, the results reported in this study show that \(P\)-\(P\) condensation reactions of anionic polyphosphido complexes and halophosphanes are a potentially powerful synthetic approach which can give rise to unusual new polyphosphorus species. NMR and single-crystal XRD experiments have revealed that \(P\)-\(P\) bond formation is facile as shown by the formation of intermediate 4 characterized by X-ray crystallography. By contrast, the subsequent elimination of the \([\text{Ga}(\text{nacnac})(\text{Me}_3\text{BIAN})\text{Co}, [\text{Ga}]=\{\text{nacnac}\}\text{Ga}\] building block from 4 seems to be associated with a considerable barrier. The reaction properties of 3a-c and 5 are currently under investigation. Moreover, efforts are underway to extend and fine tune the \(P\)-\(P\) condensation approach for the synthesis of further unprecedented polyphosphorus compounds.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We thank Dr Stefanie Gärtner (Central Analytical Services, University of Regensburg) for crystallographic assistance and Kerstin Rothermel (Gschwind group, University of Regensburg) for assistance with NMR measurements. Generous funding by the Deutsche Forschungsgemeinschaft (WE4621/3-1 and WO1496/7-1) and the Fonds der Chemischen Industrie (fellowship to T. M. Maier) is gratefully acknowledged.

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