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{(MesBIAN)Co(μ-η4-η2-P4)Ga(nacnac)}] (2). Compound 2 was prepared in good yield by reaction of [K(Et2O){(MesBIAN)Co(μ-η4-1,5-cod)}] 1. BIAN = bis(mesitylimino)acenaphthene diimine, cod = 1,5-cyclooctadiene with [Ga(nacnac)(η2-P4)][nacnac = Cl(CMMe2N2,iPr2C6H3)]. Reactions with R2PCl (R = iPr, tBu, and Cy) selectively afford [l{(MesBIAN)Co(cyclo-P-R-R)}] (3a–c), which feature η4-coordinated 1,1-diorganophosphido ligands. The mechanism of formation of these species has been studied by 31P{1H} NMR spectroscopy and DFT calculations. In the case of 3a (R = iPr), it was possible to identify the intermediate [l{(MesBIAN)Co(μ-η4-η2-P2R)-Pr2Ga(nacnac)}] (4) by single-crystal X-ray diffraction. A related, monosubstituted organopentaphosphido cobalt complex [(MesBIAN)Co(μ-η4-η1-P3Bu)GaCl(nacnac)] (5) was isolated by reacting dichloroalkylphosphane iBuPCl2 with 2. Heterobimetallic complexes such as 2 thus may enable the targeted construction of a range of new metal-coordinated polyphosphorus frameworks by P–P condensation.

metallate anions.†‡ The [Nb(OAr)3{(η1-3-P3)}]− anion (A, Ar = 2,6-iPr2C6H3) 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 phosphaalkynes, and they have been using their niobium phosphido complexes to access several further unprecedented P compounds, including the previously unknown AsP3 molecule obtained by reacting A with arsenic trichloride.6,7

While these results indicate that anionic polyphosphido complexes are attractive precursors for functionalisation reactions, there have only been scattered examples with other metals.8–11 Peruzzini and Stoppioni reported the alkylation and hydrolysis of group 8 and 9 complexes, for example using ruthenium phosphido compounds (Scheme 1b).8 Moreover, Scheer described the functionalization of cyclo-P4 and cyclo-P3 units in iron and nickel complexes by main group element nucleophiles such as amides, phosphonides, and hydrocarbyl anions (Scheme 1c).6,8 The same group recently reported the synthesis of the first triarsa- and the triphosphasilabenzenes by a successful metathesis reaction of a tetraphosphido zirconium complex with a chlorosilylene.11

Here, we describe a new strategy for the synthesis of unprecedented polyphosphido complexes, which uses heterobimetallic complexes derived from P4 as a tool for the construction of more extended Pn units. As a proof of principle, we have synthesized the new CoGaP4 complex [K(dme), {{MesBIAN)Co(μ-η4-η1-P3)Ga(nacnac)]} (2, MesBIAN = 1,2-

Introduction

Over the past decades, much effort has been invested into the synthesis of transition metal polyphosphorus complexes. An impressive and structurally diverse array of early and late transition metal polyphosphorus species has become accessible. Most commonly, such species have been prepared by reaction of low-valent transition metal precursors with white phosphorus. While these results indicate that anionic polyphosphido complexes are attractive precursors for functionalisation reactions, there have only been scattered examples with other metals.8–11 Peruzzini and Stoppioni reported the alkylation and hydrolysis of group 8 and 9 complexes, for example using ruthenium phosphido compounds (Scheme 1b).8 Moreover, Scheer described the functionalization of cyclo-P4 and cyclo-P3 units in iron and nickel complexes by main group element nucleophiles such as amides, phosphonides, and hydrocarbyl anions (Scheme 1c).6,8 The same group recently reported the synthesis of the first triarsa- and the triphosphasilabenzenes by a successful metathesis reaction of a tetraphosphido zirconium complex with a chlorosilylene.11

Here, we describe a new strategy for the synthesis of unprecedented polyphosphido complexes, which uses heterobimetallic complexes derived from P4 as a tool for the construction of more extended Pn units. As a proof of principle, we have synthesized the new CoGaP4 complex [K(dme), {{MesBIAN)Co(μ-η4-η1-P3)Ga(nacnac)]} (2, MesBIAN = 1,2-

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† Dedicated to Professor Dietmar Stalke on the occasion of his 60th birthday.
‡ Electronic supplementary information (ESI) available. CCDC 1861829–1861837 and 1874059. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c8sc04745f

Cite this: Chem. Sci., 2019, 10, 1302
We report the synthesis of \([\text{MesBIAN})Co(\text{nacnac})\] \((\text{nacnac})\) \(\text{Ga}(\text{nacnac})\) \(\text{LiCl}3\) \(\text{LiCH}_2\text{SiMe}_3\) \(\text{LiNMe}_2\) \(\text{LiPH}_2\) \(\text{NaNH}_2\) \(\text{LiPH}_2\). (top).

Functionalization of anionic heterodinuclear tetraphosphido complexes \([\text{MesBIAN})Co(\text{nacnac})\] \(\text{Ga}(\text{nacnac})\).

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bis[2,4,6-dimethylphenyllimino]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})Co(\text{cycl0-P,R})_2\] \(\text{Ga}(\text{nacnac})\). Functionalization of anionic heterodinuclear tetraphosphido complexes by P–P condensation (bottom).

**Results**

Reaction of \([\text{K(ET}2\text{O})\{\text{MesBIAN})Co(\eta^1-1,5-cod)}\] \(\text{Ga}(\text{nacnac})\) \(\text{Cl}\) \(\text{Bu}_{3}\) \(\text{Bu}_{3}\).

Hydrogen atoms are omitted for clarity and thermal ellipsoids are drawn at the 40% probability level; selected bond lengths [Å] and angles [°]: \(\text{P}1–\text{P}2 = 2.1198(7)\), \(\text{P}1–\text{P}4 = 2.1286(7)\), \(\text{P}2–\text{P}3 = 2.1755(8)\), \(\text{P}2–\text{P}3 = 2.1286(7)\), \(\text{P}1–\text{P}4 = 3.3073(6)\), \(\text{P}1–\text{P}4 = 3.3073(6)\). The dihedral angle \(\text{P}1–\text{P}2–\text{P}3–\text{P}4 = 1.3\text{°}\) indicates that the \(\text{P}4\) chain is nearly planar. The C–C and C–N bond distances of the \(\text{Bian}\) moiety suggests that it is present in its radical anionic form. The coordination sphere of the potassium cation indicates that the \(\text{P}4\) is unusual in that it contains a substituted \(\text{P}2\) ligand with a single \(\text{tBu}\) moiety and a gallyl-substituent \(\text{GaCl}(\text{nacnac})\).
(K1−P4 = 3.3430(6) Å, K1−P3 = 3.7168(7) Å, cf. the sum of the van-der-Waals radii of K and P: 4.63 Å).15

A few transition metal complexes with structures related to 2 are known. For example, Scherer’s dirhodium complex [[(Cp*Rh)(μ-n4:η2−5:π-P3)]Rh(CO)Cp*P] shows 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 n4- and an n3-fashion, respectively.16 [LSi(μ-n4:η2−5:π-P3)Ni(nacnac)] (L = CH(CH2)16CMe3, Scheme 3), 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 P5 chain observed in this trimetallic 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 systems.11 DFT calculations indicate that the multiplet at low frequency (−125.4 ppm) can be assigned to the terminal P atoms (Pα,β), while the multiplet at high frequency can be assigned to the internal P atoms (Pα, see the ESI† for details).13 Iterative fitting of the 31P(1H) NMR spectrum revealed a 1JAA coupling constant of −450.5 Hz, which is 70 Hz larger in magnitude than the 1JA’A’ coupling constant (−380.5 Hz). The 2JAA (6.6 Hz) and 3JAA (−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 R2PCI (R = iPr, tBu, and Cy) suggests the formation of pentaphosphido complexes [(Me5BIAN)Co(n4−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(Pα,β) = 74.0 ppm, δ(Pα,β) = −125.4 ppm; 1JAA = 1JAA = −380.5 Hz, 1JAA = 1JAA = −450.5 Hz, 2JAA = 3JAA = 6.6 Hz, 2JAA = 3JAA = −7.2 Hz; the spectrum of 2 is very similar (see Fig. S11 and S12, ESI†). [Co] = [Me5BIAN](Co)[Ga] = [nacnac]Ga.

Chromatographic work-up is necessary to remove the by-product [Ga(nacnac)]. 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 isostuctural and feature an unprecedented n3-coordinated cyclo-P4R2 ligand in an envelope conformation. Interestingly, 3a-c may be regarded as transition metal complexes of the corresponding [P4R2]3+ cage cations,24,25 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[Et2O](μ−3P5)(μ−3P5)(μ−3P5)(μ−3P5)] show a similar coordination environment.

Fig. 3 Solid-state molecular structure of [(Me5BIAN)Co(n4−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−P5 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 1.9480(1), N1−C3 1.32559(8), N2−C4 1.32069(8), C3−C4 1.43661(6), P1−P2−P3 103.926(5), P3−P2−P4 107.049(5), P4−P3−P5 98.104(6), P5−P4−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. ²

The ³¹P(¹H) NMR spectra of 3a-c in C₆D₆ (Fig. 4 and S16, S21, and S26, ESI†) 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, diorganosubstituted 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 JPP coupling constants for the derivatives 3a-c were obtained by the iterative simulation of the ³¹P(¹H) NMR spectra. The one-bond P-P coupling constants of the coordinated P atoms (J(AX) = −380.6 Hz and J(MX) = −414.2 Hz for 3a) are comparable to those reported for [Li(ET₃)][C₆Fe(n³-P₃CH₂SiMe₃)] (J(AMX) = −409.7 Hz, J(AM) = −382.6 Hz), but the J(AX) coupling constant (−392.9 Hz) is substantially larger (−275.3 Hz for [Li(ET₃)][C₆Fe(n³-P₃CH₂SiMe₃)])⁰. The values of the ²J(PP) (J(AX) = 39.9 Hz, J(AM) = 10.4 Hz, and J(AX) = 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 the case of iPr₂PCl (Fig. 5). The starting materials are consumed within ten minutes, while two similar ABCEDE 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 °C. Upon warming the reaction mixture above 0 °C, the signals of Int-B arise in the ³¹P(¹H) NMR spectrum. 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†). 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(n⁺-P₅iPr₂)] (3a) whereas those marked with ▲ (Int-A) and ▲ (Int-B) are assigned to intermediates; inset: section from 25 ppm to −25 ppm.

Fig. 5 ³¹P(¹H) NMR monitoring of the reaction of 2 dissolved in THF-d₈ with iPr₂PCl in a 1 : 1 ratio at room temperature over seven days; resonances marked with ▲ are assigned to product [MesBIAN]Co(n⁺-P₅iPr₂)] (3a) whereas those marked with ▲ (Int-A) and ▲ (Int-B) are assigned to intermediates; inset: section from 25 ppm to −25 ppm.

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isolated compound 5. The synthesis of 5 nevertheless is remarkable because it shows that P–P condensations also occur with monoalkylchlorophosphanes. The molecular structure of 5 determined by single-crystal XRD (Fig. 7) features an $\eta^4$-$\eta^1$-coordinated cyclo-P$_5$Bu 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-P$_5$ 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 = 2.14148(6) Å, P2–P3 = 2.14129(5) Å, P3–P4 = 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 $^{31}$P($^1$H) NMR spectrum, which was simulated using an iterative

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Fig. 6 Solid-state molecular structure of [($^{10}$MesBIAN)Co($\mu$-$\eta^4$-$\eta^1$-P$_5$Bu)$_2$]$\text{GaCl}(\text{nacnac})$ (4); hydrogen atoms are omitted for clarity and thermal ellipsoids are drawn at the 40% probability level; selected bond lengths [Å] and angles [°]: P1–P2 2.1221(1), P2–P3 2.159(2), P3–P4 2.164(1), P4–P5 2.239(1), P1–Ga1 2.3320(9), P4–Ga1 2.418(1), Ga1–N1 1.992(3), Ga1–N2 1.974(3), Co1–P1 2.348(2), Co1–P2 2.37(1), Co1–P3 2.306(1), Co1–P4 2.353(1), Co1–N3 1.919(3), Co1–N4 1.963(3), C1–N3 1.335(4), C2–N4 1.323(4), C1–C2 1.422(5), P1–P2–P3 103.59(5); P2–P3–P4 102.46(5), P3–P4–P5 95.59(5), P5–P4–Ga1 133.22(5), P1–Ga1–P5 82.28(3), Ga1–P1–P2 97.13(4).

Scheme 4 Proposed mechanism of the condensation of iPr$_2$PCI with 2 leading to product 3a. $^{31}$P($^1$H) NMR monitoring revealed two intermediates Int-A and Int-B in a 4 : 1 integral ratio at room temperature.

P$_5$ 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, iBuPCl$_2$ (Scheme 5) readily affords iBu-substituted [($^{10}$MesBIAN)Co($\mu$-$\eta^4$-$\eta^1$-iPr$_5$Bu)GaCl(nacnac)] (5) as the sole P-containing species detected by $^{31}$P($^1$H) NMR. An unidentified paramagnetic by-product was detected in the $^1$H 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

Scheme 5 Synthesis of [($^{10}$MesBIAN)Co($\mu$-$\eta^4$-$\eta^1$-P$_5$Bu)GaCl(nacnac)] (5).
fitting procedure (Fig. 8). Based on the observed P-P couplings and an additional $^{31}$P–$^1$H HMBC spectrum, the resonance at 70.3 ppm (P$_A$) can be assigned to tBu-substituted phosphorus atom. At room temperature, this resonance is broad; hence, the simulation was carried out for the spectrum recorded at –60 °C. The resulting $^{31}$P NMR data suggest that the signals at 12.0 ppm (P$_B$) and –66.8 ppm (P$_C$) can be assigned to the P atoms adjacent to the tBu-substituted P atom (P$_A$, Fig. S34, ESI†).

Conclusions

The anionic cobalt-gallium tetraphosphido complex 2 is readily accessible by reaction of [K(En)$_2$]([Me$_2$BIAN]Co($\eta^5$-1,5-cod))] (1) with [Ga(nacnac)(P$_A$)$_3$]. This unique heterobimetallic complex features an activated catena-P$_4$ unit amenable to P–P condensation reactions. Remarkably, 2 readily forms unprecedented organosubstituted pentaphosphido complexes 3a–c, 4, and 5 with R$_2$PCl (R = iPr, tBu, and Cy) and tBuPCl$_2$. Related metal-free [P$_2$R$_4$]$^{2-}$, [P$_x$R$_y$]$_{2x}$, and [P–R$_2$]$_{2x}$ cations have been prepared by phosphinum metal insertion into P$_4$.[24–27] metal complexes with monosubstituted P$_x$R ligands were accessed by reaction of nucleophiles, e.g. alkali metal alkyls, amides and phosphides, on pentaphosphaferrocene and related complexes.[8,9] 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 [Ga(nacnac)] 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 Gärnter (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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13 See the ESI‡ for further details.


