ARTICLE

# Facile synthesis of *cyclo*-($P_4{}^tBu_3$)-containing oligo- and pnictaphosphanes

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The *cyclo*-($P_4{}^tBu_3$) synthon [Li{*cyclo*-($P_4{}^tBu_3$)}(thf)(tmeda)] (**1**) (thf = tetrahydrofuran, tmeda = *N*,*N*,*N*′,*N*′-tetramethylethane-1,2-diamine) is readily accessible in a one-pot synthesis from $P_4$ and Li$^t$Bu. The use of **1** as a *cyclo*-($P_4{}^tBu_3$) building block enables the rational synthesis of *cyclo*-($P_4{}^tBu_3$)-containing oligophosphanes, namely {*cyclo*-($P_4{}^tBu_3$)}$_2$ (**2**), {*cyclo*-($P_4{}^tBu_3$)}$_2$P$^t$Bu (**3**) and {*cyclo*-($P_4{}^tBu_3$)}$_2$CH$_2$ (**4**), $C_{3v}$-symmetric pnictaphosphanes E{*cyclo*-($P_4{}^tBu_3$)}$_3$ (E = Bi, Sb, As; **5**–**7**) as well as AsCl{*cyclo*-($P_4{}^tBu_3$)}$_2$ (**8**). Compounds **5** and **6** represent the first neutral homoleptic bismuthane and stibane that contain only bonds to phosphorus. All new compounds were isolated in moderate to good yields and fully characterised. The $^{31}P\{^1H\}$ NMR spectral data of **1**, **2**, **4**, and **8** have been determined by automated line-shape analysis.

## Introduction

Like carbon, phosphorus shows a notable propensity to form a wide variety of $P_n$ frameworks due to the comparatively high bond energy of P–P single bonds (ca. 200 kJ/mol, the highest value within group 15).[1] Cyclic representatives, namely cyclooligophosphanes, *cyclo*-$(PR)_n$, which are isolobal to cycloalkanes, have received much attention lately.[2–4] While the first example of this class of compounds, *cyclo*-$(PPh)_5$, was synthesised as early as 1877,[5] but not recognised as a cyclooligophosphane until the structure was solved almost 90 years later by X-ray diffraction,[6,7] the first cyclooligophosphanide anions, *cyclo*-$(P_nR_{n-1})^-$, were reported only about 100 years later.[8,9] However, readily accessible, pure cyclooligophosphanides are still scarce.[10] While the alkali metal cyclooligophosphanides K{*cyclo*-($P_3{}^tBu_2$)},[8] K{*cyclo*-($P_5Ph_4$)}[10] and Li{*cyclo*-($P_n{}^tBu_{n-1}$)} ($n$ = 3–5)[11–14] have been reported, they were only obtained in inseparable mixtures and characterised by $^{31}P$ NMR spectroscopy. Already in 1983, Fritz *et al.* published the synthesis of the cyclotetraphosphanide [Li{*cyclo*-($P_4{}^tBu_3$)}(thf)$_n$], which was obtained from white phosphorus and Li$^t$Bu.[11,12] Although the product had not been fully characterised, some follow-up chemistry was reported.[15] In general, the chemistry of cyclooligophosphanide anions has hardly been explored until recently, as selective and facile syntheses were mostly unknown. With the high-yield synthesis of Na{*cyclo*-($P_5{}^tBu_4$)} we have paved the way for its use as *cyclo*-$P_5$ synthon in coordination and main group chemistry, as these anions can be employed in salt elimination reactions or they can undergo oxidative coupling reactions to form neutral bis-cyclooligophosphanes.[16–23]

Recently, our group reported the targeted synthesis and coordination chemistry of the octaphosphane {*cyclo*-($P_4{}^tBu_3$)}$_2$ (**2**),[24–26] which was first prepared by Baudler *et al.* in a low-yielding procedure.[27] Employing crude *cyclo*-($P_4{}^tBu_3Cl$)[28] as *cyclo*-($P_4{}^tBu_3$) synthon in the reaction with magnesium furnished **2** in moderate yield.[24] Aiming for a feasible synthesis for other compounds containing a *cyclo*-($P_4{}^tBu_3$) moiety, we adapted this protocol to the synthesis of {*cyclo*-($P_4{}^tBu_3$)}$_2$P$^t$Bu (**3**), which was first isolated in 0.4 % yield.[29] However, this attempt was less successful. As *cyclo*-($P_4{}^tBu_3Cl$) could not be isolated in pure state, although stated otherwise in the literature,[28] workup and isolation of **3** became very tedious due to similar solubility of product and by-products. Consequently, there is a need for an easily accessible *cyclo*-$P_4$ synthon for the rational synthesis of cyclooligophosphanes, and *cyclo*-($P_4{}^tBu_3$)$^-$ represents an ideal candidate.

Furthermore, using cyclooligophosphanide anions as substituents or ligands in main group element or transition metal chemistry is also highly interesting for the synthesis of the corresponding phosphorus-rich derivatives. Here, especially examples of interpnictogen compounds are quite rare and thus particularly interesting. Recently, Chitnis and Marczenko reported the first structurally characterised neutral compound with a Bi–Sb σ bond,[30] and Hänisch *et al.* synthesised a molecule that contains all five pnictogens adjacent to each other.[31] However, to the best of our knowledge there is only one example for arsenic[32] and there are no examples for the trivalent heavier group 15 elements antimony and bismuth being coordinated by phosphanido groups only.

As Li{*cyclo*-($P_4{}^tBu_3$)} seems to be a versatile *cyclo*-$P_4$ synthon and is furthermore accessible in a relatively convenient one-step synthesis from bulk chemicals, we have optimised the synthetic procedure, isolated and fully characterised the product, [Li{*cyclo*-($P_4{}^tBu_3$)}(thf)(tmeda)] (**1**) (thf = tetrahydrofuran,

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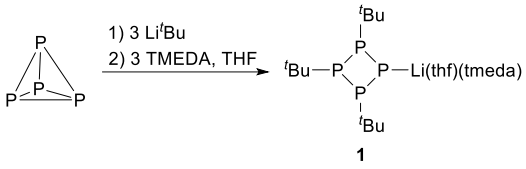
tmeda = *N*,*N*,*N'*,*N'*-tetramethylethane-1,2-diamine) and employed it in oxidative coupling and salt elimination reactions with group 14 and 15 halides.

## Results and discussion

**[Li{*cyclo*-($P_4{}^tBu_3$)}(thf)(tmeda)] (1)**

Already in the 1980s, quite some time before the activation of white phosphorus gained broad interest,[4,33–37] Fritz *et al.* described the reactions of white phosphorus with lithium alkyls. With Li$^t$Bu [Li{*cyclo*-($P_4{}^tBu_3$)}$(thf)_n$] was obtained, but not fully characterised.[11,12] The use of white phosphorus has the benefit of circumventing the formation of stoichiometric amounts of salts, as the traditional syntheses of phosphanes are often based on phosphorus halides.[2–4,38,39] Adapting the procedure of Fritz *et al.*, [Li{*cyclo*-($P_4{}^tBu_3$)}(thf)(tmeda)] (**1**) can be isolated as orange crystals in 15% yield in a one-pot reaction of $P_4$ with three equivalents of Li$^t$Bu followed by the addition of THF and three equivalents of TMEDA (Scheme 1).




**1**

**Scheme 1** White phosphorus reacts with 3 equiv. of Li$^t$Bu forming Li{*cyclo*-($P_4{}^tBu_3$)} which can be isolated from THF as **1** after the addition of 3 equiv. TMEDA.

Crystalline orange **1** can be stored under inert gas at ambient conditions. The rather low yield can be explained by the fact that the formation of **1** is just one possible reaction pathway of a cascade of many competitive reactions[40] that are initiated by the reaction of $P_4$ with Li$^t$Bu. Presumably, the first step involves a nucleophilic attack at the $P_4$ tetrahedron, forming a $P_4$ butterfly compound. Fluck *et al.* have isolated the related $P_4Mes^*_2$ derivative (Mes* = 2,4,6-$^t$Bu$_3$C$_6$H$_2$) from the reaction of $P_4$ with LiMes* and Mes*Br.[41] Isolation of this type of $P_4$ butterfly compounds is only successful with sterically very demanding substituents (this does not include the *tert*-butyl group).[42–44] A P–C bond formation does not occur with *tert*-butyl halides as their reaction with alkali metal phosphanides would result in the protonation of the phosphanide and the elimination of isobutene.[45]

The $^1$H NMR spectrum of **1** shows the coordination of TMEDA and THF at lithium confirming that there is no loss of solvent molecules upon drying *in vacuo*. In the $^{31}P\{^1H\}$ NMR spectrum, an $AM_2X$ spin system is observed. In polar aprotic deuterated solvents but also in benzene-$d^6$, no $^1J_{PLi}$ coupling can be detected, indicating the presence of solvent-separated ion pairs.

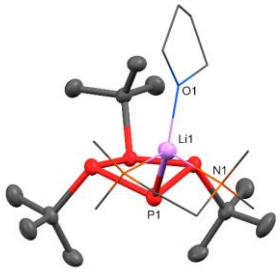



**Fig. 1** Molecular structure of **1**. Hydrogen atoms are omitted and coordinated THF and TMEDA are drawn as wireframe for clarity; thermal ellipsoids at 50 % probability level.

Compound **1** crystallises as intense orange crystals in the monoclinic space group $P2_1$ with two molecules per unit cell (Fig. 1). The P–P bond lengths (ca. 2.21 Å), endocyclic bond angles (ca. 88°), as well as the exocyclic bond angles (102° to 108°) are in the expected range for *cyclo*-$P_4$ compounds.[46] The P1–Li1 bond (2.574(4) Å) is also in the range of P–Li bonds with the lithium atom being coordinated by THF and TMEDA.[47–51]

Lithium cyclotetraphosphanide **1** can be used in salt elimination reactions with element halides as a versatile *cyclo*-($P_4{}^tBu_3$) transfer reagent with formation of lithium halide. However, oxidative coupling of two *cyclo*-($P_4{}^tBu_3$) fragments can also occur depending on the element halide used, resulting in formation of {*cyclo*-($P_4{}^tBu_3$)}$_2$ (**2**). Although the formation of **2** may also be a desirable goal, this reaction pathway slightly limits the versatility of **1**.

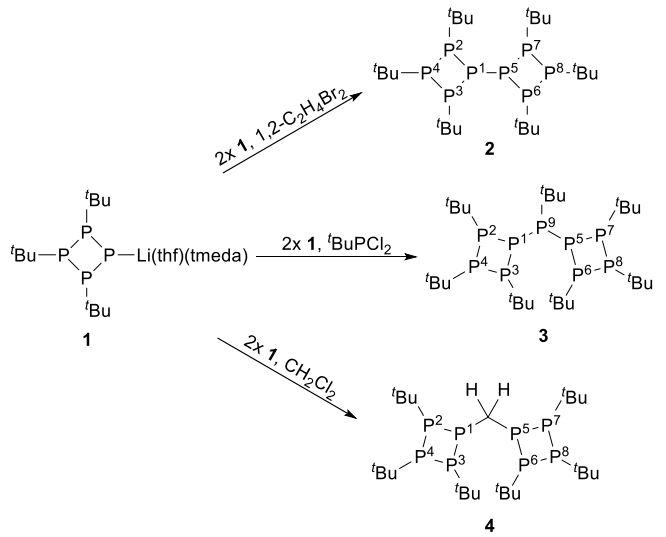
**Reactivity of 1: Synthesis of neutral oligophosphanes**

The use of **1** as a *cyclo*-($P_4{}^tBu_3$) building block enables the rational synthesis of *cyclo*-($P_4{}^tBu_3$)-containing oligophosphanes, namely {*cyclo*-($P_4{}^tBu_3$)}$_2$ (**2**),[27] {*cyclo*-($P_4{}^tBu_3$)}$_2$P$^t$Bu (**3**)[29] and {*cyclo*-($P_4{}^tBu_3$)}$_2$CH$_2$ (**4**) (Scheme 2).

Oxidative coupling of two *cyclo*-($P_4{}^tBu_3$) fragments of **1** was achieved with 0.5 equiv. 1,2-dibromoethane resulting in the clean formation of {*cyclo*-($P_4{}^tBu_3$)}$_2$ (**2**)[27] which was isolated as **2**·2 THF by recrystallisation from THF. Nonaphosphane {*cyclo*-($P_4{}^tBu_3$)}$_2$P$^t$Bu (**3**)[29] was obtained by salt elimination reaction of **1** with 0.5 equiv. $^t$BuPCl$_2$, and the methylene-bridged octaphosphane {*cyclo*-($P_4{}^tBu_3$)}$_2$CH$_2$ (**4**) was formed by reacting two equivalents of **1** with methylene chloride.

In contrast, reactions of **1** with $CHCl_3$, $CCl_4$ or $SnCl_2$ did not result in E–P bond formation (E = C, Sn) but gave **2**, though always as complex mixtures also including *cyclo*-($P_4{}^tBu_3$Cl) or elemental tin (in case of $SnCl_2$) as reduction product. This is in accordance with the reaction of Na{*cyclo*-($P_5{}^tBu_4$)} with tin(II) chloride, lead(II) chloride and bismuth(III) chloride, which resulted in the formation of {*cyclo*-($P_5{}^tBu_4$)}$_2$ and {*cyclo*-($P_4{}^tBu_3$)P$^t$Bu}$_2$ by reductive elimination with formation of the elemental metals.[17]

The number of bis-cyclooligophosphanes and bicyclic compounds obtained in pure form is still small,[27,52–60] and to the best of our knowledge only six structurally characterised compounds are known to date, namely $P_6R_4$ (R = $^t$Bu, Cp),[52,58] {*cyclo*-($P_5{}^tBu_4$)}$_2$,[17] {*cyclo*-($P_4{}^tBu_3$)P$^t$Bu}$_2$,[17] {*cyclo*-($P_4{}^tBu_3$)}$_2$[61] and its pentalane analogue[25].




**Scheme 2** Reactions of **1** to form the neutral oligophosphanes **2**–**4**.

**$^{31}P\{^{1}H\}$ NMR spectra of 2–4.** Although **2** has been known for decades,[27] the determination of the parameters of the $^{31}P\{^{1}H\}$ NMR spectrum (Fig. 2) by automated line shape analysis (Table 1) has not been reported. The large $^{2}J_{PP}$ coupling constant ($^{2}J_{1,6}$, +130.71 Hz) indicates an orientation of the respective lone pairs of electrons towards each other, as was also observed in the rhodium complex [RhCl(**2**)(CO)].[26] This is in accordance with one of the conformers predicted in solution.[24]

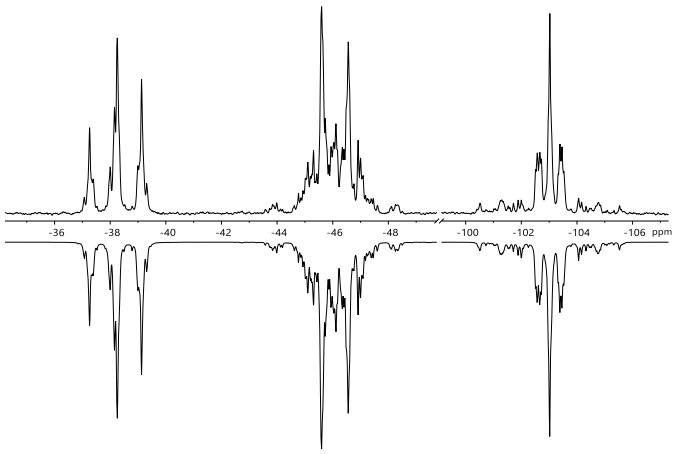



**Fig. 2** Experimental (top) and simulated (bottom) $^{31}P\{^{1}H\}$ NMR spectrum of **2** at 162 MHz ($R$ = 0.07 %).

**Table 1** $^{31}P\{^{1}H\}$ NMR parameters of **2** at 162 MHz in $C_6D_6$ at 25 °C ([AMM'X]$_2$ spin system, $C_{2h}$ symmetrisation, $R$ = 0.07 %).

| $\delta$/ppm | $J_{PP}$/Hz | $J_{PP}$/Hz (interannular) | $H$/Hz |
|---|---|---|---|
| $\delta_1$ = –103.02 | $J_{1,2}$ = –140.59 | $J_{1,5}$ = –213.95 | $H_1$ = 7.65 |
| $\delta_2$ = –46.06 | $J_{1,4}$ = 16.37 | $J_{1,6}$ = 130.71 | $H_2$ = 7.22 |
| $\delta_4$ = –38.25 | $J_{2,3}$ = 16.46 | $J_{1,8}$ = –16.21 | $H_4$ = 7.01 |
| | $J_{2,4}$ = –152.27 | $J_{2,6}$ = 24.16 | |
| | | $J_{2,7}$ = 29.93 | |
| | | $J_{2,8}$ = 0.25 | |
| | | $J_{4,8}$ = 1.16 | |

$\delta$, chemical shift; $J$, coupling constant; $H$, spectral half width. For the sake of legibility, only one parameter assignment for symmetry-equivalent values is given. $P^1 \sim P^5$, $P^2 \sim P^3 \sim P^6 \sim P^7$, $P^4 \sim P^8$ (for numbering see Scheme 2).

Due to the structural similarity of **3** and **4**, their $^{31}P\{^{1}H\}$ NMR spectra are also comparable. In the case of **3**, the atom bridging the *cyclo*-$P_4$ rings is a phosphorus atom, in the case of **4** a carbon atom. As in **2**,[24] rotation around the E–P bond (E = P (**3**), E = C (**4**)) is possible rendering the *cyclo*-($P_4{}^tBu_3$) rings equivalent. Consequently, in the $^{31}P\{^{1}H\}$ NMR spectrum of **4**, three resonances are observed, constituting an [AMM'X]$_2$ spin system (Fig. 3). For compound **3**, the [AMM'X]$_2$ spin system turns into an [AMNR]$_2$X spin system, where three resonances are degenerated by coincidence.[29] The appearance of the spectra of both compounds is additionally governed by higher-order effects. Baudler *et al.* reported a large $^{2}J_{PP}$ coupling in **3** between the bridging atom $P^9$ and the adjacent *tert*-butyl-substituted phosphorus atom (e.g., $P^2$; for numbering, see Scheme 2) which results from the orientation of their lone pairs of electrons and can also be observed in comparable compounds.[62]

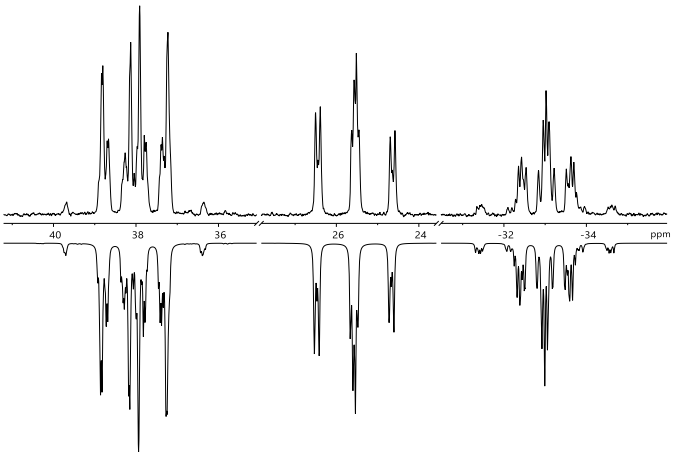



**Fig. 3** Experimental (top) and simulated (bottom) $^{31}P\{^{1}H\}$ NMR spectrum of **4** at 162 MHz ($R$ = 0.31 %).

The parameters of the $^{31}P\{^{1}H\}$ NMR spectrum of **4** (Fig. 3) were determined by simulation of the spectrum (Table 2). Strong long-range couplings between the *cyclo*-($P_4{}^tBu_3$) rings are also observed in **4**. The large interannular $^{2}J_{PP}$ coupling between $P^1$ and $P^5$ ($^{2}J_{1,5}$, +164.03 Hz) can be explained, as in **2** and **3**, by the orientation of the lone pairs of electrons of the corresponding

atoms, which are partially pointing towards each other during the rotation around the $C(H_2)$–P bonds.

**Table 2** $^{31}P\{^1H\}$ NMR parameters of **4** at 162 MHz in $C_6D_6$ at 25 °C ($[AMM'X]_2$ spin system, $C_{2v}$ symmetrisation, $R$ = 0.32 %).

| $\delta$/ppm | $J_{PP}$/Hz | $J_{PP}$/Hz (interannular) | $H$/Hz |
|---|---|---|---|
| $\delta_1$ = –107.98 | $J_{1,2}$ = –135.17 | $J_{1,5}$ = 164.03 | $H_1$ = 4.40 |
| $\delta_2$ = –36.96 | $J_{1,4}$ = 20.90 | $J_{1,6}$ = 25.31 | $H_2$ = 4.49 |
| $\delta_4$ = –49.39 | $J_{2,3}$ = 16.88 | $J_{1,8}$ = 0.13 | $H_4$ = 4.46 |
| | $J_{2,4}$ = –146.81 | $J_{2,6}$ = 1.74 | |
| | | $J_{2,7}$ = 1.67 | |
| | | $J_{2,8}$ = 0.44 | |
| | | $J_{4,8}$ = –0.01 | |

$\delta$, chemical shift; $J$, coupling constant; $H$, spectral half width. For the sake of legibility, only one parameter assignment for symmetry-equivalent values is given. $P^1 \sim P^5$, $P^2 \sim P^3 \sim P^6 \sim P^7$, $P^4 \sim P^8$ (for numbering see Scheme 2).

**Molecular structures of 3 and 4.** Colourless crystals of **3** were obtained from MeOH/THF (5:1, v/v). **3** crystallises in the triclinic space group $P\bar{1}$ with two molecules per unit cell (Fig. 4). The bond angle of the bridging phosphorus atom P4–P5–P6 (106.83(1)°) is smaller than the ideal tetrahedral angle (109.5°).

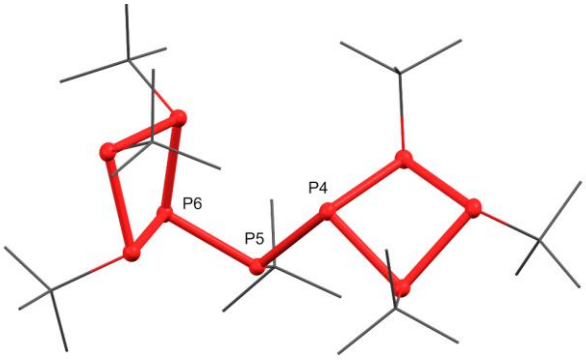



**Fig. 4** Molecular structure of **3**. Hydrogen atoms are omitted and $^t$Bu groups are drawn as wireframe for clarity; thermal ellipsoids at 50 % probability level.

Colourless crystals of **4** were obtained from MeOH/THF (1:1, v/v). **4** crystallises in the monoclinic space group $P2_1/n$ with four molecules per unit cell (Fig. 5). The structure of **4** is comparable to **3** with the atom bridging both *cyclo*-($P_4{}^tBu_3$) rings being a carbon instead of a phosphorus atom. The endocyclic P–P–P bond angles (ca. 87°) are similar to those of **1**. The P1–C1–P5 bond angle (108.9(1)°) indicates an almost perfect tetrahedral environment of C1.

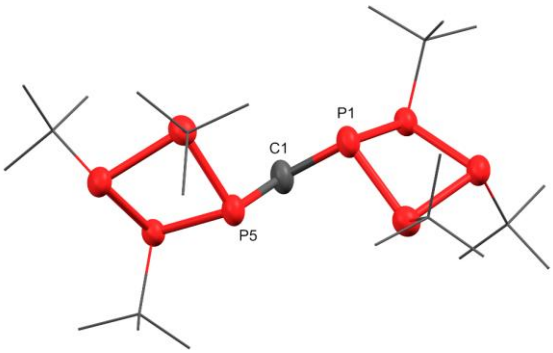
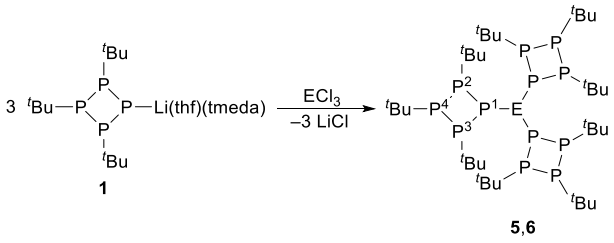



**Fig. 5** Molecular structure of **4**. Hydrogen atoms are omitted and $^t$Bu groups are drawn as wireframe for clarity; thermal ellipsoids at 50 % probability level.

**Reactivity of 1: Synthesis of pnictaphosphanes**

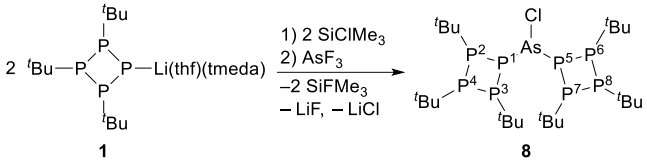
The heavier group 15 chlorides $ECl_3$ (E = Bi, Sb) react with **1** under elimination of lithium chloride, forming $C_{3v}$-symmetric compounds of the type E{*cyclo*-($P_4{}^tBu_3$)}$_3$ (E = Bi (**5**), Sb (**6**), Scheme 3) in good yields (64 % (**5**) and 74 % (**6**)).




**Scheme 3** Formation of $C_{3v}$-symmetric pnictaphosphanes **5** (E = Bi) and **6** (E = Sb) by reaction of **1** with $ECl_3$ (E = Bi, Sb).

In contrast, the formation of the analogous arsenic compound As{*cyclo*-($P_4{}^tBu_3$)}$_3$ (**7**) is more tedious. The reaction of **1** with arsenic triiodide, which was used to favour the nucleophilic substitution at the arsenic atom does not form the $C_3$-symmetric arsenic compound As{*cyclo*-($P_4{}^tBu_3$)}$_3$ (**7**) but octaphosphane **2**.

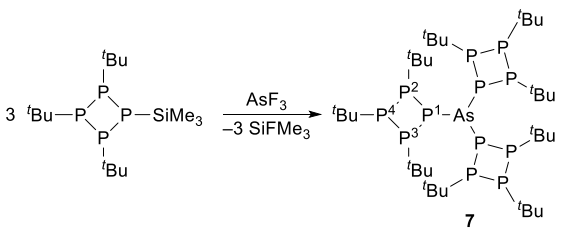
Attempts to prepare **7** in a one-pot reaction of the silylated cyclotetraphosphane *cyclo*-{$P_4{}^tBu_3(SiMe_3)$}[11,12] (prepared *in situ* from **1** and $SiClMe_3$) with arsenic trifluoride also did not furnish **7**. Instead, AsCl{*cyclo*-($P_4{}^tBu_3$)}$_2$ (**8**) was obtained (Scheme 4), which is the result of a halide exchange at the arsenic atom in one of the reaction steps, involving lithium chloride. The driving force of the substitution reaction at the arsenic atom is the formation of the energetically favoured Si–F bond; thus, the halide exchange will halt the reaction at the intermediary step.




**Scheme 4** The one-pot reaction of the silylation of **1** followed by reaction with $AsF_3$ results in formation of **8**.

However, when *cyclo*-{$P_4{}^tBu_3(SiMe_3)$} is first isolated and employed as a pure compound, the reaction with $AsF_3$ yields **7** (Scheme 5). While the reaction of *cyclo*-{$P_4{}^tBu_3(SiMe_3)$} with $AsF_3$ proceeds slowly (within hours) and at elevated temperature, in the presence of LiCl, **8** is formed within minutes. This might be explained by the activation of the P–Si bond by the formation of hypervalent silicon species – a phenomenon which is known from organic chemistry.[63]

Efforts to prepare the phosphorus analogue, P{*cyclo*-$(P_4{}^tBu_3)\}_3$, by passing $PF_3$ gas (prepared *in situ* from $AsF_3$ und $PCl_3$) into a THF solution of *cyclo*-{$P_4{}^tBu_3(SiMe_3)$} (prepared *in situ* from **1** and $SiClMe_3$) were unsuccessful. Similarly, no reaction was observed between $PCl_3$ and *cyclo*-{$P_4{}^tBu_3(SiMe_3)$}. Even after one day at 60 °C in THF, the $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture showed only the formation of traces of unidentified phosphorus compounds. Compared to E–P bonds of the higher homologues (E = As, Sb, Bi), the P–P bond is shorter resulting in larger steric interaction of the *cyclo*-$(P_4{}^tBu_3)$ rings, as already observed in **7** (see below). Presumably, this hampers the formation of the corresponding phosphane.




**Scheme 5** *Cyclo*-{$P_4{}^tBu_3(SiMe_3)$} reacts with $AsF_3$ to arsaphosphane **7**.

The bismuth compound **5** is light sensitive in solution and decomposes readily in THF, diethyl ether, benzene and *n*-hexane. When a benzene solution of **5** is exposed to sunlight, precipitation of elemental bismuth is observed within minutes. Complete decomposition is observed within one hour, resulting in a mixture of mainly **2** and **3**, but also other known phosphanes[25,29,52,54,64,65] and unidentified compounds (see ESI†, Fig. S20). Cyclooligophosphanes are known to undergo isomerisation when exposed to light.[4] Thus, this rather complex mixture might not only be the result of decomposition of **5**, but could also be due to subsequent reactions of the primary decomposition products **2** and **3** (see ESI†, Figs. S21 and S22). On recrystallisation in boiling THF, **5** partially decomposes, detectable by precipitation of elemental bismuth. With exclusion of light, solutions of **5** are stable even on heating for days in benzene at 76 °C. These findings are in accordance with observations implying that photosensitivity is a key factor regarding the stability of Bi–P bonds.[66] In comparison to **5**, the antimony compound **6** is more stable and photodecomposition is slower. In contrast, **7** does not show any decomposition at all. Although bismuth(III) compounds often exhibit coordination numbers higher than 3,[67] there are examples of lower coordination numbers.[31,66,68–72] In compound **5**, there is no evidence for a coordination number higher than 3 in potentially coordinating solvents, as indicated by $^1H$ NMR spectroscopic studies in deuterated THF or benzene. Furthermore, no intermolecular interactions (Lewis acid/base) are observed in the solid state. To the best of our knowledge, there is only one bismuth compound known in which bismuth is bound only to phosphorus atoms.[73] Therefore comparison with similar compounds is difficult.

In the mass spectra (ESI-MS, positive mode), no molecular ion peaks are observed (for **6**) or only with very low intensity (for **5** and **8**). **5**, **6** and **8** show fragmentation with loss of one *cyclo*-$(P_4{}^tBu_3)$ moiety (**5**, **6**) or a chloride anion (**8**) resulting in the fragment $[E\{cyclo\text{-}(P_4{}^tBu_3)\}_2]^+$ (E = Bi, Sb, As) and its oxides. However, oxidised species are observed with the highest intensities, probably due to facile ionisation. Compound **7** does not show strong fragmentation and can be easily observed as $[M + H]^+$ when proton sources such as trifluoroacetic acid or formic acid are added.

**NMR spectra of 5–8.** In the $^1H$ NMR spectra of **5**–**7**, the *tert*-butyl groups are observed as two doublets with an integral ratio 2:1; the observed $[AMM'X]_3$ spin systems in the $^{31}P\{^1H\}$ NMR spectra indicate free rotation around the E–P bonds. In the $^{31}P\{^1H\}$ NMR spectra, only **5** displays a distinct MM' pattern (although with extensive line broadening). The MM' part in the $^{31}P\{^1H\}$ NMR spectra of **6** and **7** is observed only as a broad singlet. In the $^1H$ NMR spectrum of **8**, three resonances are observed for the *tert*-butyl protons (ratio 1:1:1, determined in the $^1H\{^{31}P\}$ NMR spectrum due to strong overlap of the doublets). The $^{31}P\{^1H\}$ NMR spectrum changes from an $[AMM'X]_3$ (**5**–**7**) to an $[AMRX]_2$ spin system for **8**, as the phosphorus atoms $P^2$ and $P^3$ (or $P^6$ and $P^7$) are diastereotopic due to the chlorine atom as third substituent at the arsenic atom (Fig. 6). The parameter set of the $^{31}P\{^1H\}$ NMR spectrum of **8** has been determined by iterating the $[AMRX]_2$ spin system (Table 3). The $^2J_{P^1P^5}$ coupling ($^2J_{1,5}$, +94.15 Hz) *via* the arsenic atom is still large, but smaller than in **4**.

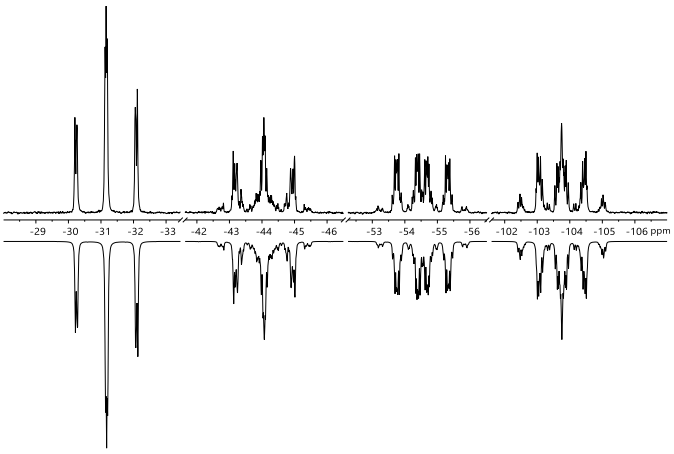



**Fig. 6** Experimental (top) and simulated (bottom) $^{31}P\{^1H\}$ NMR spectrum of **8** at 162 MHz, constituting an $[AMRX]_2$ spin system ($R$ = 0.22 %).

The simulation of the $^{31}P\{^1H\}$ NMR spectra of **5**–**7** failed due to strong line-broadening and limitations of the iteration software.

**Table 3** $^{31}P\{^{1}H\}$ NMR parameters of **8** at 162 MHz in $C_6D_6$ at 25 °C ($[AMRX]_2$ spin system, $C_s$ symmetrisation, $R$ = 0.22 %).

| $\delta$/ppm | $J_{PP}$/Hz | $J_{PP}$/Hz (interannular) | $H$/Hz |
|---|---|---|---|
| $\delta_1$ = –103.76 | $J_{1,2}$ = –152.65 | $J_{1,5}$ = 94.15 | $H_1$ = 4.10 |
| $\delta_2$ = –44.06 | $J_{1,3}$ = –126.89 | $J_{1,6}$ = 13.78 | $H_2$ = 3.68 |
| $\delta_3$ = –54.54 | $J_{1,4}$ = 11.49 | $J_{1,7}$ = 23.19 | $H_3$ = 3.81 |
| $\delta_4$ = –31.20 | $J_{2,3}$ = 15.18 | $J_{1,8}$ = 0.52 | $H_4$ = 3.41 |
| | $J_{2,4}$ = –149.94 | $J_{2,6}$ = 7.33 | |
| | $J_{3,4}$ = –150.15 | $J_{2,7}$ = 6.25 | |
| | | $J_{2,8}$ = 1.22 | |
| | | $J_{3,7}$ = 0.11 | |
| | | $J_{3,8}$ = 0.85 | |
| | | $J_{4,8}$ = –0.24 | |

$\delta$, chemical shift; $J$, coupling constant; $H$, spectral half width. For the sake of legibility, only one parameter assignment for symmetry-equivalent values is given. $P^1 \sim P^5$, $P^2 \sim P^6$, $P^3 \sim P^7$, $P^4 \sim P^8$ (for numbering see Scheme 4).

**Crystal structures of 5–7.** Compounds **5**–**7** are isotypic. They crystallise as orange (**5**), pale yellow (**6**) or almost colourless (**7**) needles from *n*-hexane solution in the monoclinic space group $P2_1/c$ with four molecules per unit cell (Fig. 7; only compound **5** is shown) and have almost identical cell parameters. The E1–P bond lengths are in the range of 2.6278(8) Å – 2.6352(8) Å for E = Bi (**5**), 2.5371(5) Å – 2.5408(5) Å for E = Sb (**6**) and 2.3529(4) Å – 2.3565(4) Å for E = As (**7**). The P1–E1–P5 bond angles (89.96(2)° (**5**) and 91.134(7)° (**6**)) are slightly smaller than those of the corresponding hydrides ($BiH_3$: 90.48°[74] and $SbH_3$: 91.56°[75]), while the P1–As1–P5 bond angle in **7** (93.34(2)°) is larger ($AsH_3$: 92.1°).[76] Additionally, the shortest distance between two *cyclo*-($P_4{}^tBu_3$) rings, *d*(P1···P12), decreases from **5** (3.499(1) Å) to **6** (3.3964(8) Å) and **7** (3.2742(6) Å). These observations can be explained by the decreasing E–P bond length from Bi–P to As–P. The As–P bond is already so short that the P–As–P bond angle widens to fulfil the space demand of the *cyclo*-($P_4{}^tBu_3$) rings.

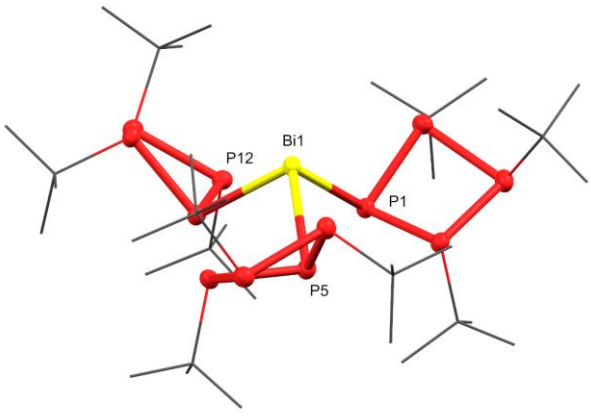



**Fig. 7** Molecular structure of **5**. Hydrogen atoms are omitted and $^t$Bu groups are drawn as wireframe for clarity; thermal ellipsoids at 50 % probability level.

**Crystal structure of 8.** Compound **8** crystallises in the triclinic space group $P\bar{1}$ with two molecules per unit cell (Fig. 8).

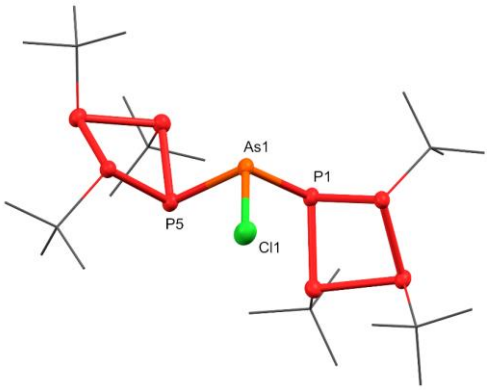



**Fig. 8** Molecular structure of **8**. Hydrogen atoms are omitted and $^t$Bu groups are drawn as wireframe for clarity; thermal ellipsoids at 50 % probability level.

The As1–P1 bond length (2.3194(5) Å) is in the same range as in **7**, while the P1–As1–P5 bond angle (94.41(2)°) is larger.

## Conclusions

Rational syntheses of oligophosphanes and pnictaphosphanes, containing *cyclo*-($P_4{}^tBu_3$) rings are facilitated by employing lithium cyclotetraphosphanide **1** which is accessible from white phosphorus and *tert*-butyl lithium. The pnictaphosphanes **5** and **6** represent the first examples of molecules containing a tri-coordinate group 15 element with an $EP_3$ (E = Sb (**6**), Bi (**5**)) substructure. Selected $^{31}P\{^{1}H\}$ NMR spectra have been simulated by automated line shape analysis. These simulations are the first iterations of $[AMM'X]_2$ ({*cyclo*-($P_4{}^tBu_3$)}$_2$ (**2**) and {*cyclo*-($P_4{}^tBu_3$)}$_2CH_2$ (**4**)) and $[AMRX]_2$ ([AsCl{*cyclo*-($P_4{}^tBu_3$)}$_2$] (**8**)) spin systems.

## Experimental

All manipulations were performed using standard Schlenk techniques under nitrogen atmosphere unless stated otherwise. Dry, oxygen-free solvents (THF, $Et_2O$, *n*-hexane, methylene chloride) were obtained from an MBraun Solvent Purification System MB SPS-800. THF, which was further treated by dynamic drying employing molecular sieve (3 Å), and $Et_2O$ were stored over molecular sieve (4 Å) and *n*-hexane was stored over a potassium mirror. Solvents used for NMR measurements (benzene-$d^6$ and THF-$d^8$) were distilled prior to use and stored over molecular sieve (4 Å). Li$^t$Bu solution, TMEDA, 1,2-$Br_2C_2H_4$, $BiCl_3$, $SbCl_3$ and $SiClMe_3$ are commercially available. $^t$BuPCl$_2$,[77] $AsF_3$,[78] and $PF_3$[79] were prepared according to literature procedures. The preparation of *cyclo*-{$P_4{}^tBu_3(SiMe_3)$} was based on the method of Fritz *et al.*[12] NMR spectra were recorded on a Bruker Avance III HD 400 MHz spectrometer with a 5 mm TBO BB-1H/D/31P Z-GRD Z5610/004 probe head at 25 °C. The coupling constants $J$ are reported in hertz (Hz) and are absolute values if no sign is indicated. The chemical shift ($\delta$) is given in ppm. $^1$H NMR spectra were either referenced to $SiMe_4$ as internal standard or to the solvent residual signal. Spectra of all other heteronuclei were referenced using the Ξ scale.[80] $^{31}$P NMR

spectra were recorded using 90° pulse angles and a $D_1$ time of 6.5 s. Iteration of NMR spectra was done by using Daisy under Bruker's TopSpin.[81] Mass spectrometry was performed on a Bruker Daltonics Esquire 3000 Plus, melting points were determined using a Gallenkamp MPD 350 BM 2.5 and are reported uncorrected. IR spectra were recorded on a Thermo Scientific Nicolet iS5 with a diamond ATR (400–4000 $cm^{-1}$), and for CHN analysis a Heraeus Vario-EL oven was used.

**Synthesis of [Li{*cyclo*-($P_4{}^tBu_3$)}(thf)(tmeda)] (1).** Teflon stir bars or teflon cannulas were only used in the first reaction step to avoid the formation of black, insoluble precipitates.

A Li$^t$Bu solution in *n*-pentane (110 ml of a 1.63 M solution, 179.3 mmol, 3 equiv.) was added over the course of 50 min to a suspension of freshly distilled $P_4$ (7.33 g, 59.1 mmol) in 150 ml *n*-hexane at 55 °C. The resulting mixture containing a red precipitate was stirred for 30 min under ambient conditions, cooled to 0 °C, and 100 ml THF were added. At room temperature, 27.10 ml TMEDA (179.6 mmol, 3 equiv.) were added and the solvents were removed under reduced pressure. The residue was dissolved in 200 ml *n*-hexane/THF (4:1 (v/v)), filtered (D4 frit) and stored at 5 °C. The crystallised $[Li_3(tmeda)_3P_7]$ was filtered off and the filtrate was stored at –30 °C, resulting in the precipitation of the crude product **1**. The mother liquor was decanted and the crystalline solid recrystallised from *n*-hexane/THF (4:1 (v/v)). Crystallisation at –30 °C and drying of the crystalline solid *in vacuo* gave 3.37 g of **1** as bright orange crystals. Removing the solvent from the mother liquor of the crude product gave a dark-red oil which formed a foam-like material *in vacuo* and is pyrophoric on contact with paper in air. This residue was dissolved in 40 ml $Et_2O$ and stored at –30 °C. The formed precipitate was isolated and subsequently recrystallised from *n*-hexane/THF (4:1 (v/v)) resulting in an additional 1.01 g of **1** (total mass: 4.38 g (8.93 mmol), 15 %, referred to $P_4$).

Mp. 128 °C (sealed tube, loss of solvent above 98 °C).

$^1$H NMR (400 MHz, benzene-$d^6$): $\delta$ 3.60 (m, O$CH_2$ (thf), 4H), 2.03 (s, C$H_3$ (tmeda), 12H), 1.79 (s, C$H_2$ (tmeda), 4H), 1.51 (m, $C_4H_9$, C$H_2$ (thf), 31H) ppm.

$^{13}$C{$^1$H} NMR (101 MHz, benzene-$d^6$): $\delta$ 68.0 (s, O$CH_2$ (thf)), 56.3 (s, $CH_2$ (tmeda)), 45.8 (s, $CH_3$ (tmeda)), 29.9 (m, $C(CH_3)_3$), 28.8 (dt, C($CH_3$)$_3^{2,4}$, $^2J_{CP}$ = 12.8, $^3J_{CP}$ = 6.2), 27.5 (dt, C($CH_3$)$_3^3$, $^2J_{CP}$ = 8.5, $^3J_{CP}$ = 2.4), 25.4 (s, $CH_2$ (thf)) ppm.

$^{31}$P{$^1$H} NMR (162 MHz, benzene-$d^6$): $AM_2X$ spin system ($C_s$, $R$ = 0.98 %): $\delta_X$ = 10.19 (td, 1P, $H_x$ = 7.82 Hz), $\delta_M$ = –56.33 (dd, 2P, $H_M$ = 5.29 Hz), $\delta_A$ = –215.28 (td, 1P, $H_A$ = 9.51 Hz) ppm; $J_{AM}$ = –189.24, $J_{AX}$ = 7.63, $J_{MX}$ = –166.58 Hz.

$^7$Li{$^1$H} NMR (156 MHz, benzene-$d^6$): $\delta$ 1.55 (s) ppm.

HR-ESI(–)-MS (THF): *m/z* 295.118 [{*cyclo*-($P_4{}^tBu_3$)}]$^-$, 311.113 [{*cyclo*-($P_4{}^tBu_3$)}O]$^-$, 327.109 [{*cyclo*-($P_4{}^tBu_3$)}$O_2$]$^-$, 343.104 [{*cyclo*-($P_4{}^tBu_3$)}$O_3$]$^-$, 359.098 [{*cyclo*-($P_4{}^tBu_3$)}$O_4$]$^-$.

IR: $\tilde{\nu}$ 2930 (m), 2886 (m), 2850 (m), 1453 (m), 1385 (w), 1356 (m), 1348 (w), 1290 (w), 1170 (m), 1129 (w), 1098 (w), 1066 (w), 1035 (m), 1019 (w), 948 (m), 893 (w), 799 (m), 556 (m), 466 (s), 435 (s) $cm^{-1}$.

CHN, Found: C, 53.5; H, 9.9; N, 5.8. $C_{22}H_{51}LiN_2OP_4$ requires C, 53.9; H, 10.5; N, 5.7 %.

**Synthesis of {*cyclo*-($P_4{}^tBu_3$)}$_2$ (2).** At 0 °C, 1.50 ml 1,2-$C_2H_4Br_2$ diluted 1:100 (v/v) in $Et_2O$ (0.116 mol/l, 0.174 mmol, 0.5 equiv.) were added to a solution of 170.3 mg (0.347 mmol) **1** in 6 ml $Et_2O$ at 0 °C. The clear orange solution turned turbid and was pale yellow after 10 min. After no further colour change was observed, the solution was washed with 2 ml $H_2O$, the solvent was removed and the residue dried *in vacuo*. Recrystallisation of the crude product (115.8 mg) in 4.9 ml THF (42.3 ml/g) and crystallisation at room temperature gave colourless crystals of **2**·2 THF (91.1 mg, 0.125 mmol, 72 % (literature 28 %)[24]). Analytical data are in agreement with those reported previously.[24,27]

**Synthesis of {*cyclo*-($P_4{}^tBu_3$)}$_2$P$^t$Bu (3).** Within 12 min, 1.2 ml of a 0.24 M solution of $^t$BuPCl$_2$ in $Et_2O$ (0.290 mmol, 0.61 equiv.) were added dropwise to a solution of 233.5 mg (0.476 mmol) **1** in 10 ml $Et_2O$. The solvent and the excess of $^t$BuPCl$_2$ were removed under reduced pressure. The residue was suspended in 12 ml *n*-pentane and washed with 2 ml $H_2O$. Recrystallisation of the crude product (159.4 mg) in 5.0 ml MeOH/THF 1:1 (v/v) and crystallisation at –30 °C yielded 87.2 mg of **3** (0.129 mmol, 54 % (literature 0.4 %)[29]). Analytical data are in agreement with those reported previously.[29] Single crystals of **3** suitable for X-ray diffraction experiments were obtained by crystallisation from MeOH/THF 5:1 (v/v) at room temperature.

**Synthesis of {*cyclo*-($P_4{}^tBu_3$)}$_2$CH$_2$ (4).** 1.68 ml of $CH_2Cl_2$ diluted 1:100 (v/v) in $Et_2O$ (0.263 mmol, 0.5 equiv.) were added to a solution of 257.8 mg (0.526 mmol) **1** in 7 ml $Et_2O$. The clear orange solution turned turbid after 1 min. The colour was slightly pale yellow after 5 h. After 24 h, the solution was washed with 2 ml $H_2O$, then the solvent of the organic phase was removed and the residue dried *in vacuo*. Recrystallisation of the crude product (155.9 mg) in 4.2 ml MeOH/THF 1:1 (v/v) (26.9 ml/g) and crystallisation at room temperature resulted in the formation of big colourless crystals (137.5 mg, 0.227 mmol, 86 %).

Mp. 174 °C (sealed tube).

$^1$H NMR (400 MHz, benzene-$d^6$): $\delta$ 2.80 (m, $N$ = 5.1 Hz, C$H_2$), 1.32 (d, $^3J_{HP}$ = 12.8, $C_4H_9$), 1.27 (d, $^3J_{HP}$ = 13.2, $C_4H_9$) ppm.

$^{13}$C{$^1$H} NMR (101 MHz, benzene-$d^6$): $\delta$ 34.4 (m, $CH_2$), 30.4 (m, $C(CH_3)_3$), 28.6 (m, $C(CH_3)_3$, C($CH_3$)$_3$) ppm.

$^{13}$C{$^1$H,$^{31}$P} NMR (101 MHz, benzene-$d^6$, 28 °C): $\delta$ 30.4 ($C(CH_3)_3$), 28.7 ($C(CH_3)_3$), 28.4 (C($CH_3$)$_3$), 28.3 ($C(CH_3)_3$) ppm. The resonance of the methylene carbon can only be observed in the $^{13}$C{$^1$H} NMR spectrum.

$^{31}$P{$^1$H} NMR (162 MHz, benzene-$d^6$): $[AMM'X]_2$ spin system ($R$ = 0.32 %, for full parameter set see Table 2): $\delta$ –36.96 (m, $P^{2,3,6,7}$, 4P), –49.51 (m, $P^{4,8}$, 2P), –107.93 (m, $P^{1,5}$, 2P) ppm.

HR-ESI(+)-MS (THF): *m/z* 605.224 $[M + H]^+$, 621.222 $[M + OH]^+$.

IR: $\tilde{\nu}$ 3287 (w), 3077 (w), 2947 (m), 2930 (m), 2887 (m), 2852 (m), 1467 (s), 1454 (s), 1383 (w), 1356 (s), 1171 (m), 1081 (w), 1011 (w), 933 (w), 806 (m), 770 (w), 695 (w), 573 (w), 492 (w), 470 (w) $cm^{-1}$.

CHN, Found: C, 50.0; H, 9.1; N, 0.0. $C_{25}H_{56}P_8$ requires C, 49.7; H, 9.3; N, 0.0 %.

**Synthesis of Bi{*cyclo*-($P_4{}^tBu_3$)}$_3$ (5).** Under vigorous stirring, a suspension of 44.7 mg $BiCl_3$ (0.141 mmol) in 3 ml $Et_2O$ was added dropwise to a solution of 255.1 mg (0.520 mmol, 3.69 equiv.) **1** in 5 ml $Et_2O$. The clear orange solution turned red-brown and a brownish precipitate was observed. After stirring for further 5 min,

the solvent was removed *in vacuo* at ambient temperature and the brown residue was extracted with 20 ml *n*-hexane. The bright-orange extract was stored at –30 °C, and **5** was obtained as an orange solid after the mother liquor was filtered off (98.8 mg, 0.090 mmol, 64 %). Suitable crystals for X-ray diffraction were obtained by storing a saturated solution of **5** in *n*-hexane at 5 °C.

Mp. decomposition above 161 °C (sealed tube).

$^1$H NMR (400 MHz, benzene-$d^6$): $\delta$ 1.41 (d, $^3J_{HP}$ = 12.3, $C_4H_9^{2,3}$), 1.28 (d, $^3J_{HP}$ = 12.9, $C_4H_9^4$) ppm.

$^{13}$C{$^1$H,$^{31}$P} NMR (101 MHz, benzene-$d^6$, 28 °C): $\delta$ 34.2 ($C$(CH$_3$)$_3$), 28.8 ($C$(CH$_3$)$_3$), 28.3 (C($C$H$_3$)$_3$), 28.1 (C($C$H$_3$)$_3$) ppm.

$^{31}$P{$^1$H} NMR (162 MHz, benzene-$d^6$): $\delta$ –20.2 (t, $^1J_{PP}$ = 153.8, $P^4$, 3P), –49.3 (m, $P^{2,3}$, 6P), –115.7 (m, $P^1$, 3P) ppm.

HR-ESI(+)-MS (THF): *m/z* 799.192 [Bi{*cyclo*-(P$_4$$^t$Bu$_3$)}$_2$]$^+$.

IR: $\tilde{\nu}$ 2928 (m), 2885 (m), 2849 (m), 1452 (m), 1465 (w), 1386 (s), 1356 (m), 1169 (m), 1008 (w), 934 (w), 803 (m), 571 (w), 463 (w) cm$^{-1}$.

CHN, Found: C, 39.8; H, 7.2; N, 0.0. $C_{36}H_{81}BiP_{12}$ requires C, 39.5; H, 7.5; N, 0.0 %.

**Synthesis of Sb{*cyclo*-(P$_4$$^t$Bu$_3$)}$_3$ (6).** Under vigorous stirring, a solution of 33.7 mg $SbCl_3$ (0.148 mmol) in 3 ml $Et_2O$ was added dropwise to a solution of 261.5 mg (0.533 mmol, 3.61 equiv.) **1** in 5 ml $Et_2O$. The clear orange solution turned into a yellow suspension. After stirring for further 5 min, the solvent was removed *in vacuo* at ambient temperature, and the orange residue was extracted with 20 ml boiling *n*-hexane. **6** (109.6 mg, 0.735 mmol, 74 %) was obtained as thin yellow needles by storing the yellow extract at –30 °C and subsequent filtration. Suitable crystals for X-ray diffraction were obtained by storing a saturated solution in *n*-hexane at 5 °C.

Mp. decomposition above 179 °C (sealed tube).

$^1$H NMR (400 MHz, benzene-$d^6$): $\delta$ 1.42 (d, $^3J_{HP}$ = 12.6, $C_4H_9^{2,3}$, 54H), 1.28 (d, $^3J_{HP}$ = 13.0, $C_4H_9^4$, 27H) ppm.

$^{13}$C{$^1$H,$^{31}$P} NMR (101 MHz, benzene-$d^6$, 28 °C): $\delta$ 32.2 ($C$(CH$_3$)$_3^{2,3}$), 29.6 ($C$(CH$_3$)$_3^4$), 28.5 (C($C$H$_3$)$_3^{2,3}$), 28.1 (C($C$H$_3$)$_3^4$) ppm.

$^{31}$P{$^1$H} NMR (162 MHz, benzene-$d^6$): $\delta$ –24.3 (t, $^1J_{PP}$ = 152.8, $P^4$, 3P), –54.9 (br s, $P^{2,3}$, 6P), –132.9 (m, $P^1$, 3P) ppm.

HR-ESI(+)-MS (THF): *m/z* 711.115 [Sb{*cyclo*-(P$_4$$^t$Bu$_3$)}$_2$]$^+$.

IR: $\tilde{\nu}$ 2929 (m), 2885 (m), 2850 (m), 1452 (s), 1386 (w), 1356 (s), 1170 (s), 1008 (w), 934 (w), 803 (m), 570 (w), 463 (w) cm$^{-1}$.

CHN, Found: C, 43.7; H, 7.6; N, 0.0. $C_{36}H_{81}P_{12}Sb$ requires C, 42.9; H, 8.1; N, 0.0 %.

**Synthesis of As{*cyclo*-(P$_4$$^t$Bu$_3$)}$_3$ (7).** 167.8 mg *cyclo*-{P$_4$$^t$Bu$_3$(SiMe$_3$)} (0.455 mmol) were dissolved in 3 ml THF and 0.75 ml $AsF_3$ solution (1 vol.-% in THF, 0.154 mmol, 0.34 equiv.) were added. The solution was heated to 50 °C for 1 d. After removal of all volatiles *in vacuo*, the yellow residue was extracted with 5 ml boiling *n*-hexane. The extract was stored at 5 °C, leading to the isolation of **7** (43.2 mg, 0.045 mmol, 30 %) as pale-yellow needles.

Mp. decomposition above 218 °C (sealed tube).

$^1$H NMR (400 MHz, benzene-$d^6$): $\delta$ 1.44 (d, $^3J_{HP}$ = 12.7, $C_4H_9^{2,3}$, 54H), 1.31 (d, $^3J_{HP}$ = 13.2, $C_4H_9^4$, 27H) ppm.

$^{13}$C{$^1$H,$^{31}$P} NMR (101 MHz, benzene-$d^6$, 28 °C): $\delta$ 32.6 ($C$(CH$_3$)$_3^{2,3}$), 29.7 ($C$(CH$_3$)$_3^4$), 29.1 (C($C$H$_3$)$_3^{2,3}$), 28.5 (C($C$H$_3$)$_3^4$) ppm.

$^{31}$P{$^1$H} NMR (162 MHz, benzene-$d^6$): $\delta$ –35.2 (t, $^1J_{PP}$ = 154.3, $P^4$, 3P), –47.9 (br s, $P^{2,3}$, 6P), –96.6 (m, $P^1$, 3P) ppm.

HR-ESI(+)-MS (THF): *m/z* 961.251 [M + H]$^+$.

IR: $\tilde{\nu}$ 2939 (m), 2885 (m), 2850 (m), 1452 (s), 1387 (w), 1356 (s), 1261 (w), 1170 (s), 1008 (m), 934 (m), 804 (s), 612 (w), 570 (m), 523 (w), 488 (w), 466 (w) cm$^{-1}$.

CHN, Found: C, 44.7; H, 8.4; N, 0.0. $C_{36}H_{81}P_{12}As$ requires C, 45.0; H, 8.5; N, 0.0 %.

**Synthesis of AsCl{*cyclo*-(P$_4$$^t$Bu$_3$)}$_2$ (8).** 0.05 ml $SiClMe_3$ (0.393 mmol, 1.49 equiv.) were added to a solution of 129.5 mg **1** (0.264 mmol) in 2.5 ml $Et_2O$. The solvent was removed, the residue dried *in vacuo* at 50 °C for 20 min and then dissolved in 3 ml THF. An $AsF_3$ solution (0.93 ml, 1 vol.-% in THF, 0.190 mmol, 0.72 equiv.) was added dropwise. All volatiles were removed *in vacuo* and the residue was extracted with 10 ml *n*-hexane. Storing of this solution at –30 °C gave pale yellow crystals of **8**. The mother liquor was decanted and the crystals were dried *in vacuo* (34.2 mg, 0.036 mmol, 40 %).

Mp. 153 °C (sealed tube).

$^1$H NMR (400 MHz, benzene-$d^6$): $\delta$ 1.29 (d, $^3J_{HP}$ = 13.2), 1.27 (d, $^3J_{HP}$ = 13.2), 1.24 (d, $^3J_{HP}$ = 13.1) ppm.

$^1$H{$^{31}$P} NMR (400 MHz, benzene-$d^6$): $\delta$ 1.29 (s, 18H), 1.27 (s, 18H), 1.24 (s, 18H) ppm.

$^{13}$C{$^1$H,$^{31}$P} NMR (101 MHz, benzene-$d^6$, 28 °C): $\delta$ 31.3 ($C$(CH$_3$)$_3$), 30.6 ($C$(CH$_3$)$_3$), 30.4 ($C$(CH$_3$)$_3$), 28.3 (C($C$H$_3$)$_3$), 28.12 (C($C$H$_3$)$_3$), 28.07 (C($C$H$_3$)$_3$) ppm.

$^{31}$P{$^1$H} NMR (162 MHz, benzene-$d^6$): [AMRX]$_2$ spin system ($R$ = 0.22 %, for full parameter set see Table 3): $\delta$ –31.20 (m, $P^4$, 2P), –44.06 (m, $P^2$, 2P), –54.54 (m, $P^3$, 2P), –103.76 (m, $P^1$, 2P) ppm.

HR-ESI(+)-MS (THF): *m/z* 665.135 [As{*cyclo*-(P$_4$$^t$Bu$_3$)}$_2$]$^+$.

IR: $\tilde{\nu}$ 2944 (m), 2929 (m), 2886 (m), 2851 (m), 1452 (s), 1386 (m), 1357 (s), 1170 (s), 1008 (m), 934 (w), 803 (m), 617 (w), 572 (m), 460 (m) cm$^{-1}$.

CHN, Found: C, 41.0; H, 7.7; N, 0.0. $C_{24}H_{54}AsClP_8$ requires C, 41.1; H, 7.8; N, 0.0 %.

**Crystallography**

The data for single crystal X-ray analysis were collected on a Gemini-CCD diffractometer (Rigaku) using Mo-K$_\alpha$ radiation. The structure solution was performed with SHELXT-2018[82] (dual-space method). Structure refinement was done with SHELXL-2018,[83] using full-matrix least-square routines against $F^2$ and anisotropic refinement of all non-hydrogen atoms. All hydrogen atoms were calculated on idealised positions. The crystallographic data (CSD codes below) and additional information can be obtained free of charge via https://summary.ccdc.cam.ac.uk/structure-summary-form (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, United Kingdom; fax: (+44)1223-336-033; or deposit@ccdc.cam.uk).

**Crystal data of 1.** $C_{22}H_{51}LiN_2OP_4$, 490.46 g mol$^{-1}$, $T$ = 130 K, $P2_1$, $a$ = 8.8751(2) Å, $b$ = 15.4665(3) Å, $c$ = 11.1923(3) Å, $V$ = 1480.93(6) Å$^3$, $Z$ = 2, $\rho$ = 1.100 g cm$^{-3}$, $\mu$ = 0.270 mm$^{-1}$, $F$(000) = 536, GooF = 1.028, $x$ = 0.00(3). A total of 19005 reflections were collected, of which 9687 were independent

($R$(int) = 0.0318). $R_1$ (w$R_2$ all data) = 0.0384 (0.0861) for 284 parameters and 9687 reflections ($I$>2$\sigma$($I$)). CCDC 2097486.

**Crystal data of 3.** $C_{28}H_{63}P_9$, 678.51 g mol$^{-1}$, $T$ = 130 K, $P\overline{1}$, $a$ = 9.8283(2) Å, $b$ = 13.4869(3) Å, $c$ = 15.1621(3) Å, $V$ = 1938.76(7) Å$^3$, $Z$ = 2, $\rho$ = 1.162 g cm$^{-3}$, $\mu$ = 0.418 mm$^{-1}$, $F$(000) = 732, GooF = 1.067. A total of 56622 reflections were collected, of which 15839 were independent ($R$(int) = 0.0188). $R_1$ (w$R_2$ all data) = 0.0316 (0.0626) for 355 parameters and 15839 reflections ($I$>2$\sigma$($I$)). CCDC 2097387.

**Crystal data of 4.** $C_{25}H_{56}P_8$, 604.45 g mol$^{-1}$, $T$ = 240 K, $P2_1$/n, $a$ = 13.0038(3) Å, $b$ = 18.2142(4) Å, $c$ = 16.2394(4) Å, $V$ = 3639.2(2) Å$^3$, $Z$ = 4, $\rho$ = 1.103 g cm$^{-3}$, $\mu$ = 0.396 mm$^{-1}$, $F$(000) = 1304, GooF = 1.013. A total of 33109 reflections were collected, of which 8716 were independent ($R$(int) = 0.0429). $R_1$ (w$R_2$ all data) = 0.0450 (0.1231) for 316 parameters and 8716 reflections ($I$>2$\sigma$($I$)). CCDC 2097487. Below 240 K, phase transformation occurs, resulting in twinning of the crystal.

**Crystal data of 5.** $C_{36}H_{81}BiP_{12}$, 1094.62 g mol$^{-1}$, $T$ = 130 K, $P2_1$/c, $a$ = 14.0955(2) Å, $b$ = 23.8832(3) Å, $c$ = 16.1985(2) Å, $V$ = 5354.8(1) Å$^3$, $Z$ = 4, $\rho$ = 1.358 g cm$^{-3}$, $\mu$ = 3.674 mm$^{-1}$, $F$(000) = 2240, GooF = 1.023. A total of 57685 reflections were collected, of which 14673 were independent ($R$(int) = 0.0538). $R_1$ (w$R_2$ all data) = 0.0359 (0.0710) for 469 parameters and 14673 reflections ($I$>2$\sigma$($I$)). CCDC 2097488.

**Crystal data of 6.** $C_{36}H_{81}P_{12}Sb$, 1007.39 g mol$^{-1}$, $T$ = 130 K, $P2_1$/c, $a$ = 14.0171(2) Å, $b$ = 23.7666(3) Å, $c$ = 16.2734(2) Å, $V$ = 5322.5(1) Å$^3$, $Z$ = 4, $\rho$ = 1.257 g cm$^{-3}$, $\mu$ = 0.902 mm$^{-1}$, $F$(000) = 2112, GooF = 0.802. A total of 40984 reflections were collected, of which 40984 were independent ($R$(int) = 0.0518). $R_1$ (w$R_2$ all data) = 0.0363 (0.0595) for 470 parameters and 40984 reflections ($I$>2$\sigma$($I$)). CCDC 2097489.

**Crystal data of 7.** $C_{36}H_{81}AsP_{12}$, 960.56 g mol$^{-1}$, $T$ = 130 K, $P2_1$/c, $a$ = 13.8340(2) Å, $b$ = 23.4873(2) Å, $c$ = 16.4233(2) Å, $V$ = 5236.5(1) Å$^3$, $Z$ = 4, $\rho$ = 1.218 g cm$^{-3}$, $\mu$ = 1.039 mm$^{-1}$, $F$(000) = 2040, GooF = 1.044. A total of 78078 reflections were collected, of which 17694 were independent ($R$(int) = 0.0458). $R_1$ (w$R_2$ all data) = 0.0348 (0.0760) for 469 parameters and 17694 reflections ($I$>2$\sigma$($I$)). CCDC 2097490.

**Crystal data of 8.** $C_{24}H_{54}AsClP_8$, 700.80 g mol$^{-1}$, $T$ = 130 K, $P\overline{1}$, $a$ = 9.0335(4) Å, $b$ = 13.3330(4) Å, $c$ = 16.5876(6) Å, $V$ = 1829.2(1) Å$^3$, $Z$ = 2, $\rho$ = 1.272 g cm$^{-3}$, $\mu$ = 1.365 mm$^{-1}$, $F$(000) = 736, GooF = 1.121. A total of 40036 reflections were collected, of which 12182 were independent ($R$(int) = 0.0366). $R_1$ (w$R_2$ all data) = 0.0415 (0.0798) for 344 parameters and 12182 reflections ($I$>2$\sigma$($I$)). CCDC 2097491.

## Conflicts of interest

There are no conflicts to declare.

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## References

1 Y.-R. Luo, *Comprehensive Handbook of Chemical Bond Energies*, CRC Press, Boca Raton, 1st edn., 2007.

2 M. Baudler and K. Glinka, Monocyclic and Polycyclic Phosphanes, *Chem. Rev.*, 1993, **93**, 1623.

3 T. Wellnitz and C. Hering-Junghans, Synthesis and Reactivity of Monocyclic Homoleptic Oligophosphanes, *Eur. J. Inorg. Chem.*, 2021, 8.

4 V. J. Eilrich and E. Hey-Hawkins, Cyclooligophosphanes and their coordination chemistry, *Coord. Chem. Rev.*, 2021, **437**, 213749.

5 H. Köhler and A. Michaelis, Ueber Phenylphosphin und Phosphobenzol (Diphosphenyl), *Ber. Dtsch. Chem. Ges.*, 1877, **10**, 807.

6 J. J. Daly, The Crystal and Molecular Structure of Phosphobenzene A, $(PC_6H_5)_5$, *J. Chem. Soc.*, 1964, 6147.

7 J. J. Daly and L. Maier, Molecular Structure of Phosphobenzene, *Nature (London, U. K.)*, 1964, **203**, 1167.

8 M. Baudler, C. Gruner, G. Fürstenberg, B. Kloth, F. Saykowski and U. Özer, Beiträge zur Chemie des Phosphors. 79. Zur Ringspaltung von Tetra-*t*-butyl-cyclotetraphosphan mit Kalium bzw. Schwefel, *Z. Anorg. Allg. Chem.*, 1978, **446**, 169.

9 M. Baudler and B. Makowka, Beiträge zur Chemie des Phosphors. 152. Funktionalisierte Cyclotriphosphane des Typs $(t\text{-BuP})_2$PX (X = K, $SiMe_3$, $SnMe_3$, Cl, Br, $PCl_2$, P(*t*-Bu)Cl, P(*t*-Bu)I), *Z. Anorg. Allg. Chem.*, 1985, **528**, 7.

10 A. Schmidpeter and G. Burget, Die Reaktion von Alkaliphosphiden mit weißem Phosphor. I. Bildung von 1,1,3,3-Tetraphenyl-triphosphid, 2,3,4,5-Tetraphenyl-cyclopentaphosphid und Phenyl-tricycloheptaphosphid, *Phosphorus Sulfur Relat. Elem.*, 1985, **22**, 323.

11 G. Fritz and J. Härer, Über Umsetzungen von weißem Phosphor mit Metallorganylen, *Z. Anorg. Allg. Chem.*, 1983, **504**, 23.

12 G. Fritz, J. Härer and K. Stoll, Untersuchungen zur Metallierung der Cyclophosphane $P_4(Cme_3)_3(Sime_3)$, $P_4(Cme_3)_2(Sime_3)_2$, $P_4(Sime_3)_4$, *Z. Anorg. Allg. Chem.*, 1983, **504**, 47.

13 G. Fritz and K. Stoll, Bildung und Reaktionen silylierter Triphosphane, *Z. Anorg. Allg. Chem.*, 1986, **538**, 78.

14 G. Fritz, R. Biastoch, K. Stoll, T. Vaahs, D. Hanke and H. W. Schneider, Synthesis and Reactions of P-Rich Silylphosphanes, *Phosphorus Sulfur Relat. Elem.*, 1987, **30**, 385.

15 G. Fritz and K. Stoll, Die Cyclotetraphosphane $(Me_3C)_3P_4H$ und $(Me_3C)_3P_4[P(CMe_3)Cl]$, *Rev. Roum. Chim.*, 1986, **31**, 949.

16 A. Schisler, P. Lönnecke, U. Huniar, R. Ahlrichs and E. Hey-Hawkins, Sodium Tetra-*tert*-butylcyclopentaphosphanide: Synthesis, Structure, and Unexpected Formation of a

Nickel(0) Tri-*tert*-butylcyclopentaphosphene Complex, *Angew. Chem., Int. Ed.*, 2001, **40**, 4217.

17 A. Schisler, P. Lönnecke, T. Gelbrich and E. Hey-Hawkins, The reactivity of *cyclo*-$(P_5{}^tBu_4)^-$ towards group 13, 14 and 15 metal chlorides: complexation and formation of cyclooligophosphanes, {*cyclo*-$(P_5{}^tBu_4)\}_2$ and {*cyclo*-$(P_4{}^tBu_3)P{}^tBu\}_2$, by reductive elimination, *Dalton Trans.*, 2004, 2895.

18 A. Schisler, P. Lönnecke and E. Hey-Hawkins, Synthesis and Molecular Structure of the First Rhodium(I) Complex Containing a Tetra-*tert*-butylcyclopentaphosphanide Ligand, *Inorg. Chem.*, 2005, **44**, 461.

19 S. Gómez-Ruiz, R. Wolf, S. Bauer, H. Bittig, A. Schisler, P. Lönnecke and E. Hey-Hawkins, Coordination Chemistry of the *cyclo*-$(P_5tBu_4)^-$ Ion: Monomeric and Oligomeric Copper(I), Silver(I) and Gold(I) Complexes, *Chem. – Eur. J.*, 2008, **14**, 4511.

20 S. Gómez-Ruiz and E. Hey-Hawkins, The Versatile Reactivity of Tetra-*tert*-butyl-cyclopentaphosphanide Monoanions, *New J. Chem.*, 2010, **34**, 1525.

21 S. Gómez-Ruiz and E. Hey-Hawkins, The unusual coordination chemistry of phosphorus-rich linear and cyclic oligophosphanide anions, *Coord. Chem. Rev.*, 2011, **255**, 1360.

22 A. Kircali, R. Frank, S. Gómez-Ruiz, B. Kirchner and E. Hey-Hawkins, Synthesis and Thermolysis of the Phosphorus-Rich Manganese(I) Complex $[Mn_2(\mu\text{-Br})\{cyclo\text{-}(P_4tBu_3)PtBu\}(CO)_6]$: From Complexes to Metal Phosphides, *ChemPlusChem*, 2012, **77**, 341.

23 A. Kırcalı Akdag, P. Lönnecke and E. Hey-Hawkins, Synthesis and Thermolysis of the Homoleptic Iron(II) Complex $[Fe\{cyclo\text{-}(P_5tBu_4)\}_2]$, *Z. Anorg. Allg. Chem.*, 2014, **640**, 271.

24 T. Grell and E. Hey-Hawkins, Dynamic Gold(I) Complexes of Hexa-*tert*-butyl-octaphosphane, *Eur. J. Inorg. Chem.*, 2020, 732.

25 T. Grell and E. Hey-Hawkins, Unexpected Isomerization of Hexa-*tert*-butyl-octaphosphane, *Chem. – Eur. J.*, 2020, **26**, 1008.

26 T. Grell and E. Hey-Hawkins, Versatile Coordination Chemistry of Hexa-*tert*-butyl-octaphosphine, *Inorg. Chem.*, 2020, **59**, 7487.

27 M. Baudler, J. Hellmann, P. Bachmann, K.-F. Tebbe, R. Fröhlich and M. Fehér, $tBu_6P_8$ and $tBu_6As_8$ — Two New Element-Homologous Bicyclic Compounds of Different Structure, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 406.

28 B. Riegel, A. Pfitzner, G. Heckmann, H. Binder and E. Fluck, In situ-Erzeugung von [PX] und Insertion in $(^tBuP)_3$, (X = Cl, Br) Synthese der funktionalisierten Cyclophosphane $(^tBuP)_3PX$, $[1\text{-}(^tBu)(X)P\text{-}2,3,4\text{-}(^tBu)_3]P_4$ und Strukturbestimmung von $(^tBuP)_3PCl$, *Z. Anorg. Allg. Chem.*, 1995, **621**, 1365.

29 M. Baudler, M. Schnalke and C. Wiaterek, Beiträge zur Chemie des Phosphors. 202. Hepta-*tert*-butyl-nonaphosphan(7), $P_9(t\text{-}Bu)_7$, und Octa-*tert*-butyl-decaphosphan(8), $P_{10}(t\text{-}Bu)_8$ Darstellung und $^{31}P$-NMR-spektroskopische Strukturbestimmung, *Z. Anorg. Allg. Chem.*, 1990, **585**, 7.

30 K. M. Marczenko and S. S. Chitnis, Bismuthanylstibanes, *Chem. Commun. (Cambridge, U. K.)*, 2020, **56**, 8015.

31 C. Ritter, F. Weigend and C. von Hänisch, Synthesis of a Molecule with Five Different Adjacent Pnictogens, *Chem. – Eur. J.*, 2020, **26**, 8536.

32 M. Stubenhofer, C. Kuntz, G. Balázs, M. Zabel and M. Scheer, 1,2,3-Triphosphole derivatives as reactive intermediates, *Chem. Commun. (Cambridge, U. K.)*, 2009, 1745.

33 M. Scheer, G. Balázs and A. Seitz, $P_4$ Activation by Main Group Elements and Compounds, *Chem. Rev.*, 2010, **110**, 4236.

34 M. Caporali, L. Gonsalvi, A. Rossin and M. Peruzzini, $P_4$ Activation by Late-Transition Metal Complexes, *Chem. Rev.*, 2010, **110**, 4178.

35 F. Scalambra, M. Peruzzini and A. Romerosa, in *Advances in Organometallic Chemistry*, ed. P. J. Perez, Academic Press, Amsterdam, 2019, vol. 72, pp. 173–222.

36 J. E. Borger, A. W. Ehlers, J. C. Slootweg and K. Lammertsma, Functionalization of $P_4$ through Direct P–C Bond Formation, *Chem. – Eur. J.*, 2017, **23**, 11738.

37 D. J. Scott, J. Cammarata, M. Schimpf and R. Wolf, Synthesis of monophosphines directly from white phosphorus, *Nat. Chem.*, 2021, **13**, 458.

38 M. Baudler and K. Glinka, Open-Chain Polyphosphorus Hydrides (Phosphanes), *Chem. Rev.*, 1994, **94**, 1273.

39 E. Hey-Hawkins and A. A. Karasik, in *Houben-Weyl – Science of Synthesis*. *Category 5, Compounds with One Saturated Carbon-Heteroatom Bond*, ed. F. Mathey and B. M. Trost, Georg Thieme Verlag, Stuttgart, 2009, pp. 71–108.

40 G. Fritz, J. Härer, K. Stoll and T. Vaahs, Formation and chemical behaviour of silylated phosphanes, *Phosphorus Sulfur Relat. Elem.*, 1983, **18**, 65.

41 E. Fluck, R. Riedel, H.-D. Hausen and G. Heckmann, Bis(2,4,6-tri-t-butylphenyl)bicyclotetraphosphan, *Z. Anorg. Allg. Chem.*, 1987, **551**, 85.

42 A. R. Fox, R. J. Wright, E. Rivard and P. P. Power, $Tl_2[Aryl_2P_4]$: A Thallium Complexed Diaryltetraphosphabutadienediide and its Two-Eelectron Oxidation to a Diaryltetraphosphabicyclobutane, $Aryl_2P_4$, *Angew. Chem., Int. Ed.*, 2005, **44**, 7729.

43 B. M. Cossairt and C. C. Cummins, Radical synthesis of trialkyl, triaryl, trisilyl and tristannyl phosphines from $P_4$, *New J. Chem.*, 2010, **34**, 1533.

44 S. Heinl, S. Reisinger, C. Schwarzmaier, M. Bodensteiner and M. Scheer, Selective Functionalization of $P_4$ by Metal-Mediated C–P Bond Formation, *Angew. Chem., Int. Ed.*, 2014, **53**, 7639.

45 A. Schisler, P. Lönnecke and E. Hey-Hawkins, Synthesis, Properties, Structure and Reactivity of Sodium 2,3,4,5-Tetra-*tert*-butylcyclopentaphosphanide, *Phosphorus, Sulfur Silicon Relat. Elem.*, 2002, **177**, 1447.

46 W. Weigand, A. W. Cordes and P. N. Swepston, Tetra-*tert*-butylcyclotetraphosphane, $[PC(CH_3)_3]_4$, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, 1981, **37**, 1631.

47 H. H. Karsch, A. Appelt and G. Müller, Functional Trimethylphosphine Derivatives. 23.

 

(Phosphinomethyl)aluminum Compounds: (Phosphinomethyl)aluminates as a Novel Type of Phosphine Ligands and X-ray Structures of [(TMEDA)(THF)Li($Me_2PCH_2$)$AlMe_3$] and [(TMEDA)Li($Me_2PCH_2$)$_2AlMe_2$], *Organometallics*, 1985, **4**, 1624.

48 K. Niediek and B. Neumüller, Darstellung und Charakterisierung von Organodilithiumphosphiden. Die Kristallstruktur von [Li(THF)(TMEDA)P(H)Mes], *Z. Anorg. Allg. Chem.*, 1993, **619**, 885.

49 J. Langer, K. Wimmer, H. Görls and M. Westerhausen, Synthesis and crystal structures of bis(diphenylphosphanyl)methanides of lithium and calcium as well as of their borane adducts, *Dalton Trans.*, 2009, 2951.

50 E. Sattler, T. Szilvási, E. Matern, P. Bombicz, M. Gamer, A. Okrut and I. Kovács, Investigations of LiP($SiMe_2CH_2SiMe_3$)–P*t*$Bu_2$, the Surprising Byproduct in the Metalation of ($Me_3Si$)$_2$P–P*t*$Bu_2$, *Eur. J. Inorg. Chem.*, 2017, 5521.

51 D. Bevern, H. Görls, S. Krieck and M. Westerhausen, Synthesis, Structure, and Stability of Lithium Arylphosphanidyldiarylphosphane Oxide, *Z. Anorg. Allg. Chem.*, 2020, **646**, 948.

52 M. Baudler, Y. Aktalay, K.-F. Tebbe and T. Heinlein, *t*$Bu_4P_6$, a Novel Bicyclic Organophosphane, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 967.

53 M. Baudler and B. Makowka, $P_6$*t*$Bu_4$ – The First 1,1′-Bicyclotriphosphane, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 987.

54 M. Baudler, M. Michels, J. Hahn and M. Pieroth, $P_7$*t*$Bu_5$ – The First Bicyclo[3.2.0]heptaphosphane, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 504.

55 M. Baudler and L. de Riese-Meyer, Beiträge zur Chemie des Phosphors. 164. (*t*-BuP)$_2$P–P(Me)–P(*t*-BuP)$_2$ – das erste Bis(cyclotriphosphano)phosphan, ein neuer $P_7R_5$-Strukturtyp, *Z. Naturforsch., B: Anorg. Chem., Org. Chem.*, 1986, **41b**, 399.

56 M. Baudler, C. Wiaterek and K. Kazmierczak, Beiträge zur Chemie des Phosphors. 198. Hexa-*tert*-butyl-decaphosphan(6), $P_{10}$(*t*-Bu)$_6$ – Darstellung und $^{31}$P-NMR-spektroskopische Strukturbestimmung, *Z. Anorg. Allg. Chem.*, 1989, **579**, 7.

57 M. Baudler, L. de Riese-Meyer and C. Wiaterek, Beiträge zur Chemie des Phosphors. 193. 1,2-Bis(di-*tert*-butylcyclotriphosphanyl)-3,4-di-*tert*-butyl-cyclotetraphosphan – ein neuer $P_{10}R_6$-Strukturtyp, *Z. Naturforsch. B*, 1989, **44b**, 375.

58 P. Jutzi, R. Kroos, A. Müller, H. Bögge and M. Penk, Synthese und Struktur der Polycyclohexaphosphane $P_6(C_5Me_5)_4$ und $P_6(C_5Me_5)_2$, *Chem. Ber.*, 1991, **124**, 75.

59 M. Baudler and H. Tschäbunin, Beiträge zur Chemie des Phosphors. 224. Zur Thermolyse von 1,2-Di-*tert*-butyldiphosphan, 1,2,3-Tri-*tert*-butyltriphosphan und Tetra-*tert*-butylcyclotetraphosphan, *Z. Anorg. Allg. Chem.*, 1992, **617**, 31.

60 N. Wiberg, A. Wörner, H.-W. Lerner, K. Karaghiosoff, D. Fenske, G. Baum, A. Dransfeld and P. von Ragué Schleyer, The Triphosphide ($t$$Bu_3Si$)$_2P_3Na$: Formation, X-ray and Ab initio Structure Analyses, Protonation and Oxidation to Triphosphane ($t$$Bu_3Si$)$_2P_3H$ and Hexaphosphanes ($t$$Bu_3Si$)$_4P_6$, *Eur. J. Inorg. Chem.*, 1998, **1998**, 833.

61 M. Fehér, R. Fröhlich and K.-F. Tebbe, Beiträge zur Strukturchemie phosphorhaltiger Ketten und Ringe, IV. Die Kristall- und Molekülstruktur des Bicyclotetraphosphans *t*-$Bu_6P_8$, *Z. Kristallogr.*, 1982, **158**, 241.

62 M. Baudler and H. Tschäbunin, Beiträge zur Chemie des Phosphors. 138. $P_5$(*t*-Bu)$_4$H – das erste Derivat von *iso*-$P_5H_5$, *Z. Anorg. Allg. Chem.*, 1984, **511**, 77.

63 S. Rendler and M. Oestreich, Hypervalent Silicon as a Reactive Site in Selective Bond-Forming Processes, *Synthesis*, 2005, **2005**, 1727.

64 K. Issleib and M. Hoffmann, Alkali-Phosphorverbindungen und ihr reaktives Verhalten. XLI. Tetra-tert.-butyl-biphosphin und Tetra-tert.-butyl-cyclotetraphosphin, *Chem. Ber.*, 1966, **99**, 1320.

65 M. Baudler, J. Hahn, H. Dietsch and G. Fürstenberg, Beiträge zur Chemie des Phosphors. 68. Tri-*t*-butyl-cyclotriphosphan, *Z. Naturforsch., B: Anorg. Chem., Org. Chem.*, 1976, **31b**, 1305.

66 R. J. Schwamm, M. Lein, M. P. Coles and C. M. Fitchett, Bi–P Bond Homolysis as a Route to Reduced Bismuth Compounds and Reversible Activation of $P_4$, *Angew. Chem., Int. Ed.*, 2016, **55**, 14798.

67 C. Silvestru, H. J. Breunig and H. Althaus, Structural Chemistry of Bismuth Compounds. I. Organobismuth Derivatives, *Chem. Rev.*, 1999, **99**, 3277.

68 C. von Hänisch and S. Stahl, Synthese und Charakterisierung von binären Molekülverbindungen der Gruppe 15 Elemente mit $P_2As_2$-, $PSb_2$-, $PBi_2$-, $PBi_3$- und $P_2Bi_4$-Gerüst, *Z. Anorg. Allg. Chem.*, 2009, **635**, 2230.

69 S. Traut, A. P. Hähnel and C. von Hänisch, Dichloro organosilicon bismuthanes as precursors for rare compounds with a bismuth–pnictogen or bismuth–tellurium bond, *Dalton Trans.*, 2011, **40**, 1365.

70 A. Hinz, A. Schulz and A. Villinger, Synthesis of Heavy Cyclodipnictadiphosphanes [ClE($\mu$-P-Ter)]$_2$ [E = P, As, Sb, or Bi; Ter = 2,6-bis(2,4,6-trimethylphenyl)phenyl], *Inorg. Chem.*, 2016, **55**, 3692.

71 M. Balmer, H. Gottschling and C. von Hänisch, Phosphaalkene-substituted organo-group 15 compounds: synthesis and characterisation of (NHC)P–E*t*$Bu_2$ (E = P, As, Sb and Bi), *Chem. Commun. (Cambridge, U. K.)*, 2018, **54**, 2659.

72 C. Ritter, B. Ringler, F. Dankert, M. Conrad, F. Kraus and C. von Hänisch, Synthesis and crystal structures of novel tertiary butyl substituted (pseudo-)halogen bismuthanes, *Dalton Trans.*, 2019, **48**, 5253.

73 M. A. Beswick, N. Choi, A. D. Hopkins, Y. G. Lawson, M. McPartlin, A. Rothenberger, D. Stalke, A. E. H. Wheatley and D. S. Wright, The First Bismuth Phosphide Complex: $[Li(thf)_4]^+[\{(tBuP)_3\}_2Bi]^-$, *Angew. Chem., Int. Ed.*, 1999, **38**, 3053.

74 W. Jerzembeck, H. Bürger, L. Constantin, L. Margulès, J. Demaison, J. Breidung and W. Thiel, Bismuthine $BiH_3$: Fact

or Fiction? High-Resolution Infrared, Millimeter-Wave, and Ab Initio Studies, *Angew. Chem., Int. Ed.*, 2002, **41**, 2550.

75 L. Fusina, G. Di Lonardo and P. de Natale, The ground state spectroscopic parameters and molecular geometry of $SbH_3$, *J. Chem. Phys.*, 1998, **109**, 997.

76 D. R. Lide, ed., *CRC Handbook of Chemistry and Physics. A Ready-Reference Book of Chemical and Physical Data: 1995–1996*, CRC Press, Boca Raton, 76th edn., 1995.

77 H. H. Karsch, W. A. Herrmann and G. Brauer, in *Synthetic Methods of Organometallic and Inorganic Chemistry*, ed. W. A. Herrmann and G. Brauer, Georg Thieme Verlag, Stuttgart, 1996, vol. 3, p. 55.

78 C. J. Hoffman, J. M. Lutton and R. W. Parry, in *Inorganic Syntheses*, ed. J. C. Bailar, McGraw-Hill, New York, 1953, pp. 150–152.

79 C. J. Hoffman, J. M. Lutton and R. W. Parry, in *Inorganic Syntheses*, ed. J. C. Bailar, McGraw-Hill, New York, 1953, pp. 149–150.

80 R. K. Harris, E. D. Becker, S. M. Cabral De Menezes, R. J. Goodfellow and P. Granger, NMR Nomenclature: Nuclear Spin Properties and Conventions for Chemical Shifts (IUPAC Recommendations 2001), *Concepts Magn. Reson.*, 2002, **14**, 326.

81 *DAISY, part of TopSpin 4.1.1*, Bruker BioSpin GmbH, Rheinstetten, 2020.

82 G. M. Sheldrick, *SHELXT* – Integrated space-group and crystal-structure determination, *Acta Crystallogr., Sect. A: Found. Adv.*, 2015, **71**, 3.

83 G. M. Sheldrick, Crystal structure refinement with *SHELXL*, *Acta Crystallogr., Sect. C: Struct. Chem.*, 2015, **71**, 3.