

## Inorganic Chemistry

New Reactivity Patterns in 3H-Phosphaallene Chemistry  
[Aryl-P=C=C(H)-tBu]: Hydroboration of the C=C Bond,  
Deprotonation and TrimerisationJonas C. Tendency,<sup>[a]</sup> Alexander Hepp,<sup>[a]</sup> Ernst-Ulrich Würthwein,<sup>\*,[b]</sup> and Werner Uhl<sup>\*,[a]</sup>

**Abstract:** 3H-Phosphaallenes, R-P=C=C(H)C-R' (**3**), are accessible in a multigram scale on a new and facile route and show a fascinating chemical reactivity. BH<sub>3</sub>(SMe<sub>2</sub>) and **3a** (R=Mes\*, R'=tBu) afforded by hydroboration of the C=C bonds of two phosphaallene molecules an unprecedented borane (**7**) with the B atom bound to two P=C double bonds. This compound represents a new FLP based on a B and two P atoms. The increased Lewis acidity of the B atom led to a different reaction course upon treatment of **3a** with H<sub>2</sub>B-C<sub>6</sub>F<sub>5</sub>(SMe<sub>2</sub>). Hydroboration of a C=C bond of a first phosphaallene is followed in a typical FLP reaction by the coordination of a second phosphaallene molecule via B-C and P-

B bond formation to yield a BP<sub>2</sub>C<sub>2</sub> heterocycle (**8**). Its B-P bond is short and the B-bound P atom has a planar surrounding. Treatment of **3a** with tBuLi resulted in deprotonation of the β-C atom of the phosphaallene (**9**). The Li atom is bound to the P atom as demonstrated by crystal structure determination, quantum chemical calculations and reactions with HCl, Cl-SiMe<sub>3</sub> or Cl-PtBu<sub>2</sub>. The thermally unstable phosphaallene Ph-P=C=C(H)-tBu gave a unique trimeric secondary product by P-P, P-C and C-C bond formation. It contains a P<sub>2</sub>C<sub>4</sub> heterocycle and was isolated as a W(CO)<sub>4</sub> complex with two P atoms coordinated to W (**15**).

## Introduction

Phosphaallenes, R-P=C=CR'<sub>2</sub>, form a fascinating class of compounds.<sup>[1,2]</sup> They have cumulated P=C and C=C double bonds, are highly reactive and only isolable with bulky substituents R such as Mes\* (2,4,6-tBu<sub>3</sub>C<sub>6</sub>H<sub>2</sub>) to prevent decomposition. They were generated for the first time about 40 years ago by the seminal work of Yoshifuji<sup>[3,4]</sup> and further studied by the groups of Appel<sup>[5,6]</sup> and Märkl.<sup>[7,8]</sup> The latter group reported in 1988 on the first 3H-phosphaallenes, R-P=C=C(H)-R' (e.g. R=Mes\*, R'=tBu), which had a H atom bound to their β-C atom and were obtained by rearrangement upon treatment of R-P(H)-C≡C-R' with a strong base.<sup>[7]</sup> With the Lewis basic P atom, the P=C

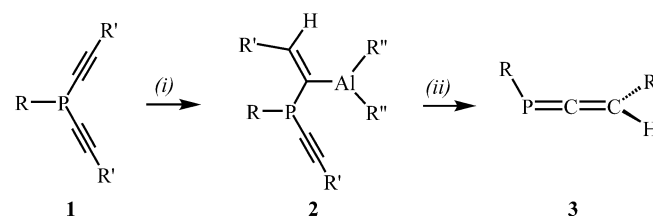
and C=C bonds and the C-H bond in β-position to phosphorus these molecules have four different functionalities and are applicable as promising starting materials in secondary processes. Reports on the reactivity of phosphaallenes are limited, and only few secondary products are reported such as transition metal complexes (η<sup>1</sup>- and η<sup>2</sup>-coordination)<sup>[1,2,9]</sup> and cyclic dimers.<sup>[7d,10,11]</sup> Few reactions with Main Group elements or their compounds, such as *n*-butyllithium, sulfur, hydrogen peroxide, protic reagents or dichlorocarbene, are known.<sup>[7e,12]</sup> The central C atom of the P=C=C moiety bears a partial negative charge and is attacked by protons.<sup>[1,13,14]</sup> Recently, we found facile access to various 3H-phosphaallenes (**3**) in a multigram scale and excellent yields by treatment of dialkynylphosphines (**1**) with commercially available dialkylaluminium hydrides (e.g. iBu<sub>2</sub>AlH; Scheme 1).<sup>[2]</sup> The products are formed via hydroalumination of an alkynyl group, generation of mixed alkenyl-alkynyl aluminium intermediates (**2**)<sup>[15]</sup> and elimination of aluminium alkynides. This method is suitable for the synthesis of persis-

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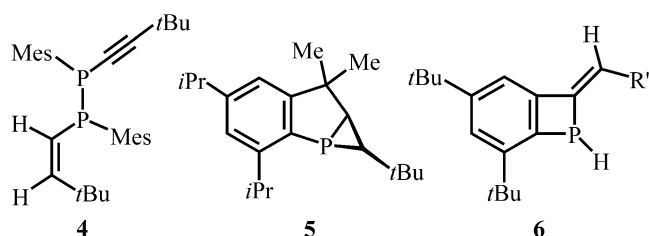
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**Scheme 1.** Synthesis of 3H-phosphaallenes: (i) + H-AlR''<sub>2</sub>; (ii) -R''<sub>2</sub>Al-C≡C-R'; R = Mes, Trip, Mes\*, CH(SiMe<sub>3</sub>)<sub>2</sub>; R' = tBu, Ph, Adamantyl, C<sub>6</sub>H<sub>11</sub>; R'' = Et, iBu, CH(SiMe<sub>3</sub>)<sub>2</sub>.

tent and transient species, the latter were trapped by coordination to transition metal atoms ( $\eta^1$ - and  $\eta^2$ -coordination).<sup>[2]</sup>

The facile accessibility of 3H-phosphaallenes enabled extensive studies on their chemical properties. A new dimer (**4**; Scheme 2) was isolated that had a P–P single bond and an alkynyl and an alkenyl group bound to the P atoms.<sup>[2]</sup> Irradiation of a transient species afforded a tricyclic compound (**5**) with a strained three-membered phosphirane ring.<sup>[14]</sup> It represents an unprecedented isomer of the starting phosphaallene. Thermolysis of two room temperature stable Mes\* compounds afforded 1-benzo-dihydrophosphetes (**6**) with annulated C<sub>6</sub> and PC<sub>3</sub> rings.<sup>[14]</sup> Their formation proceeds by an unusual intramolecular nucleophilic aromatic substitution with the replacement of an alkyl group at the aromatic ring. The phosphorus-bound H atom of **6** allowed catalyst-free hydrophosphination reactions and the generation of bulky phosphine ligands.<sup>[14]</sup> In this paper we focus on reactions at the vinylidene part of the phosphaallenes and report on the isolation of a novel trimeric product of an unstable derivative.

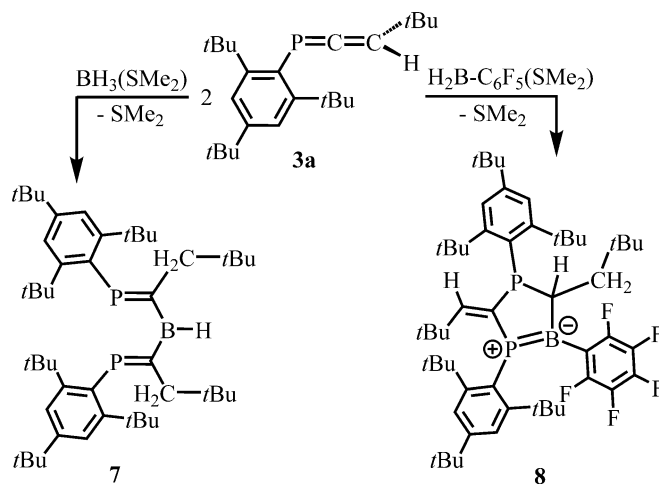


Scheme 2. Secondary products of 3H-phosphaallenes (R' = *t*Bu, adamantyl).

## Results and Discussion

### Hydroboration

Hydroboration is a powerful method for the reduction of unsaturated compounds and the generation of functional molecules<sup>[16,17]</sup> and has been applied also for the reduction of P–C double or triple bonds.<sup>[18–20]</sup> Phosphaalkenes, R–P=C(R')<sub>2</sub>, afforded preferably products with P–H and C–B bonds.<sup>[18,19]</sup> In contrast, treatment of phosphaalkynes, P≡C–R, with secondary boranes yielded both possible products with the formation of P–H or P–B bonds.<sup>[20]</sup> Hydroboration of phosphaallenes has not been reported previously. We treated Mes\*–P=C=C(H)–*t*Bu (**3a**) with equimolar quantities of H<sub>3</sub>B(SMe<sub>2</sub>) in *n*-hexane at room temperature, but based on NMR data and crystal structure determination the unexpected insertion of two phosphaallene moieties into different B–H bonds of a BH<sub>3</sub> molecule gave the di(phosphaalkenyl)borane (**7**). The reaction in the correct molar ratio of 2:1 afforded **7** in a high yield of 87% (Scheme 3). Interestingly, hydroboration of the C=C bonds is preferred over the hydroboration of the heteronuclear P=C bonds (Figure 1). The P=C distances of 1.688 Å on average correspond to standard values of phosphaalkenes.<sup>[21]</sup> Caused by the different hybridization of the central C atoms (*sp*<sup>2</sup> versus *sp*) they are slightly longer than in phosphaallene **3a** [1.651(3) Å].<sup>[2]</sup> The B atoms have a trigonal planar surrounding



Scheme 3. Hydroboration of phosphaallene **3a**.

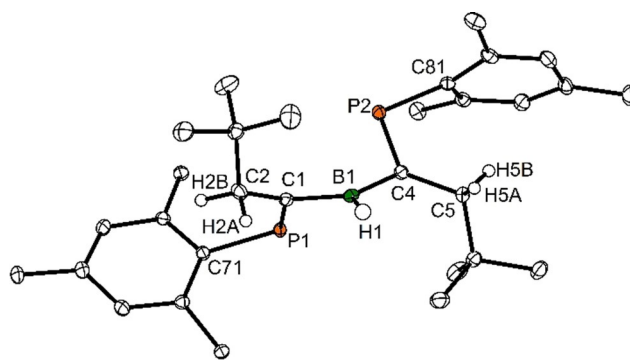


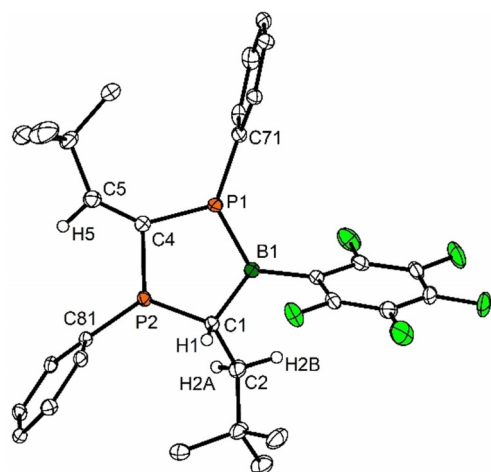
Figure 1. Molecular structure and numbering Scheme of **7**. Displacement ellipsoids are drawn at the 40% level. H atoms with exception of H1, H2A/H2B and H5A/H5B and methyl groups of the Mes\* substituents are omitted. Important bond lengths (Å) and angles (°): P1–C1 1.686(2), P2–C4 1.690(2), B1–C1 1.544(2), B2–C4 1.549(2), C1–C2 1.514(2), C4–C5 1.514(2), C1–B1–C4 126.7(1), B1–C1–P1 109.2(1), B1–C1–C2 120.5(1), B1–C4–P2 110.0(1), B1–C4–C5 128.0(1).

(sum of angles = 360°), and the B–C distances are with 1.547(av) Å in the normal range of B–C single bonds to *sp*<sup>2</sup>-C atoms.<sup>[22]</sup>

**7** showed a singlet at a low field ( $\delta$  = 326.8) of the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum. The chemical shift corresponds to values found for phosphaalkenes that have a relatively electropositive atom (Si of SiMe<sub>3</sub>, Sn of SnR<sub>3</sub> or B atoms in various groups) attached to their central C atom.<sup>[23]</sup> The <sup>13</sup>C NMR signal of the P=C moiety ( $\delta$  = 200.8) is in the normal range of phosphaalkenes, and the <sup>11</sup>B NMR spectrum shows a broad resonance in the range expected for three-coordinate B atoms ( $\delta$  = 60.4).<sup>[24]</sup> A sharp absorption of the B–H stretching vibration was observed for the terminal B–H bond in the characteristic range of the IR spectrum at 2413 cm<sup>–1</sup>. **7** has an interesting molecular structure with a coordinatively unsaturated Lewis acidic B atom and two Lewis basic P atoms in a single molecule. It represents a rare example of a frustrated Lewis pair,<sup>[25]</sup> in which the presence of two basic atoms may allow the chelating activation of substrates.<sup>[26]</sup> However, the B atom of **7** is not activated by an

electron-withdrawing group, hence, its Lewis acidity may not be high enough to act as an efficient FLP<sup>[27]</sup> and its reactivity may be somewhat limited. We, therefore, applied the borane  $H_2B-C_6F_5$  with the electron-withdrawing  $C_6F_5$  group attached to boron.<sup>[28]</sup>

Treatment of **3a** with  $H_2B-C_6F_5(SMe_2)$  in a molar ratio of 2:1 in *n*-hexane at  $-78^\circ C$  afforded (after recrystallization of the crude product from  $CH_2Cl_2$ ) yellow crystals of compound **8** in 70% yield. Crystal structure determination (Figure 2) revealed an unexpected molecular structure which is different from that one of **7**. Once again two formula units of the phosphorus compound reacted with one equivalent of the borane. But now the formation of three new bonds (B–P, P–C, B–C) afforded a five-membered  $P_2C_2B$  heterocycle, which adopted a slightly distorted envelope conformation with the atom P2 0.57 Å above the average plane of the four remaining ring atoms. Both P=C bonds of the phosphaaallenes and a C=C bond were reduced to single bonds, one of the C=C bonds [1.345(9) Å] is retained and is in an exocyclic position of the  $P_2C_2B$  ring. The atom P2 has the expected trigonal pyramidal surrounding with sum of the bond angles =  $325.9^\circ$  and shows normal endocyclic P–C bond lengths of 1.853(2) and 1.846(2) Å. In contrast, P1 has surprisingly a trigonal planar coordination sphere (sum of the angles =  $359.0^\circ$ ) with short P1–C4 [1.787(2) Å] and P1–B1 distances [1.797(2) Å]. These observations support the assumption of a  $\pi$ -interaction between the lone pair at phosphorus and the empty *p*-orbital at boron and the occurrence of a P=B double bond, which may be favored by the strong electron-withdrawing character of the  $C_6F_5$  group at boron. Few structurally authenticated compounds containing a P=B bond with planar surrounded P atoms and short P–B bond lengths are reported in the literature, in two cases the B atoms are also bound to  $C_6F_5$  groups.<sup>[29]</sup> Quantum chemical calculations on the latter compounds suggested a highly polar bonding character of the B–P bond.<sup>[29b,c]</sup> These compounds have been used



**Figure 2.** Molecular structure and numbering Scheme of **8**. Displacement ellipsoids are drawn at the 40% level. H atoms with exception of H2A/H2B and H5 and the *t*Bu groups of the Mes\* substituents are omitted. Important bond lengths (Å) and angles ( $^\circ$ ): P1–C4 1.787(2), P1–B1 1.797(2), P2–C1 1.853(2), P2–C4 1.846(2), B1–C1 1.596(2), C4–C5 1.345(2), C4–P1–B1 104.76(8), P1–B1–C1 113.6(1), B1–C1–P2 105.7(1), C1–P2–C4 103.64(7), P1–C4–P2 103.14(8).

for the heterolytic cleavage of  $H_2$  molecules and for the dehydrogenation of ammineboranes.

Two resonances were observed in a narrow range of the  $^{31}P\{^1H\}$  NMR spectrum at  $\delta = 30.3$  and 25.3. The first one is broad and did not allow the identification of a coupling pattern. It results from the atom P1, which is bound to the boron atom, and its broadness is caused by the quadrupole moment of the boron nuclei. The second P atom (P2) shows a doublet with a coupling constant  $^2J_{PP}$  of 89.2 Hz. A broad resonance was observed in the  $^{11}B$  NMR spectrum at  $\delta = 53.2$ . B and P NMR shifts are similar to those reported for B=P compounds,<sup>[29]</sup> but are not really indicative for this specific bonding situation. The  $^{13}C$  NMR signals of the exocyclic C=C bond were detected in the expected range at  $\delta = 142.2$  and 136.2 as doublets of doublets due to the coupling to two chemically different P atoms.

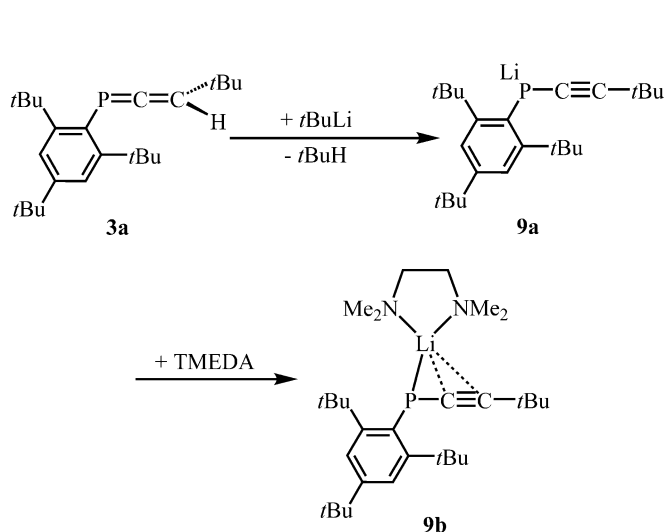
The different reaction pathways observed for the hydroboration of phosphaaallene **3a** (Scheme 3) are clearly influenced by the electron withdrawing  $C_6F_5$  group at boron. The first step of both reactions may be the same and comprise the addition of a B–H bond to the C=C double bond of the P=C=C group. The postulated intermediate has an intact P=C bond, and the B atom is bound to the inner C atom, similar to the structure of compound **7**. The resulting constitution resembles the situation in geminal Frustrated Lewis pairs.<sup>[25]</sup> In contrast to the synthesis of **7** with the insertion of a C=C double bond into the second B–H bond, the Lewis acidity of the B atom is considerably enhanced in the  $C_6F_5$  borane. It is a strongly polarizing acceptor and favors the approach of the nucleophilic P atom of a second phosphaaallene. The P=C bond becomes polarized by the P–B interaction, and the  $\alpha$ -C atom reacts as an electrophile with the P atom of the FLP-type intermediate to form the five-membered heterocycle of **8**. A similar reaction has been postulated based on quantum chemical calculations and comprises the trapping of a highly unstable phosphaaallene by a transient Al/P-based FLP analogous to **2** (Scheme 1) to yield an  $AlP_2C_2$  heterocycle (see below for further discussion).<sup>[15c]</sup> In other cases, hydroalumination of sterically less shielded alkynylphosphines with dialkylaluminum hydrides resulted in the formation of geminal Al/P FLPs, which could not be isolated, but reacted spontaneously with the triple bond of a second equivalent of the starting alkynylphosphine by generation of five-membered heterocycles.<sup>[30]</sup> In the final step of the formation of **8** 1,2-hydrogen shift from boron to the C atom of the P–C–B group is required.

### Deprotonation

While the ligand properties and the reactivity of the P=C and C=C bonds of phosphaaallenes have been reported in the literature, the reactivity of the C–H bond is almost unexplored and to the best of our knowledge lithium compounds derived from 3H-phosphaaallenes by deprotonation are not known. Yoshifuji treated a 3H-phosphaaallene with 0.5 equivalents of *n*-butyllithium and isolated a 3,4-diphosphinidenecyclobutene.<sup>[10,11a]</sup> In some cases a transient phosphaaallene was postulated to be deprotonated by a strong base.<sup>[11c,d]</sup> But no spectroscopic or

theoretical evidences were provided to support such a mechanism. A persistent phosphallene,  $R-P=C=CR'_2$ , was reported to react with *n*-butyllithium by addition of the Li–C moiety to the P=C bond.<sup>[12a]</sup> The product was not isolated and characterized, but quenched by addition of methanol. We treated **3a** with equimolar quantities of *tert*-butyllithium and isolated a colorless highly viscous liquid of **9a** (Scheme 4) which could not be purified and isolated in a crystalline form. It showed very broad resonances in the NMR spectra, which could not be assigned completely. Deprotonation of the C–H group is confirmed by the missing signal of the vinylic H atom in the characteristic range of  $^1H$  NMR spectrum at about  $\delta=5.70$ .<sup>[2]</sup> The P atom shows a broad resonance in the  $^{31}P\{^1H\}$  NMR spectrum at  $\delta=-136$ , which is considerably shifted to a higher field compared to **3a** and in the typical range of lithium phosphides.<sup>[31]</sup> Two  $^{13}C$  NMR signals at  $\delta=97.7$  and  $117.1$  confirm the presence of a  $C\equiv C$  triple bond and the missing phosphallene unit. A suggestion for the molecular constitution of **9a** is given in Scheme 4, it is based on the structures of the TMEDA adduct **9b** and of some secondary products (see below).

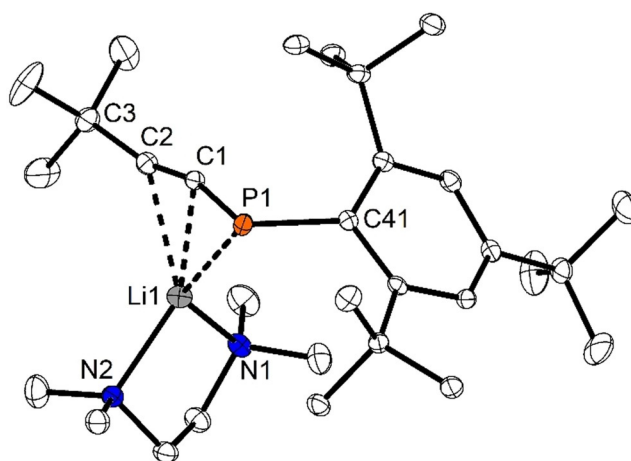
A similar lithium phosphide,  $Li[P(Mes^*)-C\equiv C-R']$  ( $R'=SiMe_3$ ), was claimed to be formed by deprotonation of the corresponding P–H alkynylphosphine with methyllithium in the presence of TMEDA.<sup>[8]</sup> It was not isolated or characterized, but immediately trapped by addition of  $Cl-SiMe_3$ .<sup>[8]</sup> A phosphallene was isolated, and from the constitution of the product an equilibrium was postulated between lithium phosphide and a deprotonated phosphallene. A similar equilibrium has been postulated for a phenyl substituted species ( $R'=Ph$ ), because quenching with  $Cl-SiMe_3$  resulted in the formation of a mixture of the phosphallene and the corresponding alkynylphosphine.<sup>[10a]</sup> NMR spectroscopy or the generation of secondary products did not confirm such an equilibrium in our case. In addition, quantum chemical calculations with **9a** (TPSSTPSS/def2tzvp + GD3BJ)<sup>[32a–g]</sup> showed that the Li phosphide structure depicted in Scheme 4 is energetically highly preferred over the isomer with Li bound to the  $\beta$ -C atom. Similar to the results of crystal structure determination of **9b** (see below) the opti-



**Scheme 4.** Deprotonation of the 3H-phosphallene **3a**.

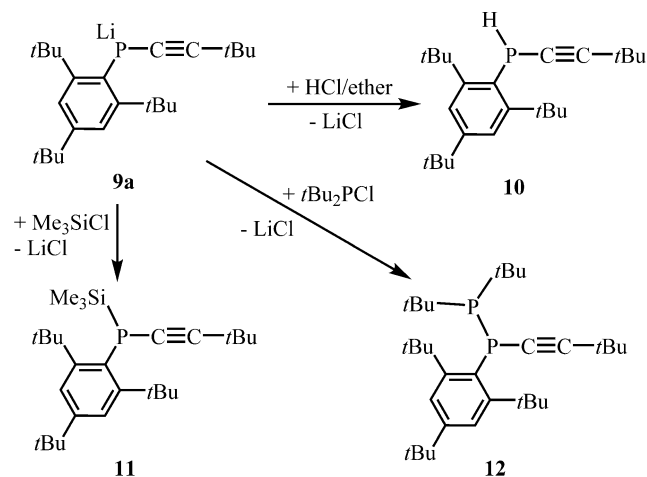
mized structure has the Li atom additionally coordinated to the  $\alpha$ - and  $\beta$ -C atoms of the ethynyl substituent. The shift of the Li atom to the  $\beta$ -C atom does not result in an energetic minimum; it is in contrast energetically highly unfavorable and can definitely be excluded. Interestingly, the H compounds behave different. The phosphallene structure is slightly favoured over the P–H phosphine tautomer by  $4.32\text{ kcal mol}^{-1}$ . These results confirm that an equilibrium between Li alkynylphosphide (**9a**, experimentally observed) and a deprotonated compound with an intact phosphallene moiety is at least in our case not to be expected.

To unambiguously characterize the deprotonated compound **9a**, we treated the reaction mixture with an equimolar quantity of *N,N,N',N'*-tetramethylethylenediamine (TMEDA, Scheme 4) and isolated yellow crystals of the TMEDA adduct **9b** in 82% yield. The  $^{31}P\{^1H\}$  NMR signal was slightly shifted to a lower field ( $\delta=-104.9$ ) compared to **9a**; a coupling to the Li atom was not observed.<sup>[33]</sup> The C atoms of the ethynyl unit resonated in a relatively narrow range at  $\delta=111.1$  and  $114.1$  and confirm the presence of a  $C\equiv C$  triple bond. The stretching vibration of the  $C\equiv C$  group was observed in the IR spectrum at  $1994\text{ cm}^{-1}$ , which is slightly outside of the characteristic range and may reflect the Li-ethynyl interaction (see below). The Li atom is coordinated by the P atom with a P–Li distance of  $2.618(3)\text{ \AA}$ , which is in the upper range of values reported for lithium phosphides in the literature (Figure 3).<sup>[33,34]</sup> It is additionally coordinated in a chelating manner by the N atoms of the TMEDA ligand and shows short contacts to the C atoms of the ethynyl group with  $Li1-C1=2.120(3)$  and  $Li1-C2=2.344(3)\text{ \AA}$ , which are in the characteristic range of Li–C interactions in organolithium derivatives.<sup>[35]</sup> The shorter one may reflect the importance of electrostatic interactions and charge separation with a relatively high negative partial charge at the  $\alpha$ -C atom of the ethynyl group. These Li–C interactions may cause the deviation of the  $C-C\equiv C-P$  group from linearity [P–C=C  $163.4(1)$  and  $C\equiv C-C$   $161.5(5)^\circ$ ; main component of the disordered group].



**Figure 3.** Molecular structure and numbering scheme of **9b**. Displacement ellipsoids are drawn at the 40% level. H atoms are omitted. Important bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ): P1–C1  $1.753(2)$ , C1–C2  $1.217(2)$ , P1–Li1  $2.618(3)$ , C1–Li1  $2.120(3)$ , C2–Li1  $2.344(3)$ , P1–C1–C2  $163.4(1)$ , C1–C2–C3  $161.5$ .

Crystal structure determination confirms the phosphide character of **9** and excludes the originally anticipated phosphallene nature. We conducted some secondary reactions with **9a** and were particularly interested in clearly excluding the equilibrium between both possible isomers in solution. Treatment of **9a** with HCl, Cl-SiMe<sub>3</sub> and Cl-PtBu<sub>2</sub> (Scheme 5)



Scheme 5. Secondary reactions of compound **9a**.

did not result in traces of products with a phosphallene structural motif. HCl yielded the P-H phosphine **10**, which has been obtained previously on another route<sup>[2,7a]</sup> and is easily identified by its characteristically large <sup>1</sup>J<sub>PH</sub> coupling constant of 245.0 Hz. Cl-SiMe<sub>3</sub> afforded the silylphosphine **11** in 70% yield, which showed relatively large coupling constants of all SiMe<sub>3</sub> atoms to phosphorus, <sup>29</sup>Si satellites in the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum and the typical resonances of an ethynyl group in the <sup>13</sup>C NMR spectrum at δ = 118.0 (P-C≡C) and 76.8 (P-C≡C). All observations are in accordance with the phosphine structure given in Scheme 5. **11** was isolated as a highly viscous liquid and could not be crystallized. P-P bond formation was observed upon treatment of **9a** with Cl-PtBu<sub>2</sub>. The crystalline compound **12** was isolated in 88% yield. It showed two doublets in the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum at δ = 42.5 (PtBu<sub>2</sub>) and -65.0 with a <sup>1</sup>J<sub>PP</sub> coupling constant of 190.5 Hz. The high field resonance is in the typical range of aryl-ethynylphosphines,<sup>[2,15c]</sup> while the signal at a lower field resembles values of dialkyldiphosphines, for example, P<sub>2</sub>tBu<sub>4</sub>.<sup>[36]</sup> The stretching vibration of the C≡C bond was detected in the normal range of the IR spectrum at 2149 cm<sup>-1</sup>. The P-P bond length of 2.245(av) Å corresponds to standard values (Figure 4).<sup>[37]</sup> The P-C distances correlate to the respective hybridization of the C atoms and are 1.755(av) (P1-C1; alkylnyl), 1.865(av) (P1-C41; aryl) and 1.902(av) Å (P-tBu). Both P atoms have a trigonal pyramidal surrounding with sum of the angles of 317.6 (P1) and 308.3° (P2; average values of two independent molecules). The difference may reflect the different bulk of the substituents.

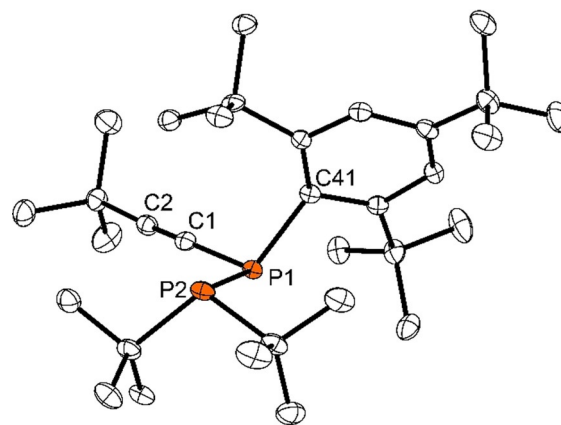
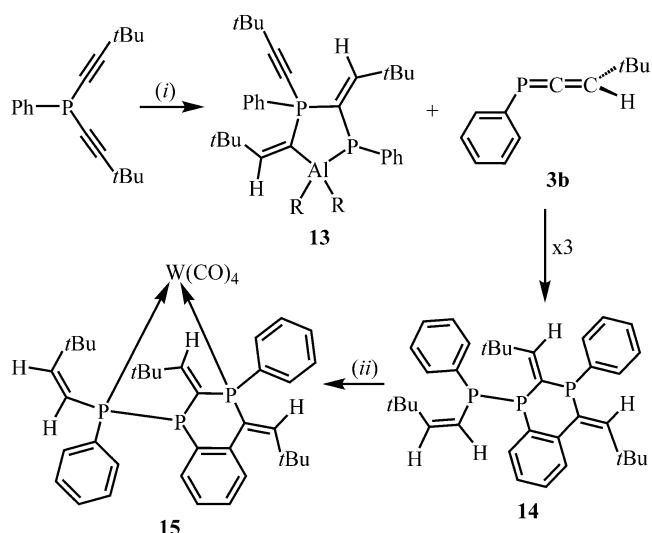


Figure 4. Molecular structure and numbering Scheme of **12**. Displacement ellipsoids are drawn at the 40% level. H atoms are omitted. Important bond lengths (Å) and angles (°), average values of two independent molecules: P1-P2 2.245, P1-C1 1.755, C1-C2 1.202, P1-C41 1.865(3), P2-tBu 1.902, C1-P1-C41 107.0, C5-P2-C6 109.5.

### A novel trimeric secondary product of an unstable phosphallene

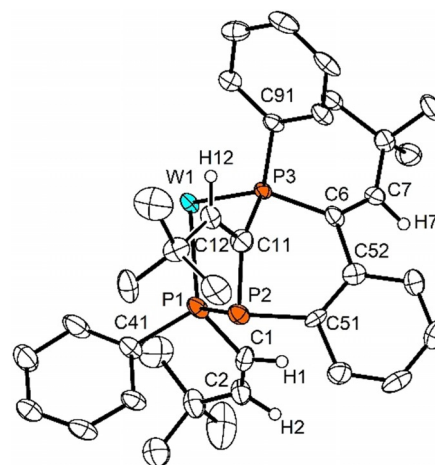
Unstable phosphallenes or persistent derivatives form various secondary products upon irradiation or in the heat. Dimers are known since many years which resulted from [2+2]- or [2+3]-cycloaddition reactions and have four-membered P<sub>2</sub>C<sub>2</sub> or C<sub>4</sub> rings (head-to-tail<sup>[6,7e]</sup> and head-to-head dimerization<sup>[10a,b,11a,b,d]</sup>) or adopt diphosphafulvene structures with five-membered P<sub>2</sub>C<sub>3</sub> heterocycles.<sup>[11b-d]</sup> Only recently we observed the formation of two unprecedented secondary products which are shown in Scheme 2 (4 and 5). The tricyclic phosphirane **5** is an isomer of a phosphallene and was obtained by rearrangement, C-H bond activation and P-C bond formation.<sup>[14]</sup> Compound **4** represents an unusual, asymmetric dimer with a P-P bond.<sup>[2]</sup> One P atom bears an alkynyl group, while the second one is bound to an alkenyl group. The generation of 3H-phosphallenes **3** by hydroalumination of dialkynylphosphines and elimination of aluminium alkynides<sup>[2]</sup> allows the generation of persistent (R = Mes\*) and transient species [R = Trip, Mes, CH(SiMe<sub>3</sub>)<sub>2</sub>], the latter could be trapped by coordination to transition metal atoms or showed a selective rearrangement reaction to yield compound **4** (Scheme 2). Ph-P=C=C(H)-tBu (**3b**) with the relatively small Ph group attached to P is accessible on a similar route (Scheme 6) and was identified by its characteristic <sup>31</sup>P NMR shift of δ = 64.6.<sup>[15a]</sup> It is very reactive and starts to decompose before the intermediately formed hydroalumination product similar to **2** was completely consumed, as was shown by thorough NMR investigations into the kinetics of these reactions.<sup>[15a]</sup> Decomposition results in the formation of several products (see Experimental Part). One of these crystallized from the reaction mixture and was identified as compound **13** (Scheme 6) which contains a five-membered AlP<sub>2</sub>C<sub>2</sub> heterocycle and results from the reaction of an intermediately formed FLP (**2**, Scheme 1) with the transient phosphallene **3b**.<sup>[15]</sup> Another secondary product (**14**) showed resonances of three different P atoms with three coupling con-



**Scheme 6.** Trimeric secondary product of phosphallaene **3b** and its  $W(CO)_4$  complex [(i) +  $HAIR_2$ – $R_2Al-C\equiv C-tBu$ ; (ii) +  $W(CO)_5(THF)$ , –THF, –CO;  $R = CH(SiMe_3)_2$ ].

starts of 12.6, 7.8 and 168.1 Hz. The latter is characteristic of a  $^1J_{PP}$  coupling and indicates the presence of a P–P bond. The concentration of **14** increased continuously, while the resonances of the phosphallaene **3b** disappeared after two days.<sup>[15a]</sup> The mixture of products with overlapping NMR signals did not allow the further characterization or unambiguous identification of **14**.

We, therefore, treated the reaction mixture with in situ generated  $W(CO)_5(THF)^{[38]}$  in order to favor crystallization and to isolate **14** by complexation (Scheme 6). Chromatographic work-up and crystallization of the oily residue from *n*-hexane afforded yellow crystals of **15** in an expectedly low yield of 17% based on diethynylphosphine. Crystal structure determination revealed a unique molecular structure with a six-membered  $P_2C_4$  heterocycle and an exocyclic P–P bond to one of the P atoms of the heterocycle. A trimer of the starting phosphallaene is formed which represents a new type of secondary products. The P–P bond length is with 2.252(2) Å in the normal range (Figure 5).<sup>[37]</sup> The central  $P_2C_4$  ring adopts an envelope conformation with the  $sp^2$ -hybridized C atoms C51, C52 and C6 and the P atoms P2 and P3 almost in a plane (maximum deviation 0.13 Å), the vinylic C atom C11 is 0.89 Å above the plane. The trimer coordinates to the W atom in a chelating manner via bonds to P1 and P3 [2.503(av) Å]. These P atoms have a distorted tetrahedral coordination sphere, while the atom P2 has a trigonal pyramidal surrounding. A benzene solution of the crystallized compound **15** showed three very similar sets of resonances in the  $^{31}P\{^1H\}$  NMR spectrum with an intensity ratio of 7:2:1 (see Experimental Part). The three P atoms have a chiral surrounding, and we assume that diastereomeric molecules are formed. Few data are discussed exclusively for the main component. The chemical shift of the P atom P2, which is not coordinated to W, is in the range of resonances observed for **14** ( $\delta = -35.1$ ). In accordance with their increased coordination numbers, the signals of the other P atoms are



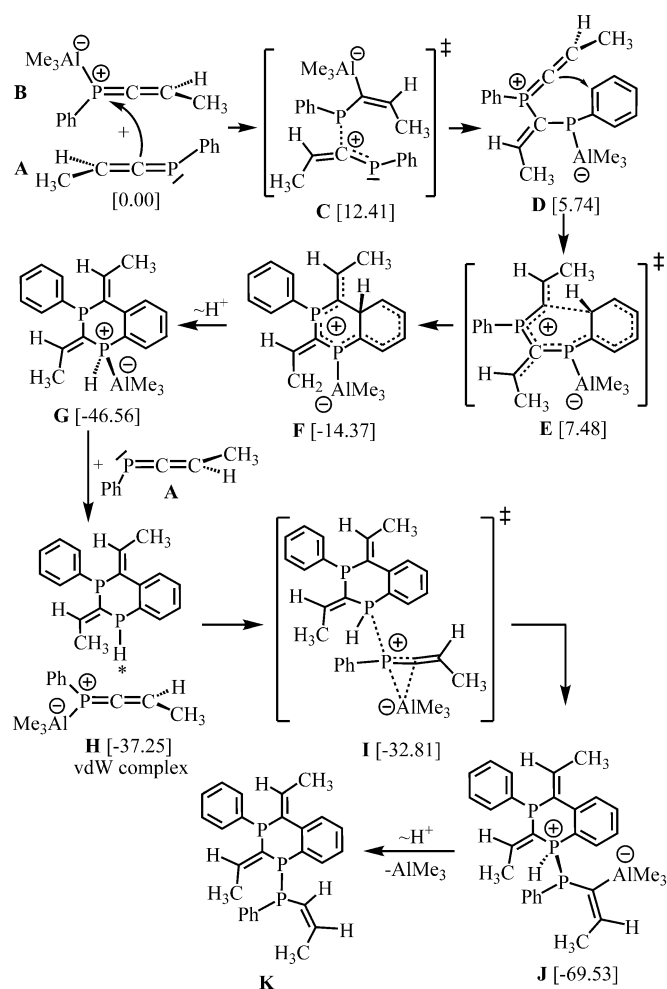
**Figure 5.** Molecular structure and numbering scheme of the W complex **15**. Displacement ellipsoids are drawn at the 40% level. H atoms with exception of the vinylic ones and CO ligands are omitted. Important bond lengths (Å) and angles (°): P1–W1 2.496(1), P3–W1 2.506(1), P1–P2 2.252(1), P2–C11 1.818(4), P3–C11 1.838(4), C51–C52 1.408(6), P1–C11–P3 113.0(2), C11–P2–C51 97.8(2), C11–P3–C6 104.1(2).

shifted to a lower field ( $\delta = 52.6$  and 12.1). The  $^1J_{PP}$  coupling constant remains almost unchanged, but the  $^2J_{PP}$  and  $^3J_{PP}$  values increase to 20.9 and 26.9 Hz.

The mechanism for the unexpected formation of trimer **14** was studied in detail by quantum chemical DFT model calculations.<sup>[32]</sup> On the basis of B3LYP/6-31G(d)<sup>[32b,c]</sup> + GD3BJ<sup>[32d,e]</sup> geometry optimizations TPSS/def2tzvp<sup>[32f,g]</sup> + GD3BJ<sup>[32d,e]</sup> calculations including the experimentally used solvent *n*-hexane (PCM<sup>[32h]</sup>) were performed. Trimerisation proceeds also in the dark, and the reaction outcome seems not to be influenced by light. Thus, in accord with the reaction conditions (thermal reactions) only closed shell calculations were performed. Discussion of relative Gibbs free energies ( $\Delta G_{298K}$ ) is based on the PCM-*n*-hexane solvent sphere model (kcal mol<sup>-1</sup>) with respect to the sum of two molecules of 1-phosphaallene **A** and one molecule of **B** (activated form of **A**; Scheme 7, see also Supporting Information for details). In all model calculations the *t*Bu group was replaced by a Me group. We used a retro-synthetic approach, starting from the final product **K** (the methyl analogue of **14**) employing reaction path calculations (stepwise varying the interatomic distances of the respective atoms) to localize transition states and minima. Their interconnections were checked by IRC-calculations.

Initial calculations showed that reactions of neutral species led to high kinetic barriers. Thus, in accordance with the reaction conditions, electrophilic catalysis was considered using Lewis acidic  $AlMe_3$  as a catalyst, which represents any electrophilic Al species present in the reaction mixture. Our suggested reaction mechanism starts with the highly reactive Lewis acid–base complex **B**, which reacted overall via several steps with two neutral phosphallaenes **A** to yield the trimeric compound **K**.

In the first step, we suggest an approach of the activated form **B** to the 1-phosphaallene **A** leading via transition state **C** and P–C bond formation to the P–C–P species **D**. **D** contains a



**Scheme 7.** Mechanism for the formation of **K** (methyl analogue of **14**); [TPSS/TPSS/def2tzvp + GD3BJ] + PCM (*n*-hexane);  $\Delta G_{298K}$  in kcal mol<sup>-1</sup> with respect to the sum of **2A** + **B**.

vinylidenephosphonium cation with cumulated P=C and C=C bonds and a highly reactive, electron rich central allene C atom (NBO charge:  $-0.3603$ ). This C atom approaches the *ortho*-C atom of a P-phenyl group to form a six-membered P<sub>2</sub>C<sub>4</sub> heterocycle **F** via transition state **E** (NBO-charge at the *ortho*-arene C atom:  $-0.2067$ ) in an unusual electrocyclization reaction. After intra- or intermolecular proton shift the intermediate **G** is formed, which already has the central structural motif of the trimer with two annulated six-membered rings, the aromatic C<sub>6</sub> ring and the P<sub>2</sub>C<sub>4</sub> heterocycle. The activating Lewis acid is coordinated by a P atom. Intermediate **G** reacts with a second 1-phosphaallene molecule **B**, which is activated by migration of AlMe<sub>3</sub>. Interestingly, we were able to localize a stationary point for the van der Waals complex **H**, which is close in energy to the transition state **I**. Relaxation and P–P bond formation results in the intermediate diphosphine **J** in a highly exothermic reaction. Compound **K**, as the analogue of the experimentally obtained trimer **14**, is finally formed after proton shift and release of AlMe<sub>3</sub>. As impressively shown, the formation of the trimeric phosphoallene requires a complicated multistep process and proceeds via relatively low activation

barriers (maximum 12.4 kcal mol<sup>-1</sup>) which are in accordance with the mild reaction conditions. Overall, the trimeric formula unit (**14**) is thermodynamically highly favoured over the starting material (**3b**), but its selective formation requires activation by a Lewis acid.

## Conclusions

3H-Phosphaallenes are highly functional molecules with Lewis basic P atoms, P=C and C=C double bonds and a C–H bond in  $\beta$ -position to phosphorus. They are known since the eighties of the last century, but their reactivity was scarcely elucidated. Recently we found facile access to persistent and reactive species in a multigram scale, which allows systematic investigations into their fascinating chemical properties. In this contribution we report on two hydroboration reactions with the persistent compound Mes<sup>\*</sup>-P=C=C(H)-*t*Bu. The insertion of C=C bonds into two B–H bonds was observed for BH<sub>3</sub>, while the electron-withdrawing C<sub>6</sub>F<sub>5</sub> groups of H<sub>2</sub>B-C<sub>6</sub>F<sub>5</sub> gave hydroboration followed by coordination of a second phosphoallene molecule and generation of a BP<sub>2</sub>C<sub>2</sub> heterocycle. The first compound represents a frustrated Lewis pair with the chelating arrangement of two P atoms and has intact P=C bonds, while in the second case an intermediate FLP with an activated Lewis acidic B atom favoured adduct formation. The B–P bond of the latter product is short, and its P atom has a planar environment. Its polarity should result in a nice reactivity as shown for a related molecule in the literature. Deprotonation of the C–H bond resulted in formation of a lithium alkynylphosphide with the Li atom coordinated to phosphorus and the P=C double bond replaced by a P–C single bond. The reactivity of the P=C bonds was demonstrated with the isolation of a trimeric secondary product of a sterically low shielded phosphoallene. It represents a nice addition to known decomposition products of phosphoallenes and results from P–P, P–C and C–C bond formation on a multistep pathway with low activation barriers, as shown by DFT calculations. Once more, these results confirm the exceptional and highly promising reactivity of phosphoallenes and their secondary products.

## Experimental Section

**General methods:** All manipulations were carried out under purified argon, using standard Schlenk techniques. Solvents were distilled from drying agents and degassed (THF and toluene over sodium/benzophenone; *n*-pentane and *n*-hexane over LiAlH<sub>4</sub>; pentafuorobenzene and dichloromethane over molecular sieves). NMR spectra were recorded in [D<sub>6</sub>]benzene and C<sub>6</sub>D<sub>5</sub>-CD<sub>3</sub> at ambient probe temperature using the following Bruker instruments: Avance I (<sup>1</sup>H, 400.13; <sup>13</sup>C, 100.62; <sup>31</sup>P, 161.98; <sup>29</sup>Si, 79.49; <sup>11</sup>B, 128.38; <sup>7</sup>Li, 155.51; <sup>15</sup>N, 40.55 MHz), Avance III (<sup>1</sup>H, 400.03; <sup>13</sup>C, 100.60; <sup>31</sup>P, 161.93; <sup>29</sup>Si, 79.47 MHz) and referenced internally to residual solvent resonances (chemical shift data in  $\delta$ ). <sup>13</sup>C, <sup>31</sup>P, <sup>7</sup>Li, <sup>11</sup>B and <sup>15</sup>N NMR spectra were all proton-decoupled. The assignment of NMR spectra is based on HSQC, HMBC, DEPT135, DEPT19.5 and H,H-ROESY data. Elemental analyses were determined by the microanalytical laboratory of the Westfälische Wilhelms Universität Münster. IR spectra were recorded as KBr pellets on a Shimadzu Prestige 21

spectrometer, electron impact mass spectra on a Finnigan MAT 95 mass spectrometer, HRMS (ESI-TOF) on Orbitrap LTQXL. The phosphallene **3a**<sup>[2]</sup> and the borane H<sub>2</sub>B-C<sub>6</sub>F<sub>5</sub>(SMe<sub>2</sub>)<sup>[28]</sup> were synthesized according to literature procedures. Improved procedures for the syntheses of Ph-P(C≡C-tBu)<sub>2</sub> and H-Al[CH(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> are given below. BH<sub>3</sub>(SMe<sub>2</sub>), Ph-PCl<sub>2</sub>, tBu<sub>2</sub>PCl, solutions of *tert*-butyl- and *n*-butyllithium in *n*-pentane, TMEDA, Me<sub>3</sub>SiCl and a solution of HCl in diethyl ether are commercially available and were used as purchased.

**Ph-P(C≡C-tBu)<sub>2</sub>**<sup>[39]</sup> A cooled (0 °C) solution of 3,3-dimethyl-1-butyne (6.42 g, 78.3 mmol) in 100 mL of diethyl ether was treated with a solution of *n*-butyllithium in *n*-hexane (1.6 M, 48.9 mL, 78.3 mmol). The solution was warmed to room temperature and stirred for 1 h. The resulting solution was added to a cooled (0 °C) solution of Ph-PCl<sub>2</sub> (7.00 g, 39.1 mmol) in 20 mL of diethyl ether. The mixture was warmed to room temperature overnight. All volatiles were removed in vacuum. The residue was extracted with 100 mL of *n*-pentane. After filtration the solvent was removed in vacuum, and the remaining highly viscous liquid was distilled in vacuum (70 °C, 10<sup>-3</sup> torr) (7.18 g, 68%). <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K): δ = -60.7.

**H-Al[CH(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>**<sup>[40]</sup> Al[CH(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub><sup>[41]</sup> (23.9 g, 47.4 mmol) was cooled with liquid N<sub>2</sub> and treated with AlH<sub>3</sub>·1.49NMe<sub>2</sub>Et (4.12 mL, 3.29 g, 23.7 mmol) without a solvent. The mixture was warmed to room temperature and heated to 120 °C for 2 h. The amine was removed in vacuum (10<sup>-3</sup> torr) at 100 °C. The residue was treated with hot *n*-hexane. Filtration and cooling afforded colorless needles of the hydride (23.5 g, 96%).

**Hydroboration of 3H-3-*tert*-butylphosphaallene 3a with BH<sub>3</sub>·SMe<sub>2</sub>; synthesis of 7:** A solution of 3H-3-*tert*-butylphosphaallene **3a** (0.35 g, 0.98 mmol) in 10 mL of *n*-hexane was cooled to -78 °C and treated with BH<sub>3</sub>·SMe<sub>2</sub> (46 μL, 0.037 g, 0.49 mmol). The mixture was warmed to room temperature overnight. All volatiles were removed in vacuum. The residue was recrystallized from 1,2-difluorobenzene at 3 °C to obtain **7** as yellow crystals (0.36 g, 87%). The crystals enclosed one molecule of difluorobenzene per formula unit of **7**. M.p. 210 °C; <sup>1</sup>H NMR (400 MHz, [D<sub>8</sub>]toluene, 300 K): δ = 7.48 (s, 4H; *m*-H), 6.30 (s br., 1H; B-H), 2.08 (overlap, m, 4H; CH<sub>2</sub>) 1.63 (s br., 36H; *o*-CMe<sub>3</sub>), 1.36 (s, 18H; *p*-CMe<sub>3</sub>), 0.96 ppm (s, 18H; CH<sub>2</sub>-tBu); <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, [D<sub>8</sub>]toluene, 300 K): δ = 200.8 (m br.; P=C), 154.6 (*o*-C Mes\*), 149.8 (*p*-C Mes\*), 141.2 (m br.; *i*-C Mes\*), 121.4 (*m*-C Mes\*), 53.3 (*pseudo-t*, <sup>2</sup>J<sub>C,P</sub> = <sup>4</sup>J<sub>C,P</sub> = 6.8 Hz; CH<sub>2</sub>), 38.4 (br.; *o*-CMe<sub>3</sub>), 35.0 (*p*-CMe<sub>3</sub>), 34.0 (br.; *o*-CMe<sub>3</sub>), 33.8 (CH<sub>2</sub>-CMe<sub>3</sub>), 31.6 (*p*-CMe<sub>3</sub>), 31.1 ppm (CH<sub>2</sub>-CMe<sub>3</sub>); <sup>11</sup>B{<sup>1</sup>H} NMR (160 MHz, [D<sub>8</sub>]toluene, 300 K): δ = 60.4 ppm; <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, [D<sub>8</sub>]toluene, 300 K): δ = 326.8 ppm; IR (KBr): ν̄ = 2957 (vs.), 2901 (vs.), 2866 (vs.) ν(CH); 2509 (vw), 2413 (m) ν(BH); 1778 (vw), 1751 (vw), 1616 (w), 1589 (m), 1508 (s) ν(C=C), aryl; 1476 (s), 1464 (m), 1393 (s), 1362 (vs.), 1258 (vs.), 1240 (s) δ(CH<sub>3</sub>); 1202 (m), 1128 (w), 1090 (m), 1045 (m), 1024 (vw), 1001 (vw), 984 (vw), 930 (vw), 903 (w), 874 (m), 845 (m), 756 (s) ν(CC), ν(BC); 646 (vw), 596 (w) aryl; 569 (vw), 488 (vw), 471 (vw), 451 (vw) cm<sup>-1</sup> ν(PC), δ(CC); MS (EI<sup>+</sup>, 20 eV, 323 K): *m/z* (%): 731 (15) [M]<sup>+</sup>, 674 (21) [M-tBu]<sup>+</sup>, 617 (9) [M-2tBu]<sup>+</sup>, 485 (22) [M-Mes-H]<sup>+</sup>; elemental analysis calcd (%) for C<sub>48</sub>H<sub>81</sub>P<sub>2</sub>B + C<sub>6</sub>H<sub>4</sub>F<sub>2</sub>: C 76.7, H 10.1; found: C 76.5, H 10.0.

**Hydroboration of 3H-3-*tert*-butylphosphaallene 3a with H<sub>2</sub>BC<sub>6</sub>F<sub>5</sub>·SMe<sub>2</sub>; synthesis of 8:** A cooled (-78 °C) solution of 3H-3-*tert*-butylphosphaallene **3a** (0.39 g, 1.09 mmol) in 10 mL of *n*-hexane was treated with BH<sub>2</sub>C<sub>6</sub>F<sub>5</sub>·SMe<sub>2</sub> (0.13 g, 0.54 mmol). The mixture was warmed to room temperature overnight. All volatiles were removed in vacuum. Compound **8** crystallized from a saturated solution in dichloromethane at 3 °C as yellow crystals (0.37 g, 70%). The crystals enclosed one molecule of CH<sub>2</sub>Cl<sub>2</sub> per formula of **8**. M.p. 137 °C; <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K): δ = 7.70 (overlap,

dd, <sup>4</sup>J<sub>H,P</sub> = 2.1 Hz, <sup>4</sup>J<sub>H,H</sub> = 2.1 Hz, 1H; *m*-H Mes\* PB), 7.70 (overlap, dd, <sup>4</sup>J<sub>H,P</sub> = 3.3 Hz, <sup>4</sup>J<sub>H,H</sub> = 2.1 Hz, 1H; *m*-H Mes\* PC<sub>2</sub>), 7.64 (dd, <sup>4</sup>J<sub>H,P</sub> = 4.6 Hz, <sup>4</sup>J<sub>H,H</sub> = 2.1 Hz, 1H; *m*-H PC<sub>2</sub>), 7.49 (dd, <sup>4</sup>J<sub>H,P</sub> = 4.6 Hz, <sup>4</sup>J<sub>H,H</sub> = 2.1 Hz, 1H; *m*-H Mes\* PB), 6.08 (dd, <sup>3</sup>J<sub>H,P</sub> = 50.4 Hz, <sup>3</sup>J<sub>H,H</sub> = 12.6 Hz, 1H; C=CH), 2.85 (dd, <sup>2</sup>J<sub>H,P</sub> = 25.4 Hz, <sup>3</sup>J<sub>H,H</sub> = 5.3 Hz, 1H; P-CH-B), 2.08 (ddd, <sup>3</sup>J<sub>H,P</sub> = 24.1 Hz, <sup>2</sup>J<sub>H,H</sub> = 14.8 Hz, <sup>3</sup>J<sub>H,H</sub> = 5.3 Hz, 1H; CH<sub>2</sub>), 1.92 (s, 9H; *o*-CMe<sub>3</sub> Mes\* PC<sub>2</sub>), 1.91 (s, 9H; *o*-CMe<sub>3</sub> Mes\* PB), 1.89 (overlap, 1H; CH<sub>2</sub>), 1.80 (s, 9H; *o*-CMe<sub>3</sub> Mes\* PC<sub>2</sub>), 1.53 (s, 9H; *o*-CMe<sub>3</sub> Mes\* PB), 1.31 (s, 9H; *p*-CMe<sub>3</sub> Mes\* PC<sub>2</sub>), 1.18 (s, 9H; *p*-CMe<sub>3</sub> Mes\* PB), 0.93 (s, 9H; C=C-CMe<sub>3</sub>), 0.45 ppm (s, 9H; CH<sub>2</sub>-CMe<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K): δ = 161.8 (dd, <sup>2</sup>J<sub>C,P</sub> = 35.8 Hz, <sup>4</sup>J<sub>C,P</sub> = 2.3 Hz; *o*-C Mes\* PC<sub>2</sub>), 158.0 (d, <sup>2</sup>J<sub>C,P</sub> = 2.8 Hz; *o*-C Mes\* PB), 157.6 (d, <sup>2</sup>J<sub>C,P</sub> = 6.2 Hz; *o*-C Mes\* PC<sub>2</sub>), 156.2 (dd, <sup>2</sup>J<sub>C,P</sub> = 10.2 Hz, <sup>4</sup>J<sub>C,P</sub> = 2.5 Hz; *o*-C Mes\* PB), 153.3 (d, <sup>4</sup>J<sub>C,P</sub> = 3.4 Hz; *p*-C Mes\* PB), 151.3 (d, <sup>4</sup>J<sub>C,P</sub> = 2.0 Hz; *p*-C Mes\* PC<sub>2</sub>), 142.2 (dd, <sup>2</sup>J<sub>C,P</sub> = 15.1 and 9.4 Hz; C=CH), 136.2 (dd, <sup>1</sup>J<sub>C,P</sub> = 53.8 and 27.8 Hz; C=CH), 131.2 (dd, <sup>1</sup>J<sub>C,P</sub> = 60.0 Hz, <sup>3</sup>J<sub>C,P</sub> = 5.8 Hz; *i*-C Mes\* PC<sub>2</sub>), 127.3 (*m*-C Mes\* PC<sub>2</sub>), 126.0 (d, <sup>3</sup>J<sub>C,P</sub> = 10.8 Hz; *m*-C Mes\* PB), 124.6 (d, <sup>3</sup>J<sub>C,P</sub> = 13.0 Hz; *m*-C Mes\* PB), 123.1 (d, <sup>3</sup>J<sub>C,P</sub> = 13.4 Hz; *m*-C Mes\* PC<sub>2</sub>), 120.8 (d, <sup>1</sup>J<sub>C,P</sub> = 39.9 Hz; *i*-C Mes\* PB), 116 (s. br.; *i*-C C<sub>6</sub>F<sub>5</sub>), 50.2 (dd, <sup>2</sup>J<sub>C,P</sub> = 9.9 Hz, <sup>3</sup>J<sub>C,P</sub> = 39.7 Hz, CH<sub>2</sub>), 41.1 (*o*-CMe<sub>3</sub> Mes\* PC<sub>2</sub>), 40.6 (d, <sup>3</sup>J<sub>C,P</sub> = 2.0 Hz; *o*-CMe<sub>3</sub> Mes\* PB), 40.1 (d, <sup>3</sup>J<sub>C,P</sub> = 9.6 Hz; *o*-CMe<sub>3</sub> Mes\* PC<sub>2</sub>), 39.4 (d, <sup>3</sup>J<sub>C,P</sub> = 3.1 Hz, *o*-CMe<sub>3</sub> Mes\* PB), 37.6 (dd, <sup>3</sup>J<sub>C,P</sub> = 6.0 and 4.2 Hz, C=CH-CMe<sub>3</sub>), 35.4 (*o*-CMe<sub>3</sub> Mes\* PC<sub>2</sub>), 35.1 (d, <sup>5</sup>J<sub>C,P</sub> = 1.0 Hz; *p*-CMe<sub>3</sub> Mes\* PB), 34.9 (overlap; *p*-CMe<sub>3</sub> Mes\* PC<sub>2</sub>), 34.9 (overlap, d, <sup>4</sup>J<sub>C,P</sub> = 13.2 Hz; *o*-CMe<sub>3</sub> Mes\* PC<sub>2</sub>), 34.6 (overlap; *o*-CMe<sub>3</sub> Mes\* PB), 34.5 (overlap; *o*-CMe<sub>3</sub> Mes\* PB), 32.0 (dd, <sup>3</sup>J<sub>C,P</sub> = 3.4 Hz, <sup>3</sup>J<sub>C,P</sub> = 1.3 Hz; CH<sub>2</sub>-CMe<sub>3</sub>), 31.2 (*p*-CMe<sub>3</sub> Mes\* PC<sub>2</sub>), 31.0 (*p*-CMe<sub>3</sub> Mes\* PB), 30.8 (br., overlap; P-CH-B), 30.3 (C=CH-CMe<sub>3</sub>), 29.0 ppm (CH<sub>2</sub>-CMe<sub>3</sub>); with the exception of *i*-C the resonances of the C<sub>6</sub>F<sub>5</sub> group are poorly resolved and could not be identified and assigned unambiguously; <sup>11</sup>B{<sup>1</sup>H} NMR (128 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K): δ = 53.2 ppm; <sup>19</sup>F{<sup>1</sup>H} NMR (376 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K): δ = -127.2 (dd, J<sub>FF</sub> = 23 and 10 Hz, 1F; *o*-F), -128.9 (dd, J<sub>FF</sub> = 24 and 8 Hz, 1F; *o*-F), -154.9 (td, J<sub>FF</sub> = 20 and 4 Hz, 1F; *p*-F), -162.1 (ddd, J<sub>FF</sub> = 25, 20 and 9 Hz, 1F; *m*-F), -163.7 ppm (ddd, J<sub>FF</sub> = 24, 20 and 9 Hz, 1F; *m*-F); <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K): δ = 30.3 (br.; B-P), 25.3 ppm (d, <sup>2</sup>J<sub>P,P</sub> = 89.2 Hz; PC<sub>2</sub>); IR (KBr): ν̄ = 2957 (vs.), 2905 (vs.), 2868 (vs.) ν(CH); 1643 (m), 1597 (s), 1514 (vs.) ν(C=C), aryl; 1474 (vs.), 1393 (vs.), 1362 (vs.), 1298 (m), 1279 (vw), 1234 (s) δ(CH<sub>3</sub>); 1211 (s), 1194 (m), 1136 (s), 1123 (s), 1061 (w), 1013 (m), 974 (vs.), 901 (vw), 880 (m), 820 (w), 770 (m), 741 (s), 704 (vw) ν(CC), ν(CF), ν(CB); 665 (w), 600 (w) aryl; 581 (vw), 525 (vw), 503 (vw), 484 (vw), 447 (vw) cm<sup>-1</sup> ν(PC), ν(BP), δ(CC); MS (EI<sup>+</sup>, 20 eV, 353 K): *m/z* (%) = 897 (25) [M]<sup>+</sup>, 651 (100) [M-Mes<sup>+</sup>-H]<sup>+</sup>; elemental analysis calcd (%) for C<sub>54</sub>H<sub>80</sub>P<sub>2</sub>BF<sub>5</sub> + CH<sub>2</sub>Cl<sub>2</sub>: C 67.3, H 8.4; found: C 67.6, H 8.5.

**Deprotonation of 3H-3-*tert*-butylphosphaallene 3a, synthesis of 9:** A solution of 3H-3-*tert*-butylphosphaallene **3a** (0.10 g, 0.28 mmol) in 5 mL of *n*-hexane was cooled to -78 °C and treated with a solution of *tert*-butyllithium (147 μL, 1.9 M, 0.28 mmol) in *n*-pentane. The mixture was warmed to room temperature overnight. Alternatively *n*-butyllithium may be used, but requires warming to 75 °C. The intermediate lithium compound **9a** was isolated as a yellow highly viscous liquid, which could not be crystallized from different solvents. It showed broad resonances in the NMR spectra, which did not allow the complete assignment. Selected NMR data: <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K): δ = 117.1 (P-C≡C), 97.7 ppm (P-C≡C); <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K): δ = -136.0 ppm. *N,N,N',N'*-Tetramethylethylenediamine (TMEDA) (42 μL, 0.28 mmol) was, therefore, added to the reaction mixture. The solution was concentrated and cooled to 3 °C to obtain yellow crystals of **9b** (0.11 g, 82%). M.p. 137 °C; <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K): δ = 7.34 (d, <sup>4</sup>J<sub>H,P</sub> = 1.7 Hz, 2H; *m*-H), 2.01 (s, 18H; *o*-CMe<sub>3</sub>), 1.71 (s, 12H;



NMe<sub>2</sub>), 1.67 (s, 4H; *N*-C<sub>2</sub>H<sub>4</sub>-N), 1.41 (s, 9H; *p*-CMe<sub>3</sub>), 1.26 ppm (s, 9H; C≡C-*t*Bu); <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K): δ = 152.3 (d, <sup>2</sup>J<sub>C,P</sub> = 6.3 Hz; *o*-C Mes\*), 146.2 (d, <sup>1</sup>J<sub>C,P</sub> = 79.1 Hz; *i*-C Mes\*), 142.0 (s; *p*-C Mes\*), 121.1 (d, <sup>3</sup>J<sub>C,P</sub> = 1.8 Hz; *m*-C Mes\*), 114.1 (d, <sup>2</sup>J<sub>C,P</sub> = 8.8 Hz; C≡C-*t*Bu), 111.1 (d, <sup>1</sup>J<sub>C,P</sub> = 89.1 Hz; C≡C-*t*Bu), 56.6 (*N*-C<sub>2</sub>H<sub>4</sub>-N), 45.8 (NMe<sub>2</sub>), 39.2 (d, <sup>3</sup>J<sub>C,P</sub> = 1.1 Hz; *o*-CMe<sub>3</sub>), 34.4 (*p*-CMe<sub>3</sub>), 33.8 (d, <sup>4</sup>J<sub>C,P</sub> = 11.3 Hz; *o*-CMe<sub>3</sub>), 32.7 (d, <sup>4</sup>J<sub>C,P</sub> = 2.6 Hz; C≡C-CMe<sub>3</sub>), 32.0 (*p*-CMe<sub>3</sub>), 31.3 ppm (d, <sup>3</sup>J<sub>C,P</sub> = 2.2 Hz; C≡C-CMe<sub>3</sub>); <sup>7</sup>Li{<sup>1</sup>H} NMR (105 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K): δ = 0.98 ppm; <sup>15</sup>N{<sup>1</sup>H} HMBC-NMR (41 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K): δ = 19 ppm; <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K): δ = -104.9 ppm; IR (KBr): ν = 2970 (vs.), 2947 (vs.), 2901 (vs.), 2864 (vs.), 2793 (s) ν(CH); 1994 (s) ν(C≡C); 1722 (vw), 1653 (vw), 1589 (m), 1528 (w) ν(C=C, aryl); 1464 (vs.), 1391 (s), 1360 (vs.), 1285 (s), 1240 (vs.) δ(CH<sub>3</sub>); 1198 (s), 1179 (m), 1157 (m), 1128 (w), 1098 (vw), 1078 (vw), 1063 (w), 1034 (s), 1020 (m), 947 (m), 930 (w), 901 (vw), 878 (m), 808 (vw), 791 (w), 770 (w), 743 (m) ν(CC), ν(CN); 648 (vw), 623 (w), 596 (w) aryl; 544 (w), 482 (m), 438 (w) cm<sup>-1</sup> ν(PC), δ(CC); MS (EI<sup>+</sup>, 20 eV, 298 K): *m/z* (%) = 357 (14) [M-Li(TMEDA)]<sup>+</sup>; elemental analysis calcd for C<sub>30</sub>H<sub>54</sub>PLiN<sub>2</sub>: C 74.9, H 11.3, N 5.8; found: C 74.5, H 11.2, N 5.4.

**Reaction of 9a with hydrogen chloride; synthesis of 10:** [2,7a] A solution of 3H-3-*tert*-butylphosphaallen **3a** (0.10 g, 0.28 mmol) in 5 mL of *n*-hexane was treated at -78 °C with a solution of *tert*-butyllithium (147 μL, 1.9 M, 0.28 mmol) in *n*-pentane. The mixture was warmed to room temperature overnight. After cooling to -78 °C, a solution of HCl in diethyl ether (280 μL, 1 M, 0.28 mmol) was added. The mixture was warmed to room temperature. All volatiles were removed in vacuum. The solid residue was treated with 10 mL of *n*-pentane. After filtration and removal of all volatiles from the filtrate compound **10** [2] was obtained as a colorless oil (0.092 g, 92%). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K): δ = 7.60 (d, <sup>3</sup>J<sub>H,P</sub> = 2.5 Hz, 2H; *m*-H), 5.94 (d, <sup>1</sup>J<sub>H,P</sub> = 245.0 Hz, 1H; *P*-H), 1.75 (s, 18H; *o*-CMe<sub>3</sub>), 1.23 (s, 9H; *p*-CMe<sub>3</sub>), 1.02 ppm (s, 9H; C≡C-CMe<sub>3</sub>); <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K): δ = -102.1 ppm.

**Reaction of 9a with chlorotrimethylsilane, synthesis of 11:** A solution of 3H-3-*tert*-butylphosphaallene **3a** (0.39 g, 1.09 mmol) in 10 mL of *n*-hexane was cooled to -78 °C and treated with a solution of *tert*-butyllithium in *n*-pentane (570 μL, 1.9 M, 1.09 mmol). The mixture was warmed to room temperature overnight. Chlorotrimethylsilane (0.12 g, 137 μL, 1.09 mmol) was added to the cooled (-78 °C) solution. Warming to room temperature, filtration and evaporation afforded a yellowish oil of **11** (0.33 g, 70%). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K): δ = 7.49 (d, <sup>4</sup>J<sub>H,P</sub> = 2.7 Hz, 2H; *m*-H), 1.76 (s, 18H; *o*-CMe<sub>3</sub>), 1.30 (s, 9H; *p*-CMe<sub>3</sub>), 1.22 (s, 9H; C≡C-*t*Bu), 0.06 ppm (d, <sup>2</sup>J<sub>H,P</sub> = 5.5 Hz, 9H; TMS); <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K): δ = 157.1 (d, <sup>2</sup>J<sub>C,P</sub> = 12.8 Hz; *o*-C Mes\*), 149.2 (d, <sup>4</sup>J<sub>C,P</sub> = 2.7 Hz; *p*-C Mes\*), 129.7 (d, <sup>1</sup>J<sub>C,P</sub> = 39.2 Hz; *i*-C Mes\*), 122.1 (d, <sup>3</sup>J<sub>C,P</sub> = 8.5 Hz; *m*-C Mes\*), 118.0 (d, <sup>2</sup>J<sub>C,P</sub> = 4.4 Hz; C≡C-*t*Bu), 76.8 (d, <sup>1</sup>J<sub>C,P</sub> = 23.5 Hz; C≡C-*t*Bu), 39.0 (d, <sup>3</sup>J<sub>C,P</sub> = 4.5 Hz; *o*-CMe<sub>3</sub>), 34.9 (d, <sup>5</sup>J<sub>C,P</sub> = 0.9 Hz; *p*-CMe<sub>3</sub>), 34.4 (d, <sup>4</sup>J<sub>C,P</sub> = 7.4 Hz; *o*-CMe<sub>3</sub>), 31.4 (*p*-CMe<sub>3</sub>), 31.0 (d, <sup>4</sup>J<sub>C,P</sub> = 1.7 Hz; C≡C-CMe<sub>3</sub>), 29.4 (d, <sup>3</sup>J<sub>C,P</sub> = 1.6 Hz; C≡C-CMe<sub>3</sub>), -0.1 ppm (d, <sup>2</sup>J<sub>C,P</sub> = 15.4 Hz; TMS); <sup>29</sup>Si{<sup>1</sup>H} NMR (79 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K): δ = 8.5 ppm (d, <sup>1</sup>J<sub>P,Si</sub> = 15.2 Hz); <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K): δ = -109.8 ppm; MS (EI<sup>+</sup>, 20 eV, 303 K): *m/z* (%) = 430 (77) [M]<sup>+</sup>, 357 (32) [M-TMS]<sup>+</sup>.

**Reaction of 9a with di-*tert*-butylchlorophosphine; synthesis of 12:** A solution of 3H-3-*tert*-butylphosphaallen **3a** (0.39 g, 1.09 mmol) in 10 mL of *n*-hexane was cooled to -78 °C and treated with a solution of *tert*-butyllithium in *n*-pentane (570 μL, 1.9 M, 1.09 mmol). The mixture was warmed to room temperature overnight. After cooling to -78 °C, di-*tert*-butylchlorophosphine (0.20 g, 205 μL, 1.11 mmol) was added. Warming to room temperature, filtration, removal of the solvents in vacuum and recrystallization of

the residue from a saturated solution in pretafluorobenzene afforded colorless crystals of **12** at -30 °C (0.48 g, 88%). M.p. 137 °C; <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K): δ = 7.50 (s br., 2H; *m*-H), 1.90 (s br., 18H; *o*-CMe<sub>3</sub>), 1.53 (d, <sup>3</sup>J<sub>H,P</sub> = 10.5 Hz, 9H; *P*-CMe<sub>3</sub>), 1.28 (s, 9H; *p*-CMe<sub>3</sub>), 1.23 (s, 9H; C≡C-*t*Bu), 0.83 ppm (d, <sup>3</sup>J<sub>H,P</sub> = 10.3 Hz, 9H; *P*-CMe<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K): δ = 159.6 (br.; *o*-C Mes\*), 150.5 (d, <sup>4</sup>J<sub>C,P</sub> = 2.5 Hz; *p*-C Mes\*), 128.8 (dd, <sup>1</sup>J<sub>C,P</sub> = 48.5 Hz, <sup>2</sup>J<sub>C,P</sub> = 13.3 Hz; *i*-C Mes\*), 125.9 (br.; *m*-C Mes\*), 122.9 (br.; *m*-C Mes\*), 116.5 (d, <sup>2</sup>J<sub>C,P</sub> = 2.7 Hz; C≡C-*t*Bu), 81.4 (dd, <sup>1</sup>J<sub>C,P</sub> = 29.1 Hz, <sup>2</sup>J<sub>C,P</sub> = 6.5 Hz; C≡C-*t*Bu), 41.9 and 40.1 (br.; *o*-CMe<sub>3</sub>), 35.3 (dd, <sup>1</sup>J<sub>C,P</sub> = 35.1 Hz, <sup>2</sup>J<sub>C,P</sub> = 4.7 Hz; *P*-CMe<sub>3</sub>), 35.1 (br.; *o*-CMe<sub>3</sub>), 34.7 (d, <sup>5</sup>J<sub>C,P</sub> = 0.9 Hz; *p*-CMe<sub>3</sub>), 34.3 (br.; *o*-CMe<sub>3</sub>), 33.6 (dd, <sup>1</sup>J<sub>C,P</sub> = 33.8 Hz, <sup>2</sup>J<sub>C,P</sub> = 22.8 Hz; *P*-CMe<sub>3</sub>), 31.5 (dd, <sup>2</sup>J<sub>C,P</sub> = 4.1 Hz, <sup>3</sup>J<sub>C,P</sub> = 13.0 Hz; *P*-CMe<sub>3</sub>), 31.3 (*p*-CMe<sub>3</sub>), 30.5 (d, <sup>4</sup>J<sub>C,P</sub> = 1.8 Hz; C≡C-CMe<sub>3</sub>), 30.0 (dd, <sup>2</sup>J<sub>C,P</sub> = 5.6 Hz, <sup>3</sup>J<sub>C,P</sub> = 13.8 Hz; *P*-CMe<sub>3</sub>), 29.2 ppm (d, <sup>3</sup>J<sub>C,P</sub> = 1.6 Hz; C≡C-CMe<sub>3</sub>); <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K): δ = 42.5 (d, <sup>1</sup>J<sub>P,P</sub> = 190.5 Hz; *Pt*Bu<sub>2</sub>), -65.0 ppm [d, <sup>1</sup>J<sub>P,P</sub> = 190.5 Hz, *P*(Mes\*)(ethynyl)]; IR (KBr): 2970 (vs.), 2949 (vs.), 2899 (vs.), 2860 (vs.), 2706 (vw) ν(CH); 2149 (w) ν(C≡C); 1707 (w), 1690 (w), 1653 (vw), 1589 (s), 1530 (m), 1514 (w) ν(C=C, aryl); 1476 (vs.), 1460 (s), 1391 (s), 1362 (vs.), 1310 (w), 1254 (vs.), 1238 (sh) δ(CH<sub>3</sub>); 1198 (m), 1175 (s), 1123 (m), 1070 (vw), 1018 (w), 984 (m), 939 (w), 926 (w), 895 (w), 872 (m), 806 (w), 770 (m), 752 (w), 716 (vw) ν(CC); 648 (w), 596 (m) aryl; 561 (w), 519 (w), 471 (vw), 453 (vw) cm<sup>-1</sup> ν(PC), δ(CC); MS (EI<sup>+</sup>, 20 eV, 313 K): *m/z* (%) = 502 (18) [M]<sup>+</sup>, 445 (16) [M-*t*Bu]<sup>+</sup>, 389 (61) [M-*t*Bu-butene]<sup>+</sup>, 357 (69) [M-*Pt*Bu<sub>2</sub>]<sup>+</sup>; elemental analysis calcd for C<sub>32</sub>H<sub>56</sub>P<sub>2</sub>: C 76.4, H 11.2; found: C 76.0; H 10.8.

**Trimer of phenyl-3H-3-*tert*-butylphosphaallene (14):** Phenyl-di(*tert*-butylethynyl)phosphine **1a** (0.64 g, 2.37 mmol) was dissolved in 15 mL of *n*-hexane and treated with a solution of H-Al[CH(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (0.82 g, 2.37 mmol) in 45 mL of *n*-hexane. The mixture was stirred for 4 d at room temperature. Several compounds were detected in its <sup>31</sup>P NMR spectrum: the phosphallene trapping product **13** [15] (δ = -10.3 and -95.0 ppm), the intermediate FLP **2** [R = Ph, R' = *t*Bu, R'' = CH(SiMe<sub>3</sub>)<sub>2</sub>] shown in Scheme 1 (δ = -43.3 ppm) [15a] and the starting dialkynylphosphine **1a** (δ = -60.8 ppm) [39]. A signal at δ = -59.6 ppm could not be assigned. The trimer **14** of the phosphallene **3b** was identified by the characteristic coupling pattern in the <sup>31</sup>P NMR spectrum: <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K): δ = -17.6 (*J*<sub>PP</sub> = 12.6 and 7.8 Hz; P3), -25.1 (<sup>1</sup>*J*<sub>PP</sub> = 168.1 Hz, *J*<sub>PP</sub> = 7.8 Hz), -43.3 ppm (<sup>1</sup>*J*<sub>PP</sub> = 168.1 Hz, *J*<sub>PP</sub> = 12.6 Hz).

**W(CO)<sub>4</sub> complex (15) of the phosphallene trimer:** A solution of impure **14** in *n*-hexane was synthesized as described in the previous section. It was treated with a solution W(CO)<sub>5</sub>(THF) which was in situ generated by irradiation of W(CO)<sub>6</sub> (1.11 g, 3.15 mmol) in 40 mL of THF. The mixture was stirred for 2 h at room temperature. All volatiles were removed in vacuum, and the crude product was purified by column chromatography (SiO<sub>2</sub>, eluent: *n*-hexane/EtOAc). The water content of the usually employed silica gel is sufficient to completely destroy the organoaluminum by-products by hydrolysis. A yellow oil of compound **15** remained after removal of the solvents. Pure **15** was obtained as yellow crystals by crystallization from a saturated solution in *n*-hexane at -45 °C (0.35 g, 17%). M.p. 172 °C. Three very similar sets of resonances were observed in the NMR spectra, which probably result from diastereomers of **15**. The ratio of the isomers is 7:2:1. Only the NMR spectra of the main isomer could be assigned completely, the remaining two isomers were identified by their characteristic <sup>31</sup>P{<sup>1</sup>H} NMR data. Assignment is based on the numbering Scheme of the atoms in the molecular structure (Figure 5): Phenyl group at P1: C41 to C46; phenyl group at P3: C91 to C96, hindered rotation results in six <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR signals; bridging aryl group: C51 to C56 with C51 and

C52 in the  $P_2C_4$  ring; vinyl group at P1: C1-C2-C3-C31/C32/C33; vinyl group bridging P2 and P3: C11 to C133; vinyl group bridging P3 and C52: C6 to C83. **Main diastereomer:**  $^1H$  NMR (400 MHz,  $C_6D_6$ , 300 K):  $\delta$  = 8.65 (dd,  $^3J_{H,P}$  = 12.3 Hz,  $^3J_{H,H}$  = 7.4 Hz, 1H; C92-H), 8.33 (dd,  $^3J_{H,P}$  = 11.4 Hz,  $^3J_{H,H}$  = 8.2 Hz, 2H; C42/C46-H), 7.71 (ddd,  $^3J_{H,P}$  = 16.0 Hz,  $^3J_{H,H}$  = 7.3 Hz,  $^4J_{H,H}$  = 1.6 Hz, 1H; C56-H), 7.56 (d,  $^3J_{H,H}$  = 7.3 Hz, 1H; C53-H), 7.48 (dd,  $^3J_{H,P}$  = 8.0 Hz,  $^3J_{H,H}$  = 6.8 Hz, 1H; C96-H), 7.21 (overlap, 1H; C93-H), 7.20 (overlap, 3H; C43/C45-H and C94-H), 7.19 (overlap, 1H; C54-H), 7.11 (ddd,  $^4J_{H,P}$  = 1.4 Hz,  $^5J_{H,P}$  = 1.4 Hz,  $^3J_{H,H}$  = 7.3 Hz, 1H; C55-H), 7.06 (overlap, 2H; C44-H and C95-H), 6.51 (d,  $^3J_{H,P}$  = 32.1 Hz, 1H; C7-H), 5.55 (overlap, dd,  $^3J_{H,P}$  = 30.9 Hz,  $^4J_{H,P}$  = 4.3 Hz, 1H; C2-H), 5.53 (overlap, dd,  $^2J_{H,P}$  = 20 Hz,  $^3J_{H,P}$  = 15 Hz, 1H; C1-H), 5.48 (dd,  $^3J_{H,P}$  = 30.0 Hz,  $^3J_{H,P}$  = 18.0 Hz, 1H; C12-H), 1.17 (s, 9H; C8-tBu), 0.88 (s, 9H; C3-tBu), 0.72 ppm (s, 9H; C13-tBu);  $^{13}C\{^1H\}$  NMR (100 MHz,  $C_6D_6$ , 300 K):  $\delta$  = 209.8 (dd,  $^2J_{C,P}$  = 26.3 Hz,  $^2J_{C,P}$  = 5.6 Hz; CO), 207.0 (dd,  $^2J_{C,P}$  = 27.8 Hz,  $^2J_{C,P}$  = 6.6 Hz; CO), 203.6 (dd,  $^2J_{C,P}$  = 6.8 Hz,  $^2J_{C,P}$  = 3.5 Hz; CO), 202.4 (dd,  $^2J_{C,P}$  = 8.9 Hz,  $^2J_{C,P}$  = 7.2 Hz; CO), 158.7 (d,  $^2J_{C,P}$  = 11.8 Hz; C7), 158.2 (ddd,  $^2J_{C,P}$  = 22.3 Hz,  $^2J_{C,P}$  = 10.3 Hz,  $^3J_{C,P}$  = 3.5 Hz; C12), 157.1 (dd,  $^2J_{C,P}$  = 2.5 Hz,  $^3J_{C,P}$  = 1.8 Hz; C2), 148.2 (ddd,  $^2J_{C,P}$  = 4.2 Hz,  $^2J_{C,P}$  = 1.5 Hz,  $^3J_{C,P}$  = 1.5 Hz; C52), 138.9 (dd,  $J_{C,P}$  = 59.0 and 4.5 Hz; C56), 138.8 (ddd,  $^1J_{C,P}$  = 30.7 Hz,  $^2J_{C,P}$  = 23.7 Hz,  $^4J_{C,P}$  = 3.9 Hz; C41), 138.3 (overlap, dd,  $J_{C,P}$  = 14 Hz,  $^1J_{C,P}$  = 12 Hz; C11), 137.0 (d,  $^2J_{C,P}$  = 22.3 Hz; C92), 136.1 (ddd,  $^1J_{C,P}$  = 29.5 Hz,  $^3J_{C,P}$  = 8.0 Hz,  $^4J_{C,P}$  = 1.5 Hz; C91), 135.7 (dd,  $^2J_{C,P}$  = 7.3 Hz,  $^3J_{C,P}$  = 12.8 Hz; C42), 133.3 (ddd,  $^1J_{C,P}$  = 27.7 Hz,  $^2J_{C,P}$  = 4.0 Hz,  $^2J_{C,P}$  = 4.0 Hz; C51), 132.5 (C96), 131.8 (d,  $^1J_{C,P}$  = 24.6 Hz; C6), 131.4 (overlap; C54 and C94), 131.2 (d,  $^3J_{C,P}$  = 2.3 Hz; C95), 130.5 (d,  $^4J_{C,P}$  = 2.4 Hz; C44), 129.5 (d,  $^3J_{C,P}$  = 13.1 Hz; C93), 129.2 (C53), 128.8 (d,  $^3J_{C,P}$  = 10.4 Hz; C43), 127.1 (d,  $^3J_{C,P}$  = 18.0 Hz; C55), 116.9 (dd,  $^1J_{C,P}$  = 28.0 Hz,  $^2J_{C,P}$  = 6.5 Hz; C1), 37.4 (d,  $^3J_{C,P}$  = 1.7 Hz; C8), 35.7 (d,  $^3J_{C,P}$  = 2.5 Hz; C3), 35.3 (dd,  $^3J_{C,P}$  = 9.6 Hz,  $^3J_{C,P}$  = 1.6 Hz,  $^3J_{C,P}$  = 1.3 Hz; C13), 31.6 (dd,  $^4J_{C,P}$  = 9.5 Hz,  $^4J_{C,P}$  = 0.9 Hz; C131-C133), 29.9 ppm (C31-C33);  $^{31}P\{^1H\}$  NMR (162 MHz,  $C_6D_6$ , 300 K):  $\delta$  = 52.6 (dd,  $^2J_{P,P}$  = 26.9 Hz,  $^3J_{P,P}$  = 20.9 Hz,  $^1J_{P,W}$  = 241.3 Hz; P3), 12.1 (dd,  $^1J_{P,P}$  = 161.8 Hz,  $^3J_{P,P}$  = 20.9 Hz,  $^1J_{P,W}$  = 223.1 Hz; P1), -35.1 ppm (dd,  $^1J_{P,P}$  = 161.8 Hz,  $^2J_{P,P}$  = 26.9 Hz; P2). **Second diastereomer:**  $^{31}P\{^1H\}$  NMR (162 MHz,  $C_6D_6$ , 300 K):  $\delta$  = 51.4 (dd,  $^2J_{P,P}$  = 27.0 Hz,  $^3J_{P,P}$  = 14.8 Hz; P3), 17.7 (dd,  $^1J_{P,P}$  = 138.2 Hz,  $^3J_{P,P}$  = 14.8 Hz; P1), -44.7 ppm (dd,  $^1J_{P,P}$  = 138.2 Hz,  $^2J_{P,P}$  = 27.0 Hz; P2). **Less abundant diastereomer:**  $^{31}P\{^1H\}$  NMR (162 MHz,  $C_6D_6$ , 300 K):  $\delta$  = 65.3 (dd,  $^2J_{P,P}$  = 26.8 Hz,  $^3J_{P,P}$  = 26.6 Hz; P3), 16.2 (dd,  $^1J_{P,P}$  = 163.6 Hz,  $^3J_{P,P}$  = 26.6 Hz; P1), -25.3 ppm (dd,  $^1J_{P,P}$  = 163.6 Hz,  $^2J_{P,P}$  = 26.8 Hz; P2). IR (KBr)  $\tilde{\nu}$  = 2961 (w), 2930 (vw), 2903 (vw), 2866 (vw)  $\nu$ (CH); 2068 (s), 2016 (w), 1977 (m), 1925 (vs.), 1869 (s)  $\nu$ (CO); 1634 (vw), 1589 (vw), 1557 (vw)  $\nu$ (C=C, aryl); 1474 (vw), 1460 (vw), 1435 (vw), 1362 (vw), 1250 (vw)  $\delta$ (CH); 1196 (vw), 1090 (vw), 941 (vw), 891 (vw), 872 (vw), 781 (vw), 758 (vw), 745 (w), 725 (vw)  $\nu$ (CC); 694 (vw), 644 (vw), 627 (vw) aryl; 596 (m), 577 (m), 538 (w), 482 (vw)  $cm^{-1}$   $\nu$ (PC),  $\delta$ (CC); MS (EI<sup>+</sup>, 20 eV, 453 K):  $m/z$  (%) = 866 (71) [M]<sup>+</sup>, 838 (100) [M-CO]<sup>+</sup>, 810 (45) [M-2CO]<sup>+</sup>, 782 (72) [M-3CO]<sup>+</sup>, 754 (88) [M-4CO]<sup>+</sup>; HRMS (ESI-ORBITRAP):  $m/z$ : calcd for  $C_{40}H_{46}O_4P_3W + H$ : 867.2120; found 867.2008; elemental analysis gave the correct hydrogen content, the carbon content was always found too low.

**X-ray crystallography:** Crystals suitable for X-ray crystallography were obtained by crystallisation from 1,2-difluorobenzene (3 °C; **7**), dichloromethane (3 °C; **8**), the reaction mixture (3 °C; **9b**), pentafluorobenzene (-30 °C; **12**) or *n*-hexane (-45 °C; **15**). Intensity data was collected on Bruker D8 Venture diffractometer with monochromated Mo  $K_{\alpha}$  radiation. The collection method involved  $\omega$ -scans. Data reduction was carried out using the program SAINT+.<sup>[42]</sup> The crystal structures were solved by direct methods using SHELXTL.<sup>[43]</sup> Non-hydrogen atoms were first refined isotropically followed by anisotropic refinement by full matrix least-squares calculation

based on  $F^2$  using SHELXTL.<sup>[43]</sup> H atoms were positioned geometrically and allowed to ride on their respective parent atoms. A tBu group of **7**, **9b** and **15** and two tBu groups of **8** were disordered; the respective atoms were refined on split positions. The crystals of **8** enclosed a molecule of  $CH_2Cl_2$  per formula unit, which was disordered over three positions (0.22:0.49:0.29). **12** crystallized with two independent molecules in the unit cell.

Deposition numbers 2001342, 2001344, 2001343, 2001341, and 2001340 (**7**, **8**, **9b**, **12**, and **15**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

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## Conflict of interest

The authors declare no conflict of interest.

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