Dalton Transactions

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Journal:	*Dalton Transactions*
Manuscript ID	DT-ART-07-2015-002825.R1
Article Type:	Paper
Date Submitted by the Author:	10-Sep-2015
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Hydroalumination of alkynyl-aminophosphines as a promising tool for the synthesis of unusual phosphines: P-N bond activation, a transient phosphaallene, a zwitterionic AlP_2C_2 heterocycle and a masked Al/P-based frustrated Lewis pair †

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Received

Treatment of the new alkynyl-chlorophosphine, Mes-P(Cl)-C≡C-CMe_3, with $LiNR_2$ afforded various unprecedented aminophosphines, Mes-P(NR_2)-C≡C-CMe_3, which showed a fascinating diversity in their reactivity towards H-Al^tBu_2. NMe_2 and NEt_2 derivatives yielded the hydroalumination products Mes-P(NR_2)-C(Al^tBu_2)=C(H)-CMe_3 which have an Al-N and an activated P-N bond. Elimination of aluminium amide yielded the transient 3H-phosphaallene, Mes-P=C=C(H)-CMe_3, which finally afforded a five-membered AlP_2C_2 heterocycle with an Al-P bond and two exocyclic C=C bonds. This heterocycle is directly formed with the sterically shielded ^{i}Pr_2N- and dimethylpiperidinophosphines. A unique R_2AlH adduct resulted from the NPh_2 and $N(SiMe_3)_2$ substituted phosphines. It may be viewed as an Al/P-based frustrated Lewis pair (FLP)

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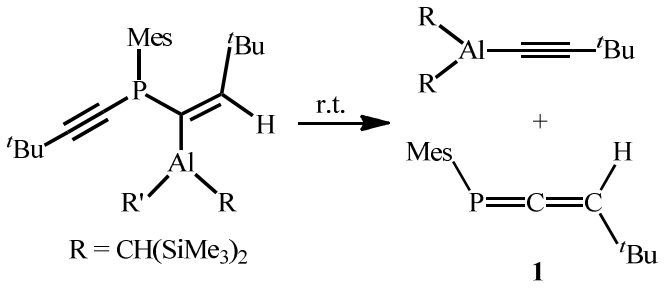
†Electronic supplementary information (ESI) available. CCDC 1057189 – 1057192. For ESI (NMR spectra of compounds **4**-**7** and **9**) and crystallographic data in CIF or other electronic format see DOI: …….

which coordinates an R_2AlH moiety. The heterocyclic AlP_2C_2 compound is formed in the final step of this reaction. Hydroalumination with Et_2AlH yielded [Mes-P(H)-$C(AlEt_2)$=C(H)-CMe_3]$_2$ which features an $Al_2P_2C_2$ heterocycle and two Al-P bonds. This dimer resembles the class of hidden or masked FLPs which show a reactivity similar to uncoordinated FLPs. Its unique structural motif is a P-H bond which may result in a new type of FLP chemistry.

Introduction

Phosphaallenes, R^1-P=C=C(R^2)(R^3), are highly interesting, functional molecules which exhibit unique structures comprising an unsaturated molecular core with cumulated P=C and C=C double bonds.[1] This specific functionality results in a unique reactivity, and these compounds undergo unprecedented secondary reactions with Main-Group or transition metal compounds.[1] 3H-phosphaallenes, R^1-P=C=C(H)(R^2), which have a hydrogen atom attached to the terminal carbon atom of the P=C=C group, have only rarely been isolated as persistent molecules.[1-3] The probably most famous compound of this type is the supermesityl substituted 3H-phosphaallene, $(Me_3C)_3H_2C_6$-P=C=C(H)-CMe_3, which has been published by the group of Märkl in 1988.[3] It was synthesized by a 1,3-hydrogen shift from a P-H functionalized alkynylphosphine and has so far not been characterized by crystal structure determination. Only recently we reported on the synthesis of the corresponding mesitylphosphaallene **1** which was obtained at room temperature by elimination of an aluminium alkynide from an alkynyl

functionalized Al/P-based frustrated Lewis pair (FLP) (Scheme 1).[4] This FLP was generated on a facile route by hydroalumination of the corresponding dialkynylmesitylphosphine with the sterically encumbered dialkylaluminium hydride H-Al[CH(SiMe$_3$)$_2$]$_2$. **1** was unambiguously identified by NMR spectroscopy, but could not be isolated in a pure form and decomposed in solution slowly over weeks, probably by the formation of dimeric species. The alkynide elimination was relatively slow and required for completion at least 8 h at room temperature. At lower temperatures the alkynyl phosphine is relatively persistent. We hoped to observe faster conversions by the use of better leaving groups. The elimination of e.g. aluminium amides may allow lower reaction temperatures, which may result in longer lifetimes of the phosphaallene, faster reactions and a better separation of the components of the product mixtures. The synthesis of the corresponding alkynyl-aminophosphines and their treatment with dialkylaluminium hydrides are reported in this article.



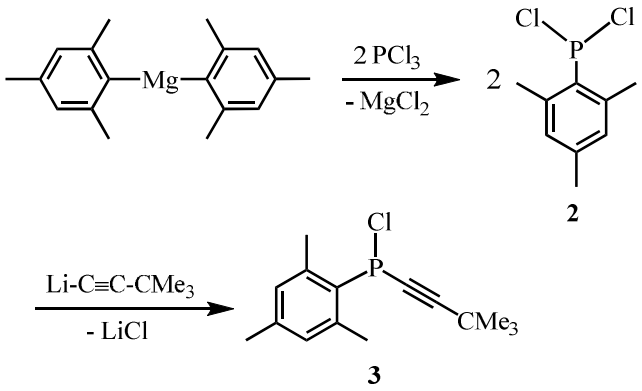
Scheme 1. Generation of the 3H-phosphaallene **1** by aluminium alkynide elimination

Results and Discussion

Synthesis of alkynyl-aminophosphines

The starting dichloro-mesitylphosphine **2** was obtained according to a literature procedure[5] by treatment of dimesitylmagnesium with two equivalents of PCl_3 (98% yield, Scheme 2). Despite of the relatively low melting point of 29 °C we were able to determine the molecular structure by X-ray diffraction (Figure 1). The data are important for comparison with the secondary products and are, therefore, briefly discussed. P-Cl (208.1 pm on average) and P-C distances [181.7(2) pm] correspond to standard values.[6] Cl-P-Cl [100.75(3)°] and the slightly larger C-P-Cl angles (102.4° on average) are in accordance with the pyramidal coordination sphere of the phosphorus atom. The chlorine atoms have almost the same distance to the plan formed by the mesityl group and the phosphorus atom (157 and -164 pm), and the C-CH_3 bond to an *ortho*-methyl group bisects the Cl-P-Cl angle [torsion angle P1-C1-C6-C61 -3.9(2)°]. Compound **2** was subsequently reacted with equimolar quantities of *in-situ* generated Li-C≡C-CMe_3 at -100 °C. After allowing the mixture to warm to room temperature and removal of the solvent in *vacuo* the organic constituents were extracted from the residue with *n*-pentane. Filtration and cooling the solution to -45 °C resulted in a colourless solid which was sublimed in *vacuo* at 60 °C to yield the alkynyl-chloro-mesitylphosphine **3** in 70% yield and a purity of >90%. This product was used without further purification in secondary reactions (see below). The dialkynyl-mesitylphosphine [$\delta(^{31}P) = -83$][7] and the starting compound **2** [$\delta(^{31}P) = +155$][5] were identified as major and minor impurities by NMR spectroscopy. They were removed completely by repeated recrystallization from *n*-pentane to yield analytically pure samples. The molecular structure (Figure 2) revealed the expected pyramidal bonding sphere of the phosphorus atom. The P1-Cl1 distance [210.70(8) pm] is slightly longer than in the dichloro compound **2**, the P1-C4(mesityl)

distance [182.5(2) pm] is almost identical. The P1-C1(alkynyl) bond length is shorter [175.3(2) pm] due to the sp-hybridisation of the alkynyl carbon atom. The C1-P1-C4 angle between the alkynyl and mesityl carbon atoms is relatively large [104.85(9)°] and may reflect some steric repulsion between the organic groups. **3** shows the expected singlet in the $^{31}P\{^{1}H\}$ NMR spectrum at $\delta = 46.4$. Two resonances in the characteristic range of the $^{13}C\{^{1}H\}$ NMR spectrum at $\delta = 77.2$ and 123.4 and an absorption at 2151 cm^{-1} in the IR spectrum confirm the presence of the C≡C triple bond. Compounds similar to the alkynyl-chlorophosphine **3** are to the best of our knowledge unknown in the literature.



Scheme 2. Synthesis of the alkynyl-chloro-mesitylphosphine **2**

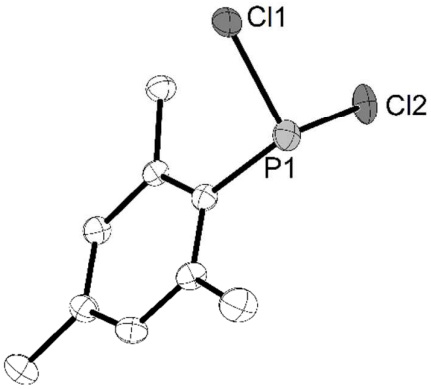


Figure 1. Molecular structure and atomic numbering scheme of compound **2**. Displacement ellipsoids are drawn at the 40% level. Hydrogen atoms are omitted for clarity. Selected bond lengths (pm) and angles (°): P1-Cl1 207.53(6), P1-Cl2 208.71(6), P1-C1 181.7(2), Cl1-P1-Cl2 100.75(3), Cl1-P1-C1 102.47(5), Cl2-P1-C1 102.29(5).

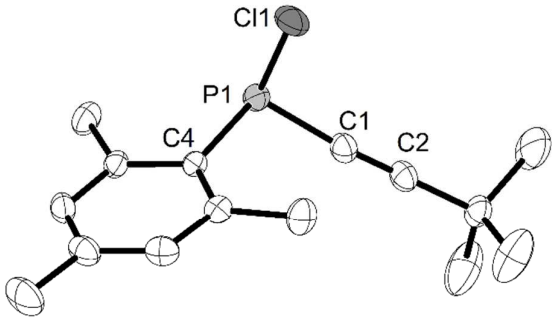
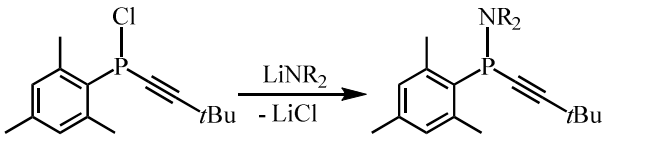


Figure 2. Molecular structure and atomic numbering scheme of compound **3**. Displacement ellipsoids are drawn at the 40% level. Hydrogen atoms are omitted for clarity. Selected bond lengths (pm) and angles (°): P1-Cl1 210.70(8), P1-C1 175.3(2), P1-C4 182.5(2), C1-C2 119.6(3), Cl1-P1-C1 99.36(8), Cl1-P1-C4 100.78(6), C1-P1-C4 104.85(9), P1-C1-C2 169.1(2), C1-C2-C3 178.0(2).

The highly functionalized compound **3** is an excellent starting material for the generation of various derivatives by salt elimination. We treated **3** with equimolar quantities of several lithium amides to generate alkynyl-aminophosphines (Scheme 3). Only the diphenylamino derivative **8** was obtained as a solid material and could be recrystallized from *n*-pentane for purification. The crystal structure determination of the greenish crystals confirmed its constitution (Figure 3). The phosphorus atom is bonded to three different substituents, an alkynyl, an amino and a mesityl group. The P-C bond lengths are similar to those observed for compound **3** [P-C(alkynyl) 176.2(1) and P-C(mesityl) 183.0(1) pm], and the P-N distance [173.4(1) pm] is in the upper range of P-N bonds reported in the literature.[6,8] The length of the C≡C bond [120.3(2) pm] corresponds to the standard value.[9] The angles at the phosphorus atom differ considerably. The smallest one is between the mesityl carbon and the nitrogen atom [C4-P1-N1 99.77(5)°], the largest one between both carbon atoms [C1-P1-C4 107.86(5)°]. Caused presumably by mesomeric interactions of the lone-pair of electrons with the aromatic ring the nitrogen atom has an almost ideally planar surrounding as indicated by the sum of the angles (358.7°). The C-N bond lengths are 142.3 pm on average. In comparison to **3** the ^{31}P NMR resonance of **8** is shifted to a higher field (δ = 11.3). The C≡C triple bond shows characteristic doublets in the ^{13}C NMR spectrum at δ = 79.0 and 120.2 and an IR absorption at 2149 cm^{-1}. All values are similar to those observed for **3**.



3

4: R = Me; **5**: R = Et; **6**: R = *i*Pr;
7: R_2 = CH(Me)-$(CH_2)_3$-CH(Me) (dimethylpiperidine);
8: R = C_6H_5; **9**: R = $SiMe_3$

Scheme 3. Synthesis of alkynyl-aminophosphines

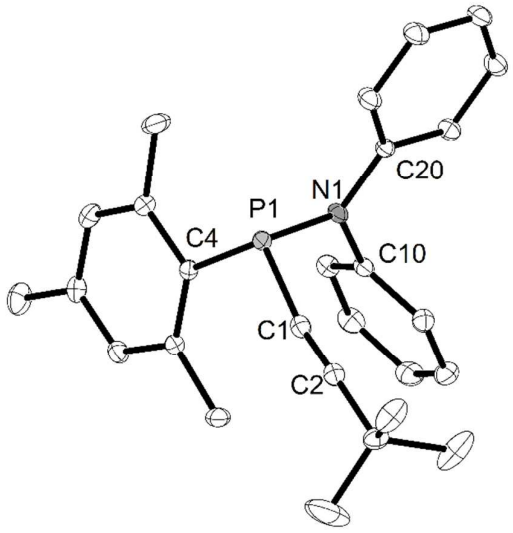


Figure 3. Molecular structure and atomic numbering scheme of compound **8**. Displacement ellipsoids are drawn at the 40% level. Hydrogen atoms are omitted for clarity. Selected bond lengths (pm) and angles (°): P1-N1 173.4(1), P1-C1 176.2(1), P1-C4 183.0(1), C1-C2 120.3(2), N1-P1-C1 101.31(5), N1-P1-C4 99.77(5), C1-P1-C4 107.86(5), P1-C1-C2 167.1(1), C1-C2-C3 174.7(1).

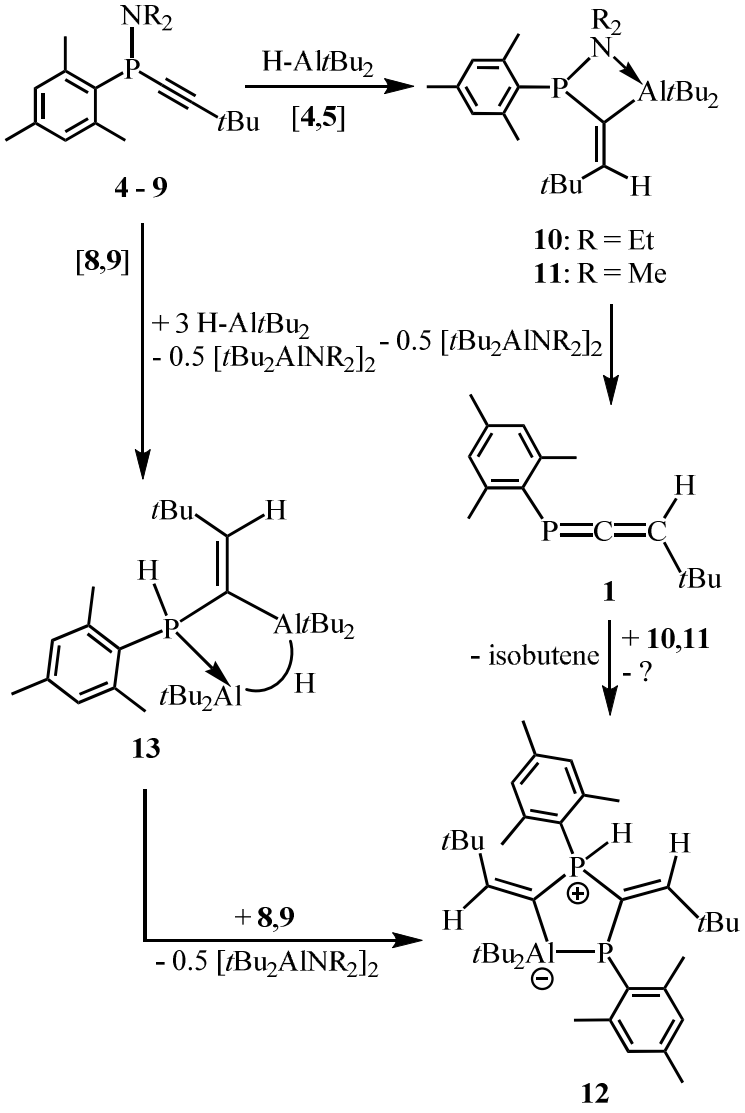
The remaining five aminophosphines (Scheme 3) were isolated as pale yellow, orange or brown oils that could not be purified by recrystallization from a variety of solvents (cyclopentane, *n*-hexane, toluene, 1,2-difluorobenzene or pentafluorobenzene). Attempts of destillative work-up resulted in complete decomposition of the products. These oils contained usually about 10% to 15% impurities with the dialkynylphosphine $MesP(C{\equiv}C\text{-}CMe_3)_2$ as the major component, but were used in secondary reactions as described below. The NMR spectroscopic characterization allowed an unambiguous assignment of the molecular constitutions, integration ratios and chemical shifts were in

accordance with expectations. Singlets were detected in the ^{31}P NMR spectra at δ = 21 to 29. A shift to a higher field was only observed for the diphenylamino compound **8** (δ = 11.3) and the diisopropylamino derivative **6** (δ = -0.3). The delocalization of the nitrogen lone pair by mesomeric interactions with the phenyl groups, the bulk of the amino group and the possible deformation of bond angles in **8** and **6** may influence these chemical shifts. The ^{13}C NMR spectra showed the resonances of the ethynyl carbon atoms in narrow ranges of δ = 77 to 85 (P-*C*≡C) and 117 to 121 (P-C≡*C*) with $^{1}J_{PC}$ and $^{2}J_{PC}$ coupling constants of 24 to 44 and 0 to 5 Hz, respectively. Only the diphenylamino compound **8** deviated from this pattern with relatively similar coupling constants of $^{1}J_{PC}$ = 12.6 and $^{2}J_{PC}$ = 10.1 Hz. Absorptions in the IR spectra at about 2145 cm^{-1} were characteristic of the C≡C stretching vibrations.

Hydroalumination of alkynylaminophosphines with di(tert-butyl)aluminium hydride

Treatment of the aminophosphines **4** to **9** with di(*tert*-butyl)aluminium hydride yielded the same final product, but different reaction courses with different intermediates have been observed. The expected simple hydroalumination product (**10**, Scheme 4) was only isolated from the reaction with diethylaminophosphine **5**. **10** crystallized in high purity from the concentrated reaction mixture in 83% yield. It is relatively stable at room temperature in solution and could be completely characterized, but decomposition became significant after about 24 h. Crystal structure determination (Figure 4) revealed the formation of the hydroalumination product with the alkynyl group in **5** reduced to an alkenyl group [C1-C2 135.7(5) pm] and the *cis*-arrangement of Al and H atoms across the C=C bond. A four-membered CPNAl heterocycle was formed by a strong intramo-

lecular Al-N bonding interaction. The Al-N bond length [212.1(1) pm] is in the upper range of values found for Al-N-E bridges[10] but corresponds to distances observed for Al/N-based active Lewis pairs which were obtained by hydroalumination of yneamines and contain C_2AlN heterocycles.[11] The P-N bond [183.5(1) pm] is activated by the coordination of the nitrogen atom to aluminium and significantly lengthened compared to the diphenylaminophosphine **8** [173.4(1) pm] or to standard bond lengths of P(III)-N bonds (about 173 pm).[8] The lengthening may be caused by the increased coordination number of the nitrogen atom and the ring strain in the small heterocycle. Results of the NMR spectroscopic characterization are in accordance with the molecular structure. The phosphorus atom showed a singlet in the $^{31}P\{^1H\}$ NMR spectrum with a chemical shift of $\delta = 98.9$ which was considerably shifted to a lower field compared to the starting aminophosphine **5** ($\delta = 22.6$). This result may in part depend on the increased coordination number of the nitrogen atom and the missing hyperconjugative interaction to the nitrogen lone pair as discussed for phosphorus trihalides.[12] The vinylic hydrogen atom showed a doublet in the expected range of the ^1H NMR spectrum ($\delta = 6.37$) with a $^3J_{PH}$ coupling constant of 35.2 Hz which is characteristic of a *trans*-arrangement of a three-coordinate phosphorus atom and the hydrogen atom.[4,7,13] The vinylic carbon atoms were observed in the ^{13}C NMR spectrum at $\delta = 146.2$ (P-*C*=C) and 153.0 (P-C=*C*). The molecular symmetry with a chiral environment of the phosphorus atom resulted in the observation of distinct resonances for two independent *tert*-butyl groups at aluminium and two different ethyl groups at nitrogen. One group is close to the lone pair of electrons at phosphorus, the other is on the same side of the heterocycle as the mesityl substituent. A further splitting into four resonances was detected for the diasterotopic methylene hydrogen atoms of the diethylamino group.



Scheme 4. Hydroalumination of alkynyl-aminophosphines; **12** is directly formed upon hydroalumination of the diisopropylamino- (**6**) and the dimethylpiperidinophosphine (**7**) without any detectable intermediate

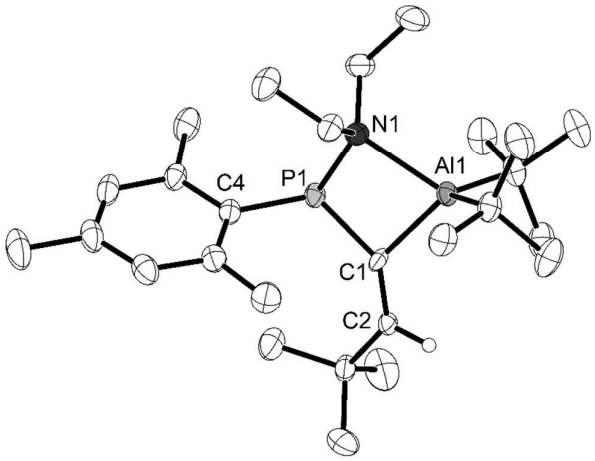


Figure 4. Molecular structure and atomic numbering scheme of compound **10**. Displacement ellipsoids are drawn at the 40% level. Hydrogen atoms with the exception of the vinylic hydrogen atom are omitted for clarity. Selected bond lengths (pm) and angles (°): Al1-N1 212.1(1), P1-N1 183.5(1), P1-C1 181.3(5), Al1-C1 198.8(6), C1-C2 135.7(5), N1-P1-C1 91.5(2), P1-N1-Al1 89.90(4), N1-Al1-C1 78.8(1), Al1-C1-P1 94.9(2).

A similar addition product (**11**) has only been obtained by hydroalumination of dimethylaminophosphine **4**. But **11** is a transient species which decomposes completely (see below) within a few hours in solution at room temperature and could not be isolated in pure form. An unambiguous identification is based on the results of NMR spectra which with the exception of the signals of the amino group (Et *vs*. Me) are almost identical to those of **10**. A singlet at $\delta = 104.4$ is observed in the $^{31}P\{^{1}H\}$ NMR spectrum, the vinylic hydrogen atom gave a doublet in the ^{1}H NMR spectrum at $\delta = 6.33$ with a $^{3}J_{PH}$ coupling constant of 36.1 Hz, and the vinylic carbon atoms showed chemical shifts of $\delta =$ 146.1 and 153.1. Two sets of resonances were observed for the *tert*-butyl groups at aluminium and the methyl groups at nitrogen.

Both compounds **10** and **11** decompose in solution with different rates to generate 3H-phosphaallene **1** by aluminium amide elimination (Scheme 4). Hence, the behavior of these hydroalumination products corresponds exactly to our expectations, but it proved impossible to isolate the non-volatile phosphaallene from the reaction mixture. **1** was only a transient intermediate under these conditions and was completely consumed in a secondary reaction (see below). It was identified by its characteristic NMR data[4] [$\delta(^{31}P)$ = 56.0; $\delta(^{1}H)$ = 5.74 (d, $^{3}J_{PH}$ = 24.9 Hz, 1H, P=C=C-*H*)]. Few single crystals of the eliminated aluminium amides were isolated and characterized by preliminary crystal structure determinations [$(Me_2NAl^tBu_2)_2$: a = 8.7464(6), b = 12.6005(9), c = 11.0658(8) pm, β = 105.478(2)°; $(Et_2NAl^tBu_2)_2$: a = 14.9346(6), b = 9.5549(4), c = 18.3708(7) pm, β = 105.478(2)°]. Both structures could not be refined to reasonable R values, but the data allowed an unambiguous assignment of the molecular constitutions with four-membered Al_2N_2 heterocycles[8a,14] in the solid state. NMR data were obtained from dilute solutions of the crystals in C_6D_6: $(^tBu_2AlNMe_2)_2$: $\delta\{^1H\}$ = 1.20 (s, 36 H, Al^tBu_2), 2.43 (s, 12 H, NMe_2). The amidophosphines **10** and **11** resemble active Lewis pairs obtained by the hydroalumination of yneamines.[11] These compounds have unsaturated C_2NAl heterocycles with relatively weak Al-N bonding interactions and show a remarkable reactivity with the catalytic oligmerisation of cyanamides or the coordination of heterocumulenes.[11] We therefore treated **10** with phenylisocyanate in *n*-pentane at room temperature and interestingly observed a fast reaction (<1 h) with the selective and quantitative formation of the 3H-phosphaallene **1** which was detected as the only species in the ^{31}P NMR spectrum. The ^{1}H NMR spectrum of the reaction mixture was relatively complicated and did not allow the identification of a specific constituent. We

were not able to isolate any component from the reaction mixture, and the course of the reaction remains unclear.

Stirring solutions of the *in-situ* generated hydroalumination product **11** (NMe_2) in *n*-pentane at room temperature for 1 d afforded a new compound **12** (Scheme 4) which was isolated as orange-red crystals in 61% yield after concentration and cooling of the reaction mixture to -70 °C. Crystal structure determination of **12** (Figure 5) confirmed the formation of a five-membered zwitterionic AlP_2C_2 heterocycle with a three-coordinate (phosphine, P1) and a four-coordinate phosphorus atom (phosphonium, P2). P2 is further coordinated to a mesityl group and a hydrogen atom in a distorted tetrahedral fashion, while P1 has a pyramidal coordination sphere. Two C=C double bonds [C11=C12 and C21=C22 with bond lengths of 134.9(3) and 134.4(3) pm] are in *exo*-positions and bridge two phosphorus atoms or a phosphorus and an aluminium atom. An Al-P bond completes the ring, its length [241.00(7) pm] corresponds to standard values.[7,15,16] The molecule has two stereogenic centers (P1 and P2) which should result in the formation of diastereomers, but the molecule with a *trans*-arrangement of the bulky mesityl groups seems to be strongly favoured and is formed exclusively. The $^{31}P\{^1H\}$ NMR spectrum of **12** shows two characteristic doublets at $\delta = 3.2$ (P1) and -88.0 (P2) with a $^2J_{PP}$ coupling constant of 103 Hz. The hydrogen atom bound to P2 resonates in the ^1H NMR spectrum at $\delta = 6.19$ with the expected large $^1J_{PH}$ coupling constant of 338 Hz ($^3J_{PH} = 21$ Hz). The vinylic hydrogen atoms were observed as doublets of doublets (H12: $^3J_{PH}$(*trans*) = 30.6 and $^3J_{PH}$(*cis*) = 9.2 Hz; H22: $^3J_{PH} = 37.5$ Hz and $^5J_{PH} = 3.3$ Hz). Interestingly, the results of 2D NMR spectroscopy of **12** do not really exclude the possibility of a tautomeric form in solution with the proton attached to the aluminium bound phosphorus atom P1.

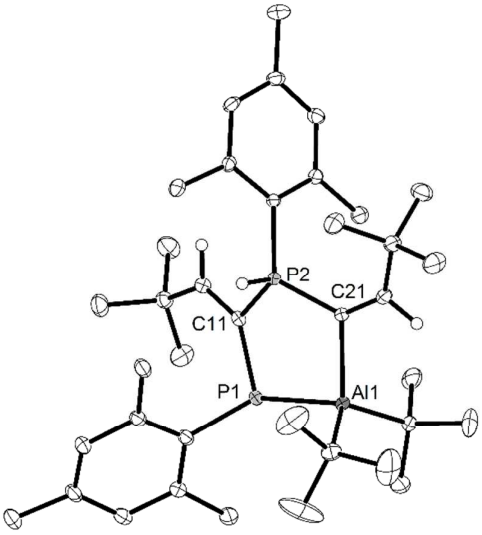


Figure 5. Molecular structure and atomic numbering scheme of compound **12**. Displacement ellipsoids are drawn at the 40% level. Hydrogen atoms with the exception of the vinylic and P-H hydrogen atoms are omitted for clarity. Selected bond lengths (pm) and angles (°): Al1-P1 241.00(7), Al1-C21 204.5(2), P1-C11 181.7(2), P2-C11 182.3(2), P2-C21 177.9(2), C11-C12 134.9(3), C21-C22 134.4(3), P1-Al1-C21 93.99(6), Al1-C21-P2 113.66(9), C11-P2-C21 109.27(9), P2-C11-P1 114.7(1), C11-P1-Al1 101.84(6).

Compound **12** was also formed when solutions of the pure NEt_2 compound **10** in *n*-pentane or C_6D_6 were stored for several days at room temperature. This decomposition is relatively slow and not very selective. An increasing concentration of unknown decomposition products was observed after a week, but **12** is the major component of the final mixture. The formation of impurities is favoured by the long reaction time, which may result as one possible side reaction in the recently reported dimerization of the

phosphaallene **1**.[4] The highly interesting and unprecedented formation of **12** may proceed in several steps which are, however, not yet fully understood in every detail. The 3H-phosphaallene **1** is formed as a reactive intermediate and may react with the hydroalumination products **10** and **11** *via* coordination of the aluminium atom by the allene phosphorus atom and of the phosphorus atom of **10** and **11** to the allene α-carbon atom to yield a five-membered AlP_2C_2 heterocycle. Such a mechanism has been suggested by quantum chemical calculations for the reactions of dialkynylphosphines with dialkylaluminium hydrides.[7] The amino group attached to phosphorus is finally replaced by a hydrogen atom probably *via β*-hydride elimination of an Al-^{t}Bu group, formation of an intermediate Al-H species and subsequent reaction of this intermediate with the P-NR_2 group to afford an aluminium amide. The identification of isobutene in the reaction mixtures by NMR spectroscopy supports such a pathway, but we were not able to identify the missing aluminium amide species [e.g. R-$Al(NR_2)_2$]. The last part is speculative, and we, therefore, abstain from a drawing of the mechanism.

Diphenylamino- (**8**) and bis(trimethylsilyl)aminophosphine (**9**; NMR experiment only) showed a different reactivity. Hydroalumination products similar to **10** and **11** as intermediates have not been detected by NMR spectroscopy. Instead the unique compound **13** was formed. It gave a singlet in the $^{31}P\{^1H\}$ NMR spectrum at δ = -79.3. A doublet at $\delta(^1H)$ = 6.40 with a large coupling constant $^1J_{PH}$ of 344.6 Hz indicated the presence of a P-H bond. Signals of five different *tert*-butyl groups (one vinylic, four attached to aluminium) were detected which indicate the presence of two Al^{t}Bu$_2$ moieties in the molecule. The non-equivalence of the *tert*-butyl resonances reflects the chiral coordination sphere of the phosphorus atom. A broad resonance in the ^1H NMR spectrum at δ = 3.2 ($^3J_{PH}$ = 34.0 Hz) is characteristic of a hydrogen atom bridging two alu-

minium atoms. The vinylic hydrogen atom resonated at δ = 6.82, and the relatively large $^{3}J_{PH}$ coupling constant of 65.6 Hz confirms the *trans*-arrangement of hydrogen and four-coordinate phosphorus atoms across the C=C bond.[17] Resonances of phenyl or trimethylsilyl groups are missing for the products, obviously the amino groups have been eliminated. These data resembles those of adducts which were obtained only recently from Al/P-based frustrated Lewis pairs and dialkylaluminium hydrides.[18] In these adducts the phosphorus atoms are bonded to two mesityl groups, while **13** is unique in featuring a mesityl group and a hydrogen atom bonded to phosphorus. This functionalization may allow the application of **13** in secondary reactions including the insertion of substrates into the P-H bond. Treatment of **8** with three equivalents of di(*tert*-butyl)aluminium hydride afforded **13** in a very selective reaction. It is stable in solution at room temperature for several days, but attempts to crystallize it for purification and structure determination failed. Its formation may tentatively be described by hydroalumination of the aminophosphine, aluminium amide elimination and the intermediate formation of the phosphaallene **1**. In a fast secondary reaction **1** may be consumed by hydroalumination with di(*tert*-butyl)aluminium hydride to afford the transient species Mes(H)P-C(Al^{t}Bu$_2$)=C(H)^{t}Bu. **13** may finally be formed by coordination of a third equivalent of hydride *via* an Al-P and a 3c-2e Al-H-Al bond. The reaction of the hydride with the alkynyl-aminophosphines may in these cases be hindered by steric shielding or the delocalization of the lone pair of electrons at nitrogen which could result in a considerable concentration of unreacted H-Al*t*Bu$_2$ in the reaction mixture. In contrast to the formation of **12** *via* **10** or **11** and **1** we could not identify any intermediates by NMR spectroscopy which makes the suggestion of a mechanism highly speculative. Further reaction of this intermediate (**13**) with the aminophosphines **8** and **9** afforded the five-

membered heterocycle **12**, but it was contaminated by a number of impurities, even when the reaction was carried out in the ideal stoichiometric ratio of 2 to 3.

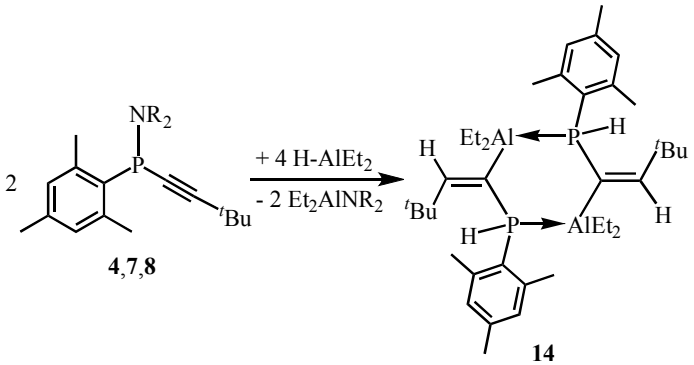
The diisopropylamine (**6**) and dimethylpiperidine derivatives (**7**) have the highest steric shielding of the aminophosphines employed in this study. They behaved similar in their reactions with di(*tert*-butyl)aluminium hydride (for **7**: NMR experiment only). Compound **12** was formed directly after short reaction times, and we were not able to detect any intermediate by NMR spectroscopy. The reaction of **6** is actually the most efficient method (85% yield) for the generation of crystalline **12** in high purity.

Hydroalumination of alkynylaminophosphines with diethylaluminium hydride

In the following reactions we used the sterically less shielded hydride H-$AlEt_2$ as a reductant. The low steric shielding of the aluminium atoms compared to Al^tBu_2 moieties should lead to different reaction courses, may help to stabilize reactive intermediates by dimerization as observed previously[7] and may allow to isolate functionalized derivatives different from those described above. Treatment of solutions of the aminophosphines **4** (NMe_2), **7** (dimethylpiperidine) and **8** (NPh_2) in *n*-pentane with H-$AlEt_2$ afforded a different and unique functionalized product (**14**, Scheme 6) after crystallization from the concentrated reaction mixtures in yields of 40 to 79%. Optimized conditions comprise two equivalents of the hydride (a slight excess), cooling the aminophosphine solution to 0 °C and stirring the mixture at room temperature for 30 min. The crystal structure determination (Figure 6) revealed a dimeric aluminium-phosphorus compound featuring a six-membered $Al_2P_2C_2$ heterocycle in a chair conformation. **14** is formed by hydroalumination of the C≡C triple bond and amino-hydrogen exchange. Aluminium

and phosphorus atoms have coordination numbers of four with distorted tetrahedral coordination spheres. Particularly interesting is the chiral coordination of both phosphorus atoms which are bonded to the aluminium atom, the vinylic carbon atom, the terminal mesityl group and a terminal hydrogen atom. The Al-P distances [251.83(5) pm] are longer than in **12**, but correspond to standard values of Al-P donor-acceptor bonds.[15,16] All other bonding parameters are unexceptional and do not require a detailed discussion. The NMR spectra of **14** in C_6D_6 solution are rather complicated. Resonances of at least two different species were observed, remaining, not assignable signals may indicate the presence of further compounds. We assume that as a consequence of two chiral centers in the molecules there are two diastereomeric forms present in solution and that partial monomerisation may result in a further set of resonances. Addition of a drop of THF to such solutions resulted in simple NMR spectra probably caused by cleavage of the Al-P bonds, coordination of the aluminium atoms by an ether molecule and monomerisation. A singlet was observed in the $^{31}P\{^1H\}$ NMR spectrum at δ = -79.1. The hydrogen atom bonded to phosphorus resonated at δ = 5.26 with a $^1J_{PH}$ coupling constant of 220 Hz which is indicative of a three-coordinate phosphorus atom. Coupling constants of about 330 Hz were detected for the dimeric diastereomers of the THF-free compound. The vinylic hydrogen atom of **14·THF** gave a doublet of doublets at δ = 6.47 with $^3J_{PH}$ = 34.1 Hz, characteristic of a *trans*-arrangement of hydrogen and phosphorus, and $^4J_{HH}$ = 2.2 Hz. **14** is a highly fascinating compound which may be described as a dimeric Al/P-based frustrated Lewis pair. Such dimeric species have been reported to show a reactivity similar to the monomeric compounds which have coordinatively unsaturated aluminium and phosphorus atoms.[15,19] They have been applied in various secondary reactions such as the coordination of carbon dioxide or isocyanates.[15,19] Two functionalities are

combined in **14**. The frustrated Lewis pair capability may help to coordinate and activate substrates, and the P-H function may allow the insertion into the P-H bond and the reduction of unsaturated molecules.



Scheme 6. Synthesis of the P-H functionalized compound **14**

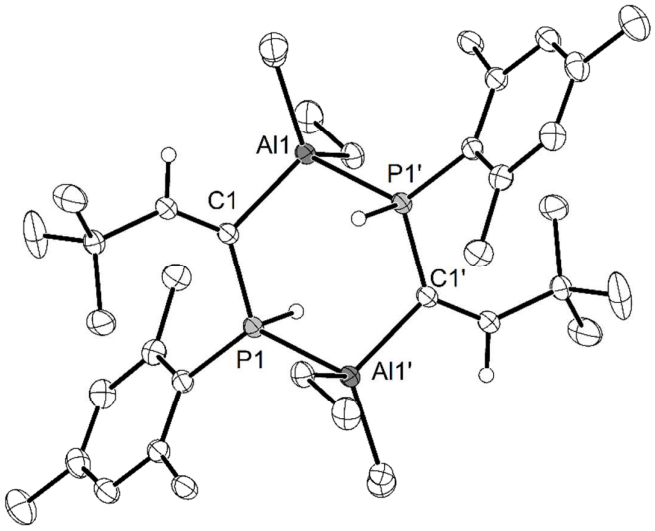


Figure 6. Molecular structure and atomic numbering scheme of compound **14**. Displacement ellipsoids are drawn at the 40% level. Hydrogen atoms with the exception of the vinylic and P-H hydrogen atoms are omitted for clarity. Selected bond lengths (pm) and angles (°): P1-Al1' 251.83(5), Al1-C1 202.3(1), P1-C1 181.2(1), C1-C2 134.4(2), P1'-Al1-C1 96.54(4), Al1-C1-P1 115.88(7), Al1'-P1-C1 109.65(4); Al1' and P1' generated by –x, –y+1, –z+1.

Conclusion

The new alkynyl-chlorophosphine (**3**) and alkynyl-aminophosphines (**4** to **9**) were obtained on facile routes by treatment of dichloro-mesitylphosphine (**2**) with lithium alkynide (**3**) and subsequent reaction with lithium amides by salt elimination (**4** to **9**). They are promising starting materials for an application in various secondary reactions. Hydroalumination of the alkynyl group with di(*tert*-butyl)aluminium hydride resulted in three different and unprecedented reaction courses depending on steric shielding and the electronic properties of the amino groups. The less shielded dimethyl- and diethylamino derivatives allow the approach of the aluminium atom to the α-carbon atom of the ethynyl group to yield the simple hydroalumination products **10** and **11** in which the P-N bonds are activated by an intramolecular Al-N interaction. This is the key structural motif for the following aluminium amide elimination and formation of an intermediate 3H-phosphaallene (**1**) which has cumulated P=C and C=C double bonds and was identified by NMR spectroscopy. **1** is highly reactive and reacts with **10** or **11** to afford a five-membered AlP_2C_2 heterocycle (**12**) with an endocyclic Al-P bond. This bond is predisposed to secondary reactions by insertion of substrates as recently shown for $AlPC_2$ four-membered rings.[20] **12** is directly formed in high yield by hydroalumination of the sterically shielded diisopropylamino and dimethylpiperidine substituted alkynylphosphines. In these reactions hydroalumination of the aminophosphine or the formation of intramolecular Al-N bonds may be sterically hindered and amino-

hydrogen exchange may be favoured. But any suggestion for a mechanism is highly speculative because we were not able to detect any intermediate by NMR spectroscopy. The fact that we did not observe specific intermediates (aminophosphine, phosphaallene) does not exclude their existence as short lived intermediates. For instance, compound **13** may be formed by dual hydroalumination of the phosphaallene **1**. Diphenyl- and bis(trimethylsilyl)aminophosphines have the lone pairs of electrons at nitrogen delocalized by mesomeric or hyperconjugative effects, and the formation of an intermediate compound with an intramolecular Al-N bond analogous to **10** or **11** may be unfavourable. The nitrogen atoms of these compounds are relatively hard (NPh_2) or bear a relatively high partial negative charge [$N(SiMe_3)_2$] and may favour aluminium-amide elimination and the formation of a P-H compound. Hydroaluminiation of such a phosphine and reaction with excess hydride affords the dialkylaluminium hydride adduct of an Al/P-based frustrated Lewis pair (**14**) which has a hydrogen atom as a functional group bonded to the chiral phosphorus atom. **14** was formed selectively by treatment of the aminophosphine **8** with three equivalents of the hydride but could not be isolated. Reaction with excess alkynylphosphine afforded the heterocyclic compound **12** as the major product.

Hydroalumination of alkynyl-aminophosphines (**4**, **7** and **8**) with two equivalents of the sterically less shielded diethylaluminium hydride afforded a dimeric Al/P-based frustrated Lewis pair (**14**). Dimerisation may help to stabilize these compounds and may prevent the relatively complicated secondary chemistry reported for the di(*tert*-butyl)aluminium derivatives. Compounds such as **14** (masked or hidden FLPs) show a reactivity similar to those of the highly active monomeric FLPs and have been applied in various secondary reactions.[15,19] The unique characteristic of **14** is the presence of a

P-H bond as an additional functionality. This may allow the coordination of ambiphilic molecules as a result of the characteristic donor-acceptor capability of the aluminium and phosphorus atoms and the transfer of the hydrogen atom on phosphorus to the activated substrates. This is a very promising perspective for future investigations and a preliminary reaction with phenyl isocyanate showed indeed the expected behavior. In this article we have reported on a wide variety of new functional phosphorus compounds which show a fascinating structural chemistry and reactivity and are promising starting compounds for an application in various secondary reactions.

Experimental Section

All procedures were carried out under an atmosphere of purified argon in dried solvents (*n*-pentane and *n*-hexane with $LiAlH_4$; Et_2O, THF, and toluene with Na/benzophenone; pentafluorobenzene with molecular sieves). *n*-BuLi and H-C≡C-CMe_3 were used as purchased. $MesPCl_2$ (**2**),[5] H-Al^{t}Bu$_2$[21] and H-AlEt_2[22] were obtained according to literature procedures. Microanalyses were carried out by the microanalytical laboratory of the Westfälische Wilhelms-Universität Münster. NMR spectra were recorded in C_6D_6 or C_7D_8 at ambient probe temperature using the following Bruker instruments: Avance I (^{1}H, 400.13; ^{13}C, 100.62; ^{31}P, 161.98 MHz) or Avance III (^{1}H, 400.03; ^{13}C, 100.59; ^{31}P, 161.93 MHz) and referenced internally to residual solvent resonances (chemical shift data in δ). ^{13}C NMR spectra were all proton decoupled. The assignment of NMR spectra is based on HSQC, HMBC, DEPT135, and H,H-ROESY data. IR spectra were recorded

as paraffin mulls between KBr plates on a Shimadzu Prestige 21 spectrometer, electron impact mass spectra with a Varian mass spectrometer.

Mes(Cl)P-C≡C-^{t}Bu (3). A solution of H-C≡C-^{t}Bu (1.20 g, 14.6 mmol) in Et_2O (10 mL) was treated at 0 ºC with *n*-BuLi (9.0 mL, 14.4 mmol, 1.6 M in *n*-hexane). The ice bath was removed and the mixture stirred for 2 h. This solution was slowly added at -100 ºC to a solution of $MesPCl_2$ (**2**, 3.20 g, 14.5 mmol) in Et_2O (20 mL). The mixture was slowly warmed to room temperature, the solvent was removed *in vacuo*, the residue was treated with *n*-pentane (10 mL) and the suspension was filtered. Concentrating the filtrate and storing it at -45 ºC yielded a crystalline material of impure Mes(Cl)P-C≡C-^{t}Bu (**3**) which was sublimed (10^{-3} mbar, 60 ºC) to yield **3** (2.68 g, 70%) with a purity of >90% based on ^{31}P NMR spectroscopy [$MesPCl_2$ and $MesP(C{\equiv}C\text{-}^tBu)_2$ as impurities]. This product was used for further reactions. The analytically pure compound was accessible by repeated recrystallization from *n*-pentane. Microanalysis: found C 67.2, H 7.5; [$C_{15}H_{20}ClP$ (266.75)] requires C 67.5, H 7.6. ^{1}H NMR (C_6D_6, 300 K): δ = 1.04 (9H, s, ^{t}Bu) 1.93 (3H, s, *p*-Me), 2.75 (6H, s, *o*-Me), 6.64 (2H, d, $^4J_{PH}$ = 3.4 Hz, *m*-H). ^{13}C{^{1}H} NMR (C_6D_6, 300 K): δ = 21.1 (*p*-Me), 21.2 (d, $^3J_{PC}$ = 22.0 Hz, *o*-Me), 29.1 (d, $^4J_{PC}$ = 2.2 Hz, C*Me*$_3$), 30.7 (*C*Me$_3$), 77.2 (d, $^1J_{PC}$ = 39.9 Hz, *C*≡C-^{t}Bu), 123.4 (d, $^2J_{PC}$ = 4.5 Hz, C≡*C*-^{t}Bu), 130.4 (d, $^3J_{PC}$ = 4.7 Hz, *m*-C), 130.4 (d, $^1J_{PC}$ = 41.0 Hz, *ipso*-C), 142.0 (*p*-C), 144.4 (d, $^2J_{PC}$ = 23.5 Hz, *o*-C). ^{31}P{^{1}H} NMR (C_6D_6, 300 K): δ = 46.4. IR (cm^{-1}; paraffin, KBr plates): 2199 w, 2151 m ν(C≡C); 1603 s aromatic ring; 1466 vs, 1410 w, 1375 vs (paraffin); 1364 vs, 1302 w, 1290 m, 1254 s δ(CH$_3$); 1202 m, 1155 vw, 1059 m, 1030 m, 955 w, 943 m, 889 vw, 849 m, 772 s δ(CH), ν(CC); 721 s (paraffin); 615 s, 577

m, 552 m, 540 w, 473 s, 413 m ν(PC), ν(PCl). Mass spectrum (EI+; 20 eV; 298 K): *m/z* (%) = 266 (50) [M^+], 251 (86) [$M^+ - CH_3$], 231 (39) [M^+ – Cl], 210 (91) [M^+ – butene].

Me_2N(Mes)P-C≡C-^{t}Bu (4). A solution of Me_2NLi (0.20 g, 3.82 mmol) in Et_2O (10 mL) was added at -30 ºC to a solution of Mes(Cl)P-C≡C-CMe_3 (**3**, 1.02 g, 3.82 mmol) in Et_2O (10 mL). The mixture was allowed to warm to room temperature and stirred for 30 min. The solvent was removed *in vacuo*, the solid extracted with *n*-pentane (20 mL) and the obtained mixture filtered by means of a canula. The solvent was removed from the filtrate *in vacuo* to yield compound **4** as an orange oil [0.90 g, 86%, MesP(C≡C-^{t}Bu)$_2$ as an impurity]. ^{1}H NMR (C_6D_6, 300 K): δ = 1.17 (9H, s, ^{t}Bu), 2.09 (3H, s, *p*-Me), 2.57 (6H, d, $^3J_{PH}$ = 11.9 Hz, NMe), 2.80 (6H, s, *o*-Me), 6.79 (2H, s, *m-H*). ^{13}C{^{1}H} NMR (C_6D_6, 300 K): δ = 20.9 (*p*-Me), 23.6 (d, $^3J_{PC}$ = 16.8 Hz, *o*-Me), 29.8 (*C*Me_3), 30.7 (C*Me*$_3$), 41.7 (d, $^2J_{PC}$ = 11.6 Hz, NMe), 77.2 (d, $^1J_{PC}$ = 44.0 Hz, *C*≡C-^{t}Bu), 120.8 (C≡*C*-^{t}Bu), 130.5 (d, $^3J_{PC}$ = 3.4 Hz, *m*-C), 131.3 (d, $^1J_{PC}$ = 13.4 Hz, *ipso*-C), 139.1 (*p*-C), 143.2 (d, $^2J_{CP}$ = 17.4 Hz, *o*-C). ^{31}P{^{1}H} NMR (C_6D_6, 300 K): δ = 29.3. IR (cm^{-1}; paraffin, KBr plates): 2170 m, 2143 s ν(C≡C); 1603 vs, 1550 m aromatic ring; 1456 vs, 1412 m, 1375 s (paraffin); 1362 s, 1288 m, 1252 s $\delta(CH_3)$; 1200 s, 1192 s, 1139 w, 1098 w, 1051 s, 1030 s, 961 vs, 934 m, 849 s, 764 s δ(CH), ν(CC), ν(CN); 719 w (paraffin); 702 w, 656 s, 613 s, 577 s, 554 m, 529 w, 511 w, 463 m, 440 s ν(PN), ν(PC). Mass spectrum (EI+; 20 eV; 298 K): *m/z* (%) = 275 (100) [M^+], 260 (61) [$M^+ - CH_3$].

Et_2N(Mes)P-C≡C-^{t}Bu (5), **$^i Pr_2N$(Mes)P-C≡C-^{t}Bu (6)** and **$(Me_3Si)_2N$(Mes)P-C≡C-^{t}Bu (9)** were prepared accordingly from Mes(Cl)P-C≡C-^{t}Bu **3** and the corresponding lithium amide. In the case of **Me_2Pip(Mes)P-C≡C-C-^{t}Bu (7)** and **Ph_2N(Mes)P-C≡C-^{t}Bu (8)** the lithium amide was synthesized *in situ* from *n*-BuLi and the respective amine (stirring for 30 min at -30 ºC in Et_2O) before adding the solution to Mes(Cl)P-C≡C-^{t}Bu **3**.

$Et_2N(Mes)P\text{-}C{\equiv}C\text{-}CMe_3$ (5): **5** was obtained from Mes(Cl)P-C≡C-CMe_3 (**3**, 1.05 g, 3.94 mmol) and $LiNEt_2$ (0.31 g, 3.92 mmol) as a brown oil [0.72 g, 61%, MesP(C≡C-^{t}Bu)$_2$ and other unknown impurities]. ^{1}H NMR (C_6D_6, 300 K): δ = 1.05 (6H, t, $^3J_{HH}$ = 7.1 Hz, $NCH_2\mathit{Me}$), 1.17 (9H, s, ^{t}Bu), 2.10 (3H, s, *p*-Me), 2.82 (6H, s, *o*-Me), 3.08 (4H, m, NCH_2Me), 6.80 (2H, s, *m-H*). $^{13}C\{^1H\}$ NMR (C_6D_6, 300 K): δ = 14.4 (d, $^3J_{PC}$ = 5.3 Hz, $NCH_2\mathit{Me}$), 21.0 (*p*-Me), 23.7 (d, $^3J_{PC}$ = 16.8 Hz, *o*-Me), 29.0 ($\mathit{C}Me_3$), 30.5 ($C\mathit{Me_3}$), 45.6 (d, $^2J_{PC}$ = 14.1 Hz, $N\mathit{C}H_2Me$), 81.2 (d, $^1J_{PC}$ = 30.5 Hz, *C*≡C-^{t}Bu), 118.9 (d, $^2J_{PC}$ = 4.4 Hz, C≡*C*-^{t}Bu), 130.5 (d, $^3J_{PC}$ = 3.4 Hz, *m*-C), 131.5 (d, $^1J_{PC}$ = 6.9 Hz, *ipso*-C), 138.8 (*p*-C), 142.9 (d, $^2J_{PC}$ = 17.9 Hz, *o*-C). $^{31}P\{^1H\}$ NMR (C_6D_6, 300 K): δ = 22.6. IR (cm^{-1}; paraffin, KBr plates): 2170 m, 2143 m *v*(C≡C); 1684 w, 1605 s, 1555 w aromatic ring; 1456 vs, 1410 w, 1375 s (paraffin); 1362 s, 1342 w, 1288 w, 1252 s $\delta(CH_3)$; 1219 m, 1194 s, 1180 s, 1094 w, 1074 w, 1055 w, 1020 s, 920 m, 849 s, 785 w, 764 m δ(CH), *v*(CC), *v*(CN); 719 vw (paraffin); 685 w, 654 m, 640 m, 613 m, 575 w, 556 w, 513 w, 494 vw, 459 w, 420 w *v*(PN), *v*(PC). Mass spectrum (EI+; 20 eV; 298 K): *m/z* (%) = 303 (100) [M^+], 288 (30) [$M^+ - CH_3$], 246 (6) [$M^+ - {}^t$Bu], 231 (45) [$M^+ - NEt_2$].

$^i Pr_2N(Mes)P\text{-}C{\equiv}C\text{-}^t Bu$ (6): **6** was obtained from Mes(Cl)P-C≡C-CMe_3 (**3**, 0.49 g, 1.87 mmol) and LiN^iPr_2 (0.20 g, 1.87 mmol) as a pale yellow oil (0.51 g, 82%, impurities up to 15%). ^{1}H NMR (C_6D_6, 300 K): δ = 1.04 (6H, d, $^3J_{HH}$ = 6.9 Hz, $NCH\mathit{Me}$), 1.17 (9H, s, ^{t}Bu), 1.44 (6H, d, $^3J_{HH}$ = 6.7 Hz, $NCH\mathit{Me}$), 2.09 (3H, s, *p*-Me), 2.86 (6H, s, *o*-Me), 3.42 (2H, m, $^3J_{PH}$ = ca. 11 Hz, $NC\mathit{H}Me$), 6.80 (2H, d, $^4J_{PH}$ = 3.3 Hz, *m*-H). $^{13}C\{^1H\}$ NMR (C_6D_6, 300 K): δ = 21.0 (*p*-Me), 23.2 (d, $^3J_{PC}$ = 11.1 Hz, $NCH\mathit{Me}$), 23.7 (d, $^3J_{PC}$ = 3.9 Hz, $NCH\mathit{Me}$), 24.0 (d, $^3J_{PC}$ = 17.3 Hz, *o*-Me), 28.9 (d, $^3J_{PC}$ = 1.7 Hz, $\mathit{C}Me_3$), 30.4 (d, $^4J_{PC}$ = 1.9 Hz, $C\mathit{Me_3}$), 49.0 (d, $^2J_{PC}$ = 7.3 Hz, $N\mathit{C}HMe$), 84.6 (d, $^1J_{PC}$ = 37.9 Hz, *C*≡C-CMe_3), 117.1 (d, $^2J_{PC}$ = 3.5 Hz, C≡*C*-CMe_3), 130.2 (*ipso*-C), 130.5 (d, $^3J_{PC}$ = 3.8 Hz, *m*-

C), 138.9 (*p*-C), 143.6 (d, $^{2}J_{PC}$ = 17.3 Hz, *o*-C). $^{31}P\{^{1}H\}$ NMR (C_6D_6, 300 K): δ = -0.3. IR (cm^{-1}; paraffin, KBr plates): 2172 m, 2143 m ν(C≡C); 1719 vw, 1605 s, 1557 m aromatic ring; 1462vs, 1410 s, 1377 vs (paraffin); 1362 vs, 1310 m, 1288 m; 1252 s $\delta(CH_3)$; 1194 s, 1175 s, 1155 m, 1123 s, 1074 w, 1059 m, 1030 s, 1016 s, 961 s, 932 m, 864 m, 847 s, 762 s δ(CH), ν(CC), ν(CN); 719 m (paraffin); 664 w, 635 m, 611 s, 575 s, 556 s, 521 s, 492 s, 461 m, 434 s ν(PN), ν(PC). Mass spectrum (EI+; 20 eV; 298 K): *m/z* (%) = 331 (70) [M^+], 316 (12) [$M^+ - CH_3$], 288 (8) [$M^+ - {}^{i}Pr$], 231 (28) [$M^+ - N{}^{i}Pr_2$].

Me_2pip(Mes)P-C≡C-^{t}Bu (7): **7** was obtained from Mes(Cl)P-C≡C-^{t}Bu (**3**, 0.29 g, 1.09 mmol), H$(Me)_2$pip (0.118, 1.04 mmol) and *n*-BuLi (0.67 mL, 1.07 mmol, 1.6 M in *n*-hexane) as pale brown oil (0.28 g, 78%; about 10% impurities, $MesP(C{\equiv}C\text{-}{}^{t}Bu)_2$ as the main component). ^{1}H NMR (C_6D_6, 300 K): δ = 1.14 [1H, m, NCH(Me)CH_2], 1.18 (9H, s, CMe_3), 1.20 [1H, m, $NCH(Me)CH_2CH_2$], 1.29 and 1.33 [each 1H, m, NCH(Me)CH_2], 1.33 [3H, d, $^{3}J_{HH}$ = 7.1 Hz, NCH(*Me*)], 1.49 [3H, d, $^{3}J_{HH}$ = 7.0 Hz, NCH(*Me*)], 1.64 [1H, m, $NCH(Me)CH_2CH_2$], 1.67 [1H, m, NCH(Me)CH_2], 2.10 (3H, s, *p*-Me), 2.83 (6H, s, *o*-Me), 3.56 and 3.84 (each 1H, m, $^{3}J_{PH}$ = 3.2 Hz, NC*H*), 6.84 (2H, d, $^{4}J_{PH}$ = 3.0 Hz, *m*-H). $^{13}C\{^{1}H\}$ NMR (C_6D_6, 300 K): δ = 14.2 [$NCH(Me)CH_2CH_2$], 21.0 (*p*-Me), 21.7 (NCH*Me*), 23.2 (d, $^{3}J_{PC}$ = 1.9 Hz, NCH*Me*), 23.8 (d, $^{3}J_{PC}$ = 17.8 Hz, *o*-Me), 29.0 (d, $^{3}J_{PC}$ = 1.8 Hz, CMe_3), 30.4 (d, $^{4}J_{PC}$ = 2.0 Hz, CMe_3), 32.0 [d, $^{3}J_{PC}$ = 10.4 Hz, $NCH(Me)CH_2$], 32.2 [$NCH(Me)CH_2$], 51.1 [N*CH*(Me)], 54.9 [d, $^{2}J_{PC}$ = 34.2 Hz, N*CH*(Me)], 83.4 (d, $^{1}J_{PC}$ = 33.2 Hz, *C*≡C-^{t}Bu), 118.9 (d, $^{2}J_{PC}$ = 5.4 Hz, C≡*C*-^{t}Bu), 130.4 (d, $^{3}J_{PC}$ = 3.1 Hz, *m*-C), 131.3 (d, $^{1}J_{PC}$ = 4.9 Hz, *ipso*-C), 138.7 (*p*-C), 143.1 (d, $^{2}J_{PC}$ = 18.2 Hz, *o*-C). $^{31}P\{^{1}H\}$ NMR (C_6D_6, 300 K): δ = 23.0. IR (cm^{-1}; paraffin; KBr plates): 2187 w, 2141 s ν(C≡C); 1603 s, 1578 m, 1551 m aromatic ring; 1433 vs, 1406 s, 1376 vs (paraffin); 1314 m, 1252 s $\delta(CH_3)$; 1231 s, 1202 m, 1146 vs, 1125 s, 1103 w, 1076 s,

1059 w, 1030 s, 997 s, 972 m, 957 m, 932 m, 866 s, 849 s, 804 m, 764 s, 735 m δ(CH), ν(CC), ν(CN); 719 m (paraffin); 698 w, 613 s, 579 s, 567 s, 556 m, 529 m, 515 m, 490 m, 455 s, 434 s ν(PN), ν(PC). Mass spectrum (EI+; 20 eV; 313 K): *m/z* (%) = 343 (40) [M^+], 328 (10) [$M^+ - CH_3$], 231 (21) [$M^+ - Me_2pip$].

$Ph_2N(Mes)P\text{-}C{\equiv}C\text{-}^tBu$ (8): **8** was obtained from Mes(Cl)P-C≡C-^{t}Bu (**3**, 0.53 g, 1.99 mmol), $HNPh_2$ (0.33, 1.95 mmol) and *n*-BuLi (1.23 mL, 1.97 mmol, 1.6 M in *n*-hexane) as pale green crystals after recrystallization from *n*-pentane (0.44 g, 57%). M.p.: 140 °C. Microanalysis: found C 80.9, H 7.6, N 3.4; [$C_{27}H_{30}NP$ (399.5)] requires C 81.2, H 7.6, N 3.5. ^{1}H NMR (C_6D_6, 300 K): δ = 1.10 (9H, s, CMe_3), 2.04 (3H, s, *p*-Me), 2.35 (6H, s, *o*-Me), 6.67 (2H, d, $^4J_{PH}$ = 1.0 Hz, *m*-Mes), 6.89 (2H, t, $^3J_{HH}$ = 7.8 Hz, *p*-Ph), 7.08 (4H, *pseudo*-t, $^3J_{HH}$ = 7.8 Hz, *p*-Ph), 7.19 (4H, d, $^3J_{HH}$ = 7.6 Hz, *p*-Ph). $^{13}C\{^1H\}$ NMR (C_6D_6, 300 K): δ = 21.0 (*p*-Me), 23.1 (d, $^3J_{PC}$ = 17.7 Hz, *o*-Me), 29.0 (d, $^3J_{PC}$ = 1.9 Hz, *C*Me_3), 30.2 (d, $^4J_{PC}$ = 2.3 Hz, C*Me*$_3$), 79.0 (d, $^1J_{PC}$ = 12.6 Hz, *C*≡C-^{t}Bu), 120.2 (d, $^2J_{PC}$ = 10.1 Hz, C≡*C*-^{t}Bu), 123.3 (*p*-Ph), 124.6 (d, $^3J_{PC}$ = 9.6 Hz, *o*-Ph), 129.2 (*m*-Ph), 130.3 (d, $^3J_{PC}$ = 4.0 Hz, *m*-Mes), 130.4 (overlap, *ipso*-Mes), 139.8 (*p*-Mes), 144.1 (d, $^2J_{PC}$ = 20.2 Hz, *o*-Mes), 148.2 (d, $^2J_{PC}$ = 9.4 Hz, *ipso*-Ph). $^{31}P\{^1H\}$ NMR (C_6D_6, 300 K): δ = 11.3. IR (cm^{-1}; paraffin, KBr plates**)**: 2193 w, 2173 w, 2149 m ν(C≡C); 1591 s aromatic rings; 1454 vs, 1377 vs (paraffin); 1310 s, 1273 vs, 1252 vs $\delta(CH_3)$; 1196 s, 1179 s, 1167 s, 1155 s, 1113 w, 1082 m, 1071 m, 1061 w, 1042 m, 972 sh w, 949 s, 901 m, 885 m, 847 m, 837 w, 770 s, 746 vs δ(CH), ν(CC), ν(CN); 721 vs (paraffin); 695 vs, 692 vs, 617 m, 602 m, 575 m, 569 m, 552 m, 527 s, 511 m, 495 m, 415 m ν(PN), ν(PC). Mass spectrum (EI+; 20 eV; 303 K): *m/z* (%) = 399 (53) [M^+], 384 (3) [$M^+ - CH_3$], 342 (6) [$M^+ - {}^tBu$], 231 (100) [$M^+ - NPh_2$].

$(Me_3Si)_2N(Mes)P\text{-}C{\equiv}C\text{-}^tBu$ (9): **9** was obtained from Mes(Cl)P-C≡C-^{t}Bu (**3**, 0.19 g, 0.71 mmol) and $LiN(SiMe_3)_2$ (0.12 g, 0.72 mmol) as an orange oil [0.20 g, 72%, about 10% impurities, $MesP(C{\equiv}C\text{-}^tBu)_2$ as one of the components]. ^{1}H NMR (C_6D_6, 300 K): δ = 0.36 (18H, d, $^4J_{PH}$ = 0.9 Hz, $^2J_{SiH}$ = 7.0 Hz, $SiMe_3$), 1.16 (9H, s, CMe_3), 2.07 (3H, d, $^6J_{PH}$ = 1.6 Hz, *p*-Me), 2.70 (6H, d, $^4J_{PH}$ = 1.5 Hz, *o*-Me), 6.70 (2H, d, $^4J_{PH}$ = 3.3 Hz *m*-H). ^{13}C NMR (C_6D_6, 300 K): δ = 3.9 (d, $^3J_{PC}$ = 7.0 Hz, $^1J_{SiC}$ = 56.8 Hz, $SiMe_3$), 20.8 (*p*-Me), 24.1 (d, $^3J_{PC}$ = 10.8 Hz, *o*-Me), 28.9 (d, $^3J_{PC}$ = 1.8 Hz, CMe_3), 30.3 (d, $^4J_{CP}$ = 1.9 Hz, CMe_3), 83.2 (d, $^1J_{CP}$ = 24.1 Hz, $C{\equiv}C\text{-}^tBu$), 118.3 (d, $^2J_{PC}$ = 5.3 Hz, $C{\equiv}C\text{-}^tBu$), 130.9 (d, $^3J_{PC}$ = 1.2 Hz, *o*-C), 134.5 (d, $^1J_{CP}$ = 27.1 Hz, *ipso*-C), 137.6 (d, $^4J_{CP}$ = 1.7 Hz, *p*-C), 140.4 (d, $^2J_{PC}$ = 10.8 Hz, *o*-C). $^{31}P\{^1H\}$ NMR (C_6D_6, 300 K): δ = 20.6. IR (cm^{-1}; neat; KBr plates): 2193 w, 2149 m ν(C≡C); 1605 s, 1558 m aromatic ring; 1469 s, 1454 vs, 1447 s, 1404 m, 1377 w, 1362 s, 1250 vs $\delta(CH_3)$; 1202 w, 1180 w, 1030 m, 903 vs, 876 vs, 845 vs, 829 vs, 766 s, 717 w δ(CH), ν(CC), ρ(CH_3Si); 681 m, 610 w, 575 w, 552 vw ν(PN), ν(PC), ν(SiN), ν(SiC). Mass spectrum (EI+; 20 eV; 298 K): *m/z* (%) = 391 (61) [M^+], 376 (100) [M^+ – Me], 334 (46) [M^+ – ^{t}Bu].

$Et_2N(Mes)PC(Al^tBu_2){=}C(H)\text{-}^tBu$ (10): A solution of $^tBu_2AlH$ (0.90 g, 6.34 mmol) in *n*-pentane (10 mL) was added at -30 ºC to a solution of $Et_2N(Mes)P\text{-}C{\equiv}C\text{-}^tBu$ (**5**, 1.92 g, 6.34 mmol) in *n*-pentane (20 mL). The mixture was stirred for 1 h and allowed to warm to room temperature. The solution was concentrated and stored at -70 ºC to afford colourless crystals of compound **10** (2.34 g, 83%). **10** decomposes slowly at room temperature in solution and the solid state; the crystals turn yellow. M.p.: 65 °C. Microanalysis: found C 72.2, H 10.8; [$C_{27}H_{49}AlNP$ (445.651)] requires C 72.8, H 11.1. ^{1}H NMR (C_6D_6, 300 K): δ = 0.17 (3H, t, $^3J_{HH}$ = 7.1 Hz, NCH_2Me), 0.80 (3H, m, NCH_2Me), 0.96 (9H, s, C=CH-CMe_3), 1.39 and 1.45 (each 9H, s, $AlCMe_3$), 2.02 (3H, s, *p*-Me), 2.66 and 2.79

(each 3H, s, *o*-Me), 2.90, 3.03, 3.27 and 3.39 (each 1H, br., NCH_2), 6.37 (1H, d, $^3J_{PH}$ = 35.2 Hz, C=CH), 6.72 (2H, overlap, *m*-H). $^{13}C\{^1H\}$ NMR (C_6D_6, 300 K): δ = 9.0 and 13.5 (NCH_2Me), 17.4 and 18.7 (br., AlCMe$_3$), 21.0 (*p*-Me), 23.7 and 24.3 (overlap, *o*-Me), 29.5 (d, $^4J_{PC}$ = 7.2 Hz, C=CH-CMe_3), 32.6 (AlCMe_3), 38.1 (C=CH-CMe$_3$), 45.5 (d, $^2J_{PC}$ = 3.0 Hz, NCH$_2$), 45.5 (d, $^2J_{PC}$ = 31.9 Hz, NCH$_2$), 129.9 (overlap, *m*-C), 140.6 (*p*-C), 144.0 and 144.9 (*o*-C), 146.2 (d, $^1J_{PC}$ = 81.8 Hz, C=CH), 153.0 (d, $^2J_{PC}$ = 11.5 Hz, C=CH), *ipso*-C not observed. $^{31}P\{^1H\}$ NMR (C_6D_6, 300 K): δ = 98.9. IR (cm^{-1}; paraffin, KBr plates): 1572 s, 1555 m ν(C=C), aromatic ring; 1450 vs, 1404 m, 1375 vs (paraffin); 1306 w, 1248 w δ(CH$_3$); 1196 w, 1169 w, 1153 w, 1136 w, 1109 w, 1074 w, 1043 w, 1005 vw, 962 vw, 932 vw, 851 w, 808 w, 779 w ν(CC), δ(CH); 719 s (paraffin); 650 vw, 600 vw, 559 w, 478 w, 446 m ν(AlC), ν(PC), ν(AlN), ν(PN). Mass spectrum (EI+; 20 eV; 298 K): *m/z* (%) = 417 (2) [M$^+$ – ethene], 388 (17) [M$^+$ – ^{t}Bu], 359 (2) [M$^+$ – ^{t}Bu – Et].

Me$_2$N(Mes)PC(Al^{t}Bu$_2$)=C(H)-^{t}Bu (11) and the heterocyclic compound 12: A solution of HAl^{t}Bu$_2$ (0.47 g, 3.31 mmol) in *n*-pentane (15 mL) was treated at 0 ºC with a solution of compound **4** (0.90 g, 3.27 mmol) in *n*-pentane (8 mL). The mixture was stirred for 30 min and allowed to warm to room temperature. NMR spectra of the mixture showed mainly compound **11** with small quantities of the starting material **4** and the secondary product **12**. Concentrating the solution and storing at -70 ºC yielded after several days compound **12** as orange-red needles (0.60 g, 61%). At room temperature the conversion from compound **11** to **12** was complete after about 1 d in pentane. NMR characterisation of compound **11**: ^1H NMR (C_6D_6, 300 K): δ = 0.97 (9H, s, C=CH-CMe_3), 1.35 and 1.44 (each 9H, s AlCMe$_3$), 2.04 (3H, s, *p*-Me), 2.10 (3H, d, $^3J_{PH}$ = 1.9 Hz, NMe), 2.42 (3H, d, $^3J_{PH}$ = 15.6 Hz, NMe), 2.53 and 2.68 (each 3H, s, *o*-Me), 6.33

(1H, d, $^{3}J_{PH}$ = 36.1 Hz, C=CH), 6.70 (1H, s, *m*-H), 6.72 (1H, d, $^{4}J_{PH}$ = 4.0 Hz, *m*-H). $^{13}C\{^{1}H\}$ NMR (C_6D_6, 300 K): δ = 16.8 and 18.6 (each br., Al*C*Me$_3$), 21.0 (*p*-Me), 24.3 (d, $^{3}J_{PC}$ = 33.3 Hz, *o*-Me), 25.2 (*o*-Me), 29.4 (d, $^{4}J_{PC}$ = 7.7 Hz, C=CH-C*Me$_3$*), 32.1 (d, $^{4}J_{CP}$ = 2.5 Hz, AlC*Me$_3$*), 32.7 (AlC*Me$_3$*), 38.2 (d, $^{3}J_{PC}$ = 2.3 Hz, C=CH-*C*Me$_3$), 44.4 (d, $^{2}J_{PC}$ = 3.4 Hz, NMe), 48.2 (d, $^{3}J_{PC}$ = 27.5 Hz, NMe), 129.8 (d, $^{3}J_{PC}$ = 5.8 Hz, *m*-C), 131.1 (*m*-C), 131.2 (d, $^{1}J_{PC}$ = 53.3 Hz, *ipso*-C), 140.4 (*p*-C), 144.4, (d, $^{2}J_{PC}$ = 36.8 Hz, *o*-C), 145.3 (d, $^{2}J_{PC}$ = 2.1 Hz, *o*-C), 146.1 (br., d, $^{1}J_{PC}$ = 46.0 Hz, *C*=CH), 153.1 (d, $^{2}J_{PC}$ = 11.2 Hz, C=*C*H). $^{31}P\{^{1}H\}$ NMR (C_6D_6, 300 K): δ = 104.4.

Synthesis of the heterocyclic compound 12 from diisopropylaminophosphine 6: A solution of $^{t}Bu_2AlH$ (0.31 g, 2.18 mmol) in *n*-pentane (10 mL) was added at 0 ºC to a solution of $^{i}Pr_2N(Mes)P$-C≡C-^{t}Bu (**6**, 0.73 g, 2.20 mmol) in *n*-pentane (10 mL). The mixture was warmed to room temperature and stirred for 1 h. The solution was concentrated and stored at -30 ºC to afford colourless crystals of compound **12** (0.57 g, 85%). M.p.: 212 °C. Microanalysis: found C 74.5, H 10.4; [$C_{38}H_{61}AlP_2$ (606.84)] requires C 75.2, H 10.1. ^{1}H NMR (C_6D_6, 300 K): δ = 0.71 (9H, s, P_2C=CH-*CMe$_3$*), 1.06 (9H, s, Al(P)C=CH-*CMe$_3$*), 1.27 and 1.52 (each 9H, s AlCMe$_3$), 1.92 [3H, s, *p*-Me(PH)], 2.07 [3H, s, *p*-Me(P)], 2.35 [3H, s, *o*-Me(PH)], 2.53 and 2.79 [each 3H, s, *o*-Me(P)], 2.88 [3H, d, $^{4}J_{PH}$ = 4.8 Hz, *o*-Me(PH)], 5.82 (1H, dd, $^{3}J_{PH}$ = 30.6 and 9.2 Hz, P_2C=CH), 6.19 (1H, dd overlap, $^{1}J_{PH}$ = 337.7 Hz, $^{3}J_{PH}$ = 21.0 Hz, PH), 6.53 [1H, dd, $^{3}J_{PH}$ = 37.5 Hz, $^{5}J_{PH}$ = 3.3 Hz, Al(P)C=CH], 6.61 and 6.65 [each 1H, s, *m*-H(PH)], 6.85 [1H, d, $^{4}J_{PH}$ = 5.2 Hz, *m*-H(P)], 6.89 [1H, s, *m*-H(P)]. $^{13}C\{^{1}H\}$ NMR (C_6D_6, 300 K): δ = 17.0 (br., Al*C*Me$_3$), 20.8 [*p*-Me(PH)], 21.2 [*p*-Me(P)], 23.2 [d, $^{3}J_{PC}$ = 11.9 Hz, *o*-Me(PH)], 23.6 [d, $^{3}J_{PC}$ = 28.3 Hz, *o*-Me(P)], 24.8 [*o*-Me(PH)], 24.8 [dd, $^{3}J_{PC}$ = 20.0 Hz, $^{5}J_{PC}$ = 5.0 Hz, *o*-Me(P)], 29.7 (d, $^{4}J_{PC}$ = 3.0 Hz, P_2C=CH-C*Me$_3$*), 29.9 [d, $^{4}J_{PC}$ = 4.0 Hz, Al(P)C=CH-

C*Me₃*], 31.5 and 32.6 (AlC*Me₃*), 37.0 (dd, $^{3}J_{PC}$ = 2.0 Hz, $^{3}J_{PC}$ = 4.0 Hz, P_2C=CH-*C*Me_3), 37.4 [dd, $^{3}J_{PC}$ = 4.0 Hz, $^{5}J_{PC}$ = 3.0 Hz, Al(P)C=CH-*C*Me_3], 122.7 [d, $^{1}J_{PC}$ = 23.3 Hz, *ipso*-C(PH)], 129.0 [d, $^{3}J_{PC}$ = 7.5 Hz, *m*-C(P)], 130.4 [d, $^{3}J_{PC}$ = 6.1 Hz, *m*-C(PH)], 130.5 [*m*-C(P)], 131.5 [d, $^{3}J_{PC}$ = 7.2 Hz, *m*-C(PH)], 135.6 [dd, $^{1}J_{PC}$ = 26.0 Hz, $^{3}J_{PC}$ = 8.0 Hz, *ipso*-C(P)], 139.4 [d, $^{2}J_{PC}$ = 10.5 Hz, *o*-C(PH)], 139.9 [*p*-C(PH) and *p*-C(P)], 142.0 [d, $^{2}J_{PC}$ = 8.0 Hz, *o*-C(PH)], 142.1 (d, $^{1}J_{PC}$ = 8.1 Hz, P_2C=CH), 143.2 [br., Al(P)*C*=CH], 144.0 [d, $^{2}J_{PC}$ = 4.0 Hz, *o*-C(P)], 145.0 [d, $^{2}J_{PC}$ = 33.1 Hz, *o*-C(P)], 151.8 [dd, $^{2}J_{PC}$ = 8.6 Hz, $^{4}J_{PC}$ = 6.2 Hz, Al(P)C=*C*H], 155.7 (dd, $^{2}J_{PC}$ = 6.8 Hz, $^{2}J_{PC}$ = 13.7 Hz, P_2C=*C*H). $^{31}P\{^{1}H\}$ NMR (C_6D_6, 300 K): δ = -88.0 (d, $^{2}J_{PP}$ = 103 Hz, PH), 3.2 (d, $^{2}J_{PP}$ = 103 Hz, P). IR (cm^{-1}; paraffin, KBr plates): 1578 s, 1558 m ν(C=C), aromatic rings; 1456 vs, 1404 w, 1377 s (paraffin); 1341 w, 1306 vw, 1250 sh $\delta(CH_3)$; 1119 br., w, 810 vw ν(CC), δ(CH), δ(CC); 719 w (paraffin); 561 vw, 473 vw ν(AlC), ν(PC). Mass spectrum (EI+; 20 eV; 353 K): *m/z* (%) = 549 (100) [$M^+ - CMe_3$].

Mes(H)P-C(Al^{t}Bu$_2$)=C(H)-^{t}Bu·HAl^{t}Bu$_2$ (13): **13** was observed by NMR spectroscopy as an intermediate upon treatment of the diphenylaminophosphine **8** with HAl^{t}Bu$_2$ in a molar ratio of 1 to 3. ^{1}H NMR (C_6D_6, 300 K): δ = 0.81 (9H, s, C=CH-C*Me₃*), 1.19 and 1.29 (each 9H, s, PAl^{t}Bu$_2$), 1.40 and 1.43 (each 9H, s, C=CAl^{t}Bu$_2$) 1.93 (3H, s, *p*-Me), 2.25 and 2.49 (each 3H, s, *o*-Me), 3.20 (1H, d, br., $^{3}J_{PH}$ = 34.0 Hz, AlH), 6.40 (1H, dd, $^{1}J_{PH}$ = 344.6 Hz, $^{4}J_{HH}$ = 2.2 Hz, PH), 6.58 (1H, s, *m*-H), 6.59 (1H, d, $^{4}J_{PH}$ = 2.0 Hz, *m*-H), 6.82 (d, $^{3}J_{PH}$ = 65.6 Hz, $^{4}J_{HH}$ = 2.0 Hz, C=CH). $^{13}C\{^{1}H\}$ NMR (C_6D_6, 300 K): δ = 17.2 (HC=CAl*C*Me_3), 17.5 (PAl*C*Me_3), 17.7 (HC=CAl*C*Me_3 and PAl*C*Me_3), 20.9 (*p*-Me), 23.3 (d, $^{3}J_{PC}$ = 6.1 Hz, *o*-Me), 25.7 (d, $^{3}J_{PC}$ = 10.0 Hz, *o*-Me), 29.4 (C=CH-C*Me₃*), 31.2 and 31.8 (PAlC*Me₃*), 32.4 and 32.5 (HC=CAlC*Me₃*), 38.9 (d, $^{3}J_{PC}$ = 13.9 Hz, C=CH-*C*Me_3), 125.1 (d, $^{1}J_{PC}$ = 17.5 Hz, *ipso*-C), 126.9 (d, br., $^{1}J_{PC}$ = 40.1 Hz, *C*=CH-

^{t}Bu), 130.3 (d, br., $^3J_{PC}$ = 5.9 Hz, *m*-C), 130.6 (d, $^3J_{PC}$ = 8.0 Hz, *m*-C), 140.4 (d, $^2J_{PC}$ = 4.0 Hz, *o*-C), 140.9 (d, $^4J_{PC}$ = 2.0 Hz, *p*-C), 141.8 (d, $^2J_{PC}$ = 13.5 Hz, *o*-C), 166.8 (d, $^2J_{PC}$ = 19.2 Hz, C=*C*H). $^{31}P\{^1H\}$ NMR (C_6D_6, 300 K): δ = -79.3.

[Mes(H)PC(AlEt$_2$)=C(H)-^{t}Bu]$_2$ (14): Et_2AlH (0.15 g, 0.18 mL, 1.74 mmol) was added at 0 ºC to a solution of Me_2N(Mes)P-C≡C-^{t}Bu (**4**) (0.21 g, 0.76 mmol) in *n*-pentane (10 mL). The mixture was stirred for 2 h, allowed to warm to room temperature and stirred for 30 min. Concentration and cooling to -30 ºC afforded colourless crystals of compound **14** (0.097 g, 40%). Compound **14** was similarly obtained from Et_2AlH (0.12 g, 0.15 mL, 1.40 mmol) and Mes(NPh_2)PC≡C-^{t}Bu (0.27 g, 0.68 mmol) or Et_2AlH (0.15 g, 0.19 ml, 1.74 mmol) and Mes(Me_2pip)PC≡C-^{t}Bu (0.30 g, 0.87 mmol) in yields of 79% (0.17 g) and 40% (0.11 g), respectively. M.p.: 131 ºC. Microanalysis: found C 72.3, H 10.1; [$C_{38}H_{64}Al_2P_2$ (636.84)] requires C 71.7, H 10.1. Complete assignment of the complicated spectra with different species was impossible. The phosphorus atoms are chiral and different diastereomers are possible. Further, the formation of monomeric formula units in solution may also not be excluded. Only those resonances are given which could be assigned unambiguously to the dimeric compounds. ^1H NMR (C_6D_6, 300 K): Diastereomer 1: δ = 0.93 (9H, s, C=CH-C*Me$_3$*), 1.36 and 1.52 (each 3H, t, $^3J_{HH}$ = 8.1 Hz, AlCH$_2$*Me*), 1.97 (3H, s, *p*-Me), 2.64 (6H, s, *o*-Me), 5.78 (1H, d, $^1J_{PH}$ = 341.0 Hz, PH), 6.68 (2H, s, *m*-H), 7.11 (d, $^3J_{PH}$ = 56.4 Hz, C=CH). $^{31}P\{^1H\}$ NMR (C_6D_6, 300 K): δ = -66.5. Diastereomer 2: δ = 0.97 (9H, s, C=CH-C*Me$_3$*), 1.98 (3H, s, *p*-Me), 2.62 (6H, s, *o*-Me), 6.03 (1H, d, $^1J_{PH}$ = 326.3 Hz, PH), 6.68 (2H, m, *m*-H), 6.95 (d, $^3J_{PH}$ = 57.0 Hz, C=CH). $^{31}P\{^1H\}$ NMR (C_6D_6, 300 K): δ = -70.7. IR (cm^{-1}; paraffin, KBr plates): 1603 m, 1549 m, 1519 w ν(C=C), aromatic ring; 1447 vs, 1408 m, 1377 vs (paraffin); 1314 m, 1292 m, 1250 w δ(CH_3); 1229 w, 1198 m, 1177 w, 1148 w, 1128 w, 1103 w, 1076

w, 1063 m, 1030 m, 986 s, 974 m, 953 m, 918 m, 866 w, 849 s, 833 m, 795 m, 762 m, 746 m ν(CC), δ(CH), δ(CC); 714 m (paraffin); 644 vs, 625 sh, 615 sh, 534 m, 511 w ν(AlC), ν(PC). **14·THF**: ^{1}H NMR (C_4D_8O, 300 K): δ = -0.34 (4H, s, br., AlC*H*$_2$), 0.88 (9H, s, C=CH-C*Me*$_3$), 1.23, (6H, t, $^{3}J_{HH}$ = 7.0 Hz AlCH$_2$*Me*), 2.19 (3H, s, *p*-Me), 2.46 (6H, s, *o*-Me), 5.02 (1H, d, $^{1}J_{PH}$ = 217 Hz, PH), 6.31 (d, $^{3}J_{PH}$ = 34.9 Hz, C=CH), 6.80 (2H, s, *m*-H). ^{1}H NMR (C_6D_6, one drop OC_4D_8, 300 K): δ = -0.09 (4H, m, $^{3}J_{HH}$ = 8.1 Hz, AlC*H*$_2$), 1.15 (6H, t, $^{3}J_{HH}$ = 8.1 Hz, AlCH$_2$*Me*), 1.27 (9H, s, C=CH-C*Me*$_3$), 2.09 (3H, s, *p*-Me), 2.60 (6H, s, *o*-Me), 5.26 (1H, d, $^{1}J_{PH}$ = 218.7 Hz, PH), 6.47 (dd, $^{3}J_{PH}$ = 34.1 Hz, $^{4}J_{HH}$ = 2.2 Hz, C=CH), 6.77 (2H, s, *m*-H). ^{13}C{^{1}H} NMR (C_6D_6, 300 K): δ = 0.0 (br., AlCH$_2$), 9.9 (AlCH$_2$*Me*), 21.0 (*p*-Me), 24.0 (d, $^{3}J_{PC}$ = 12.8 Hz, *o*-Me), 30.2 (d, $^{4}J_{PC}$ = 4.8 Hz, C=CH-C*Me*$_3$), 37.0 (d, $^{3}J_{PC}$ = 3.6 Hz, C=CH-*C*Me$_3$), 129.0 (d, $^{3}J_{PC}$ = 3.7 Hz, *m*-C), 133.0 (d, $^{1}J_{PC}$ = 11.7 Hz, *ipso*-C), 137.9 (*p*-C), 144.2 (d, $^{2}J_{PC}$ = 12.6 Hz, *o*-C), 144.3 (s, br., *C*=CH), 157.1 (d, $^{2}J_{PC}$ = 5.6 Hz, C=*C*H). ^{31}P{^{1}H} NMR (C_6D_6, 300 K): δ = -79.1.

X-Ray crystallography. Crystals suitable for X-ray crystallography were obtained in most cases directly from the concentrated reaction mixtures in *n*-pentane upon cooling (see above). Colourless crystals of MesPCl$_2$ **2** were isolated from the melt at room temperature, and crystals of the dimeric compound **14** precipitated from a C_6D_6 solution in an NMR tube at room temperature. Intensity data was collected on Bruker APEX II and D8-Venture diffractometers with MoK_α radiation. The collection method involved ω scans. Data reduction was carried out using the program SAINT+.[23] The crystal structures were solved by Direct Methods using SHELXTL.[24,25] Non-hydrogen atoms were first refined isotropically followed by anisotropic refinement by full matrix least-squares calculation based on F^2 using SHELXTL.[24,25] Hydrogen atoms with the exception

of those attached to P or Al were positioned geometrically and allowed to ride on their respective parent atoms. The vinyl group of compound **8** was disordered and refined on split positions (0.67 : 0.33). The molecules of compound **14** are located on inversion centers. **14** crystallized with two benzene molecules per formula unit of the dimer. Molecular structures were drawn with the DIAMOND program package.[26]

Crystal data for $MesPCl_2$ **2**: $C_9H_{11}Cl_2P$, $M = 221.05$, monoclinic, $a = 814.45(3)$ pm, $b = 711.78(3)$ pm, $c = 1840.60(8)$ pm, $\alpha = 90°$, $\beta = 101.823(1)°$, $\beta = 90°$, $V = 1.04438(7)$ nm^3, $T = 153(2)$ K, space group $P2_1/n$, $Z = 4$, $\mu(MoK\alpha) = 0.719$ mm^{-1}, 10452 reflections measured, 3026 independent reflections ($R_{int} = 0.0207$). The final R values were $R_1 = 0.0357$ ($I > 2\sigma(I)$; 2710) and $wR(F^2) = 0.0988$ (all data). The goodness of fit on $F^2 = 1.093$.

Crystal data for Mes(Cl)P-C≡C-^{t}Bu **3**: $C_{15}H_{20}ClP$, $M = 266.73$, monoclinic, $a = 884.46(5)$ pm, $b = 1363.8(1)$ pm, $c = 1279.0(1)$ pm, $\alpha = 90°$, $\beta = 95.263(3)°$, $\gamma = 90°$, $V = 1.5362(2)$ nm^3, $T = 153(2)$ K, space group $P2_1/n$, $Z = 4$, $\mu(MoK\alpha) = 0.331$ mm^{-1}, 22519 reflections measured, 4504 independent reflections ($R_{int} = 0.0407$). The final R values were $R_1 = 0.0546$ ($I > 2\sigma(I)$; 3184) and $wR(F^2) = 0.1550$ (all data). The goodness of fit on $F^2 = 1.023$.

Crystal data for $Mes(NPh_2)P$-C≡C-CMe_3 **8**: $C_{27}H_{30}NP$, $M = 399.49$, triclinic, $a = 863.69(3)$ pm, $b = 998.98(4)$ pm, $c = 1389.08(6)$ pm, $\alpha = 76.356(1)°$, $\beta = 79.679(1)°$, $\gamma = 80.886(1)°$, $V = 1.13736(8)$ nm^3, $T = 153(2)$ K, space group $P\bar{1}$, $Z = 2$, $\mu(MoK\alpha) = 0.133$ mm^{-1}, 18334 reflections measured, 6566 independent reflections ($R_{int} = 0.0204$). The final R values were $R_1 = 0.0431$ ($I > 2\sigma(I)$, 5704) and $wR(F^2) = 0.1182$ (all data). The goodness of fit on $F^2 = 1.043$.

Crystal data for the heterocycle **10**: $C_{27}H_{49}AlNP$, M = 445.62, triclinic, a = 1082.18(5) pm, b = 1140.57(5) pm, c = 1260.79(6) pm, α = 74.341(1)°, β = 70.402(1)°, γ = 78.671(1)°, V = 1.4116(1) nm^3, T = 153(2) K, space group $P\bar{1}$, Z = 2, μ(MoKα) = 0.142 mm^{-1}, 19636 reflections measured, 6903 independent reflections (R_{int} = 0.0193). The final R values were R_1 = 0.0387 ($I > 2\sigma(I)$; 6138) and w$R(F^2)$ = 0.1137 (all data). The goodness of fit on F^2 = 1.055.

Crystal data for the heterocycle **12**: $C_{38}H_{61}AlP_2$, M = 606.78, monoclinic, a = 879.59(4) pm, b = 1912.09(8) pm. c = 2199.57(9) pm, α = 90°, β = 94.433(2)°, γ = 90°, V = 3.6883(3) nm^3, T = 153(2) K, space group $P2_1/n$, Z = 4, μ(MoKα) = 0.165 mm^{-1}, 52283 reflections measured, 10795 independent reflections (R_{int} = 0.0665). The final R values were R_1 = 0.0584 ($I > 2\sigma(I)$; 7493) and w$R(F^2)$ = 0.1457 (all data). The goodness of fit on F^2 = 1.034.

Crystal data for the heterocycle **14**·$(C_6H_6)_2$: $C_{50}H_{76}Al_2P_2$, M = 793.00, triclinic, a = 967.42(4) pm, b = 1055.05(4) pm, c = 1221.07(5) pm, α = 92.185(1)°, β = 106.351(1)°, γ = 92.279(1)°, V = 1.19338(8) nm^3, T = 153(2) K, space group $P\bar{1}$, Z = 1, μ(MoKα) = 0.159 mm^{-1}, 16216 reflections measured, 5648 independent reflections (R_{int} = 0.0173). The final R values were R_1 = 0.0406 ($I > 2\sigma(I)$; 5015) and w$R(F^2)$ = 0.1100 (all data). The goodness of fit on F^2 = 1.061.

Further details of the crystal structure determinations are available from the Cambridge Crystallographic Data Center on quoting the depository numbers CCDC–1414316 to –1414321 (**2**, **3**, **8**, **10**, **12**, **14**).

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Graphical Abstract:

Hydroalumination of alkynyl-aminophosphines as a promising tool for the synthesis of unusual phosphines: P-N bond activation, a transient phosphaallene, a zwitterionic AlP_2C_2 heterocycle and a masked Al/P-based frustrated Lewis pair

Hans Klöcker, Marcus Layh, Alexander Hepp and Werner Uhl

Reactions of alkynyl-aminophosphines with H-Al^{t}Bu$_2$ afforded an AlP_2C_2 heterocycle on three routes. Small amino groups gave an aluminium-amino intermediate with an Al-N bond which resulted in aluminium amide elimination and formation of a transient 3H-phosphaallene. H-AlEt$_2$ gave a masked, P-H functionalized, FLP.