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C≡C Triple Bond Activation by Heterocyclic Aluminum Phosphinides

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Treatment of aryl-di(*tert*-butylethynyl)phosphines Aryl-P(C≡C-CMe$_3$)$_2$ [Aryl = C$_6$H$_5$ (**4**) 2,4,6-Me$_3$C$_6$H$_2$ (**5**)] with dialkylaluminum hydrides, R$_2$Al−H (R = CMe$_3$, CH$_2$CMe$_3$), afforded heterocyclic, zwitterionic compounds **6**−**9** by hydroalumination and release of the corresponding dimeric *tert*-butylethynyl-dialkylaluminum derivatives, [R$_2$Al-C≡C-CMe$_3$]$_2$ (**10** and **11**). The molecular structures of **6**−**8** reveal a P$_2$C$_2$Al ring with a tetracoordinated aluminum atom, two exocyclic C=C double bonds, a tricoordinated phosphorus atom, and a phosphonium cation carrying an aryl and an alkynyl group. The C≡C triple bond of **7** was inserted into the Al−P bonds of the heterocycles upon warming to give the bicyclic compound **13**. A similar compound (**12**) was directly formed when the bisalkyne **4** was treated with dineopentylaluminum hydride. Their molecular structures show the annulated four- (AlC$_2$P) and five-membered heterocycles (P$_2$C$_3$) to contain three different C=C double bonds. The sterically most shielded monocyclic compound (**8**; Aryl = 2,4,5-Me$_3$C$_6$H$_2$; R = CMe$_3$) decomposed upon warming. DFT calculations were used to examine these reactions.

Introduction

Hydroalumination is an effective method to reduce homo- or heteronuclear double or triple bonds,[1] but in most cases the organoaluminum intermediates have not been isolated and characterized. Recently, in examining the reactions with alkynes we found, besides the expected addition of R$_2$Al−H to the triple bond,[2] unprecedented secondary processes leading to aluminum/carbon clusters (carbaalanes **1**, Scheme 1),[3] cyclophane-type cages with bridging Al−R groups (**2**),[4] and carbocations resulting from C−H bond activation (**3**).[5] We have also shown that dipolar-induced *cis*/*trans* isomerization of the resulting olefins can occur depending on the nature of the substituents.[6] These reactions are mimicked by the selective hydrogallation of alkynes.[2,7] Here we extend these studies by addressing the influence of phosphine substituents on the hydroalumination reaction. We anticipated that their presence might lead to systems containing both donor (P) and acceptor (Al) groups, which in the context of frustrated Lewis pairs are of interest for the activation of small molecules.[8]

Results and Discussion

Phosphine-substituted alkynes are common building blocks for the synthesis of molecular frames and cages, a topic that has been reviewed recently,[9] and are capable of undergoing the so-called "click" reaction.[10] Here we describe the unconventional hydroalumination of phosphines carrying two

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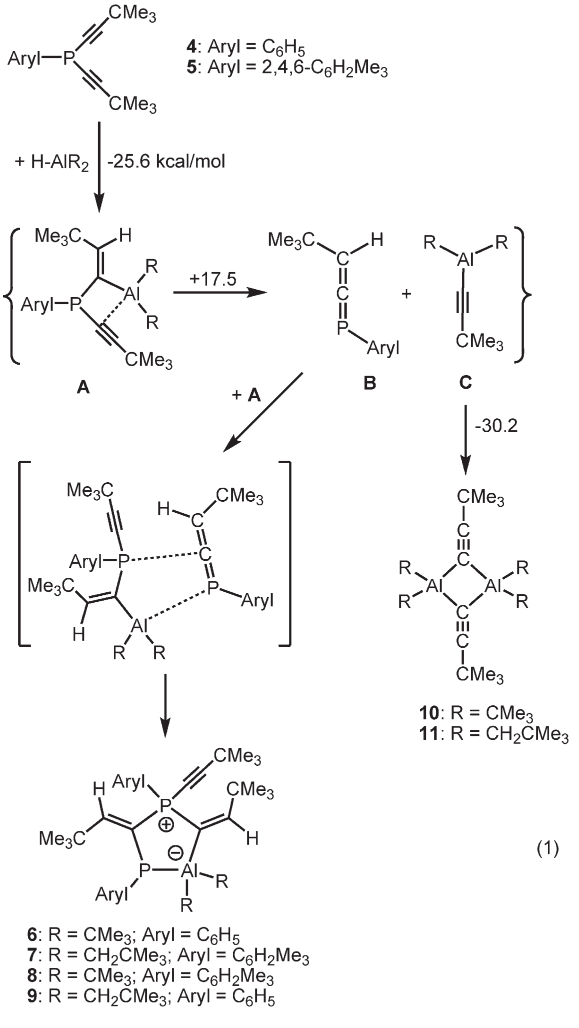
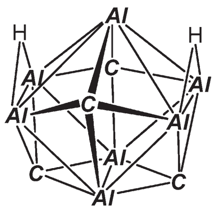
alkyne groups and examine the course of events by which the novel heterocyclic products are formed.

Hydroalumination of Dialkynylphosphines: Generating AlP_2C_2 Heterocycles. Reaction of the readily available aryl-di(*tert*-butylethynyl)phosphines, Aryl-P(C≡C-CMe_3)$_2$ [Aryl = C_6H_5 (**4**),[11] -2,4,6-$Me_3C_6H_2$ (**5**)], in *n*-hexane at room temperature with an equimolar amount of dineopentyl- and di(*tert*-butyl)aluminum hydride gave upon isolation red crystals of compounds **6**−**8** in 70−80% yield (eq 1). In addition, upon concentration of the mother liquors, the colorless dimeric dialkyl-ethynylaluminum compounds (R_2Al-C≡C-CMe_3)$_2$ [R = CMe_3 (**10**), CH_2CMe_3 (**11**)] could be isolated, as for **10**, on which one of us reported recently,[12] or identified by its characteristic ^{1}H NMR parameters, as for **11** [δ = 0.81 (Al-CH_2), 1.05 (C≡C-CMe_3), and 1.36 (CMe_3 of neopentyl) with a molar ratio of 2:1:2].



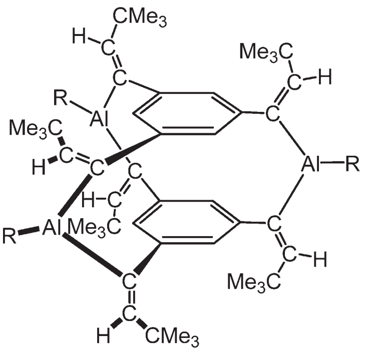
(1)

Scheme 1

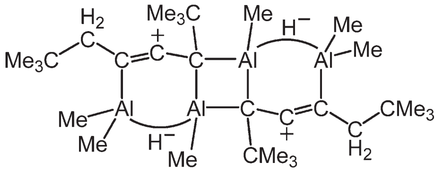


(***Al*** = AlMe; ***C*** = CCH_2CH_3)

1



2 (R = CMe_3)



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The complex NMR spectra of each of the three isolated reaction products (**6**−**8**) reveal the unexpected presence of five nonequivalent *tert*-butyl groups, making clear that the reaction was not a simple hydroalumination. This is also evident from the two observed ^{31}P NMR resonances at δ = −90 to −100 and −9 to −12 ($^2J_{PP}$ = 4 to 30 Hz), indicating that two phosphine molecules were used in the product formation. The ^{13}C NMR spectra reveal the presence of one C≡C bond (δ at about 73 and 123) and two different C═C bonds (δ at about 133 and 165). Hindered rotation causes two clearly resolved resonances for each set of *ortho*-methyl groups of the mesityl substituents of compound **8**. These NMR data suggest an exceptional five-membered AlC_2P_2 ring structure with two exocyclic double bonds as depicted in eq 1. The molecular structure of these compounds was established unequivocally by single-crystal X-ray structure determinations (Figures 1−3), each revealing that the AlC_2P_2 heterocycle deviates only slightly, up to about 0.20 Å, from planarity. The aluminum atom is tetracoordinated, carrying two alkyl groups. One of the phosphorus atoms is tricoordinated and has a trigonal-pyramidal conformation (average sum of the angles 315° for **6** and **7**; 334° for the more congested **8**), while the other is best described as a phosphonium cation carrying an aryl and an ethynyl group (C≡C 1.180 Å on average). This suggests zwitterionic character for these compounds, as shown in eq 1. The two heterocyclic P−C bonds of the phosphonium center differ in lengths by 0.06 to 0.09 Å, with the shortest being about 1.76 Å long. Each of the ring carbon atoms is part of an exocyclic C═C bond (C═C 1.342 Å on average). The *cis* Al,H arrangement of one of these bonds suggests that *cis*-addition has occurred to the C≡C bonds of **4** and **5**. The two bulky mesityl groups in **7** and **8** are at opposite sides of the AlC_2P_2 ring, probably due to steric crowding, as a *cis*-arrangement is found

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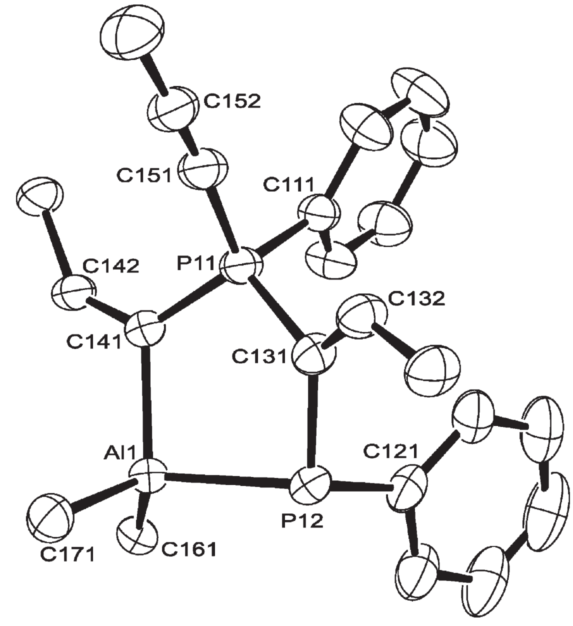

Figure 1. Molecular structure and numbering scheme of **6**. Thermal ellipsoids are drawn at the 40% probability level; hydrogen atoms and methyl groups are omitted for clarity. Important bond lengths [Å] and angles [deg] (values of the two other independent molecules in square brackets): P(11)−C(141) 1.764(3) [1.753(3), 1.761(3)], P(11)−C(131) 1.831(2) [1.826(3), 1.817(3)], P(12)−C(131) 1.842(3) [1.854(3), 1.826(3)], Al(1)−P(12) 2.431(1) [2.414(1), 2.426(1)], Al(1)−C(141) 2.037(2) [2.039(2), 2.042(3)], C(131)−C(132) 1.338(4) [1.335(4), 1.359(4)], C(141)−C(142) 1.345(4) [1.352(3), 1.341(4)], C(151)−C(152) 1.180(4) [1.186(4), 1.171(4)], P−C−Al 114.8 (av), P−C−P 119.3 (av), C−P−C 108.1 (av), P−Al−C 96.1 (av), Al−P−C 95.8 (av).

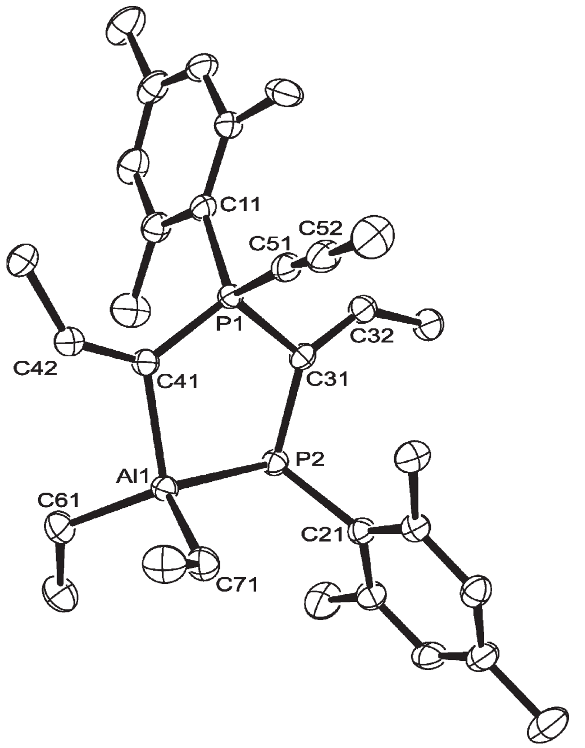

Figure 2. Molecular structure and numbering scheme of **7**. Thermal ellipsoids are drawn at the 40% probability level; hydrogen atoms and methyl groups of *tert*-butyl substituents are omitted for clarity. Important bond lengths [Å] and angles [deg]: P(1)−C(31) 1.837(1), P(1)−C(41) 1.775(1), Al(1)−C(41) 2.045(1), Al(1)−P(2) 2.4138(7), P(2)−C(31) 1.832(1), C(31)−C(32) 1.349(2), C(41)−C(42) 1.342(2), C(51)−C(52) 1.195(2), P(1)−C(41)−Al(1) 115.60(7), P(1)−C(31)−P(2) 116.98(7), C(31)−P(1)−C(41) 109.14(6), P(2)−Al(1)−C(41) 93.26(4), Al(1)−P(2)−C(31) 100.74(5).

for the two phenyl groups in **6**. Nevertheless, steric crowding is a stabilizing factor, which is evident from the inability to isolate the heterocyclic system from the reaction of the sterically less demanding combination of **4** and dineopentylaluminum hydride. Yet, monitoring this reaction at room temperature by ^{31}P NMR spectroscopy did show the formation of the five-membered heterocycle **9** (δ = −7.8 and −99.1; $^3J_{PP}$ = 35.4 Hz), but after two hours its concentration steadily diminished to give a different product, which we discuss in the next section.

First, how are the novel AlC_2P_2 heterocyclic compounds containing two phosphanyl fragments but only one dialkyaluminum group formed? Hydroalumination of one of the C≡C bonds of the starting dialkynylphosphines **4** and **5** is expected to give monoadduct **A** (eq 1) with an alkynyl and an alkenyl group attached to the central phosphorus atom. The exothermicity of this process is evident from the −25.6 kcal/mol calculated for the reaction of **4** with one-half of a di(*tert*-butyl)aluminum hydride dimer. The phosphorus-induced difference in charge separation between the two alkyne carbon atoms (NBO charges α-C −0.40; β-C +0.03; P +0.93) in **4** suggests a selective attack of the aluminum atom at the α-carbon atom. The DFT calculations (B3LYP/6-31G(d)) reveal a weak electrostatic interaction (Al···C 2.56 Å; Wiberg bond index 0.1) between the coordinatively unsaturated aluminum atom and the α-carbon atom of the intact ethynyl group of **A**, based on the NBO charges of the respective atoms, i.e., Al +1.93, α-C (C≡C) −0.49, β-C (C≡C) +0.08, α-C (C=C) −0.99, β-C (C=C) −0.18, P +0.95. Similar interactions and Al−C distances have been reported for several molecular structures of related silicon-centered compounds.[13] This close intramolecular Al,C-contact reflects the frustrated Lewis pair nature of **A** and likely initiates the elimination of the alkynyl-dialkylaluminum compounds **C**, which were detected as dimeric byproduct **10** and **11**, to afford the phosphaallene **B** as reactive intermediate. Phosphaallenes with their cumulated C=C and P=C bonds are well-known in the literature[14,15] and can be formed, for example, from congested dialkynyl-tri(*tert*-butyl)phenylphosphines by treatment with *tert*-butyllithium under expulsion of an ethynyllithium derivative.[15] The elimination of the

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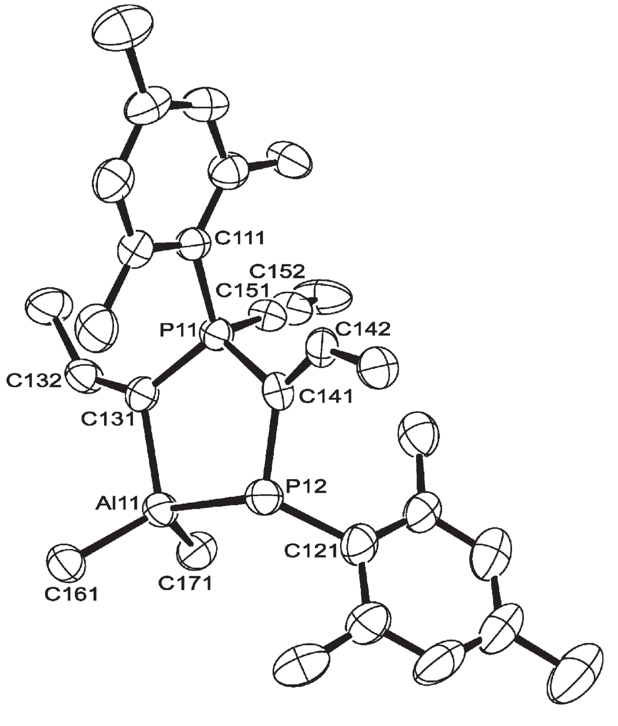


Figure 3. Molecular structure and numbering scheme of **8**. Thermal ellipsoids are drawn at the 40% probability level; hydrogen atoms and methyl groups of *tert*-butyl substituents are omitted for clarity. Important bond lengths [Å] and angles [deg] (values of the second molecule in square brackets): P(11)−C(141) 1.848(3) [1.825(3)], P(11)−C(131) 1.780(3) [1.778(3)], Al(11)−C(131) 2.053(3) [2.038(3)], Al(11)−P(12) 2.395(1) [2.399(2)], P(12)−C(141) 1.814(3) [1.804(3)], C(131)−C(132) 1.331(4) [1.341(4)], C(141)−C(142) 1.326(4) [1.339(4)], C(151)−C(152) 1.175(4) [1.171(5)], P(11)−C(131)−Al(11) 116.1(2) [117.9(2)], P(11)−C(141)−P(12) 115.6(2) [115.6(2)], C(131)−P(11)−C(141) 108.2(1) [108.4(2)], P(12)−Al(11)−C(131) 92.7(1) [91.2(1)], Al(11)−P(12)−C(141) 103.5(1) [104.7(1)].

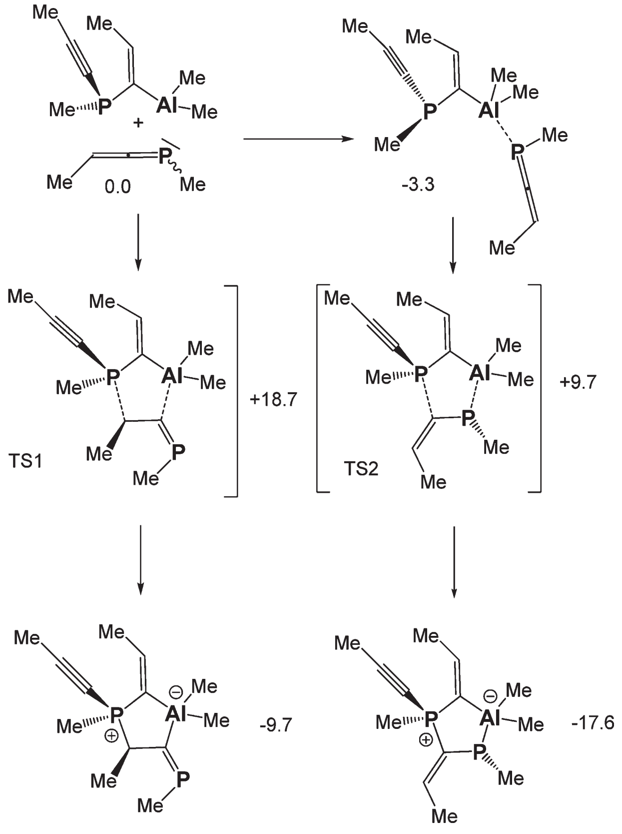
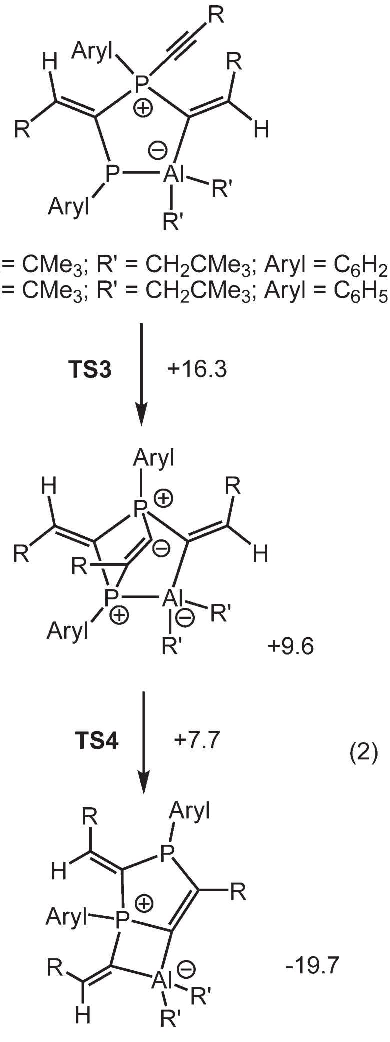


Figure 4. Calculated reaction pathways for the cycloaddition of the hydroalumintion product **A** with phosphallene **B** at the B3LYP/6-31G(d) level of theory utilizing all-methyl-substituted model systems.

alkynylaluminum fragment **C** and the formation of the unsaturated phosphorus intermediate **B** shows resemblance with this process. The likelihood of the fragmentation of **A** at room temperature is supported by the B3LYP-calculated modest endothermicity of +17.5 kcal/mol and is further facilitated by the dimerization of **C** (−30.2 kcal/mol). However, so far we have not been able to detect any in situ formed phosphaallene. This could mean that the phosphaallene **B** never reaches detectable concentrations during the reaction, as it is consumed immediately. The process by which this occurs is a 1,3-cycloaddition with the initial hydroalumination product **A** to give the observed heterocyclic compounds **6**−**9**. The likely path by which this happens is by coordinating first the aluminum atom of the frustrated Lewis pair **A** to the phosphorus atom of phosphaallene **B** with subsequent ring closure on P−C bond formation between the activated P=C bond and the tricoordinate phosphorus center (Figure 4). The cycloaddition is calculated to have a barrier of only 9.7 kcal/mol for the all-methyl-substituted model system and is exothermic by −17.6 kcal/mol. The alternative cycloaddition with the C=C bond of the phosphaallene that would give an $AlPC_3$ heterocycle with exocyclic C=C and C=P bonds instead is both kinetically and thermodynamically disfavored with a barrier of 18.7 kcal/mol and a reaction energy of −9.7 kcal/mol (Figure 4). The calculated structure of **6** is −13.6 kcal/mol more stable than **A** and **B** and shows a slightly longer Al−P bond (2.468 Å) than the experimental one (2.424 Å, Figure 1).

Bicyclic AlP_2C_3 Heterocycles: C≡C Insertion into AlP_2C_2 Monocycles. We return to the room-temperature reaction of phenyl-di(*tert*-butylethynyl)phosphine **4** with dineopentylaluminum hydride. Whereas this reaction also afforded the dialkyl-ethynylaluminum dimer **11**, the AlC_2P_2 heterocycle **9** that was observed only by ^{31}P NMR spectroscopy converted within 18 h fully into a single colorless product **12**, isolated in 51% yield. Its ^{31}P NMR spectrum showed two resonances with chemical shifts at $\delta = +56.0$ and +11.5 that differ greatly from those of **6**−**9**. The ^{13}C NMR spectrum showed the absence of ethynyl carbon resonances and instead ones attributable to three different C=C bonds, suggesting that an isomeric structure of the five-membered AlC_2P_2 heterocycle was formed with the monocyclic compound only as a reactive intermediate. This hypothesis was supported by the formation of a similar yellow compound (**13**) in 65% yield upon warming an *n*-hexane solution of **7** to 60 °C for 14 h (eq 2). Instead, the more congested monocyclic **8** (Aryl = 2,4,6-$Me_3C_6H_2$; R = CMe_3) decomposed under these conditions, resulting in di(*tert*-butyl)-*tert*-butylethynylaluminum **10** as the main component in the ^1H NMR spectrum together with unidentified products [$\delta(^{31}P)$ 56.0 (s), −10.2 (s), −47.1 and −69.8 (d; $J_{PP} = 126.2$ Hz; −52.3 and −72.8 (d; $J_{PP} = 119.0$ Hz), −95.5 (s)]. Also a mixture of two unidentified products

[$\delta(^{31}P)$ 54.3 and 12.0, J_{PP} = 15.1 Hz; δ = 44.5 and 14.7, J_{PP} = 5.6 Hz] resulted upon heating of **6**.



7: R= CMe_3; R' = CH_2CMe_3; Aryl = $C_6H_2Me_3$
9: R= CMe_3; R' = CH_2CMe_3; Aryl = C_6H_5

(2)

12: R= CMe_3; R' = CH_2CMe_3; Aryl = C_6H_5
13: R= CMe_3; R' = CH_2CMe_3; Aryl = $C_6H_2Me_3$

The constitution of **12** was revealed by crystal structure determination (Figure 5) and showed it to be a bicyclic structure in which a four- (AlC_2P) and a five-membered heterocycle (C_3P_2) are annulated across a central P−C bond. The structure of the five-membered ring is essentially planar with a deviation of only up to 0.05 Å. The angle between the planes of the two rings amounts to 31.6°. The aluminum atoms have a coordination number of four. One phosphorus atom is attached to three carbon atoms (trigonal pyramidal, sum of the angles 298.7°), and the other is best described as a phosphonium atom bearing a formal positive charge. Hence, also **12** is a zwitterionic compound. The three different C=C double bonds have similar lengths [1.326(4) to 1.339(4) Å] that are independent of their endo- or exocyclic position. The phenyl groups attached to the phosphorus atoms adopt a *cis* arrangement. In contrast, the NMR spectroscopic data suggest that the mesityl groups of **13** are in *trans* positions. Hence, we observe different diastereomeric forms similar to the discussed monocyclic compounds **6**−**8**. The mixture obtained upon heating of **6** may, in fact, contain both forms, but we were unable to isolate them. The steric congestion of the hypothetical bicyclic product is intermediate between that of **12** and **13**.

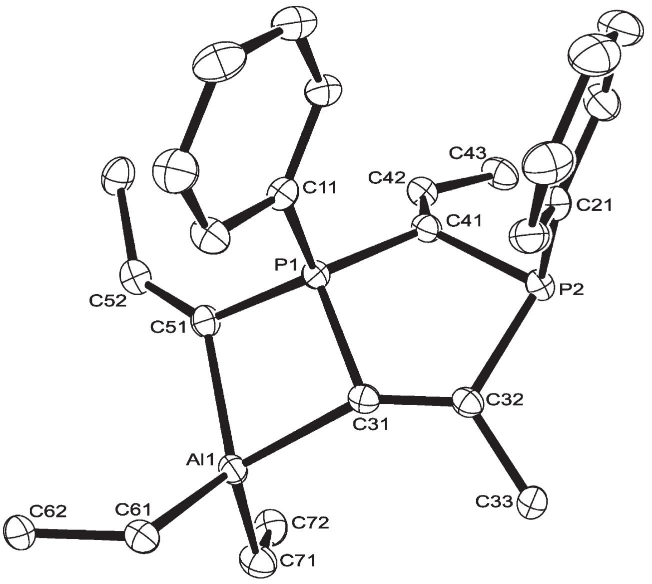


Figure 5. Molecular structure and numbering scheme of **12**. Thermal ellipsoids are drawn at the 40% probability level; hydrogen atoms and methyl groups are omitted for clarity. Important bond lengths [Å] and angles [deg]: P(1)−C(31) 1.790(3), P(1)−C(51) 1.797(3), P(1)−C(41) 1.808(3), P(2)−C(41) 1.865(3), P(2)−C(32) 1.873(3), Al(1)−C(51) 2.081(3), Al(1)−C(31) 2.069(3), C(31)−C(32) 1.339(4), C(41)−C(42) 1.326(4), C(51)−C(52) 1.336(4), Al(1)−C(31)−C(32) 146.7(2), Al(1)−C(31)−P(1) 92.4(1), P(1)−C(31)−C(32) 113.4(2), C(31)−P(1)−C(41) 98.6(1), C(31)−P(1)−C(51) 95.6(1), C(41)−P(1)−C(51) 127.0(1).

Bicyclic compounds **12** and **13** represent isomeric forms of monocyclic **6**−**9** and are formed by the formal insertion of the ethynyl group into the Al−P bond. An unprecedented cooperative activation of the triple bond appears to play an essential role. Bending the alkynyl substituent out of its axial position over the five-membered ring leads to overlap between the phosphorus lone pair and the ethynyl π^* orbital at the β-carbon to form a bicyclic intermediate (+9.6 kcal/mol) with an activation barrier of 16.3 kcal/mol (TS3, R, R', Aryl = Me) and a weakened Al−P bond of 2.547 Å. Breaking this bond (TS4) requires only 7.7 kcal/mol to form the more stable (−19.7 kcal/mol) bicyclic compound with the aluminum atom favoring the α-carbon atom of the former C≡C bond (eq 2; the calculated energies are given for the all-methyl-substituted model systems). The first step (**7** or **9** to TS3) resembles the nucleophilic activation of alkynes by electron-rich phosphines,[16] which in our case is followed by an unusual migration of the AlR_2 fragment from P to C.

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Recent investigations describe similar activations by so-called frustrated Lewis-acid Lewis-base pairs in which the interactions between the donor and acceptor atoms are negligibly small.[8] In the compounds presented here this activation may be particularly favorable, as a phosphinide anion is stabilized by adduct formation with a dialkylaluminum group. The negative charge localized at the phosphorus atom of the activated species with a weakened Al−P bond is balanced by the zwitterionic character.

Experimental Section

All procedures were carried out under an atmosphere of purified argon in dried solvents (*n*-hexane and *n*-pentane over $LiAlH_4$; diethyl ether over Na/benzophenone). Di(*tert*-butylethynyl)phenylphosphine,[9] dihalomesitylphosphine ($MesPX_2$, mixture with X = Cl, Br),[17] and di(neopentyl)-[18] and di(*tert*-butyl)aluminum hydride[19] were obtained according to literature procedures. Commercially available *tert*-butylethyne (3,3-dimethyl-1-butyne) was degassed, saturated with argon, and stored over molecular sieves. The assignment of the NMR spectra is based on HMBC, HSQC, ROESY, and DEPT135 data. Mass spectra were recorded with a Micromass Quattro LC-Z; IR spectra, with a Shimadzu IR PRESTIGE 21.

Synthesis of 5. A solution of 3,3-dimethyl-1-butyne (1.84 mL, 15.0 mmol) in 50 mL of diethyl ether was treated dropwise with a solution of *n*-butyllihium in *n*-hexane (1.6 M, 8.75 mL, 14 mmol) at −78 °C. The reaction mixture was allowed to warm to room temperature and further stirred for 1 h. After cooling to −78 °C dihalomesitylphosphine (1.51 g, 5.80 mmol) dissolved in 25 mL of diethyl ether was added dropwise. After 30 min at −78 °C the solution was warmed to room temperature and stirred for 14 h. Water was added. The organic layer was separated and washed with 25 mL of water. The aqueous phase was extracted three times with 25 mL of diethyl ether. The organic layers were dried over $MgSO_4$, and all volatiles were removed under vacuum. The remaining solid was thoroughly evacuated and dissolved in a mixture of 10 mL of diethyl ether and 10 mL of *n*-pentane. Colorless crystals of **5** were obtained upon cooling of the solution to −45 °C. Yield: 1.61 g (89%). Mp (argon, closed capillary): 147 °C. Anal. Calcd [$C_{21}H_{29}P$] (312.4): C, 80.7; H, 9.4. Found: C, 80.5; H, 9.5. ^{1}H NMR (C_6D_6, 400 MHz): δ 1.06 (18 H, s, C*Me*$_3$), 2.02 (3 H, s, *p*-Me of phenyl), 2.91 (6 H, s, *o*-Me of phenyl), 6.74 (2 H, d, $^{4}J_{PH}$ = 2.9 Hz, Aryl-*H*). ^{13}C NMR (C_6D_6, 100 MHz): δ 21.0 (*p*-Me), 23.1 (d, $^{3}J_{CP}$ = 19.7 Hz, *o*-Me), 28.9 (d, $^{3}J_{CP}$ = 1.1 Hz, *C*Me$_3$), 30.5 (d, $^{4}J_{CP}$ = 1.2 Hz, C*Me*$_3$), 73.8 (P-*C*≡C; coupling to phosphorus not detectable), 115.0 (d, $^{2}J_{CP}$ = 8.2 Hz, P-C≡*C*), 127.8 (*ipso*-C), 130.0 (d, $^{3}J_{CP}$ = 5.5 Hz, *m*-C), 140.2 (*p*-C), 144.6 (d, $^{2}J_{CP}$ = 19.1 Hz, *o*-C). ^{31}P NMR (C_6D_6; 81 MHz): δ −83.4. IR (paraffin, CsI plates, cm^{-1}): 2195 vs, 2149 vs νC≡C, 2012 vw, 1946 vw, 1911 w, 1883 w, 1792 w, 1759 m, 1726 s, 1694 w, 1630 w, 1601 s, 1566 m, 1551 s, 1533 m (aromatic ring); 1460 vs, 1356 vs (paraffin); 1290 m, 1238 vs δCH_3; 1200 vs, 1109 m, 1072 m, 1055 s, 1030 s, 937 vs, 849 vs, 768 vs νCC, δCH; 721 s (paraffin); 685 w, 640 vs, 613 vs, 571 vs, 530 vs, 509 s, 486 m, 436 s, 413 s νPC, δCC. MS (EI, 20 eV, 25 °C): *m*/*z* 312 (40%) (M^+), 297 (88%) (M^+ − Me), 255 (100%) (M^+ − CMe_3).

Synthesis of 6. Di(*tert*-butylethynyl)phenylphosphine **4** (0.303 g, 1.12 mmol) was dissolved in 10 mL of *n*-hexane and treated with a solution of di(*tert*-butyl)aluminum hydride (0.159 g, 1.12 mmol) in 10 mL of *n*-hexane at room temperature. The reaction mixture adopted a bright red color. Stirring was continued for 24 h. The solution was concentrated and cooled to 4 °C to obtain bright red crystals of compound **6**. Yield: 0.226 g (68%). Mp (argon, closed capillary): 116 °C (dec). Anal. Calcd [$C_{38}H_{57}AlP_2$] (602.8): C, 75.7; H, 9.5. Found: C, 75.3; H, 9.4. ^{1}H NMR (C_6D_6, 400 MHz): δ 0.98 (9 H, s, P-(Al)C=C(H)C*Me*$_3$), 1.01 (9 H, s, P-C≡C-C*Me*$_3$), 1.32 (9 H, s, P_2C=C(H)C*Me*$_3$), 1.44 and 1.58 (each 9 H, s, Al-C*Me*$_3$), 6.78 (1 H, m, *p*-H of Al-P-*Ph*), 6.87 (2 H, m, *m*-H of Al-P-*Ph*), 6.92 (2 H, m, *m*-H of C≡C-P-*Ph*), 6.94 (1 H, m, *p*-H C≡C-P-*Ph*), 7.24 (2 H, m, *o*-H of Al-P-*Ph*), 7.45 (1 H, dd, $^{3}J_{HP}$ = 31.4 and 16.9 Hz, P_2C=C(*H*)CMe$_3$), 7.59 (1 H, d, $^{3}J_{HP}$ = 74.9 Hz, P-(Al)C=C(*H*)CMe$_3$), 7.79 (2 H, dd, $^{3}J_{HH}$ = 7.5 Hz and $^{3}J_{HP}$ = 12.7 Hz, *o*-H of C≡C-P-*Ph*). ^{13}C NMR (C_6D_6, 100 MHz): δ 17.9 and 18.6 (each br, Al*C*Me$_3$), 28.9 (d, $^{3}J_{CP}$ = 18.1 Hz, P-C≡C-*C*Me$_3$), 29.3 (P-C≡C-C*Me*$_3$), 29.9 (P-(Al)C=C(H)-C*Me*$_3$), 30.1 (P_2C=C(H)C*Me*$_3$), 32.2 and 32.9 (each AlC*Me*$_3$), 37.7 (d, $^{3}J_{CP}$ = 20.1 Hz, P_2C=C(H)*C*Me$_3$), 40.9 (d, $^{3}J_{CP}$ = 12.0 Hz, P-(Al)C=C(H)*C*Me$_3$), 69.9 (dd, $^{1}J_{CP}$ = 129.8 Hz and $^{3}J_{CP}$ = 1.2 Hz, P-*C*≡C), 123.7 (d, $^{2}J_{CP}$ = 14.4 Hz, P-C≡*C*), 127.4 (d, $^{3}J_{CP}$ = 6.4 Hz, *m*-C of Al-P-*Ph*), 128.0 (*p*-C of Al-P-*Ph*), 128.7 (d, $^{1}J_{CP}$ = 10.7 Hz, P-(Al)*C*=C(H)CMe$_3$), 129.1 (d, $^{3}J_{CP}$ = 12.0 Hz, *m*-C of C≡C-P-*Ph*), 130.3 (d, $^{2}J_{CP}$ = 19.0 Hz, *o*-C of Al−P-*Ph*), 131.1 (d, $^{1}J_{CP}$ = 79.4 Hz, *ipso*-C of C≡C-P-*Ph*), 131.8 (d, $^{2}J_{CP}$ = 10.5 Hz, *o*-C of C≡C-P-*Ph*), 132.4 (d, $^{4}J_{CP}$ = 2.9 Hz, *p*-C of C≡C-P-*Ph*), 133.4 (dd, $^{1}J_{CP}$ = 67.8 and 62.8 Hz, P_2*C*=C(H)CMe$_3$), 144.0 (d, $^{1}J_{CP}$ = 32.3 Hz, *ipso*-C of Al-P-*Ph*), 173.5 (dd, $^{2}J_{CP}$ = 15.0 and 12.4 Hz, P_2C=*C*(H)CMe$_3$), 174.4. (d, $^{2}J_{CP}$ = 6.4 Hz, P-(Al)C=*C*(H)CMe$_3$). ^{31}P NMR (C_6D_6, 162 MHz): δ −100.4 (d, $^{2}J_{PP}$ = 29.8 Hz, *P*-Al), −8.5 (d, $^{2}J_{PP}$ = 29.8 Hz, *P*-C≡C). IR (paraffin, CsI plates, cm^{-1}): 2210 s, 2166 s νC≡C; 2062 m, 1985 w, 1964 w, 1935 w, 1910 w, 1890 w, 1861 w, 1838 w, 1589 s, 1568 s, 1551 vs, 1533 s aromatic ring, νC=C; 1452 (vs), 1375 vs (paraffin); 1308 m, 1252 s δCH_3; 1202 s, 1103 m, 1067 w, 1026 m, 1001 m, 957 m, 935 m, 897 w, 880 w, 845 w, 812 m, 777 m νCC, δCH, δCC; 721 s (paraffin); 692 m, 629 w, 588 m, 579 m, 534 w, 505 w, 461 vw νPC, νAlC, δCC. MS (EI, 20 eV, 90 °C): *m*/*z* 545 (100%) (M^+ − CMe_3), 489 (16%) (M^+ − CMe_3 − butene).

Synthesis of 7. A solution of di(*tert*-butylethynyl)mesitylphosphine **5** (0.102 g, 0.327 mmol) in 10 mL of *n*-hexane was treated with a solution of dineopentylaluminum hydride (0.056 g, 0.327 mmol) in 10 mL of *n*-hexane at room temperature. The reaction mixture became orange-red in a few minutes and was stirred for 24 h. Orange crystals were obtained upon concentration of the solution and cooling to 4 °C. Yield: 0.095 mg (81%). Mp (argon, closed capillary): 136 °C (dec). Anal. Calcd [$C_{46}H_{73}AlP_2$] (715.0): C, 77.3; H, 10.3. Found: C, 76.7; H, 10.1. ^{1}H NMR (C_6D_6, 400 MHz): δ 0.65 and 0.69 (each 1 H, s, C*H*$_2$CMe$_3$), 0.88 (9 H, s, P_2C=C(H)C*Me*$_3$), 0.95 (9 H, s, P-(Al)C=C(H)C*Me*$_3$), 0.97 and 1.07 (each 1 H, s, C*H*$_2$CMe$_3$), 1.15 (9 H, s, P-C≡C-C*Me*$_3$), 1.29 and 1.59 (9 H, s, CH$_2$C*Me*$_3$), 1.89 (3 H, s, *p*-Me of C≡C-P-*Mes*), 2.15 (3 H, s, *p*-Me of Al-P-*Mes*), 2.5−3.0 (12 H, br, m, *o*-Me), 6.15 (1 H, dd, $^{3}J_{HP}$ = 36.2 and 7.0 Hz, P_2C=C(*H*)CMe$_3$), 6.60 (2 H, br, *m*-H of C≡C-P-*Mes*), 6.93 (2 H, br., *m*-H of Al-P-*Mes*), 7.21 (1 H, d, $^{3}J_{HP}$ = 76.1 Hz, P-(Al)C=C(*H*)CMe$_3$). ^{13}C NMR (C_6D_6, 100 MHz): δ 20.8 (*p*-Me of C≡C-P-*Mes*), 21.1 (*p*-Me of Al-P-*Mes*), 25.0 (br, *o*-Me of C≡C-P-*Mes* and of Al-P-*Mes*), 28.4 (dd, $^{4}J_{CP}$ = 4.6 and 1.3 Hz, P_2C=C(H)C*Me*$_3$), 29.0 (P-C≡C-C*Me*$_3$) 29.2 (d, $^{3}J_{CP}$ = 2.6 Hz, P-C≡C-*C*Me$_3$) 29.4 (P-(Al)C=C(H)C*Me*$_3$), 32.3 and 32.9 (CH$_2$*C*Me$_3$), 33.9 and 34.4 (*C*H$_2$CMe$_3$), 35.6 and 35.9 (CH$_2$C*Me*$_3$), 36.7 (dd, $^{3}J_{CP}$ = 22.0 and 3.3 Hz, P_2C=C-(H)*C*Me$_3$), 39.6 (dd, $^{3}J_{CP}$ = 12.7 and $^{5}J_{CP}$ = 1.7 Hz, P(Al)C=C-(H)*C*Me$_3$), 73.2 (d, $^{1}J_{CP}$ = 138.5 Hz and $^{3}J_{CP}$ = 3.2 Hz, P-*C*≡C-CMe$_3$), 122.4 (d, $^{2}J_{CP}$ = 18.6 Hz, P-C≡*C*-CMe$_3$), 129.3 (br, *m*-C of Al-P-*Mes*), 131.5 (br, *m*-C of C≡C-P-*Mes*), 135.4 (*p*-C of Al-P-*Mes*), 135.6 (pseudo-t, $^{1}J_{CP}$ = 67.2 and 67.2 Hz, P_2*C*=C-(H)CMe$_3$), 136.2 (d, br, $^{1}J_{CP}$ = 19 Hz, P-(Al)*C*=C(H)CMe$_3$), 137.5 (dd, $^{1}J_{CP}$ = 30.5 Hz and $^{3}J_{CP}$ = 4.1 Hz, *ipso*-C of Al-P-*Mes*), 138.5 (dd, $^{1}J_{CP}$ = 86.7 Hz and $^{3}J_{CP}$ = 3.0 Hz, *ipso*-C of C≡C-P-*Mes*), 142.1 (d, $^{4}J_{CP}$ = 2.9 Hz, *p*-C of C≡C-P-*Mes*), 142.6 (br, *o*-C of C≡C-P-*Mes*), 144.8 (br, *o*-C of Al-P-*Mes*), 160.5 (pseudo-t, $^{2}J_{CP}$ = 9.8 and 9.8 Hz, P_2C=*C*(H)CMe$_3$),

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168.1 (dd, J_{CP} = 8.2 and 5.1 Hz, P-(Al)C═*C*(H)CMe$_3$). ^{31}P NMR (C$_6$D$_6$, 162 MHz): δ −89.4 (d, $^2J_{PP}$ = 8.9 Hz, *P*-Al), −12.1 (d, $^2J_{PP}$ = 8.9 Hz, *P*-C≡C). IR (paraffin, CsI plates, cm^{-1}): 2205 m, 2162 s νC≡C; 2127 w, 1726 w, 1694 w, 1645 w, 1601 s, 1553 s, 1537 m aromatic ring, νC═C; 1460 vs (paraffin); 1406 w δCH$_3$; 1375 vs (paraffin); 1306 w, 1288 m, 1246 s δCH$_3$, 1221 s, 1196 s, 1119 m, 1099 m, 1055 m, 1028 s, 1013 s, 1001 sh, 949 m, 930 m, 910 w, 897 w, 880 m, 849 vs, 791 vs, 775 vs, 743 vs νCC, δCH, δCC; 718 s (paraffin); 704 s, 677 vs, 648 s, 629 s, 608 m, 581 m, 550 w, 519 m, 501 m, 468 s, 457 s νPC, νAlC, δCC. MS (EI, 20 eV, 100 °C): *m*/*z* 715 (0.5%) (M$^+$ + H), 644 (100%) (M$^+$ − CHCMe$_3$).

Synthesis of 8. Di(*tert*-butylethynyl)mesitylphosphine **5** (0.131 g, 0.419 mmol) was dissolved in 10 mL of *n*-hexane and treated with a solution of di(*tert*-butyl)aluminum hydride (0.059 g, 0.419 mmol) dissolved in 10 mL of *n*-hexane at room temperature. The reaction mixture adopted immediately a red color. After 24 h the solution was concentrated and cooled to +4 °C to afford red crystals of the heterocyclic product **8**. Yield: 0.100 g (69%). Mp (argon, closed capillary): 114 °C (dec). Anal. Calcd [C$_{44}$H$_{69}$AlP$_2$] (687.0): C, 76.9; H, 10.1. Found: C, 76.6; H, 9.9. ^{1}H NMR (C$_6$D$_6$, 400 MHz): δ 0.88 (9 H, s, P$_2$C═C(H)C*Me*$_3$), 0.95 (9 H, s, P-(Al)C═C(H)C*Me*$_3$), 1.10 (9 H, s, P-C≡C-C*Me*$_3$), 1.32 and 1.66 (each 9 H, s, AlC*Me*$_3$), 1.90 (3 H, s, *p*-Me of C≡C-P-*Mes*), 2.16 (3 H, s, *p*-Me of Al-P-*Mes*), 2.47 (3 H, s, *o*-Me of C≡C-P-*Mes*), 2.82 (3 H, s, *o*-Me of Al-P-*Mes*), 2.83 (3 H, s, *o*-Me of C≡C-P-*Mes*), 2.99 (3 H, s, *o*-Me of Al-P-*Mes*), 6.09 (1 H, dd, $^3J_{HP}$ = 35.5 and 8.7 Hz, PC═C(*H*)CMe$_3$), 6.56 and 6.65 (each 1 H, s, *m*-H of C≡C-P-*Mes*), 6.90 and 6.91 (each 1 H, s, *m*-H of Al-P-*Mes*), 7.14 (1 H, dd, $^3J_{HP}$ = 77.5 Hz and $^4J_{HP}$ = 1.1 Hz, P-(Al)C═C(*H*)CMe$_3$). ^{13}C NMR (C$_6$D$_6$, 100 MHz): δ 17.7 (d, $^2J_{CP}$ = 30 Hz, Al*C*Me$_3$), 18.0 (d, $^2J_{CP}$ = 40 Hz, Al*C*Me$_3$), 20.8 (*p*-Me of C≡C-P-*Mes*), 21.1 (*p*-Me of Al-P-*Mes*), 25.0 (d, $^3J_{CP}$ = 31 Hz, *o*-Me of Al-P-*Mes*), 25.2 (d, *o*-Me of C≡C-P-*Mes*), 26.1 (dd, J_{CP} = 9.1 and 4.0 Hz, *o*-Me of C≡C-P-*Mes*), 27.5 (*o*-Me of Al-P-*Mes*), 28.4 (dd, $^4J_{CP}$ = 5.4 and 1.2 Hz, P-(Al)C═C(H)C*Me*$_3$), 28.9 (d, $^4J_{CP}$ = 1.9 Hz, P-C≡C-C*Me*$_3$), 29.3 (dd, $^3J_{CP}$ = 21.6 Hz, $^5J_{CP}$ = 1.4 Hz, P-C≡C-*C*Me$_3$), 29.5 (P-(Al)C═C(H)C*Me*$_3$), 32.9 (AlC*Me*$_3$), 33.4 (d, $^3J_{CP}$ = 3.5 Hz, AlC*Me*$_3$), 37.0 (dd, $^3J_{CP}$ = 21.6 and 3.0 Hz, P$_2$C═C(H)*C*Me$_3$), 40.1 (dd, $^3J_{CP}$ = 12.7 and 1.7 Hz, P-(Al)C═C(H)*C*Me$_3$), 73.1 (dd, $^1J_{CP}$ = 139.8 Hz and $^3J_{CP}$ = 3.9 Hz, P-*C*≡C-CMe$_3$), 122.5 (d, $^2J_{CP}$ = 17.9 Hz, P-C≡*C*-CMe$_3$), 127.1 (d, $^1J_{CP}$ = 71.4 Hz, *ipso*-C of C≡C-P-*Mes*), 129.5 (dd, $^3J_{CP}$ = 4.6 Hz and $^4J_{CP}$ = 5.0 Hz, *m*-C of Al-P-*Mes*), 129.5 (d, $^3J_{CP}$ = 1.9 Hz, *m*-C of Al-P-*Mes*), 131.4 (d, $^3J_{CP}$ = 5.2 Hz, *m*-C of C≡C−P-*Mes*), 131.5 (d, $^3J_{CP}$ = 1.6 Hz, *m*-C of C≡C−P-*Mes*), 132.5 (d, $^1J_{CP}$ = 19 Hz, P-(Al)*C*═C(H)CMe$_3$), 132.6 (dd, $^1J_{CP}$ = 65.9 and 61.3 Hz, P$_2$*C*═C(H)CMe$_3$), 134.9 (*p*-C of Al-P-*Mes*), 137.2 (d, $^1J_{CP}$ = 24.5 Hz, *ipso*-C of Al-P-*Mes*), 141.2 (dd, $^2J_{CP}$ = 32.5 Hz and $^4J_{CP}$ = 3.4 Hz, *o*-C of Al-P-*Mes*), 141.4 (d, $^2J_{CP}$ = 6.9 Hz, *o*-C of Al-P-*Mes*), 141.8 (*o*-C of C≡C-P-*Mes*), 142.3 (d, $^4J_{CP}$ = 2.9 Hz, *p*-C of C≡C−P-*Mes*), 143.0 (d, $^2J_{CP}$ = 15.2 Hz, *o*-C of C≡C−P-*Mes*), 159.9 (t, $^2J_{CP}$ = 12.0 Hz, P$_2$C═*C*(H)CMe$_3$), 167.3 (d, $^2J_{CP}$ = 8.8 and 6.0 Hz, P-(Al)C═*C*(H)CMe$_3$). ^{31}P NMR (C$_6$D$_6$, 162 MHz): δ −95.6 (d, $^2J_{PP}$ = 4.4 Hz, Al-*P*), −10.2 (d, $^2J_{PP}$ = 4.4 Hz, *P*-C≡C). IR (paraffin, CsI plates, cm^{-1}): 2205 s, 2162 s νC≡C; 2070 w, 1981 vw, 1886 w, 1746 w, 1728 w, 1697 w, 1649 vw, 1603 m, 1553 s, 1537 s, 1520 s aromatic ring, νC═C; 1454 vs, 1371 vs (paraffin); 1292 s, 1248 vs δCH$_3$; 1198 s, 1175 m, 1053 m, 1030 s, 1007 s, 949 s, 935 s, 912 m, 893 m, 849 s, 810 m, 777 m, 741 m νCC, δCH, δCC; 719 vs (paraffin); 673 m, 627 s, 583 s, 569 s, 554 s, 536 s, 519 m, 467 m, 419 m νPC, νAlC, δCC. MS (EI, 20 eV, 100 °C): *m*/*z* 630 (19%) (M$^+$ − butene), 550 (100%) (M$^+$ − C≡C-CMe$_3$ − butene + H).

Synthesis of 12. A solution of di(*tert*-butylethynyl)phenylphosphine **4** (0.200 g, 0.741 mmol) in 10 mL of *n*-hexane was treated with a solution of dineopentylaluminium hydride (0.126 g, 0.741 mmol) in 10 mL of *n*-hexane at room temperature. The pale yellow solution was stirred for 18 h, concentrated, and cooled to −30 °C to yield a colorless powder of compound **12**; repeated crystallization gave colorless crystals. Yield: 0.118 g (51%). Mp (argon, closed capillary): 138 °C (dec); color change to yellow at 128 °C. Anal. Calcd [C$_{40}$H$_{61}$AlP$_2$] (630.9): C, 76.2; H, 9.7. Found: C, 75.9; H, 9.7. ^{1}H NMR (C$_6$D$_6$, 400 MHz): δ 0.79 and 1.05 (each 1 H, s, C*H*$_2$CMe$_3$), 0.82 (9 H, s, P-(Al)C═C-(H)C*Me*$_3$), 0.96 and 1.04 (each 1 H, s, C*H*$_2$CMe$_3$), 1.32 (9 H, s, P$_2$C═C(H)C*Me*$_3$), 1.34 (9 H, s, CH$_2$C*Me*$_3$), 1.39 (9 H, s, Al-(P)C═C(P)C*Me*$_3$), 1.53 (9 H, s, CH$_2$C*Me*$_3$), 6.70 (2 H, m, *m*-H of (C═C)$_2$P-*Ph*), 6.75 (2 H, m, *m*-H of (C═C)$_3$P-*Ph*), 6.78 (1 H, m, *p*-H of (C═C)$_2$P-*Ph*), 6.80 (1 H, m, *p*-H of (C═C)$_3$P-*Ph*), 7.13 (1 H, dd, $^3J_{HP}$ = 23.0 and 22.0 Hz, P$_2$C═C(*H*)CMe$_3$), 7.24 (1 H, d, $^3J_{HP}$ = 77.2 Hz, P-(Al)C═C(*H*)CMe$_3$), 7.28 (2 H, m, $^3J_{HP}$ = 6.9 Hz, *o*-H of (C═C)$_2$P-*Ph*), 7.46 (2 H, pseudo-t, *o*-H of (C═C)$_3$P-*Ph*). ^{13}C NMR (C$_6$D$_6$, 100 MHz): δ 29.6 (d, $^4J_{CP}$ = 1.6 Hz, P-(Al)C═C(H)C*Me*$_3$), 30.6 (d, $^4J_{CP}$ = 7.4 Hz, Al-(P)C═C(P)C*Me*$_3$), 31.0 (d, $^4J_{CP}$ = 7.9 Hz, P$_2$C═C(H)C*Me*$_3$), 32.2 (*C*H$_2$CMe$_3$), 32.5 and 32.9 (CH$_2$*C*Me$_3$), 35.0 (br, *C*H$_2$CMe$_3$), 35.4 and 35.8 (CH$_2$C*Me*$_3$), 37.3 (d, $^3J_{CP}$ = 12.9 Hz, P$_2$C═C-(H)*C*Me$_3$), 38.2 (d, $^3J_{CP}$ = 16.2 Hz, P-(Al)C═C(H)*C*Me$_3$), 41.6 (dd, J_{CP} = 29.6 and 26.7 Hz, Al-(P)C═C(P)*C*Me$_3$), 127.9 (d, $^3J_{CP}$ = 6.0 Hz, *m*-C of (C═C)$_2$P-*Ph*), 128.1 (d, $^3J_{CP}$ = 10.7 Hz, *m*-C of (C═C)$_3$P-*Ph*), 128.6 (*p*-C of (C═C)$_2$P-*Ph*), 130.4 (d, $^4J_{CP}$ = 2.8 Hz, *p*-C of (C═C)$_3$P-*Ph*), 131.7 (d, $^2J_{CP}$ = 9.0 Hz, *o*-C (C═C)$_3$P-*Ph*), 131.8 (d, $^1J_{CP}$ = 35 and 3 Hz, P$_2$*C*═C-(H)CMe$_3$), 133.8 (d, $^4J_{CP}$ = 17.6 Hz, *o*-C of (C═C)$_2$P-*Ph*), 133.9 (d, $^1J_{CP}$ = 53.8 Hz, *ipso*-C of (C═C)$_3$P-*Ph*), 135.3 (d, $^1J_{CP}$ = 25.7 Hz, *ipso*-C of (C═C)$_2$P-*Ph*), 139.2 (d, $^1J_{CP}$ = 24.7 Hz, P-(Al)*C*═C(H)CMe$_3$), 164.3 (dd, $^2J_{CP}$ = 23.3 and 4.3 Hz, P$_2$C═*C*(H)CMe$_3$), 168.7 (d, $^2J_{CP}$ = 13.7 Hz, P-(Al)C═*C*-(H)CMe$_3$), 170.5 (br, Al-(P)*C*═C(P)CMe$_3$), 179.9 (d, $^1J_{CP}$ = 25.8 Hz, Al-(P)C═*C*(P)CMe$_3$). ^{31}P NMR (162 MHz, C$_6$D$_6$): δ 56.0 (d, $^2J_{PP}$ = 13.7 Hz, (C═C)$_3$*P*), 11.4 (d, $^2J_{PP}$ = 13.7 Hz, (C═C)$_2$*P*). IR (paraffin, CsI plates, cm^{-1}): 2073 w, 1967 w, 1950 w, 1898 w, 1883 w, 1823 w, 1809 m, 1780 vw, 1694 m, 1661 m, 1595 vs, 1568 s, 1551 m, 1508 vs aromatic ring, νC═C; 1466 vs, 1356 vs (paraffin); 1306 m, 1244 s δCH$_3$; 1221 s, 1202 s, 1157 w, 1109 s, 1069 w, 1028 s, 1011 s, 995 s, 964 vs, 941 vs, 932 s, 920 s, 905 vs, 878 vs, 860 vs, 847 vs, 775 s, 741 s νCC, δCH, δCC; 712 m (paraffin); 692 w, 677 w, 669 w, 638 w, 606 m, 559 s, 542 s, 530 s, 490 m, 465 s, 436 m νPC, νAlC, δCC. MS (EI, 20 eV, 90 °C): *m*/*z* 560 (100%) (M$^+$ − CHCMe$_3$), 502 (6%) (M$^+$ − CH$_2$CMe$_3$ − CMe$_3$).

Synthesis of 13. A solution of the monocyclic aluminum phosphinide **7** (0.048 g, 0.067 mmol) in 10 mL of *n*-hexane was heated to 60 °C for 14 h. Concentration at room temperature and cooling to +4 °C gave yellow crystals of **13**. Yield: 0.031 g (65%). Mp (argon, closed capillary): 94 °C (dec). Anal. Calcd [C$_{46}$H$_{73}$AlP$_2$] (715.0): C, 77.3; H, 10.3. Found: C, 76.9; H, 10.1. ^{1}H NMR (C$_6$D$_6$, 400 MHz): δ 0.72 (9 H, s, P$_2$C═C(H)C*Me*$_3$), 0.77 (2 H, s, C*H*$_2$CMe$_3$), 0.89 and 0.95 (each 1 H, s, C*H*$_2$CMe$_3$), 1.10 (9 H, s, CH$_2$C*Me*$_3$), 1.36 (9 H, s, P-(Al)C═C(H)C*Me*$_3$), 1.39 (9 H, s, Al-(P)C═C(P)C*Me*$_3$), 1.49 (9 H, s, CH$_2$C*Me*$_3$), 1.93 (3 H, s, *p*-Me of (C═C)$_2$P-*Mes*), 2.01 (3 H, s, *p*-Me of (C═C)$_3$P-*Mes*), 2.30 (3 H, s, *o*-Me of (C═C)$_3$P-*Mes*), 2.73 (6 H, s, *o*-Me of (C═C)$_2$P-*Mes*), 2.92 (3 H, s, *o*-Me of (C═C)$_3$P-*Mes*), 6.59 (1 H, s, *m*-H of (C═C)$_3$P-*Mes*), 6.65 (2 H, br, *m*-H of (C═C)$_2$P-*Mes*), 6.74 (1 H, dd, $^3J_{HP}$ = 21.6 and 17.2 Hz, P$_2$C═C*H*CMe$_3$), 6.79 (1 H, s, *m*-H of (C═C)$_3$P-*Mes*), 7.04 (1 H, d, $^3J_{HP}$ = 48.0 Hz, P-(Al)C═C(*H*)CMe$_3$). ^{13}C NMR (C$_6$D$_6$, 100 MHz): δ 20.7 (*p*-Me of (C═C)$_2$P-*Mes*), 21.0 (*p*-Me of (C═C)$_3$P-*Mes*), 23.0 and 24.5 (*o*-Me of (C═C)$_3$P-*Mes*), 23.3 and 27.2 (*o*-Me of (C═C)$_2$P-*Mes*), 28.4 (dd, $^4J_{CP}$ = 4.6 and 1.5 Hz, P$_2$C═C(H)C*Me*$_3$), 29.4 (d, $^4J_{CP}$ = 1.4 Hz, P-(Al)C═C(H)C*Me*$_3$), 31.4 (d, $^3J_{CP}$ = 7.2 Hz, Al-(P)C═C(P)C*Me*$_3$), 31.6 (CH$_2$*C*Me$_3$), 32.1 (*C*H$_2$CMe$_3$), 32.7 (*C*H$_2$CMe$_3$), 35.4 (CH$_2$C*Me*$_3$), 35.8 (CH$_2$C*Me*$_3$), 36.3 (dd, $^3J_{CP}$ = 11.8 and 2.0 Hz, P$_2$C═C(H)*C*Me$_3$), 37.6 (d, $^3J_{HP}$ = 30.0 Hz, P-(Al)C═C(H)*C*Me$_3$), 37.7 (CH$_2$*C*Me$_3$), 41.5 (dd, J_{CP} = 29.9 and 19.3 Hz, P-(Al)C═C(H)*C*Me$_3$), 126.7 (dd, $^1J_{CP}$ = 67.8 Hz and $^3J_{CP}$ = 3.7 Hz, *ipso*-C of (C═C)$_2$P-*Mes*), 130.3 (d, $^3J_{CP}$ = 8.1 Hz, *m*-C of (C═C)$_3$P-*Mes*), 130.5 (br, *m*-C of (C═C)$_3$P-*Mes*), 131.8 (d, $^1J_{CP}$ = 31.8 Hz, *ipso*-C of (C═C)$_3$P-*Mes*), 131.8 (br, *m*-C of (C═C)$_2$P-*Mes*), 135.4 (dd, $^1J_{CP}$ = 38.9 and 10.0 Hz, P$_2$*C*═C(H)CMe$_3$), 140.6 (d, $^4J_{CP}$ = 1.3 Hz, *p*-C of

Table 1. Crystal Data, Data Collection Parameters, and Structure Refinement Details of Compounds 6, 7, 8, and 12

	6	7	8	12
formula	$C_{38}H_{57}AlP_2$	$C_{46}H_{73}AlP_2$	$C_{44}H_{69}AlP_2$	$C_{40}H_{61}AlP_2$
cryst syst	triclinic	monoclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P2_1/n$	$P2_1/c$	$P\bar{1}$
Z	6	4	8	2
temp, K	153(2)	153(2)	153(2)	153(2)
D_{calcd}, Mg m^{-3}	1.013	1.032	1.018	1.068
a, Å	10.9603(4)	12.956(3)	23.453(5)	10.4008(5)
b, Å	23.8441(8)	20.415(4)	18.823(4)	10.9142(5)
c, Å	24.3899(7)	17.439(4)	22.344(5)	18.2195(8)
α, deg	74.501(3)	90	90	76.269(3)
β, deg	77.708(3)	93.87(3)	114.66(3)	79.021(3)
γ, deg	78.105(3)	90	90	81.930(3)
V, nm^3	5.9256(3)	4.602(2)	8.96(1)	1.9625(2)
μ, mm^{-1}	0.154 (Mo Kα)	0.141 (Mo Kα)	0.143 (Mo Kα)	1.388 (Cu Kα)
cryst dimens, mm	0.24 × 0.15 × 0.12	0.35 × 0.21 × 0.16	0.29 × 0.20 × 0.11	0.14 × 0.10 × 0.08
θ_{max}, deg	27.98	29.24	29.35	72.21
no. unique reflns	26 250	12 415	24 288	6654
no. of params	1217	463	920	403
R1 [reflns $I > 2\sigma(I)$]	0.0566 (13 355)	0.0375 (7920)	0.0507 (5347)	0.0564 (5778)
wR2 (all data)	0.1447	0.0925	0.0863	0.1437
max./min. residual electron density, 10^{30} e/m^3	0.398/−0.389	0.381/−0.342	0.355/−0.277	0.448/−0.255

(C═C)$_3$P-*Mes*), 141.9 (d, $^4J_{CP}$ = 2.6 Hz, *p*-C of (C═C)$_2$P-*Mes*), 142.9 (br, *o*-C of (C═C)$_2$P-*Mes*), 144.2 (d, $^2J_{CP}$ = 3.4 Hz, *o*-C of (C═C)$_3$P-*Mes*), 144.7 (br, *o*-C of (C═C)$_2$P-*Mes*), 145.4 (d, $^2J_{CP}$ = 5.4 Hz, *o*-C of (C═C)$_3$P-*Mes*), 147.2 (d, $^1J_{CP}$ = 24.1 Hz, P-(Al)*C*═C(H)CMe$_3$), 159.3 (br, P-(Al)*C*═C(P)CMe$_3$), 160.5 (d, $^2J_{CP}$ = 15.4 Hz, P$_2$C═*C*(H)CMe$_3$), 165.3 (d, $^2J_{CP}$ = 10.1 Hz, P-(Al)C═*C*(H)CMe$_3$), 175.4 (dd, $^1J_{CP}$ = 30.1 Hz and $^2J_{CP}$ = 2.2 Hz, Al-(P)C═*C*(P)CMe$_3$). ^{31}P NMR (C$_6$D$_6$; 162 MHz): δ 61.6 (d, $^2J_{PP}$ = 25.0 Hz, (C═C)$_3$*P*), 13.7 (d, $^2J_{PP}$ = 26.0 Hz, (C═C)$_2$*P*). IR (paraffin, CsI plates, cm^{-1}): 1726 w, 1713 w, 1694 w, 1661 w, 1645 w, 1605 m, 1578 m, 1557 w, 1520 w aromatic ring, νC═C; 1463 vs, 1378 vs (paraffin); 1304 (s), 1250 sh δCH$_3$; 1225 s, 1206 m, 1167 s, 1155 s, 1118 m, 1101 w, 1080 m, 1057 w, 1032 m, 1011 w, 964 s, 935 s, 891 m, 849 s, 770 m νCC, δCH, δCC; 723 s (paraffin); 685 w, 652 m, 626 m, 563 m, 521 m, 461 m νPC, νAlC, δCC. MS (EI, 20 eV, 90 °C): *m*/*z* 644 (100%) (M$^+$ − CHCMe$_3$).

Crystal Structure Determinations. Single crystals were obtained directly after concentration of the reaction mixture and cooling of the solutions as described with the synthetic procedures. The crystallographic data were collected with Bruker SMART APEX-II (Mo), STOE IPDS (Mo), and Bruker SMART 6000 (Cu) diffractometers. The crystals were coated with a perfluoropolyether, picked up with a glass fiber, and immediately mounted in the cooled nitrogen stream of the diffractometer. The crystallographic data and details of the final R values are provided in Table 1. All structures were solved by direct methods using the program system SHELXTL PLUS[20] and refined with the SHELXL-97[20] program via full-matrix least-squares calculations based on F^2. All non-hydrogen atoms were refined with anisotropic displacement parameters; hydrogen atoms attached to carbon were calculated on ideal positions and allowed to ride on the bonded atom with U = 1.2U_{eq}(C). Three *tert*-butyl groups of compound **6** were disordered; their methyl groups were refined on split positions (C153: site occupation factors 0.25:0.75; C343 0.34:0.66; C353 0.80:0.20). Compound **8** showed a similar disorder of four *tert*-butyl groups (C133 0.48:0.52; C153 0.41:0.59; C161 0.56:0.44; C253 0.33:0.67). Compound **8** was obtained as only weakly scattering crystals. Further details of the crystal structure determinations are also available from the Cambridge Crystallographic Data Center on quoting the depository numbers CCDC-755342 (**6**), -755343 (**7**), -755344 (**8**), and -755345 (**12**).

Quantum-Chemical Calculations. DFT calculations at the B3LYP/6-31G(d) level[21] were conducted by applying the Gaussian03 program package.[22] Second derivative calculations have been performed to ensure that the transition states have only one imaginary frequency. The calculations have been performed utilizing all-methyl-substituted model systems in order to establish the principal mechanistic pathways. Therefore we have chosen a standard DFT scheme being aware that substituent effects have been neglected for which dispersion-corrected density functional theory (DFT-D) would be a more appropriate approach.

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Supporting Information Available: CIF files giving the crystal data of compounds **6**, **7**, **8**, and **12**. Geometries of TS3 and TS4. This material is available free of charge via the Internet at http://pubs.acs.org.

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