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To be cited as: *ChemPlusChem* 10.1002/cplu.202000239

Link to VoR: https://doi.org/10.1002/cplu.202000239

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FULL PAPER

Additive-free Conversions of Internal Alkynes by Phosphanylalumanes Producing Phosphorus/Aluminum Frustrated Lewis Pairs

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Abstract: Alkyne-insertion into hetero element–element bond is recognized as one of the most atom economical routes in the synthesis of multi-substituted alkenes. Transition metal-catalyzed additions of bonds between Group 13 (B), 14 (Si, Ge, Sn), and 16 (S, Se) elements and radical additions of bonds between Group 14-16 elements with initiator/light have been widely investigated. On the other hand, the bond between Group 13 and 15 elements, *that is*, Lewis acid–Lewis base bond, is essentially promising to activate alkynes without additives, and the additions are quite useful for the direct synthesis of LA/LB-substituted alkenes applicable to intermolecular frustrated Lewis pairs (FLPs). However, there is no report on the addition reaction of such bonds toward alkyne. In this work, the reactions of alkynes with phosphanylalumanes, P–Al single-bond species, were investigated. The reactions with internal alkynes afforded the corresponding adducts with *cis*-1,2-form in moderate yields (54-80%). In addition, alkyne-adducts thus obtained work as new P/Al-based C_2-*vicinal* FLPs, and the FLP addition reactions with benzaldehyde and CO_2 were found. In the reaction of alkyne-adducts with dimethyl acetylenedicarboxylate, furthermore, we found an unexpected C_{Ar}–C_{Me} bond cleavage characteristic of this system.

Introduction

Conversions of small molecules such as carbon dioxide and hydrocarbons by chemical reactions is essential to synthesize useful compounds from various simple resources. Transformation of organic molecules using transition metal complexes is a powerful and practical method, but transition metals are rare[1] and often difficult to use in chemical industrial processes due to the high costs and the problem of resource depletion. Therefore, in recent years, the research which adapts naturally abundant main group elements to play the role of transition metals has been emphasized. For achieving this purpose, the use of frustrated Lewis pairs (FLPs)[2] and low-coordinated species[3] as reactive main group compounds has been promoted. In particular, the similarity of low-coordinated species of heavy main group element compounds that mimic the function of transition metal complexes has attracted considerable attention. The key is the synergistic orbital interaction with small molecules.[4] For example, the orbital interaction between a dimetallyne and ethylene is similar to the transition metal-ethylene interaction interpreted by the Dewar-Chatt-Duncanson model (Figure 1a).[5]

Based on this background, the direct bonding between a Lewis acid (LA) and a Lewis base (LB) (*e.g.*, Group 13 elements as a Lewis acid and Group 15 elements as a Lewis base) can acquire promising interactions toward small molecules (Figure 1b). Actually, P–B compounds, phosphanylboranes, show not only cycloaddition reactions but also "FLP-like" reactivity such as H_2 split.[6] Like aminoboranes (N–B), phosphanylboranes show distinct double-bond character. Although the degree of double-bond character of phosphanylboranes depends on the substituents on the P and B atoms, they have a significant P→B contribution irrespective of the substituents, indicating the decrease of their Lewis acidity/basicity.

Our working hypothesis is that the decrease of such π-interaction, which can be overcome with utilizing the longer σ-bond between the heavier main group elements, enhances the reactivity of LA–LB compounds and their substrate scope.[7] In this context, P–Al single-bond compounds (phosphanylalumanes) having a bond between the third-row elements can be suitable for the purpose. However, the reactivity of phosphanylalumanes has been hardly studied to date.[8]

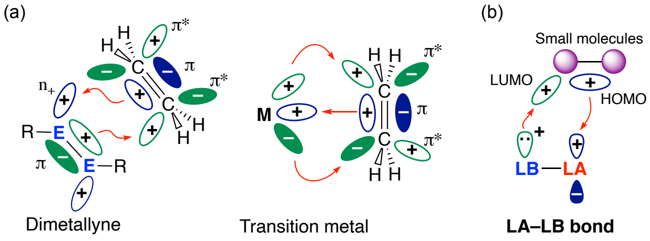


Figure 1. (a) Similarity of ethylene interactions of dimetallynes and transition metal compounds. (b) Postulated interactions of LA–LB bond with small molecules. E = heavier Group 14 elements, M = transition metals, LA = Lewis acid, LB = Lewis base.

Recently, we have reported the syntheses and structures of λ^3,λ^3-phosphanylalumane **1PAl** and λ^4,λ^4-phosphanylalumane **2PAl·LiCl** with carbon-based protecting groups on the P and Al atoms.[9] In particular, well separated LA–LB bond of **1PAl** has been revealed experimentally and theoretically.

Here, we report the reactions of phosphanylalumanes **1PAl** and **2PAl·LiCl** with alkynes as the start of a novel small molecule activation reaction using saturated species. In terms of the addition reactions of heteroatom-heteroatom bond (E–E'; E, E' = Group 13-16 element, not C) to alkynes are atom-efficient approaches in which two heteroatoms can be introduced at the same time. They are valuable from the viewpoints of the synthesis of multi-substituted alkenes [(E)C=C(E')] and their conversions.[10] However, most of the addition reactions of E–E' bonds toward alkynes require the help of additives, *e.g.*, transition metals,[11] radical initiators.[12] For the addition reactions of bonds between Group 13 (B), 14 (Si, Ge, Sn), and 16 (S, Se) elements to alkynes, transition metal (typically Pd, Pt) catalysts are necessary. Radical addition reactions of bonds between Group 14-16 elements need initiator or light. By contrast, several additive-free addition reactions of E–E bonds, such as P–P and B–B bonds, have been developed to date, the scope of the alkynes is pretty limited, *e.g.*, activated alkynes for the P–P and dialkyl- or alkyl,aryl-substituted acetylene for the B–B compounds.[13] The bonds between Group 13 and 15 elements (LA–LB bond) are essentially promising to activate alkynes without additives. However, there is no report on the addition reactions of such bonds toward alkynes. In addition, alkenes substituted with LA and LB moieties are valuable as new reactive species, FLPs. Therefore, the application of the addition reaction of phosphanylalumanes, "phosphanylalumination", with less reactive alkynes provides significant benefits as the development of simultaneously introduction of the LA/LB moieties. In this paper, we report the reactions of phosphanylalumanes with internal alkynes (RC≡CR; R = Ph, Et) giving the corresponding *cis*-1,2-adducts without any additives. Moreover, we demonstrate further investigation on the application of the resulting alkyne-adducts as a new type of C$_2$-*vicinal* P/Al-based FLPs (Figure 2).

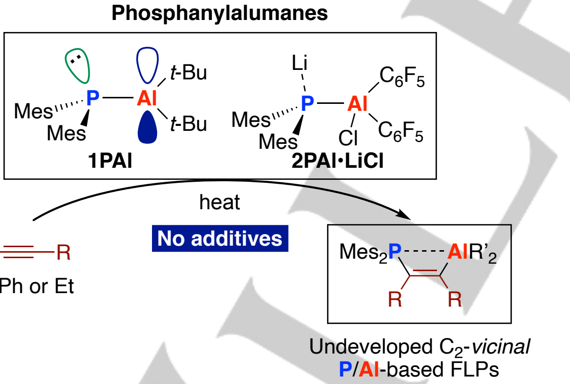
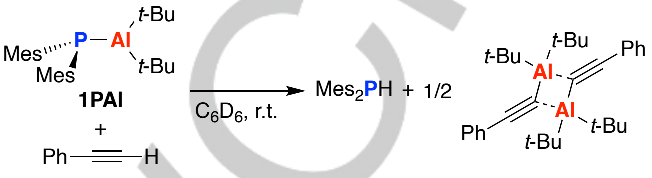


Figure 2. The summary of this work: Additive-free addition of P–Al bond to internal alkynes and development of unknown C$_2$-vicinal P/Al-based FLP chemistry. Mes = 2,4,6-trimethylphenyl.

Results and Discussion

Reaction with a terminal alkyne

Phosphanylalumane **1PAl** was treated with phenylacetylene (PhC≡CH) to give Mes$_2$PH quantitatively, as judged by NMR spectroscopy (Scheme 1). The corresponding product containing an Al moiety was assigned to be the alkynylaluminium dimer [PhC≡CAl(*t*-Bu)$_2$]$_2$,[14] the structure of which was suggested by the results of ^{1}H NMR spectroscopy and X-ray structural analysis. This result showed the deprotonation reaction of phenylacetylene, reflecting the high Lewis basicity of the P moiety of **1PAl**. Similar deprotonation reaction of phenylacetylene has been reported in the cases of P/Al-based intermolecular FLPs[15] and intramolecular FLPs.[2a,16] Therefore, it can be demonstrated that the high Lewis basicity of **1PAl** is comparable to that of P/Al-based FLPs.

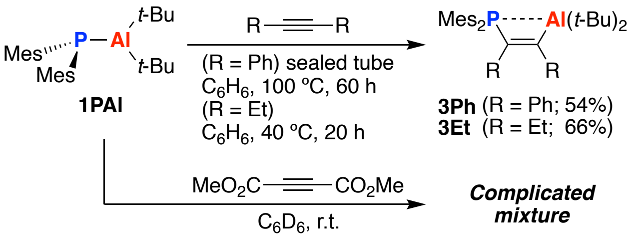


Scheme 1. Reaction of λ^3,λ^3-phosphanylalumane **1PAl** with phenylacetylene.

Reaction with internal alkynes

Next, we examined the addition reactions of **1PAl** toward internal alkynes to avoid the undesired deprotonation reaction.

When a mixture of diphenylacetylene and **1PAl** was heated in C$_6$D$_6$ at 70 °C, the consumption of **1PAl** and the increase one new major signal were observed by the monitoring of ^{31}P{^{1}H} NMR spectra. As a result of careful examination of conditions, *cis*-1,2-adduct **3Ph** was isolated in a moderate yield (54%) by heating in C$_6$H$_6$ at 100 °C for 60 h using a degassed *J.* Young Schlenk tube (Scheme 2). Similarly, the reaction of **1PAl** with dialkylacetylene, hex-3-yne, afforded the similar product **3Et** under more moderate conditions (in C$_6$H$_6$, 40 °C, 20 h; 66%) as compared with the case of diphenylacetylene. Single crystals of **3Ph** and **3Et** were obtained by recrystallization from benzene. Adduct **3Ph** is the first example of the product by the additive-free 1,2-addition of the heteroatom–heteroatom bond toward a diarylacetylene. On the other hand, the reaction of **1PAl** with an activated alkyne, such as dimethyl acetylenedicarboxylate (DMAD), gave a complicated mixture. As seen in the reaction of **1PAl** with benzophenone,[9] the presence of the carbonyl moiety promotes the homolysis of **1PAl**, and undesired decomposition is considered to proceed.



Scheme 2. Reactions of λ^3,λ^3-phosphanylalumane **1PAl** with internal alkynes.

Surprisingly, the reaction of λ^4,λ^4-phosphanylalumane **2PAl·LiCl** with diphenylacetylene gently proceeded even at room temperature (12 h in C$_6$H$_6$) to give the corresponding 1,2-addtion product **4Ph** almost quantitatively, as judged by ^{31}P{^{1}H} NMR spectroscopy (Figure 3a). As a result of recrystallization, a slight amount of single crystals encapsulating 0.5 molecules of diphenylacetylene **4Ph·0.5(PhCCPh)** were obtained (Figure 3b). These results suggested that **2PAl·LiCl** reacted with diphenylacetylene in accompany with the elimination of LiCl to give **4Ph**. Therefore, **2PAl·LiCl** is valued as an equivalent of λ^3,λ^3-phosphanylalumane **2PAl**. We speculate that the high Lewis acidity of **2PAl** with strongly electron-withdrawing groups enabled the rapid reaction at room temperature.

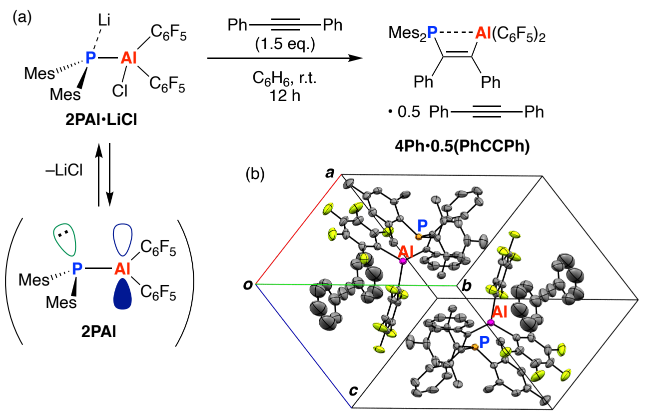
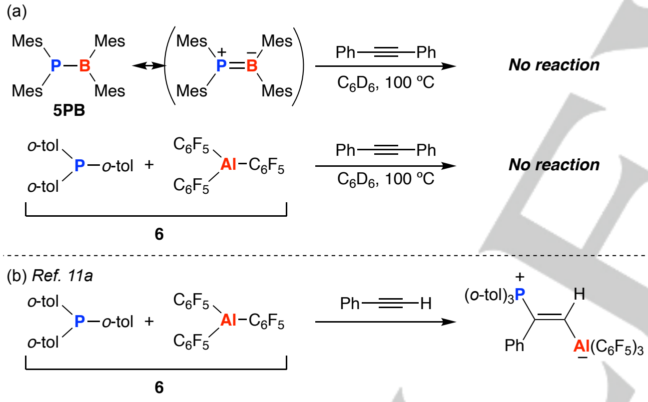


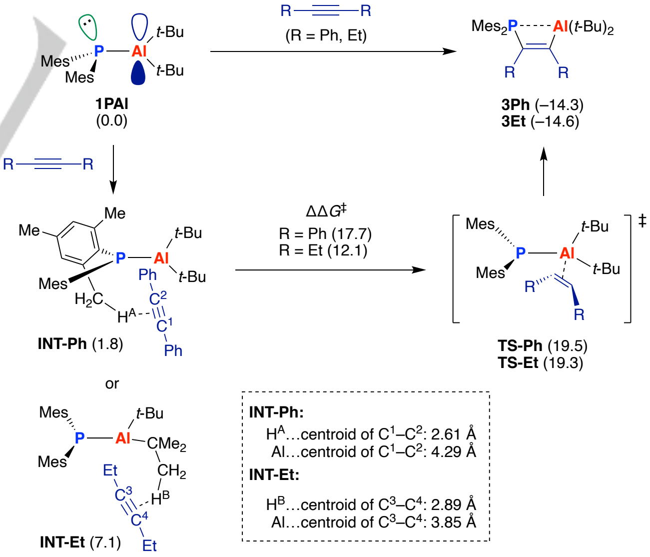
Figure 3. (a) Reaction of phosphanylalumane LiCl complex **2PAl·LiCl** with diphenylacetylene. (b) Crystal packing for **4Ph·0.5(PhCCPh)**. Hydrogen atoms are omitted for clarity.



Scheme 3. (a) Reactions of phosphanylborane **5PB** and a P/Al-based intermolecular FLP **6** with diphenylacetylene. (b) Activation of terminal alkyne by FLP **6** (Ref. 11a).

To clear the essentiality of phosphanylalumane for the activation of internal alkynes, we examined the reactions of diphenylacetylene with a λ^3,λ^3-phosphanylborane and an intermolecular P/Al-based FLP since such reactions have not been reported so far (Scheme 3). For the λ^3,λ^3-phosphanylborane, **5PB**[17] was selected due to the difficulty in the synthesis of [$Mes_2P–B(t\text{-}Bu)_2$] (**1PB**). The most common combination of [(o-tol)$_3$P and (C_6F_5)$_3$Al] (**6**) was selected for an intermolecular FLP. The reaction of a terminal alkyne (PhC≡CH) with FLP **6** gave a *trans*-1,2-adduct,[11a] while the reaction with internal alkynes remained unclear. However, these species did not react with diphenylacetylene even on heating up to 100 ºC in a sealed tube. Although we should consider the differences in the substituents and steric congestion among these systems, **5PB** and **6** are not preferred for the activation of diphenylacetylene. On the other hand, phosphanylalumanes have enough ability to activate less reactive internal alkynes, resulted from the retention of the functions of well-separated but single-bonded Lewis acid and base moieties close to each other to interact with alkynes effectively.

The reaction mechanism based on calculations is shown in Scheme 4. First, reactant complexes (**INT-Ph** and **INT-Et**) were formed. Probably due to steric hindrance, the CH(substituents)-π(alkyne) interactions were predominant in both **INT**s at this stage. Thus, the Al atom and alkynes were well separated (**INT-Ph**: 4.29 Å and **INT-Et**: 3.85 Å). It is noteworthy that the formation of **INT-Ph** proceeded with a very small barrier (1.8 kcal mol^{-1}). The transition states (**TS-Ph** and **TS-Et**) were concerned with the interaction between the 3p(Al) orbital of **1PAl** and the π orbital of alkynes, and their energies were almost the same (**TS-Ph**: 19.5 kcal mol^{-1} and **TS-Et**: 19.3 kcal mol^{-1}). Such transition state, which is formed by the interaction of the 3p(Al) orbital and π orbitals of alkynes, has also been seen in the case of an alumole with an alkyne,[18] supporting the presence of **TS** in these systems. Charge distribution should be important in the formation of π-complexes involving the 3p(Al) orbital and π-orbital of alkynes, where the initial CH(substituents)–π(alkyne) intermediate may be affected by steric hindrance. Even if the substituents involved are different (Mes or *t*-Bu), the charge distribution is unlikely to result in greater selectivity in the formation of the CH–π intermediate. In addition, no stability changes of the products are observed in both cases (**3Ph**: –14.3 kcal mol^{-1} and **3Et**: –14.6 kcal mol^{-1}). However, the barrier from **INT** to **TS** was found to be much higher for **TS-Ph** than that for **TS-Et** (R = Ph: 17.7 kcal mol^{-1} > R = Et: 12.1 kcal mol^{-1}), being consistent with the requirement of severe heating in the synthesis of **3Ph**.



Scheme 4. (a) Calculated reaction mechanism for the reaction of **1PAl** with internal alkynes. Relative Gibbs free energies (Δ*G* in kcal mol^{-1}) were calculated at the B3LYP-D3/6-31G(d) level of theory and are shown in parentheses.

Structures and properties of alkyne-adducts 3 and 4

The alkyne-addition products **3Ph**, **3Et**, and **4Ph·0.5(PhCCPh)** were characterized by NMR spectroscopy and X-ray crystallography. The molecular structures of **3Ph**, **3Et**, and

4Ph (a selected part from **4Ph·0.5(PhCCPh)**) are shown in Figures 4a-c. All compounds contain the P and Al moieties bound at the *cis*-1,2-position of C–C double bonds. In the case of **4Ph**, two of the aryl rings on the P and Al atoms are facing each other in parallel reflecting the intramolecular π-π interactions whose distance between the two aryl planes (3.613 Å) is within the range of typical face-to-face interactions (3.3-3.8 Å) (Figure 4d).[19] The P···Al distances of alkyne-adducts [**3Ph**: 2.614(1) Å, **3Et**: 2.5848(7) Å, and **4Ph**: 2.441(1) Å] are longer than those of **1PAl** [2.343(1) and 2.347(1) Å, for the two independent molecules][9] and the sum of the covalent radii ($r_{\mathrm{cov,Al}} + r_{\mathrm{cov,P}}$ = 2.37 Å).[20] The sum of the bond angles around the Al moiety in **3Ph** (349.0°) indicates slightly pyramidalized geometry toward the P moiety in contrast to that of **1PAl** (356.6°) which has a planar Al structure. These values indicated the existence of the non-bonding P→Al interactions and their pseudo four-membered ring structures, which have already been known in the P/B systems.[21]

The ^{31}P{^{1}H} NMR signals of **3Ph**, **3Et**, and **4Ph** [**3Ph**: –2.9 ppm, **3Et**: –11.4 ppm, and **4Ph·0.5(PhCCPh)**: 8.6 ppm] appeared in lower magnetic field than that of $Mes_2PCH{=}CH_2$ (–22.0 ppm).[22] These values indicated the lower electron deficiency in the Mes_2P moieties of **3** and **4** compared to that of $Mes_2PCH{=}CH_2$, demonstrating the presence of P→Al interaction.

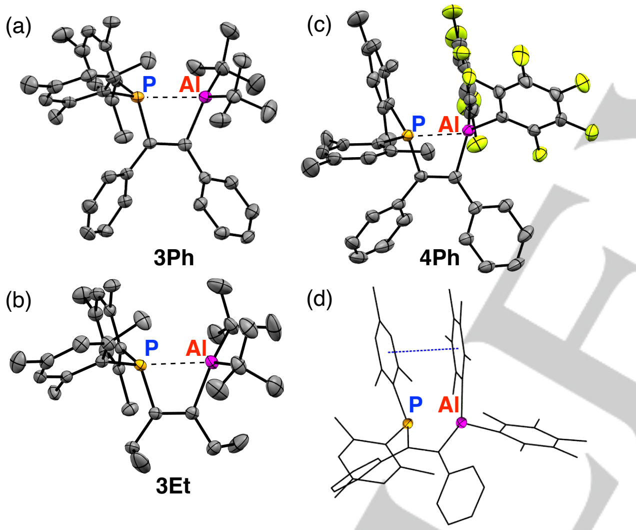
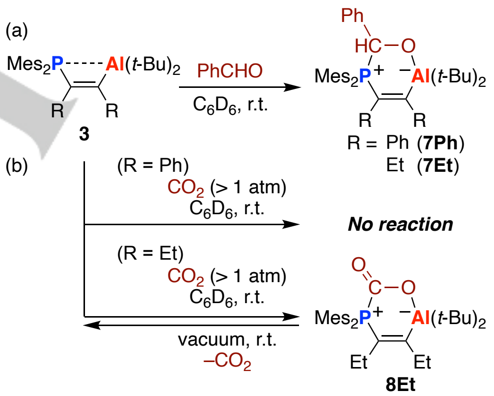


Figure 4. Structures of **3Ph** (a), **3Et** (b), and **4Ph** (c) (a selected part from **4Ph·0.5(PhCCPh)**) (thermal ellipsoids at the 50% probability level). Hydrogen atoms and disordered molecules of **3Ph** are omitted for clarity. Color code: Al, magenta; C, gray; F, light yellow; P, orange. (d) Intramolecular π-π interactions in **4Ph**.

The C–C bond lengths of the [P*CC*Al] moiety [**3Ph**: 1.357(4) Å, **3Et**: 1.352(2) Å, and **4Ph**: 1.365(4) Å] were almost identical to that of the C–C double bond (ca. 1.35 Å). The ^{13}C{^{1}H} NMR signals of Al-bound carbon atoms ($=C^{Al}$) displayed low-field shifted resonances (**3Ph**: 192.6 ppm and **3Et**: 193.1 ppm) as compared with those of P-bound carbon atoms ($^{P}C=$) (**3Ph**: 145.7 ppm and **3Et**: 148.4 ppm), and those of B-bound carbon atoms ($=C^{B}$) in a P/B analogue (159.4 ppm).[21b] The ^{13}C signal of a vinyl carbon atom connected to a main-group element is known to appear in the range of 120-210 ppm. Such extremely low-field NMR signals of the Al-bound alkenyl C atoms are also seen in other alkenylaluminum species.[23]

Reactivity of alkyne-adducts 3Ph and 3Et as intramolecular P/Al-based FLPs

Compounds **3Ph** and **3Et** are the first Al-analogues of the known unsaturated C_2-bridged P/B Lewis pairs developed by Erker *et al.,*[24] which were synthesized by the cooperative 1,1-addition reactions of $B(C_6F_5)_3$ to P-substituted alkynes.[2,24] As for the previous studies on Al-containing C-bridged FLPs, Uhl *et al.* have developed the chemistry of C_1-*geminal* P/Al-FLPs by hydroalumination of alkynes.[25] Compounds **3Ph** and **3Et** are considered to act as unexplored C_2-*vicinal* P/Al-based FLPs, a new family of C-bridged FLPs. The detailed comparison of the structures and spectroscopic properties between **3Ph** and **3Et** will allow us to discuss the P→Al interactions and their reactivity depending on the substituents on C_2-backbone. Although the P···Al distance of **3Et** is shorter than that of **3Ph** [**3Et**: 2.5848(7) Å < **3Ph**: 2.614(1) Å], the n(P)→3p(Al) orbital interactions are estimated to be much smaller than that of **3Ph** (**3Et**: 10.3 kcal mol^{-1} < **3Ph**: 23.5 kcal mol^{-1}) by theoretical calculations. These values reflected more twisted structure of **3Et** than that of **3Ph** (P–C=C–Al; **3Et**: 18.4° > **3Ph**: 9.7°). These results were also supported by the ^{31}P{1H} NMR resonance of **3Et** appeared at higher magnetic field than that of **3Ph** (**3Et**: –11.4 ppm < **3Ph**: –2.9 ppm). Therefore, **3Et** can be considered to be more reactive than **3Ph**.



Scheme 5. Reactions of alkyne-adduct **3** with benzaldehyde (a) and CO_2 (b).

When the C_6D_6 solutions of **3Ph** and **3Et** were treated with benzaldehyde, the reactions proceeded instantaneously to give the corresponding 6-membered ring compounds **7Ph** and **7Et**, respectively, in quantitative yields (Scheme 5a). They showed the typical 1,2-addition reaction to benzaldehyde as intramolecular FLPs.[26,27] At room temperature, broadened or complicated ^{1}H, ^{13}C, and ^{31}P signals of **7Ph** and **7Et** were observed probably due to the presence of rotamers and/or partial cleavage of the P–C bond. Therefore, we could not observe the splitting of resonances of the diastereotopic *t*-Bu groups. While we could observe simple spectra at the reported temperatures (**7Ph**: 368 K, **7Et**: 268 K), rapid ring inversion with the P–C bond cleavage would occur at the temperature to show the single signals for the *t*-Bu group. These reactions were overwhelmingly faster than the known *vicinal*-P/B system,[26] reflecting the weaker orbital interaction in n(P)→3p(Al) than n(P)→2p(B) and the higher Lewis acidity of Al than B. However, as well as the cases of the corresponding *vicinal*-P/B analogues, **3Ph** or even **3Et** was unreactive toward the industrially important gases (H_2, CO, NO_2) and a terminal alkyne (PhC≡CH). On the other hand, the C_6D_6 solution of **3Et** was subjected to the reaction with CO_2 at room temperature to afford CO_2-adduct **8Et** as judged by NMR spectroscopy, while no reaction was observed in the case of **3Ph** (Scheme 5b). The $^{13}C\{^1H\}$ signals corresponding to the carbonyl moiety in a mixture of **3Et** and excess CO_2 are observed as doublet signals at 159.7 ppm ($^1J_{CP}$ = 102.7 Hz), which are comparable to those of the CO_2-adducts of saturated C_2-*vicinal* P/B system (160.5 ppm, d, $^1J_{CP}$ = 89.0 Hz)[28] and C_1-*geminal* P/Al system (165.1 ppm, d, $^1J_{CP}$ = 106.5 Hz).[2a] However, the captured CO_2 is very labile to dissociate from **8Et**, and **3Et** quickly regenerated in the absence of excess amount of CO_2. Therefore, the isolation of **8Et** in the solid state has not been achieved yet by any attempts. It should be noted that this is the first binding of CO_2 in unsaturated C_2-*vicinal* FLPs. This study demonstrates the extension of the FLP chemistry by the use of Al.

X-Ray crystallographic analysis for **7Ph** and **7Et** showed the distorted six-membered ring structures as well as the case of *vicinal* P/B-based FLPs[26] (Figure 6). The P⋯Al distances of **7** are much longer than those of **3** [**3Ph**: 2.614(1) Å → **7Ph**: 3.5575(9) Å and **3Et**: 2.5848(7) Å → **7Et**: 3.5021(6) Å], being consistent with that the chemical shifts of the $^{31}P\{^1H\}$ NMR in **7** were shifted to lower fields (**3Ph**: –2.9 ppm → **7Ph**: –0.99 ppm and **3Et**: –11.4 ppm → **7Et**: 6.4 ppm).

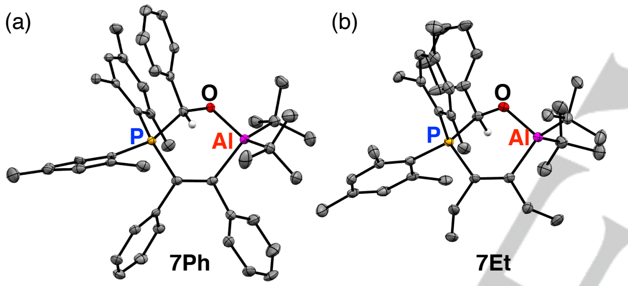
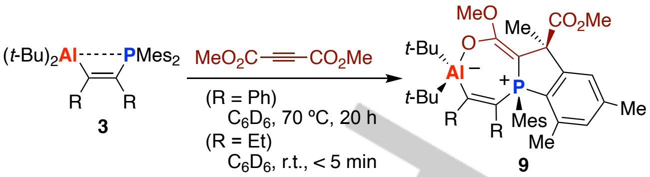


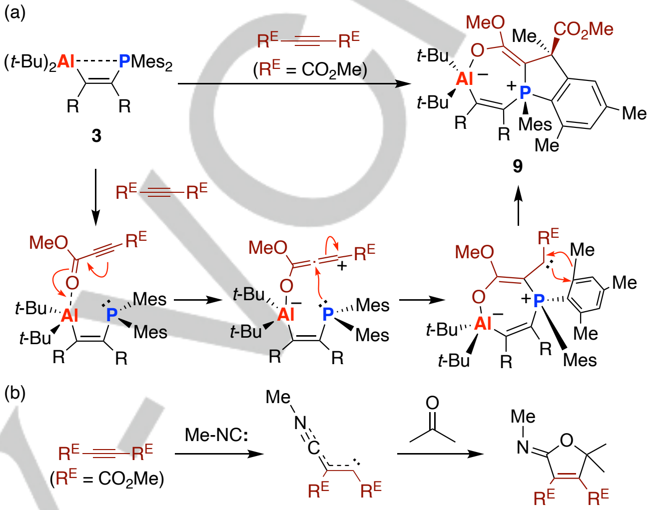
Figure 5. Structures of **7Ph** (a) and **7Et** (b) (thermal ellipsoids at the 50% probability level). Hydrogen atoms except for a C–H of benzaldehyde moieties and disordered molecules of **7Et** are omitted for clarity. Color code: Al, magenta; C, gray; H, white; O, red; P, orange.

Reactions of 3 with DMAD: Unexpected C–C bond cleavage

Alkyne-adducts **3** did not react with the second molecule of internal alkyne, and the reaction of **1PAl** with DMAD gave a complicated mixture as described in Scheme 2. However, the reaction of **3Et** with DMAD at room temperature gave the signals assignable to quantitatively formed one product as judged by the ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. X-Ray crystallographic analysis revealed the structure of the fused heterocyclic compound **9Et**, in which an ethynyl carbon atom of DMAD was inserted into the C_{Ar}–C_{Me} bond of the Mes group bound to the P atom (Scheme 6). On the other hand, the treatment of **3Ph** with DMAD at room temperature gave two major signals (18.7 ppm and –7.7 ppm) as judged by the $^{31}P\{^1H\}$ NMR spectroscopy reflecting the difference of reactivity between **3Ph** and **3Et**, but the mixture was converted into the major product **9Ph** (18.7 ppm) after heating to 70 ºC for 20 h. Thus, the compound corresponding to the signal at –7.7 ppm in the $^{31}P\{^1H\}$ NMR spectroscopy is assumed to be an intermediate in this reaction, although this species has not yet been isolated.



Scheme 6. Reactions of **3** with DMAD.



Scheme 7. Reactions of a P/Al-based intermolecular FLP **5** (a) and phosphanylborane **6PB** with diphenylacetylene (b).

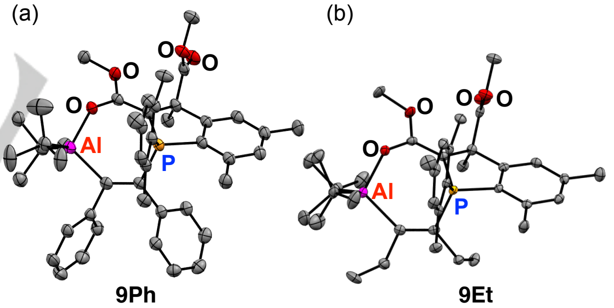


Figure 6. Structures of (a) **9Ph** and (b) **9Et** (thermal ellipsoids at the 50% probability level). Hydrogen atoms and solvent molecules of **9Ph** are omitted for clarity. Color code: Al, magenta; C, gray; O, red; P, orange.

To date, several studies have been reported for the activation of a C_{Ar}–C_{Ar} bond in main group species (Al(I) anion[29] and Si(II)[30]). However, the formation of **9** mentioned above is noteworthy as the first example of the transition metal-free C_{Ar}–C_{Me} bond cleavage. In the activation of the C_{Ar}–C_{Me} bond (stronger than the benzylic C–H bond[31]) using transition metal complexes, the oxidative addition was promoted by bringing the transition metals spatially close to the C_{Ar}–C_{Me} bond by the chelation.[32] This characteristic C_{Ar}–C_{Me} bond activation by P/Al-based FLPs would be postulated to be caused by the formation of highly reactive carbenoid, which may insert into the spatially close C_{Ar}–C_{Me} bond (Scheme 7a). On the other hand, it has been reported that some isocyanides coordinated to the adjacent carbon atom of DMAD to generate carbenoid intermediate (Scheme 7b).[33] Based on this

10.1002/cplu.202000239

result, it is considered that a carbenoid-type species is generated by the electron donation from the P atom in our system. To the best of our knowledge, however, such carbenes (or carbenoids) have never inserted into the $\mathrm{C_{Ar}}$–$\mathrm{C_{Me}}$ bond so far. Furthermore, no reaction was observed when **3Et** was treated with methyl tetrolate ($\mathrm{MeC{\equiv}CCO_2Me}$) or methyl phenylpropiolate ($\mathrm{PhC{\equiv}CCO_2Me}$). These results suggested that the reaction did not proceed unless carbenoid-type species generated in the presence of a sufficient electron-withdrawing moiety.

X-Ray crystallographic analysis of **9Ph** and **9Et** revealed the fused ring structures with 7, 5, and 6-membered rings. (Figure 6). The 7-membered rings are highly distorted as compared with the nearly planar 5 and 6-membered rings.

Conclusion

In summary, the reactions of phosphanylalumanes, P–Al single-bond species, with alkynes were investigated. In the reaction of **1PAl** with phenylacetylene (a terminal alkyne), deprotonation reaction proceeded, demonstrating the high Lewis basicity of **1PAl**. On the other hand, in the reaction with internal alkynes on heating, **1PAl** achieved the activation of internal alkynes, which was not realized with a P–B single-bond compound **5PB** and a common intermolecular FLP **6**. Similarly, **2PAl·LiCl** was found to serve as an equivalent of λ^3,λ^3-phosphanylalumane **2PAl** to activate diphenylacetylene at room temperature, reflecting its high Lewis acidity.

Moreover, the chemistry of P/Al-based $\mathrm{C_2}$-*geminal* FLPs was greatly developed by using alkyne-adducts **3Ph** and **3Et**. They were found to undergo the typical FLP-addition reactions with benzaldehyde and the reversible binding with $\mathrm{CO_2}$ as can be seen in P/B-based $\mathrm{C_2}$-*vicinal* and P/Al-based $\mathrm{C_1}$-*geminal* FLPs. Quite interestingly, the reactions of **3** with dimethyl acetylenedicarboxylate (DMAD) afforded a very unique fused ring compounds **9**, in which the $\mathrm{C_{Ar}}$–$\mathrm{C_{Me}}$ bond of a Mes substituent was cleaved at room temperature. Further small molecule activation reactions using phosphanylalumanes are currently in progress.

Experimental Section

General

All the manipulations were performed under a dry argon atmosphere using standard Schlenk techniques or gloveboxes. Solvents were purified by the Ultimate Solvent System, Glass Contour Company (THF, toluene, and hexane)[34] or by trap-to-trap distillation from a potassium mirror prior to use ($\mathrm{C_6D_6}$ and toluene-d_8). NMR spectra were measured on a JEOL JMM-ECA600 (^{1}H: 600 MHz, ^{7}Li: 233 Hz, ^{13}C: 151 MHz, ^{19}F: 565 MHz, ^{27}Al: 156 MHz, ^{31}P: 243 MHz) in the Joint Usage/Research Center (JURC, Institute for Chemical Research, Kyoto University) or on a JEOL AL-300 spectrometer (^{1}H: 300 MHz, ^{13}C: 75 MHz, ^{19}F: 282 MHz, ^{31}P: 121 MHz). For the ^{1}H NMR spectra, signal arising from residual partially hydrogenated $\mathrm{C_6D_5H}$ (7.15 ppm for ^{1}H) and $\mathrm{C_6D_5CD_2H}$ (2.03 ppm for ^{1}H) was used as references. $\mathrm{C_6D_6}$ (128.0 ppm for ^{13}C), toluene-d_8 (20.4 ppm for ^{13}C), and $\mathrm{Al(NO_3)_3}$ in $\mathrm{D_2O}$ (0 ppm for ^{27}Al) were used as references. ^{1}H and ^{13}C NMR signals were assigned with the aids of the ^{1}H-^{1}H COSY, ^{1}H-^{13}C HSQC, and ^{1}H-^{13}C HMBC spectra. Melting points were determined on a Yanaco micro melting point apparatus and uncorrected. Elemental analyses were carried out at the Microanalytical Laboratory, Institute for Chemical Research, Kyoto University. Phenylacetylene, hex-3-yne, benzaldehyde, and dimethyl acetylenedicarboxylate were purified by the trap-to-trap distillation prior to use. Diphenylacetylene was purified by recrystallization from ethanol and dried *in vacuo* prior to use. $\mathrm{CO_2}$ gas is dried thorough the column packing molecular sieves 3A prior to use. The system of the gas reaction maintained a high vacuum (below 7.5×10^{-4} Torr) before exposure of gases. Although we have tried collecting mass spectrometric data of the obtained novel compounds by using DART, FAB, and EI ionization methods, the corresponding molecular ion peaks could not be observed due to the extremely high sensitivity of Al compounds towards the air. The purity of novel compounds was estimated by the ^{1}H and ^{31}P NMR spectrum.

Reaction of 1PAl with phenylacetylene

In a *J.* Young NMR tube, phenylacetylene (10.6 mg, 0.104 mmol, 1.1 eq.) was added to a $\mathrm{C_6H_6}$ (0.6 mL) solution of **1PAl** (40.0 mg, 0.0974 mmol) at room temperature. The reaction was monitored by NMR spectroscopy, resulting in the quantitative conversion to $\mathrm{Mes_2PH}$ as judged by the ^{1}H and ^{31}P{^{1}H} NMR spectrum. The mixture was washed with hexane to remove $\mathrm{Mes_2PH}$ and phenylacetylene, and the residual material was recrystallized from hexane at –35 ºC to afford $[(t\text{-Bu})_2\mathrm{AlC{\equiv}CPh}]_2$ (5.7 mg, 0.024 mmol, 24%) as judged by ^{1}H NMR spectroscopy and X-ray crystallography.

Reaction of 1PAl with internal alkynes

With diphenylacetylene

In a *J.* Young Schlenk tube, a solution of **1PAl** (205 mg, 0.500 mmol) and diphenylacetylene (89.0 mg, 0.499 mmol) in $\mathrm{C_6H_6}$ (3 mL) was degassed by freeze-pump-thaw cycles and stirred at 100 ºC over 60 h. After all volatiles were removed under reduced pressure at room temperature, the residue was washed with hexane to afford **3Ph** as a colorless solid (159 mg, 0.269 mmol, 54%). Single crystals of **3Ph** suitable for X-ray crystallographic analysis were obtained by recrystallization from benzene at room temperature. **3Ph**: A colorless solid, mp. 224-225 ºC (dec.). ^{1}H NMR (600 MHz, $\mathrm{C_6D_6}$, 298 K): δ = 1.25 (s, 18H, $\mathrm{C(C}\boldsymbol{H}_3)_3$), 1.98 (s, 6H, Mes *p*-$\mathrm{C}\boldsymbol{H}_3$), 2.36 (s, 12H, Mes *o*-$\mathrm{C}\boldsymbol{H}_3$), 6.61 (d, $^{4}J_{\mathrm{HP}}$ = 3.0 Hz, 4H, Mes *m*-$\mathrm{C}\boldsymbol{H}$), 6.75 (2H, d(AA'), $^{3}J_{\mathrm{HH}}$ = 8.4 Hz, *o*-$\boldsymbol{H}$ of $(\underline{\mathrm{Ph}})\mathrm{C^{P}{=}C^{Al}}$ moiety), 6.83 (2H, t(BB'), $^{3}J_{\mathrm{HH}}$ = 15.0 Hz, *m*-$\boldsymbol{H}$ of $(\underline{\mathrm{Ph}})\mathrm{C^{P}{=}C^{Al}}$ moiety), 6.87-6.90 (2H, m, *p*-$\boldsymbol{H}$ of $(\underline{\mathrm{Ph}})\mathrm{C^{P}{=}C^{Al}}$ moiety and $\mathrm{C^{P}{=}C^{Al}(Ph)}$ moiety moiety), 7.03-7.04 (m, 4H, *o*-$\boldsymbol{H}$ and *m*-$\boldsymbol{H}$ of $\mathrm{C^{P}{=}C^{Al}(Ph)}$ moiety) ppm. ^{13}C{^{1}H} NMR (151 MHz, $\mathrm{C_6D_6}$, 298 K): δ = 19.4 (d, J_{CP} = 6.0 Hz, $\mathrm{Al}\boldsymbol{C}\mathrm{Me_3}$), 20.8 (Mes *p*-$\boldsymbol{C}\mathrm{H_3}$), 23.8 (d, $^{3}J_{\mathrm{CP}}$ = 9.1 Hz, Mes *o*-$\boldsymbol{C}\mathrm{H_3}$), 31.4 (d, J_{CP} = 0.9 Hz, $\mathrm{AlC(}\boldsymbol{C}\mathrm{H_3)_3}$), 125.6 (*p*-$\boldsymbol{C}$ of $\mathrm{C^{Al}}$-$\underline{\mathrm{Ph}}$ moiety), 126.6 (*p*-$\boldsymbol{C}$ of $\mathrm{C^{P}}$-$\underline{\mathrm{Ph}}$ moiety), 126.7 (*m*-$\boldsymbol{C}$ of $\mathrm{C^{Al}}$-$\underline{\mathrm{Ph}}$ moiety), 127.8 (*m*-$\boldsymbol{C}$ of $\mathrm{C^{P}}$-$\underline{\mathrm{Ph}}$ moiety), 128.4 (*o*-$\boldsymbol{C}$ of $\mathrm{C^{Al}}$-$\underline{\mathrm{Ph}}$ moiety), 129.4 (d, $^{4}J_{\mathrm{CP}}$ = 1.4 Hz, *o*-$\boldsymbol{C}$ of $\mathrm{C^{P}}$-$\underline{\mathrm{Ph}}$ moiety), 129.7 (d, $^{2}J_{\mathrm{CP}}$ = 15.1 Hz, Mes *o*-$\boldsymbol{C}$), 130.8 (d, $^{3}J_{\mathrm{CP}}$ = 6.0 Hz, Mes *m*-$\boldsymbol{C}$), 139.0 (d, $^{2}J_{\mathrm{CP}}$ = 6.0 Hz, *ipso*-$\boldsymbol{C}$ of $\mathrm{C^{P}}$-$\underline{\mathrm{Ph}}$ moiety), 139.7 (d, $^{4}J_{\mathrm{CP}}$ = 1.5 Hz, Mes *p*-$\boldsymbol{C}$), 142.4 (d, $^{1}J_{\mathrm{CP}}$ = 10.6 Hz, Mes *ipso*-$\boldsymbol{C}$), 145.6 (d, $^{3}J_{\mathrm{CP}}$ = 46.8 Hz, *ipso*-$\boldsymbol{C}$ of $\mathrm{C^{Al}}$-$\underline{\mathrm{Ph}}$ moiety), 145.7 (d, $^{1}J_{\mathrm{CP}}$ = 34.7 Hz, $\boldsymbol{C}^{\mathrm{P}}{=}\mathrm{C^{Al}}$), 192.6 (d, $^{2}J_{\mathrm{CP}}$ = 107.2 Hz, $\mathrm{C^{P}}{=}\boldsymbol{C}^{\mathrm{Al}}$) ppm. ^{31}P{^{1}H} NMR (243 MHz, $\mathrm{C_6D_6}$, 298 K): δ = –2.9 ppm. No ^{27}Al{^{1}H} NMR signal was observed even after long-time measurement (number of scans: 44720 times). Anal. Calcd for $\mathrm{C_{40}H_{50}AlP}$: C, 81.60 H, 8.56. Found: C, 81.68; H, 8.83.

With hex-3-yne

In a *J.* Young NMR tube, a solution of **1PAl** (46.4 mg, 0.113 mmol) and hex-3-yne (9.3 mg, 0.11 mmol) in $\mathrm{C_6H_6}$ (0.5 mL) was heated at 40 ºC for 24 h. After all volatiles were removed under reduced pressure, the residue was recrystallized form $\mathrm{C_6H_6}$ at room temperature. The precipitate was washed with hexane to afford **3Et** as colorless crystals suitable for X-ray crystallographic analysis (36.7 mg, 0.0745 mmol, 66%). **3Et**: Colorless crystals, mp. 175-177 ºC (dec.). ^{1}H NMR (600 MHz, $\mathrm{C_6D_6}$, 298 K): δ = 0.59 (t, 3H, $^{3}J_{\mathrm{HH}}$ = 7.5 Hz, $\mathrm{C^{Al}\text{-}CH_2C}\boldsymbol{H}_{\boldsymbol{3}}$), 1.20-1.23 (m, 3H+18H, $\mathrm{C^{P}\text{-}CH_2C}\boldsymbol{H}_{\boldsymbol{3}}\mathrm{+AlC(C}\boldsymbol{H}_{\boldsymbol{3}}\mathrm{)_3}$), 1.98 (s, 6H, Mes *p*-$\mathrm{C}\boldsymbol{H}_3$), 2.36 (s, 12H, Mes *o*-$\mathrm{C}\boldsymbol{H}_3$), 2.45-2.53 (m, 2H+2H, $\mathrm{C^{P}\text{-}C}\boldsymbol{H}_{\boldsymbol{2}}\mathrm{CH_3+C^{Al}\text{-}C}\boldsymbol{H}_{\boldsymbol{2}}\mathrm{CH_3}$), 6.63 (m, 4H, Mes *m*-Ar$\boldsymbol{H}$) ppm. ^{13}C{^{1}H} NMR (151 MHz, $\mathrm{C_6D_6}$, 298 K): δ = 15.0 (d, $^{3}J_{\mathrm{CP}}$ = 2.3 Hz, $\mathrm{C^{P}}$-

$CH_2\boldsymbol{C}H_3$), 15.2 (s, C^{Al}-$CH_2\boldsymbol{C}H_3$), 18.9 ($Al\boldsymbol{C}Me_3$), 20.7 (Mes *p*-$\boldsymbol{C}H_3$), 23.8 (d, $^3J_{CP}$ = 10.6 Hz, Mes *o*-$\boldsymbol{C}H_3$), 25.7 (d, $^3J_{CP}$ = 4.5 Hz, C^{Al}-$\boldsymbol{C}H_2CH_3$), 28.6 (d, $^2J_{CP}$ = 45.3 Hz, C^P-$\boldsymbol{C}H_2CH_3$), 31.5 (d, J_{CP} = 1.1 Hz, $AlC(\boldsymbol{C}H_3)_3$), 130.1 (d, $^2J_{CP}$ = 10.7 Hz, Mes *o*-$\boldsymbol{C}$), 130.9 (d, $^3J_{CP}$ = 4.5 Hz, Mes *m*-$\boldsymbol{C}$), 133.1 (d, $^4J_{CP}$ = 1.5 Hz, Mes *p*-$\boldsymbol{C}$), 141.6 (d, $^1J_{CP}$ = 10.6 Hz, Mes *ipso*-$\boldsymbol{C}$), 148.4 (d, $^1J_{CP}$ = 33.2 Hz, $\boldsymbol{C}^P=C^{Al}$), 193.1 (d, $^2J_{CP}$ = 105.7 Hz, $C^P=\boldsymbol{C}^{Al}$) ppm. $^{27}Al\{^1H\}$ NMR (156 MHz, C_6D_6, 298 K): δ = 194.0 ppm. $^{31}P\{^1H\}$ NMR (243 MHz, C_6D_6, 298 K): δ = –11.4 ppm. Anal. Calcd for $C_{32}H_{50}AlP$: C, 78.01 H, 10.23. Found: C, 77.70; H, 10.37.

With dimethyl acetylenedicarboxylate (DMAD)

In a *J.* Young NMR tube, DMAD (5.2 mg, 0.037 mmol, 1.0 eq.) was added to a C_6D_6 (0.6 mL) solution of **1PAl** (15.0 mg, 0.0365 mmol) at room temperature. The reaction was monitored by NMR spectroscopy, resulting in a complicated mixture.

Reaction of 2PAl•LiCl with diphenylacetylene

In a *J.* Young NMR tube, diphenylacetylene (5.8 mg, 0.033 mmol, 1.5 eq.) was added to a C_6H_6 (0.6 mL) solution of **2PAl·LiCl** (14.8 mg, 0.0220 mmol) at room temperature. After 24 h, insoluble materials were removed by the filtration through glass fiber using benzene as an eluent. The filtrate was concentrated and washed with hexane (16.3 mg, 0.0165 mmol, 80% as **4Ph·0.5(PhCCPh)**). Single crystals of **4Ph·0.5(PhCCPh)** suitable for X-ray crystallographic analysis were obtained from recrystallization from toluene at –35 ºC. **4Ph·0.5(PhCCPh)**: A colorless solid, mp. 149-150 ºC (dec.). ^1H NMR (300 MHz, C_6D_6, 298 K): δ = 1.96 (s, 6H, Mes *p*-CH_3), 2.14 (s, 12H, Mes *o*-CH_3), 6.48 (d, $^3J_{HP}$ = 6 Hz, 4H, Mes *m*-H), 6.80 (s, 5H, Ph), 6.93-6.96 (m, 1H, Ph), 6.96-7.01 (m, 1.5H, free 0.5(PhCCPh)), 7.08 (br. t, J_{HH} = 7.5 Hz, 2H, Ph), 7.31 (br. d, J_{HH} = 4.5 Hz, 2H, Ph-*o*-C***H***), 7.49-7.53 (m, 1H, free 0.5(PhCCPh)) ppm. ^{19}F NMR (282 MHz, C_6D_6, 298 K): δ = –118.5 (m, 4F, C_6F_5 *m*-F), –153.0 (t, *J* = 18 Hz, 2F, C_6F_5 *p*-F), –161.3 (m, 4F, C_6F_5 *m*-F) ppm. $^{31}P\{^1H\}$ NMR (121 MHz, C_6D_6, 298 K): δ = 8.6 ppm. Satisfactory data of $^{13}C\{^1H\}$ NMR could not be obtained due to the impurities and decomposition. Due to the flame retardancy of fluorocarbons and the extremely high air- and moisture-sensitivity, satisfactory data of elemental analysis could not be obtained.

Reaction of a phosphanylborane 5PB with diphenylacetylene

In a *J.* Young NMR tube, a mixture of **5PB** (4.7 mg, 0.0091 mmol) and diphenylacetylene (1.7 mg, 0.0095 mmol) in C_6D_6 (0.6 mL) was degassed by freeze-pump-thaw cycles. The reaction was monitored by^1H and $^{31}P\{^1H\}$ NMR spectroscopy, showing no reaction even on heating up to 100 ºC.

Reaction of a P/Al-based intermolecular FLP 6 with diphenylacetylene

In a *J.* Young NMR tube, diphenylacetylene (1.7 mg, 0.0095 mmol) was added to a C_6D_6 (0.6 mL) solution of FLP **6** [(*o*-tol)$_3$P (2.8 mg, 0.0092 mmol) + (C_6F_5)$_3$Al) (4.8 mg, 0.0091 mmol)] at room temperature. The mixture was degassed by freeze-pump-thaw cycles. The reaction was monitored by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy, showing no change of diphenylacetylene and (*o*-tol)$_3$P even on heating up to 100 ºC. Instead, the decomposition of $Al(C_6F_5)_3$ was observed.

General procedure of reactions of 3 with benzaldehyde

In a *J.* Young NMR tube, a small excess amount of benzaldehyde (3.2 mg, 0.030 mmol, 1.1 eq.) was added to a C_6H_6 (0.6 mL) solution of **3Ph** (15.9 mg, 0.0270 mmol) at room temperature. The reaction was monitored by NMR spectroscopy, resulting in the quantitative formation of **7Ph**. After all volatiles were removed under reduced pressure at room temperature, the residue was recrystallized from hexane at room temperature to afford **7Ph** as a pale yellow solid (4.8 mg, 0.0069 mmol, 26%).

7Ph: A pale yellow solid, mp. 111-113 ºC (dec.). ^1H NMR (300 MHz, C_6D_6, 363 K): δ = 1.22 (s, 18H, $AlC(C\boldsymbol{H}_3)_3$), 2.00 (s, 6H, Mes *p*-$C\boldsymbol{H}_3$), 2.34 (s, 12H, Mes *o*-$C\boldsymbol{H}_3$), 6.62 (d, $^4J_{HP}$ = 3 Hz, Mes *m*-***H***), 6.6-7.1 (m, 16H, 3($C_6\boldsymbol{H}_5$) + C(***H***)Ph) ppm. $^{31}P\{^1H\}$ NMR (121 MHz, C_6D_6, 363 K): δ = 1.0 (br. s) ppm. Satisfactory data of ^{13}C NMR could not be obtained due to the decomposition by heating at 70 ºC for a long-time. Similarly, satisfactory data of ^1H and $^{13}C\{^1H\}$ NMR could not be obtained due to the broadening of peaks even by cooling at –90 ºC in toluene-*d*$_8$. Due to the extremely high air- and moisture-sensitivity, satisfactory data of elemental analysis and mass spectrometry could not be obtained.

7Et: A colorless solid, mp. 80 ºC (dec.). ^1H NMR (600 MHz, toluene-*d*$_8$, 268 K): δ = 0.47 (t, $^3J_{HH}$ = 7.2 Hz, 3H, C^{Al}-$CH_2C\boldsymbol{H}_3$), 1.39 (t, $^3J_{HH}$ = 7.8 Hz; determined by $^1H\{^{31}P\}$ NMR spectrum, 3H, C^P-$CH_2C\boldsymbol{H}_3$), 1.48 (s, 18H, $AlC(C\boldsymbol{H}_3)_3$), 1.91 (s, 6H, Mes *p*-$C\boldsymbol{H}_3$), 2.29 (br. s, 2H, C^{Al}–$C\boldsymbol{H}_2CH_3$), 2.84 (qd, $^3J_{HH}$ = 7.6 Hz (determined by $^1H\{^{31}P\}$ NMR spectrum), $^3J_{HP}$ = 2.6 Hz, 2H, C^P-$C\boldsymbol{H}_2CH_3$), 6.45 (s, 4H, Mes *m*-***H***), 6.92-6.96 (m, 2H, CH***Ph***), 7.14 (s, 3H, CH***Ph***), 7.17 (d, $^1J_{HP}$ = 12 Hz, 1H, PC(***H***)Ph) ppm. The ^1H signal corresponding to *o*-CH_3 of the Mes substituents appeared as very broadened signal at 1.9-2.4 ppm. $^{13}C\{^1H\}$ NMR (151 MHz, toluene-*d*$_8$, 268 K): δ = 12.3 (s, C^P–$CH_2\boldsymbol{C}H_3$), 15.2 (s, C^{Al}-$CH_2\boldsymbol{C}H_3$), 20.8 (d, $^5J_{CP}$ = 1.5 Hz, Mes *p*-$\boldsymbol{C}$), 26.8 (d, $^2J_{CP}$ = 16.6 Hz, C^P-$\boldsymbol{C}H_2CH_3$), 30.4 (d, $^3J_{CP}$ = 27.2 Hz, C^{Al}-$\boldsymbol{C}H_2CH_3$), 33.2 (s, $AlC(\boldsymbol{C}H_3)_3$), 86.8 (br. s, P***C***(H)Ph), 128.3 (s, C(H)***Ph***), 128.6 (s, C(H)***Ph***), 128.8 (s, C(H)***Ph***), 131.3 (br. d, $^1J_{CP}$ = 68.0 Hz, $\boldsymbol{C}^P=C^{Al}$), 131.7 (d, $^3J_{CP}$ =10.6 Hz, Mes *m*-$\boldsymbol{C}$), 140.7 (s, Ph *ipso*-$\boldsymbol{C}$), 141.8 (s, Mes *p*-$\boldsymbol{C}$), 143.4 (s, Mes ipso-$\boldsymbol{C}^i$), 200.3 (br. d, $^2J_{CP}$ = 30.2 Hz, $C^P=\boldsymbol{C}^{Al}$) ppm. $^{27}Al\{^1H\}$ NMR (156 MHz, toluene-*d*$_8$, 268 K): δ = 136.0 ppm. $^{31}P\{^1H\}$ NMR (243 MHz, toluene-*d*$_8$, 268 K): δ = –6.5 ppm. Due to the extremely high air- and moisture-sensitivity, satisfactory data of elemental analysis and mass spectrometry could not be obtained.

Reaction of 3Ph with CO_2

In a *J.* Young NMR tube, a solution of **3Ph** (7.4 mg, 0013. mmol) in C_6D_6 (0.5 mL) was degassed, and an excess amount of CO_2 (approximately 2 times of the NMR tube volume) was condensed into the frozen mixture at –78 ºC. After a mixture was warmed to room temperature, the reaction was monitored by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy, showing no reaction even on heating up of a mixture.

Reaction of 3Et with CO_2

In a *J.* Young NMR tube, a solution of **3Et** (7.7 mg, 0.016 mmol) in C_6D_6 (0.5 mL) was degassed, and an excess amount of CO_2 (approximately 2 times of the NMR tube volume) was condensed into the frozen mixture at –78 ºC. After the mixture was warmed to room temperature, the reaction was monitored by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy, suggesting the formation of **8Et**. Isolation of **8Et** in the solid state was not successful because **3Et** was immediately regenerated after removal of an excess amount of CO_2. Therefore, NMR spectroscopic data were collected in the presence of an excess amount of CO_2. **8Et**: Only NMR data are shown here. ^1H NMR (600 MHz, C_6D_6, 298 K): δ = 0.64 (t, $^3J_{HH}$ = 7.2 Hz, 3H, C^{Al}-$CH_2C\boldsymbol{H}_3$), 1.29 (m, 18H+3H, $AlC(C\boldsymbol{H}_3)_3$+C^P-$CH_2C\boldsymbol{H}_3$), 1.86 (s, 6H, Mes *p*-$C\boldsymbol{H}_3$), 2.15 (br. q, $^3J_{HH}$ = 7.2 Hz (determined by $^1H\{^{31}P\}$ NMR spectrum), 2H, C^P-$C\boldsymbol{H}_2CH_3$), 2.24 (s, 12H, Mes *o*-$C\boldsymbol{H}_3$), 2.70 (qd, $^3J_{HH}$ = 7.8 Hz (determined by $^1H\{^{31}P\}$ NMR spectrum), $^4J_{HP}$ = 3.5 Hz, 2H, C^{Al}-$C\boldsymbol{H}_2CH_3$), 6.52 (s, $^4J_{HP}$ = 3.6 Hz, 4H, Mes *m*-***H***) ppm. $^{13}C\{^1H\}$ NMR (151 MHz, C_6D_6, 298 K): δ = 12.9 (d, $^3J_{CP}$ = 3.0 Hz, C^P-$CH_2\boldsymbol{C}H_3$), 14.5 (d, $^4J_{CP}$ = 3.0 Hz, C^{Al}-$CH_2\boldsymbol{C}H_3$), 16.4 (br. s, $Al\boldsymbol{C}(CH_3)_3$), 20.7 (s, Mes *p*-$\boldsymbol{C}H_3$), 24.5 (d, $^3J_{CP}$ = 6.0 Hz, Mes *o*-$\boldsymbol{C}H_3$), 28.4 (d, $^2J_{CP}$ = 39.3 Hz, C^P-$\boldsymbol{C}H_2CH_3$), 30.7 (d, $^3J_{CP}$ = 27.2 Hz, C^{Al}-$\boldsymbol{C}H_2CH_3$), 31.8 (s, $AlC(\boldsymbol{C}H_3)_3$), 119.5 (d, $^2J_{CP}$ = 66.4 Hz, Mes *o*-$\boldsymbol{C}$), 127.5-127.8 ($\boldsymbol{C}^P=C^{Al}$, determined by the HMBC spectra. The correct chemical shifts and coupling constants could not be determined due to the overlapping with the residual C_6D_6 signals.), 132.2 (d, $^{3}J_{CP}$ = 10.6 Hz, Mes *m*-***C***), 144.75 (d, $^{1}J_{CP}$ = 9.1 Hz, Mes *ipso*-***C***), 159.7 (d, $^{1}J_{CP}$ = 102.7 Hz, P***C***O_2), 199.7 (d, $^{2}J_{CP}$ = 33.2 Hz, C^{P}=$\boldsymbol{C}^{Al}$) ppm. ^{27}Al{^{1}H} NMR (156 MHz, C_6D_6, 298 K): δ = 145.7 ppm. ^{31}P{^{1}H} NMR (243 MHz, C_6D_6, 298 K): δ = –12.9 ppm. The NMR spectra for pure **8Et** could not be obtained due to the decomposition and easy dissociation of CO_2.

Reactions of 3Ph with DMAD

In a *J*. Young NMR tube, a mixture of **3Ph** (14.5 mg, 0.0246 mmol) and DMAD (10.2 mg, 0.0718 mmol, 2.9 eq.) in C_6D_6 (0.6 mL) was heated to 70 ºC for 20 h. The formation of **9Ph** in 87% yield was estimated as judged by ^{31}P{^{1}H} NMR spectroscopy. After all volatiles were removed under reduced pressure at room temperature, the residue was washed with hexane to afford **9Ph** as a red solid (4.1 mg, 0.0056 mmol, 23%). Single crystals of **9Ph** suitable for X-ray crystallographic analysis were obtained from recrystallization in benzene. **9Ph**: A pink solid, mp. 131 ºC (dec.). ^{1}H NMR (600 MHz, C_6D_6, 298 K): δ = 0.98 (s, 9H, AlC(C$\boldsymbol{H}^{U}_{3}$), 1.24 (s, 3H, fused Mes *o*-C$\boldsymbol{H}^{G}_{3}$), 1.33 (s, 9H, AlC(C$\boldsymbol{H}^{L}_{3}$)), 1.87 (s, 3H, fused Mes *p*-C$\boldsymbol{H}^{I}_{3}$), 1.92 (s, 3H, PMes *p*-C$\boldsymbol{H}^{F}_{3}$), 2.36 (s, 3H, activated Mes C$\boldsymbol{H}^{E}_{3}$), 2.63 (s, 3H, PMes *o*-C$\boldsymbol{H}^{J}_{3}$), 3.05 (s, 3H, PMes *o*-C$\boldsymbol{H}^{H}_{3}$), 3.53 (s, 3H, CO_2C$\boldsymbol{H}_{3}$), 3.66 (s, 3H, O$\boldsymbol{CH}_{3}$), 6.25 (m, 1H, fused *m*-$\boldsymbol{H}^{B}$), 6.40 (d, ^{1}H, $^{3}J_{HH}$ = 7.2 Hz, Ph), 6.59 (t, 1H, $^{3}J_{HH}$ = 6.9 Hz, Ph), 6.64 (br. s, 1H, PMes *m*-$\boldsymbol{H}^{D}$), 6.69-6.73 (m, 3H, Ph), 6.80 (d, 1H, $^{4}J_{HP}$ = 53.6 Hz, PMes *m*-$\boldsymbol{H}^{C}$), 6.82 (d, 1H, $^{3}J_{HH}$ = 7.2 Hz, Ph), 6.88 (t, 1H, $^{3}J_{HH}$ = 7.2 Hz, Ph), 7.02-7.06 (m, 3H, Ph), 7.19 (s, 1H, fused *m*-$\boldsymbol{H}^{A}$) ppm. ^{13}C{^{1}H} NMR (151 MHz, C_6D_6, 298 K): δ = 17.0 (br. s, Al$\boldsymbol{C}^{L}$$Me_3$), 17.4 (br. s, Al$\boldsymbol{C}^{U}$$Me_3$), 19.6 (d, $^{3}J_{CP}$ = 3.0 Hz, fused Mes *o*-$\boldsymbol{C}^{3}H_3$), 20.6 (d, $^{5}J_{CP}$ = 1.5 Hz, PMes *p*-$\boldsymbol{C}^{7}H_3$), 21.3 (d, $^{5}J_{CP}$ = 1.5 Hz, fused Mes *p*-$\boldsymbol{C}^{2}H_3$), 25.9 (d, $^{3}J_{CP}$ = 6.0 Hz, PMes *o*-$\boldsymbol{C}^{6}H_3$), 29.5 (d, $^{3}J_{CP}$ = 3.0 Hz, PMes *o*-$\boldsymbol{C}^{8}H_3$), 30.2 (s, activated $\boldsymbol{C}^{1}H_3$), 31.6 (s, AlC($\boldsymbol{C}^{U}H_3)_3$), 32.8 (s, AlC($\boldsymbol{C}^{L}H_3)_3$), 51.8 (s, CO_2***C***H_3), 53.1 (s, O***C***H_3), 57.2 (d, $^{2}J_{CP}$ = 15.1 Hz, $\boldsymbol{C}^{4}(CH_3)CO_2Me$), 75.1 (d, $^{1}J_{CP}$ = 114.8 Hz, P$\boldsymbol{C}^{5}$-C(CH_3)CO_2Me), 119.4 (d, $^{1}J_{CP}$ = 78.5 Hz, PMes *ipso*-$\boldsymbol{C}^{Mi}$), 123.4 (d, $^{3}J_{CP}$ = 9.1 Hz, fused Mes *m*-$\boldsymbol{C}^{FUm}$), 124.2 (d, $^{1}J_{CP}$ = 84.6 Hz, fused Mes *ipso*-$\boldsymbol{C}^{Fi}$), 125.3 (s, Ph), 126.2 (s, Ph), 126.6 (s, Ph), 127.0 (s, Ph), 128.1 (s, Ph), 130.6 (s, Ph), 131.7 (d, $^{3}J_{CP}$ = 10.8 Hz, fused Mes *m*-$\boldsymbol{C}^{FLm}$), 132.9 (d, $^{3}J_{CP}$ = 10.8 Hz, PMes *m*-$\boldsymbol{C}^{MLm}$), 133.3 (d, $^{3}J_{CP}$ = 12.1 Hz, PMes *m*-$\boldsymbol{C}^{MUm}$), 134.0 (d, J_{CP} = 6.0 Hz, Ph), 137.5 (d, $^{2}J_{CP}$ = 21.1 Hz, Ph^{P}-*ipso*-***C***), 139.8 (d, $^{1}J_{CP}$ = 87.6 Hz, C^{Al}=$\boldsymbol{C}^{P}$), 142.3 (d, $^{2}J_{CP}$ = 7.6 Hz, fused Mes *o*-$\boldsymbol{C}^{Flo}$), 143.1 (d, $^{4}J_{CP}$ = 3.0 Hz, PMes *p*-$\mathbf{C}^{Mp}$), 144.8 (d, $^{4}J_{CP}$ = 3.0 Hz, fused Mes *p*-$\boldsymbol{C}^{Fp}$), 146.1 (d, $^{2}J_{CP}$ = 13.6 Hz, PMes *o*-$\boldsymbol{C}^{MUo}$), 146.7 (d, $^{2}J_{CP}$ = 10.6 Hz, PMes *o*-$\boldsymbol{C}^{MLo}$), 148.9 (d, $^{3}J_{CP}$ = 30.2 Hz, Ph^{Al}-*ipso*-***C***), 154.6 (d, $^{2}J_{CP}$ =21.1 Hz, fused Mes *o*-$\boldsymbol{C}^{FUo}$), 168.1 (d, $^{2}J_{CP}$ = 16.6 Hz, H_3CO-***C***), 174.5 (d, $^{3}J_{CP}$ = 9.1 Hz, ***C***O_2CH_3), 191.7 (d, $^{2}J_{CP}$ = 37.8 Hz, $\boldsymbol{C}^{Al}$=C^{P}) ppm. ^{31}P{^{1}H} NMR (243 MHz, C_6D_6, 298 K): δ = 18.7 ppm. No ^{27}Al NMR signal was observed even after long-time measurement (number of scans: 2048 times). See Figures S19 and S20 for details of NMR assignments of **9Ph**. Anal. Calcd for $C_{46}H_{56}AlO_4P$: C, 75.59 H, 7.72. Found: C, 75.30; H, 7.86.

Reactions of 3Et with DMAD

In a *J*. Young NMR tube, a solution of **3Et** (11.2 mg, 0.0227 mmol) in C_6H_6 (0.6 mL) was treated with DMAD (4.0 mg, 0.0.281 mmol, 1.2 eq.). The reaction was monitored by NMR spectroscopy, suggesting the quantitative formation of **9Et**. After all volatiles were removed under reduced pressure at room temperature, the residue was recrystallization from benzene to afford **9Et** as a red solid (7.2 mg, 0.011 mmol, 50%). **9Et**: A red solid, mp. 107 ºC (dec.). ^{1}H NMR (600 MHz, C_6D_6, 298 K): δ = 0.59 (t, 3H, $^{3}J_{HH}$ = 7.2 Hz, ^{Al}C-CH_2C$\boldsymbol{H}_3$), 1.14 (s, 9H, AlC(C$\boldsymbol{H}^{U}{}_{3})_3$), 1.27 (td, 3H, $^{3}J_{HH}$ = 7.5 Hz, $^{4}J_{HP}$ = 0.6 Hz, ^{P}C-CH_2C$\boldsymbol{H}_3$), 1.40 (s, 9H, AlC(C$\boldsymbol{H}^{L}{}_{3})_3$, 1.85 (s, 3H, fused-Mes *p*-C$\boldsymbol{H}^{F}{}_{3}$), 1.92 (s with m, 3H+1H, PMes *p*-C$\boldsymbol{H}_3$+^{Al}C-C***H***CH_3), 1.98 (s, 3H, fused Mes *o*-C$\boldsymbol{H}^{G}{}_{3}$), 2.10 (s, 3H, activated C$\boldsymbol{H}^{E}{}_{3}$), 2.56 (s, 6H, PMes *o*-C$\boldsymbol{H}_3$), 2.65-2.93 (m, 2H+1H, ^{P}C-C$\boldsymbol{H}_2$$CH_3$+^{Al}C-C***H***$CH_3$), 3.42 (s, 3H CO_2C$\boldsymbol{H}_3$), 3.60 (s, 3H, OCH_3), 6.46 (dm, 1H, $^{4}J_{HP}$ = 3.6 Hz, fused Mes *m*-$\boldsymbol{H}^{B}$), 6.61 (br. s, 1H, PMes *m*-$\boldsymbol{H}^{D}$), 6.69 (dm, 1H, $^{4}J_{HP}$ = 5.4 Hz, PMes *m*-$\boldsymbol{H}^{C}$), 7.09 (s, 1H, fused *m*-$\boldsymbol{H}^{A}$) ppm. ^{13}C{^{1}H} NMR (151 MHz, C_6D_6, 298 K): δ = 12.9 (d, $^{3}J_{CP}$ = 3.0 Hz, ^{P}C-CH_2***C***H_3), 16.2 (br. s, Al$\boldsymbol{C}^{U}$$Me_3$), 16.3 (s, ^{Al}C-$CH_2$***C***$H_3$), 16.9 (br. s, Al$\boldsymbol{C}^{L}$$Me_3$), 20.5-20.6 (two doublets, fused Mes *o*-***C***H_3 + PMes *p*-***C***H_3), 21.1 (d, $^{5}J_{CP}$ = 1.1 Hz, fused Mes *p*-$\boldsymbol{C}^{2}H_3$), 25.5 (d, $^{3}J_{CP}$ = 6.0 Hz, PMes *o*-$\boldsymbol{C}^{8}H_3$), 25.7 (d, $^{3}J_{CP}$ = 24.2 Hz, ^{Al}C-***C***H_2CH_3), 27.3 (d, $^{3}J_{CP}$ = 3.0 Hz, PMes *o*-$\boldsymbol{C}^{6}H_3$), 29.5 (s, activated $\boldsymbol{C}^{1}H_3$), 32.1 (AlC($\boldsymbol{C}^{U}H_3)_3$), 33.0 (AlC($\boldsymbol{C}^{L}H_3)_3$), 51.6 (s, CO_2***C***H_3), 52.9 (d, $^{4}J_{CP}$ =1.2 Hz, O***C***H_3), 56.7 (d, $^{2}J_{CP}$ = 15.1 Hz, $\boldsymbol{C}^{4}(CH_3)CO_2Me$), 74.8 (d, $^{1}J_{CP}$ = 114.8 Hz, P$\boldsymbol{C}^{5}$-C(CH_3)CO_2Me), 120.2 (d, $^{1}J_{CP}$ = 80.0 Hz, PMes *ipso*-$\boldsymbol{C}^{Mi}$), 123.2 (d, $^{1}J_{CP}$ = 81.5 Hz, fused Mes *ispo*-$\boldsymbol{C}^{Fi}$), 123.7 (d, $^{3}J_{CP}$ = 9.1 Hz, fused Mes *m*-$\boldsymbol{C}^{FUm}$), 132.3-132.4 (two doublets, PMes *m*-$\boldsymbol{C}^{MUm}$ + fused Mes *m*-$\boldsymbol{C}^{FLm}$), 133.3 (PMes *m*-$\boldsymbol{C}^{MLm}$), 140.0 (d, $^{1}J_{CP}$ = 84.6 Hz, C^{Al}=$\boldsymbol{C}^{P}$), 140.4 (d, $^{2}J_{CP}$ = 9.1 Hz, fused Mes *o*-$\boldsymbol{C}^{FLo}$), 142.6 (d, $^{4}J_{CP}$ = 3.0 Hz, PMes *p*-$\boldsymbol{C}^{Mp}$), 144.1 (d, $^{4}J_{CP}$ = 2.3 Hz, fused Mes *p*-$\boldsymbol{C}^{2}$), 145.8 (d, $^{3}J_{CP}$ = 12.1 Hz, PMes *o*-$\boldsymbol{C}^{MLo}$), 146.1 (d, $^{3}J_{CP}$ = 9.1 Hz, PMes *o*-$\boldsymbol{C}^{MUo}$), 155.2 (d, $^{2}J_{CP}$ = 21.1 Hz, fused Mes *o*-$\boldsymbol{C}^{FUo}$), 168.2 (d, $^{2}J_{CP}$ = 18.1 Hz, ***C***-OMe), 174.6 (d, $^{3}J_{CP}$ = 7.6 Hz, ***C***O_2Me), 188.2 (br. d, $^{2}J_{CP}$ = 33.2 Hz, $\boldsymbol{C}^{Al}$=C^{P}) ppm. ^{31}P{^{1}H} NMR (243 MHz, C_6D_6, 298 K): δ = 15.9 ppm. No ^{27}Al{^{1}H} NMR signal was observed even after long-time measurement (number of scans: 8880 times). See Figures S23 and S24 for details of the NMR assignments of **9Et**. Due to the extremely high air- and moisture-sensitivity, satisfactory data of elemental analysis and mass spectrometry could not be obtained.

X-Ray crystallographic analysis

The intensity data were collected on a Saturn 70 CCD diffractometer with a VariMax Mo optic system using Mo Kα radiation (λ = 0.71073 Å) (for **3Ph**, **7Et**, and **9Et**), a Mercury CCD diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71069 Å) [for **3Et**, **7Ph**, and **4Ph·0.5(PhCCPh)**], and the BL02B1 beamline of Spring-8 (2019B1774B and 2019B1578B) on a large cylindrical camera using synchrotron radiation (λ = 0.4119 Å) (for **9Ph**). All frame images (Dectris) were converted to the SFRM format using *Henkankun-R*.[35] Data reduction was performed using Bruker SAINT (for **9Ph**). An empirical absorption correction was applied to the diffraction data using ABSPACK[36] [for **3Ph**, **3Et**, **4Ph·0.5(PhCCPh)**, **7Ph**, **7Et**, and **9Et**]. The structure was solved by a direct method (SHELXT)[37] and refined by a full-matrix least-squares method on F^2 for all reflections (SHELXL-2016/4 or 2018/1).[38] All hydrogen atoms were placed using AFIX instructions, while all other atoms were refined anisotropically. CCDC-1970130 (**3Ph**), CCDC-1970132 (**3Et**), CCDC-1970131 [**4Ph·0.5(PhCCPh)**], CCDC-1970129 (**7Ph**), CCDC-1970134 (**7Et**), CCDC-1970128 (**9Ph**) and CCDC-1970133 (**9Et**) contain the supplementary crystallographic data.

Computational details

All calculations were performed using the Gaussian 16 (Rev. B. 01 or Rev. C. 01)[39] program package with B3LYP functional[40] including Grimme dispersion correction (D3)[41] along with combined basis sets: 6-31G(d) level. All the geometry optimizations have been performed until the residual mean force is smaller than 1.0×10^{-5} a.u. (*tight* threshold in Gaussian). The frequency calculations were carried out for each optimized structure to confirm the absence of any imaginary frequencies. Similarly, hessians, calculated for the transition states, were confirmed to have one imaginary frequency corresponding to the reaction coordinates. The reaction pathways for the structures of transition states were investigated and confirmed by intrinsic reaction coordinate (IRC) calculations. Natural bond orbital (NBO) analysis have been carried out with the NBO 6.0 program package,[42] linked to single-point calculations using Gaussian 16.

Acknowledgements

This work was supported by KAKENHI (JP24109013, JP26620028, JP19H05528, JP18H01963, and JP19H05635), Integrated Research Consortium on Chemical Science (IRCCS). T. Y. gratefully acknowledges a Research Fellowship for Young

Scientists (JP19J14359) from the Japan Society for the Promotion of Science (JSPS). We would also like to express our gratitude to the SPring-8 synchrotron facility, where synchrotron radiation experiments were performed at the BL02B1 beamlines with the approval of the Japan Synchrotron Radiation Research Institute (JASRI) under proposal numbers 2019B1774B and 2019B1578B. This study was supported by the Joint Usage/Research Center [JURC, Institute for Chemical Research (ICR), Kyoto University] by providing access to a JEOL JNM-ECA600 NMR spectrometer. The authors are furthermore grateful for computation time, which was provided by the Super Computer System (ICR, Kyoto University). Elemental analyses were carried out at the Microanalytical Laboratory of the ICR (Kyoto University).

Conflict of interest

The authors declare no conflict of interest.

Keywords: alkyne • aluminum • frustrated Lewis pairs • phosphanylalumane • small-molecule activation

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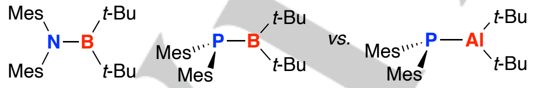
Orbital interactions (lone pair → p orbital; kcal mol^{-1})



1NB 48.5 **1PB** 37.3 **1PAl** **6.2**

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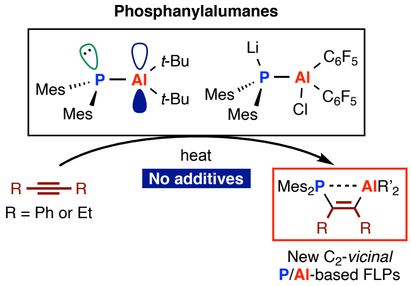

Phosphanylalumanes, P–Al single-bond species, can transform less reactive internal alkynes into new C_2-*vicinal* P–Al frustrated Lewis pairs by heating without any additives. These results demonstrated the ability of phosphanylalumanes to keep sufficiently functional Lewis acids and Lewis bases close enough to each other to interact effectively with alkynes.

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