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Al/P-Based Frustrated Lewis Pairs: Limitations of Their Synthesis by Hydroalumination and Formation of Dialkylaluminum Hydride Adducts

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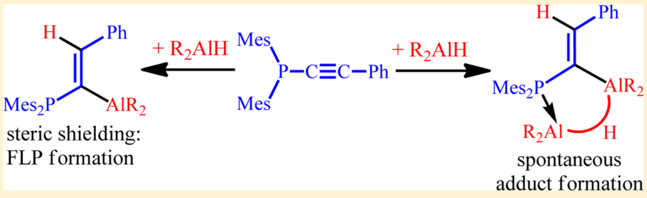
Supporting Information

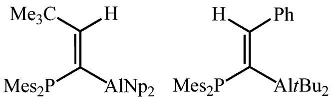


ABSTRACT: Aluminum−phosphorus-based frustrated Lewis pairs (Al/P FLPs) are valuable reagents for the dipolar activation or coordination of small molecules or ionic compounds. They are accessible by hydroalumination of alkynylphosphines. However, as reported in this article, the application of this simple method for the synthesis of a broad variety of different compounds is limited to sterically shielded systems. Hydroalumination of $Mes_2PC{\equiv}CPh$ with small dialkyl- or diarylaluminum hydrides $HAlR_2$ (R = Me, *i*Bu, Ph) afforded unique adducts in which an $HAlR_2$ molecule was coordinated by the Al/P FLP $Mes_2PC({=}CHPh)AlR_2$ via an Al−P and an Al−H−Al 3c bond. A new Al/P FLP was obtained with equimolar quantities of dineopentylaluminum hydride. The less shielded alkynylphosphine $Ph_2PC{\equiv}CPh$ yielded a hydride adduct with $HAlNp_2$ and an alkyne adduct with $HAl\mathit{t}Bu_2$. The latter compound resulted from triple-bond activation and had a five-membered $AlPC_3$ heterocycle in which a C=C bond was bonded to the P and Al atoms of an Al/P FLP. Both compounds were isolated in high yields by application of the appropriate stoichiometric ratios of the starting materials.

INTRODUCTION

Aluminum−phosphorus-based frustrated Lewis pairs (Al/P FLPs) have attracted considerable interest in current research as powerful alternatives to the well-established class of corresponding boron−phosphorus compounds.[1] These Al/P FLPs effectively coordinate and activate small molecules such as carbon dioxide,[2−4] terminal alkynes,[2,5] alkenes,[6] hydrogen,[7] carbonyl compounds,[8] and isocyanates.[4] They have been successfully applied as ion-pair receptors for the coordination of strongly polar alkali-metal hydrides and in hydride transfer reactions by phase transfer catalysis,[9] and they proved to be efficient catalysts for the dehydrogenation of amine−boranes.[10] Unimolecular Al/P FLPs were conveniently obtained in high yield by hydroalumination of ethynyldimesitylphosphines with dineopentyl- or di-*tert*-butylaluminum hydride.[2] The polarity of the phosphorus−alkynyl bonds with a partial negative charge at the α-carbon atoms causes the selective arrangement of the Al and P atoms in geminal positions (**1** and **2**; Scheme 1). The high steric shielding by two mesityl and two neopentyl or *tert*-butyl groups prevents direct Al−P interactions by adduct formation, and the conflicting Lewis acidic and basic functionalities are preserved. The simple method for the generation of these compounds by hydroalumination of easily accessible alkynylphosphines with versatile dialkylaluminum hydrides should allow the facile synthesis of a broad variety of different Al/P FLPs and an optimization of their properties with respect to steric shielding and inductive or mesomeric effects. Systematic investigations into the course of such reactions are reported in this article. The unique geminal arrangement of donor and acceptor atoms in compounds **1** and **2** favors their specific and in part unprecedented reactivity; a similar structure has in the meantime been reported also for a B/P system.[11]

Scheme 1. Al/P FLPs Obtained by Hydroalumination of Alkynyldimesitylphosphines[a]



1 (*Z*) **2** (*E*)

[a] Abbreviations: Np, neopentyl; Mes, mesityl; Ph, phenyl.

RESULTS AND DISCUSSION

Reactions of Dimesityl(phenylethynyl)phosphine with Dialkyl- and Diarylaluminum Hydrides. Reactions of $Mes_2PC{\equiv}CPh$ with equimolar quantities of R_2AlH bearing relatively small alkyl or aryl groups (R = Me, *i*Bu, Ph) resulted in the formation of new Al/P compounds, but 50% of the starting phosphine remained unchanged. Its complete consumption was only observed with an excess of the hydride of at least 100% (eq 1). The solid products **3**−**5** were isolated in high yields of 66−95%. Crystal structure determinations (Figures 1 and 2) verified the formation of adducts of an Al/

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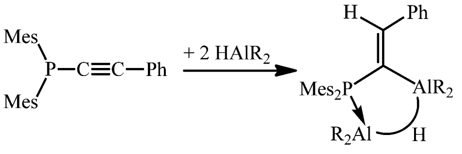


3: R = Me
4: R = *i*Bu
5: R = Ph

(1)

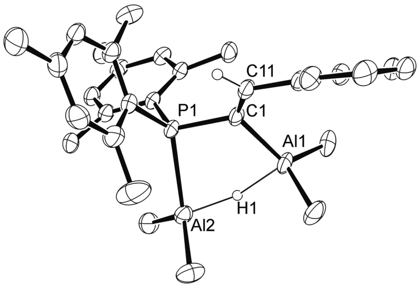


Figure 1. Molecular structure and atomic numbering scheme of compound **3**. A similar structure was observed for compound **4**. Displacement ellipsoids are drawn at the 40% level. Hydrogen atoms (except H(1) and the vinylic H atom, arbitrary radius) are omitted for clarity. Important bond lengths (Å) and angles (deg): compound **3**, Al(1)–C(1) 2.013(3), Al(1)–H(1) 1.81(3), P(1)–C(1) 1.812(3), C(1)–C(11) 1.344(4), P(1)–Al(2) 2.505(1), Al(2)–H(1) 1.64(3), P(1)–C(1)–Al(1) 114.5(3), C(1)–P(1)–Al(2) 98.05(9); compound **4**, Al(1)–C(1) 2.027(2), Al(1)–H(1) 1.78(2), P(1)–C(1) 1.812(2), C(1)–C(2) 1.344(2), P(1)–Al(2) 2.5214(7), Al(2)–H(1) 1.61(2), P(1)–C(1)–Al(1) 114.85(8), C(1)–P(1)–Al(2) 99.96(5).

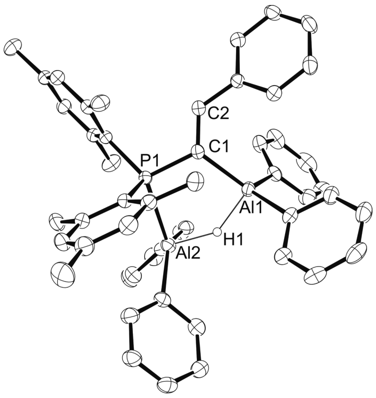
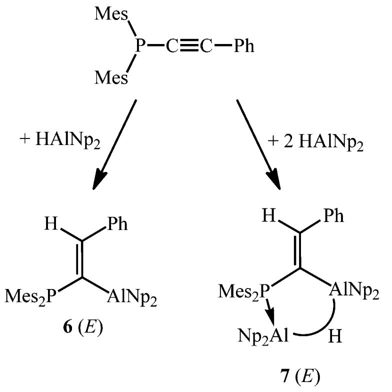


Figure 2. Molecular structure and atomic numbering scheme of compound **5**. Displacement ellipsoids are drawn at the 40% level. Hydrogen atoms (except H(1), arbitrary radius) are omitted for clarity. Important bond lengths (Å) and angles (deg): Al(1)–C(1) 2.014(2), Al(1)–H(1) 1.74(2), P(1)–C(1) 1.809(2), C(1)–C(2) 1.348(2), P(1)–Al(2) 2.5318(7), Al(2)–H(1) 1.63(2), P(1)–C(1)–Al(1) 115.87(9), C(1)–P(1)–Al(2) 98.79(6).

P FLP with a molecule of $HAlR_2$. Five-membered Al_2HPC heterocycles resulted which have an almost planar arrangement of the five ring atoms (maximum deviation from the average plane: 0.11 Å (**4**) or 0.09 Å (**5**); C(1)) or an envelope conformation (**3**; Al(2) 0.80 Å above the plane of the four remaining atoms). The Al atoms of the bridging R_2AlH moieties are coordinated by the P atoms and are further involved in 3c-2e Al–H–Al bonds to the metal atoms of the FLP backbone. The Al–P bond lengths (2.505(1) (**3**), 2.5214(7) (**4**), and 2.5318(7) Å (**5**)) are in a narrow range and correspond to standard values.[12] The Al–H distances differ, the smaller values were found to the Al atoms bonded to P (1.63 vs 1.78 Å on average; Al···Al 3.17 Å). Al and H atoms at the C=C double bonds adopt *trans* positions in all cases (similar to the case for **2**; Scheme 1). Other structural parameters are unexceptional (P–C in the heterocycle 1.811 Å (on average); Al–C in the heterocycle 2.018 Å; C=C 1.345 Å; Al–C–P 115.1°). The NMR spectra were in accordance with these molecular structures and exhibited the resonances of the bridging H atoms between both Al atoms (δ 3.96 (**3**), 3.84 (**4**), and 5.11 (**5**)) and of two different AlR_2 groups. The Al–H resonances were split into doublets caused by coupling to the P atoms ($^2J_{PH}$ = 36.0, 36.7, and 43.0 Hz). The unusual low-field shift of the bridging H atom in the spectrum of **5** was similarly observed for the starting compound diphenylaluminum hydride (δ 4.63).[13] The vinylic H atoms resonated at δ 7.57 (**3**), 7.58 (**4**), and 7.87 (**5**) with $^3J_{PH}$ coupling constants of 37.2, 37.8, and 37.0 Hz. These values are characteristic of a *cis*-arrangement of H and four-coordinate P atoms across C=C double bonds and were observed in the same range for cyclic adducts of FLP **2** and related compounds.[3,6] The ^{31}P NMR shifts (δ −10.4 to −11.8) were in the expected range of Al/P-based FLP adducts.[3,8−10] The Al–H–Al bridges gave broad absorptions in the IR spectra at about 1700 cm^{-1}. Only the mass spectrum of the dimethylaluminum compound **3** is indicative of the formation of the adduct ($M^+ - CH_3$), while in all other cases only fragments of the aluminum-free vinylphosphine backbone were detected. In attempts to generate the free FLPs, we heated reaction mixtures containing equimolar quantities of the alkynylphosphine and the corresponding dialkylaluminum hydride adducts **3**–**5** in toluene for several days (50–75 °C). In no case did we observe any alteration of the NMR intensities, and there was no indication for the formation of an FLP similar to **1** or **2**.

The steric demand of neopentyl groups is intermediate between those of *tert*-butyl and isobutyl groups, which causes a unique behavior of dineopentylaluminum hydride. Treatment of $Mes_2PC{\equiv}CPh$ with equimolar quantities of the hydride afforded a mixture of three compounds which were identified by their characteristic ^1H and ^{31}P NMR resonances as the starting alkynylphosphine, the noncoordinated FLP **6**, and the hydride adduct **7**. Only in this case warming of the mixture in toluene to 75 °C for 31 h gave further reaction with the complete consumption of the starting phosphine and the quantitative formation of the Al/P FLP **6** (eq 2). **6** was isolated



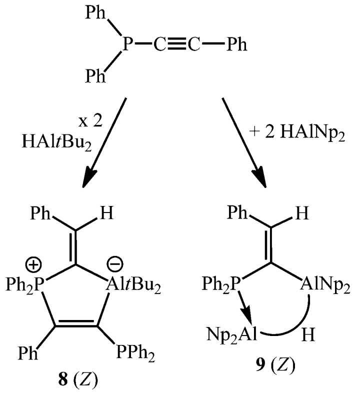
6 (*E*)

7 (*E*)

(2)

as a yellow oil and could not be purified by crystallization from several noncoordinating solvents. Its purity was sufficient for an unambiguous spectroscopic characterization and may allow its application in secondary reactions. Treatment of the alkynylphosphine with 2 equiv of the hydride afforded a similar mixture of all three components, but prolonged heating to 75 °C did not result in the quantitative formation of adduct **7**. Instead, unreacted hydride was detected in the NMR spectra. Almost complete consumption of the alkyne and the FLP **6** was only observed with a large excess of the hydride (molar ratio 1:3; concentration of residual **6** ~4%). We suppose that in solution an equilibrium exists in which the adduct **7** dissociates partially into the FLP **6** and dineopentylaluminum hydride. A large excess of the hydride shifted it toward adduct **7**. In addition, compound **7** could not be obtained in a pure, crystalline form. The ^{1}H NMR spectrum of Al/P FLP **6** showed the expected integration ratio of two neopentyl to two mesityl groups. The vinylic H atom gave a doublet at δ 7.33 with a $^3J_{PH}$ coupling constant of 20.6 Hz, which is similar to that of the analogous compound **2** (17.7 Hz, *cis* arrangement of P and H; see for comparison **1** with 37.9 Hz).[3] The P atom resonated at δ −21.0 in the ^{31}P{^{1}H} NMR spectrum. Adduct **7** showed NMR parameters closely related to those of compounds **3**−**5** with two sets of resonances of different neopentyl groups. The ^{31}P NMR signal was shifted to δ −6.9. In the ^{1}H NMR spectrum the vinylic H atom gave a doublet at δ 7.66 with a $^3J_{PH}$ coupling constant of 37.5 Hz (37−38 Hz in **3**−**5**; *cis* arrangement of P and H), which indicates retention of the configuration at the C=C double bond upon complex formation. The bridging H atom of the Al−H−Al group was detected as a doublet at δ 4.03 ($^2J_{PH}$ = 38.3 Hz) in the expected range. The mass spectrum of FLP **6** gave the molecular ion peak, while only an unspecific fragmentation pattern was observed for the relatively impure (excess hydride) adduct **7**.

Reactions of Diphenyl(phenylethynyl)phosphine. Steric shielding of the Al/P FLPs may be influenced not only by the size of the alkyl or aryl groups attached to Al but also by the substituents at the P atom. We therefore replaced the mesityl with phenyl groups and applied the alkynylphosphine $Ph_2PC{\equiv}CPh$ in further reactions. Di-*tert*-butylaluminum hydride and equimolar quantities of $Mes_2PC{\equiv}CPh$ afforded the Al/P FLP **2** in a selective reaction in more than 80% yield (Scheme 1).[2] It has been applied in many secondary transformations.[2,8−10] The similar reaction of sterically less shielded $Ph_2PC{\equiv}CPh$ (eq 3) gave surprisingly a mixture of a new compound (**8**) with excess $HAltBu_2$. **8** was isolated in 83% yield by treatment of $HAltBu_2$ with 2 equiv of $Ph_2PC{\equiv}CPh$ (eq 3). The formation of **8** may be described by the coordination of an alkyne molecule to an intermediately formed FLP ($Ph_2PC(=C(H)Ph)AlNp_2$). A crystal structure determination (Figure 3) revealed a central unsaturated five-membered $AlPC_3$ heterocycle with a C=C double bond coordinated by a P and an Al atom. Similar compounds were obtained by treatment of FLP **2** with terminal alkynes.[2] The Al atom binds to that C atom of the alkyne which is attached to the phosphine substituent. A relatively high partial negative charge[2] strongly favors the attack of the Al atom at this position. The P−C and Al−C bonds to the endocyclic ethenyl moiety are longer than those to the sp^2-C atom of the exocyclic double bond (1.816(3) vs 1.768(3) Å and 2.080(3) vs 2.039(3) Å; C(61)−P(2) (exocyclic) 1.805(3) Å). The C=C bond lengths (C(11)−C(12) 1.359(5); C(61)−C(62) 1.356(5)) are closely related to the standard value. The ring deviates slightly from planarity with the atoms of the endocyclic C=C bond 0.10 and 0.09 Å above the average plane. The alkenyl group has a *Z* configuration, which is also evident from the ^{1}H NMR parameters of the vinylic hydrogen atom (δ 8.71; $^3J_{PH}$ = 67.7 Hz). The ^{31}P NMR resonances of the three- and four-coordinate phosphorus atoms differ only slightly with values of δ 9.8 and 8.9 ($^3J_{PP}$ = 30.4 Hz).



(3)

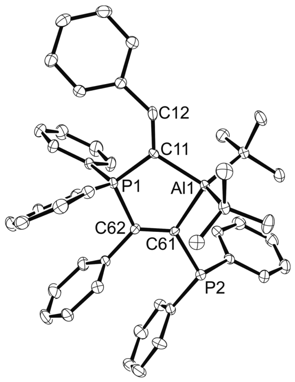


Figure 3. Molecular structure and atomic numbering scheme of compound **8**. Displacement ellipsoids are drawn at the 40% level. Hydrogen atoms are omitted for clarity. Important bond lengths (Å) and angles (deg): Al(1)−C(11) 2.039(3), Al(1)−C(61) 2.080(3), P(1)−C(11) 1.768(3), C(11)−C(12) 1.359(5), C(61)−C(62) 1.356(5), P(1)−C(62) 1.816(3), C(61)−P(2) 1.805(3), P(1)−C(11)−Al(1) 109.3(2), C(11)−P(1)−C(62) 104.4(2), P(1)−C(62)−C(61) 118.6(3), C(62)−C(61)−Al(1) 113.5(2), C(61)−Al(1)−C(11) 92.0(1), Al(1)−C(61)−P(2) 118.5(2).

Less shielded dineopentylaluminum hydride gave another reaction under similar conditions. Complete consumption of $Ph_2PC{\equiv}CPh$ was only observed with 2 equiv of the hydride. An adduct (**9**) analogous to those described above (eq 1; **3**−**5**, **7**) was isolated in 81% yield after concentration and cooling of the reaction mixture to −30 °C. A crystal structure determination (Figure 4) revealed the expected parameters (Al−P 2.476; Al−H 1.75 and 1.67 Å; Al···Al 3.19 Å; average values). In contrast to compounds **3**−**5** and **7** with the relatively bulky mesityl groups attached to P the diphenyl compound **9** has the *Z* configuration at its C=C double bond with Al and H atoms on the same side. In the ^{1}H NMR spectrum the vinylic H atom gave a doublet at δ 8.26 with a relatively large $^3J_{PH}$ coupling constant of 53.9 Hz, which verifies the *Z* configuration (37−38 Hz in **3**−**5** and **7**). The H atom of the Al−H−Al bridge resonated at δ 3.74 ($^2J_{PH}$ = 28.3 Hz). We did not find any evidence for the intermediate formation of a simple FLP corresponding to compounds **1**, **2**, and **6**.

■ CONCLUSION

Al/P FLPs contain coordinatively unsaturated Al and P atoms and are highly reactive amphiphilic compounds which are

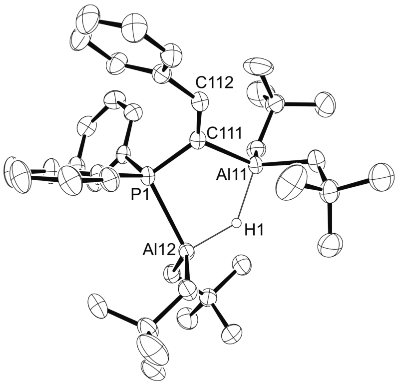


Figure 4. Molecular structure and atomic numbering scheme of compound **9**. Displacement ellipsoids are drawn at the 40% level. Hydrogen atoms (except H(1), arbitrary radius) are omitted for clarity; only one of the two independent molecules is considered. Important bond lengths (Å) and angles (deg): Al(11)−C(111) 2.009(2), Al(11)−H(1) 1.76(2), P(1)−C(111) 1.804(2), C(111)−C(112) 1.343(3), P(1)−Al(12) 2.4759(9), Al(12)−H(1) 1.66(2), P(1)−C(111)−Al(11) 111.5(1), C(111)−P(1)−Al(12) 100.14(8).

applicable in many stoichiometric or catalytic secondary reactions. Monomolecular derivatives such as **1**,[2] **2**,[2] and **6** are easily accessible by hydroalumination of alkynylphosphines. They have bulky mesityl groups attached to P and *tert*-butyl or neopentyl groups bonded to Al. However, there are important steric limitations for their syntheses. Small groups at Al gave persistent adducts of the Al/P FLP with the corresponding dialkylaluminum hydrides, even in those cases where stoichiometric 1:1 ratios of the starting compounds were applied. This observation demonstrates impressively the capability of these FLPs to act as bifunctional ligands for the effective coordination of polar or ionic compounds. Only neopentyl groups with a size between those of *tert*-butyl and isobutyl groups allowed the generation of both the uncoordinated FLP and the hydride adduct and their mutual transformation. The hydride adduct **7** seems to be relatively unstable and dissociated partially in solution to give an equilibrium mixture with the free FLP and $HAlNp_2$. Interestingly, the expected formation of dimeric compounds via intermolecular Al−P interactions was not observed. We isolated such dimeric Al/P FLPs from the reaction of sterically less shielded dialkynylphosphines with dialkylaluminum hydrides,[4] which alternatively gave heterocyclic compounds by condensation.[14] These dimeric compounds are still active Lewis pairs and are capable of coordinating CO_2 or PhN=C=O after dissociation.[4] The compounds described in this paper will stimulate further investigations. Compound **6** is important for systematic investigations into the influence of steric shielding on the reactivity of Al/P FLPs, and the unique hydride adducts may be applicable to the deprotonation of acidic compounds and the chelating coordination of the resulting anions or to hydroalumination reactions.

■ EXPERIMENTAL SECTION

All procedures were carried out under an atmosphere of purified argon in dried solvents (toluene with Na/benzophenone, *n*-hexane with $LiAlH_4$, 1,2-difluorobenzene with molecular sieves). $Mes_2PC{\equiv}CPh$,[2] $Ph_2PC{\equiv}CPh$,[15] $HAlMe_2$,[16] $HAl\textit{t}Bu_2$,[17] $HAlNp_2$,[18] and $HAlPh_2$[13] were obtained according to literature procedures. Commercially available $HAl\textit{i}Bu_2$ was distilled under vacuum at room temperature and trapped with liquid nitrogen. The assignment of the NMR spectra is based on HMBC, HSQC, ROESY, and DEPT135 data.

Synthesis of the Dimethylaluminum Hydride Adduct 3. A solution of $Mes_2PC{\equiv}CPh$ (0.362 g, 0.98 mmol) in 10 mL of toluene was added to a solution of excess dimethylaluminum hydride (0.170 g, 2.93 mmol) in 5 mL of toluene at room temperature. The mixture was stirred for 14 h at 75 °C. All volatiles (excess hydride, solvent) were removed in vacuo. The residue was dissolved in cyclopentane. Colorless crystals of **3** precipitated slowly at room temperature. Yield: 0.316 g (66%; based on alkyne). Mp (argon, sealed capillary): 161 °C dec. Anal. Calcd for $C_{30}H_{41}Al_2P$ (486.58): C, 74.1; H, 8.5. Found: C, 74.2; H, 8.7. $^{31}P\{^1H\}$ NMR (C_6D_6, 162 MHz, 300 K): δ −11.8 (s, br). ^1H NMR (C_6D_6, 400 MHz, 300 K): δ −0.34 (6 H, d, br, $^3J_{PH}$ = 2.9 Hz, $PAlMe_2$), −0.19 (6 H, s, $CAlMe_2$), 2.00 (6 H, s, *p*-CH_3), 2.67 (12 H, s, *o*-CH_3), 3.96 (1 H, d, br, $^2J_{PH}$ = 36.0 Hz, Al−H−Al), 6.62 (4 H, d, $^4J_{PH}$ = 2.6 Hz, *m*-H_{Mes}), 7.02 (1 H, m, *p*-$H_{vinylPh}$), 7.08 (2 H, t, $^3J_{HH}$ = 7.4 Hz, *m*-$H_{vinylPh}$), 7.35 (2 H, d, $^3J_{HH}$ = 7.3 Hz, *o*-$H_{vinylPh}$), 7.57 (1 H, d, $^3J_{PH}$ = 37.2 Hz, PC=CH). $^{13}C\{^1H\}$ NMR (C_6D_6, 101 MHz, 300K): δ −7.5 (s, br, $AlMe_2$, both resonances coincide), 20.8 (s, *p*-CH_3), 24.1 (d, $^3J_{PC}$ = 7.9 Hz, *o*-CH_3), 125.4 (d, $^1J_{PC}$ = 31.2 Hz, *i*-C_{Mes}), 128.1 (s, covered, *o*-$C_{vinylPh}$), 128.88 (s, *m*-$C_{vinylPh}$), 128.91 (s, *p*-$C_{vinylPh}$), 131.1 (d, $^3J_{PC}$ = 7.5 Hz, *m*-C_{Mes}), 140.4 (d, $^4J_{PC}$ = 1.9 Hz, *p*-C_{Mes}), 141.6 (d, $^3J_{PC}$ = 24.7 Hz, *i*-$C_{vinylPh}$), 142.6 (d, $^2J_{PC}$ = 9.1 Hz, *o*-C_{Mes}), 146.0 (d, br, $^1J_{PC}$ = 29.0 Hz, PC=CH), 156.0 (d, $^2J_{PC}$ = 9.6 Hz, PC=CH). IR (paraffin, CsI, cm^{-1}): 1890 w, br ν(AlH); 1688 vw, 1580 vs, 1558 vs ν(C=C), phenyl; 1470 vs (paraffin); 1402 (vs) $\delta(CH_3)$; 1377 vs (paraffin); 1339 m, 1321 w, 1306 m $\delta(CH_3)$; 1152 vs, br ν(AlHAl); 970 vw, 930 vw, 889 vw, 849 vw, 814 w, 785 vw, 762 vw δ(aromatic), ν(CC); 721 vs (paraffin); 592 w, 559 m, 511 w, 482 m, 447 m δ(CC), ν(AlC), ν(PC). MS (EI, 30 eV, 373 K): *m*/*z* (%) 471 (1), 472 (0.3) $[M^+ - CH_3]$, 428 (6), 429 (2) $[M^+ - HAlMe_2]$, 413 (7), 414 (3) $[M^+ - HAlMe_2 - CH_3]$, 372 (36), 373 (10) $[Mes_2PC(H){=}C(H)Ph^+]$, 357 (22), 358 (6) $[Mes_2PC(H){=}C(H)Ph^+ - CH_3]$, 280 (100), 281 (21) $[Mes_2PC(H){=}C(H)Ph^+ - CH_3 - Ph]$, 119 (25) $[Mes^+]$, 57 (7) $[Me_2Al^+]$.

Synthesis of the Diisobutylaluminum Hydride Adduct 4. A solution of $Mes_2PC{\equiv}CPh$ (0.500 g, 1.35 mmol) in 20 mL of toluene was treated with diisobutylaluminum hydride (0.384 g, 2.70 mmol) at room temperature. The mixture was stirred at 65 °C for 17 h. All volatiles were removed in vacuo. The residue was dissolved in 1,2-difluorobenzene and cooled to −20 °C to afford colorless crystals of **4**. Yield: 0.842 g (95%). Mp (argon, sealed capillary): 125 °C dec. Anal. Calcd for $C_{42}H_{65}Al_2P$ (654.90): C, 77.0; H, 10.0. Found: C, 77.2; H, 10.1. $^{31}P\{^1H\}$ NMR (C_6D_6, 162 MHz, 300 K): δ −11.3. ^1H NMR (C_6D_6, 400 MHz, 300 K): δ 0.30 and 0.44 (each 2 H, m, CH_2 of $PAl\textit{i}Bu_2$), 0.51 (4 H, m, CH_2 of $CAl\textit{i}Bu_2$), 1.12 (6 H, d, $^3J_{HH}$ = 6.5 Hz, CH_3 of $PAl\textit{i}Bu_2$), 1.16 (6 H, d, $^3J_{HH}$ = 6.5 Hz, CH_3 of $PAl\textit{i}Bu_2$), 1.19 (6 H, d, $^3J_{HH}$ = 6.5 Hz, CH_3 of $CAl\textit{i}Bu_2$), 1.25 (6 H, d, $^3J_{HH}$ = 6.4 Hz, CH_3 of $CAl\textit{i}Bu_2$), 2.02 (2 H, m, CH of $PAl\textit{i}Bu_2$), 2.02 (6 H, s, *p*-CH_3), 2.12 (2 H, m, CH of $CAl\textit{i}Bu_2$), 2.25 (12 H, s, br, *o*-CH_3), 3.84 (1 H, d, br, $^2J_{PH}$ = 36.7 Hz, Al−H−Al), 6.63 (4 H, d, $^4J_{PH}$ = 2.8 Hz, *m*-H_{Mes}), 7.03 (1 H, m, *p*-$H_{vinylPh}$), 7.11 (2 H, m, *m*-$H_{vinylPh}$), 7.33 (2 H, m, *o*-$H_{vinylPh}$), 7.58 (1 H, d, $^3J_{PH}$ = 37.8 Hz, PC=CH). $^{13}C\{^1H\}$ NMR (C_6D_6, 101 MHz, 300 K): δ 20.8 (s, *p*-CH_3), 23.7 (d, $^2J_{PC}$ = 12.4 Hz, CH_2 of $PAl\textit{i}Bu_2$), 24.4 (s, CH_2 of $CAl\textit{i}Bu_2$), 24.5 (s, br, *o*-CH_3), 26.8 (d, $^3J_{PC}$ = 2.9 Hz, CH_2 of $PAl\textit{i}Bu_2$), 27.4 (s, CH of $CAl\textit{i}Bu_2$), 28.2 and 28.4 (s, CH_3 of $PAl\textit{i}Bu_2$), 28.6 and 28.7 (s, CH_3 of $CAl\textit{i}Bu_2$), 126.4 (d, $^1J_{PC}$ = 29.3 Hz, *i*-C_{Mes}), 128.2 (d, $^4J_{PC}$ = 1.5 Hz, *o*-$C_{vinylPh}$), 128.9 (s, *m*-$C_{vinylPh}$), 129.0 (s, *p*-$C_{vinylPh}$), 131.0 (d, $^3J_{PC}$ = 7.4 Hz, *m*-C_{Mes}), 140.3 (d, $^4J_{PC}$ = 1.9 Hz, *p*-C_{Mes}), 141.6 (d, $^3J_{PC}$ = 24.6 Hz, *i*-$C_{vinylPh}$), 142.3 (d, $^2J_{PC}$ = 9.0 Hz, *o*-C_{Mes}), 146.1 (d, $^1J_{PC}$ = 33.9 Hz, PC=CH), 157.6 (d, $^2J_{PC}$ = 10.5 Hz, PC=CH). IR (paraffin, CsI, cm^{-1}): 1724 m, br ν(Al−H); 1601 s, 1580 m, 1533 s ν(C=C), phenyl; 1462 vs (paraffin); 1402 s $\delta(CH_3)$; 1377 vs (paraffin); 1317 s, 1292 m, 1244 w $\delta(CH_3)$; 1200 m, 1173 m, 1157 m, 1063 s, 1013 s, 943 s, 924 s, 886 w, 864 m, 847 s, 812 m, 789 m, 746 s δ(aromatic), ν(CC); 721 vs (paraffin); 702 s, 662 s, 627 s, 611 sh, 592 m, 559 m, 538 sh, 488 m, 451 w, 411 w δ(CC), ν(AlC), ν(PC). MS (EI, 30 eV, 298−573 K): *m*/

z (%) 373 (100), 374 (27) [$\mathrm{Mes_2PC(H){=}C(H)Ph^+ + H}$], 297 (85), 298 (18) [$\mathrm{Mes_2PC(H){=}C(H)Ph^+ - Ph + 2\ H}$], 119 (5) [$\mathrm{Mes^+}$].

Synthesis of the Diphenylaluminum Hydride Adduct 5. A solution of $\mathrm{Mes_2PC{\equiv}CPh}$ (0.255 g, 0.69 mmol) in 20 mL of toluene was treated with a solution of excess diphenylaluminum hydride (0.326 g, 1.79 mmol) in 20 mL of toluene at room temperature. The mixture was stirred at room temperature for 24 h. All volatiles were removed in vacuo. The residue was treated with 20 mL of *n*-pentane and filtered to separate the excess diphenylaluminium hydride. The solvent was removed in vacuo to afford a colorless solid of **5** in high purity. Yield: 0.470 g (93%, based on alkyne). Mp (argon, sealed capillary): 104 °C dec. Anal. Calcd for $\mathrm{C_{50}H_{49}Al_2P}$ (734.86): C, 81.7; H, 6.7. Found: C, 80.9; H, 6.7. ^{31}P{^{1}H} NMR ($\mathrm{C_6D_6}$, 162 MHz, 300 K): δ −10.4. ^{1}H NMR ($\mathrm{C_6D_6}$, 400 MHz, 300 K): δ 1.93 (6 H, s, *p*-$\mathrm{CH_3}$), 2.21 (12 H, s, *o*-$\mathrm{CH_3}$), 5.11 (1 H, d, br, $^2J_{\mathrm{PH}}$ = 43.0 Hz, Al–H–Al), 6.44 (4 H, d, $^4J_{\mathrm{PH}}$ = 3.0 Hz, *m*-$\mathrm{H_{Mes}}$), 6.86 (1 H, m, *p*-$\mathrm{H_{vinylPh}}$), 6.97 (2 H, m, *m*-$\mathrm{H_{vinylPh}}$), 7.07 (4 H, m, *m*-H of $\mathrm{PAlPh_2}$), 7.13 (2 H, m, *p*-H of $\mathrm{PAlPh_2}$), 7.27 (2 H, m, *p*-H of $\mathrm{CAlPh_2}$), 7.29 (4 H, m, *m*-H of $\mathrm{CAlPh_2}$), 7.53 (4 H, m, *o*-H of $\mathrm{PAlPh_2}$), 7.57 (2 H, m, *o*-$\mathrm{H_{vinylPh}}$), 7.87 (1 H, d, $^3J_{\mathrm{PH}}$ = 37.0 Hz, PC=CH), 7.91 (4 H, m, *o*-H of $\mathrm{CAlPh_2}$). ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$, 101 MHz, 300 K): δ 20.7 (d, $^5J_{\mathrm{PC}}$ = 7.8 Hz, *p*-$\mathrm{CH_3}$), 25.0 (d, $^3J_{\mathrm{PC}}$ = 8.0 Hz, *o*-$\mathrm{CH_3}$), 124.2 (d, $^1J_{\mathrm{PC}}$ = 33.6 Hz, *i*-$\mathrm{C_{Mes}}$), 127.4 (s, *m*-C of $\mathrm{PAlPh_2}$), 127.7 (s, *m*-C of $\mathrm{CAlPh_2}$), 128.2 (s, overlap, *o*-$\mathrm{C_{vinylPh}}$), 128.3 (s, overlap, *o*-C of $\mathrm{PAlPh_2}$), 128.3 (s, overlap, *o*-C of $\mathrm{CAlPh_2}$), 129.3 (s, *m*-$\mathrm{C_{vinylPh}}$), 129.7 (s, *p*-$\mathrm{C_{vinylPh}}$), 131.3 (d, $^3J_{\mathrm{PC}}$ = 7.8 Hz, *m*-$\mathrm{C_{Mes}}$), 138.5 (s, *o*-C of $\mathrm{PAlPh_2}$), 138.9 (s, *o*-C of $\mathrm{CAlPh_2}$), 141.0 (d, $^4J_{\mathrm{PC}}$ = 1.8 Hz, *p*-$\mathrm{C_{Mes}}$), 141.1 (d, $^3J_{\mathrm{PC}}$ = 24.5 Hz, *i*-$\mathrm{C_{vinylPh}}$), 142.9 (d, $^3J_{\mathrm{PC}}$ = 9.3 Hz, *o*-$\mathrm{C_{Mes}}$), 144.0 (s, br, *i*-C of $\mathrm{PAlPh_2}$), 145.9 (s, br, *i*-C of $\mathrm{CAlPh_2}$), 159.0 (d, $^2J_{\mathrm{PC}}$ = 9.5 Hz, PC=CH); PC=CH not detected. IR (paraffin, CsI, cm^{-1}): 1697 m, br ν(AlH); 1603 m, 1580 w, 1557 w, 1535 m ν(C=C), phenyl; 1458 vs (paraffin); 1420 s δ($\mathrm{CH_3}$); 1375 vs (paraffin), 1292 m, 1246 m δ($\mathrm{CH_3}$); 1192 w, 1153 w, 1086 s, 1047 vw, 1026 w, 995 w, 945 m, 931 m, 893 vw, 870 w, 849 m, 795 w, 770 vw, 748 m δ(aromatic), ν(CC); 727 s (paraffin); 700 vs, 665 m, 652 m phenyl; 629 m, 611 vw, 592 w, 579 m, 554 vw, 498 w, 465 m, 453 sh, 419 w δ(CC), ν(AlC), ν(PC). MS (EI, 20 eV, 483 K): m/z (%) 372 (26), 373 (22) [$\mathrm{Mes_2PC(H){=}C(H)Ph^+}$], 357 (16), 358 (4) [$\mathrm{Mes_2PC(H){=}C(H)Ph^+ - CH_3}$], 119 (7) [$\mathrm{Mes^+}$].

Synthesis of (*E*)-$\mathrm{Mes_2P[C{=}C(H)Ph]AlNp_2}$ (6). A solution of dineopentylaluminum hydride (0.071 g, 0.42 mmol) in 6 mL of toluene was treated with a solution of $\mathrm{Mes_2PC{\equiv}CPh}$ (0.154 g, 0.42 mmol) in 6 mL of toluene at room temperature. The mixture was stirred for 31 h at 75 °C. The ^{31}P{^{1}H} NMR spectrum showed 10% of unreacted $\mathrm{Mes_2PC{\equiv}CPh}$. To achieve full conversion, a solution of dineopentylaluminum hydride (0.007 g, 0.04 mmol) in 2 mL of toluene was added at room temperature. The mixture was stirred for 29 h at 75 °C. All volatiles were removed in vacuo. Compound **6** could not be purified by crystallization from different noncoordinating solvents and remained as a yellow waxy material. ^{31}P{^{1}H} NMR ($\mathrm{C_6D_6}$, 162 MHz, 300 K): δ −21.0 (s, br). ^{1}H NMR ($\mathrm{C_6D_6}$, 400 MHz, 300 K): δ 0.41 (4 H, s, $\mathrm{CH_2CMe_3}$), 1.08 (18 H, s, $\mathrm{CMe_3}$), 2.10 (6 H, s, *p*-$\mathrm{CH_3}$), 2.54 (12 H, s, *o*-$\mathrm{CH_3}$), 6.77 (4 H, d, $^4J_{\mathrm{PH}}$ = 2.4 Hz, *m*-$\mathrm{H_{Mes}}$), 6.95 (1 H, t, $^3J_{\mathrm{HH}}$ = 7.6 Hz, *p*-$\mathrm{H_{vinylPh}}$), 7.07 (2 H, pseudo-t, *m*-$\mathrm{H_{vinylPh}}$), 7.12 (2 H, d, $^3J_{\mathrm{HH}}$ = 9.0 Hz, *o*-$\mathrm{H_{vinylPh}}$), 7.33 (1 H, d, $^3J_{\mathrm{PH}}$ = 20.6 Hz, PC=CH). ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$, 101 MHz, 300 K): δ 20.9 (s, *p*-$\mathrm{CH_3}$), 23.9 (d, $^3J_{\mathrm{PC}}$ = 14.1 Hz, *o*-$\mathrm{CH_3}$), 31.7 (s, $\mathrm{CMe_3}$), 33.8 (s, $\mathrm{AlCH_2}$), 34.9 (s, C*Me*$_3$), 125.2 (d, $^4J_{\mathrm{PC}}$ = 1.7 Hz, *o*-$\mathrm{C_{vinylPh}}$), 127.8 (s, *p*-$\mathrm{C_{vinylPh}}$), 130.41 (s, *m*-$\mathrm{C_{Mes}}$), 130.44 (s, *m*-$\mathrm{C_{vinylPh}}$), 131.1 (d, $^1J_{\mathrm{PC}}$ = 22.4 Hz, *ipso*-$\mathrm{C_{Mes}}$), 138.6 (s, *p*-$\mathrm{C_{Mes}}$), 143.7 (two resonances coincide, d, $^2J_{\mathrm{PC}}$ = 14.5 Hz, *o*-$\mathrm{C_{Mes}}$ and PC=*C*H), 145.3 (d, $^3J_{\mathrm{PC}}$ = 13.7 Hz, *ipso*-$\mathrm{C_{vinylPh}}$), 157.6 (d, $^1J_{\mathrm{PC}}$ = 55.2 Hz, PC=CH). MS (EI, 20 eV, 393 K): m/z (%) 540 (2), 541 (0.5) [$\mathrm{M^+}$], 469 (6), 470 (2) [$\mathrm{M^+ - CH_2CMe_3}$], 372 (33), 373 (10) [$\mathrm{Mes_2PC(H){=}C(H)\text{-}^+}$], 357 (15), 358 (4) [$\mathrm{Mes_2PC(H){=}C(H)Ph^+ - CH_3}$].

Synthesis of the Dineopentylaluminum Hydride Adduct 7. A solution of excess dineopentylaluminum hydride (0.146 g, 0.86 mmol) in 15 mL of toluene was treated with a solution of $\mathrm{Mes_2PC{\equiv}CPh}$ (0.103 g, 0.28 mmol) in 6 mL of toluene at room temperature. The mixture was stirred for 16 h at 75 °C. All volatiles were removed in vacuo. An oily residue remained which could not be crystallized from noncoordinating solvents. It consisted of the hydride adduct **7**, the excess dineopentylaluminum hydride (dimeric and trimeric formula units:[12] δ 0.65 ($\mathrm{CH_2}$), 1.15 ($\mathrm{CMe_3}$), 3.34 (AlH) and 0.75, 1.17 and 3.15), and residual solvent. ^{31}P{^{1}H} NMR ($\mathrm{C_6D_6}$, 162 MHz, 300 K): δ −6.9 (s). ^{1}H NMR ($\mathrm{C_6D_6}$, 400 MHz, 300 K): δ 0.60 and 0.74 (4 H, AB spin system, $^2J_{\mathrm{HH}}$ = 15.2 Hz, $\mathrm{PAlCH_2}$), 0.89 (4 H, s, $\mathrm{CAlCH_2}$), 1.23 (18 H, s, PAl($\mathrm{CH_2C}$*Me*$_3$)$_2$), 1.30 (18 H, s, CAl($\mathrm{CH_2C}$*Me*$_3$)$_2$), 2.02 (6 H, s, *p*-$\mathrm{CH_3}$), 2.27 (12 H, s, *o*-$\mathrm{CH_3}$), 4.03 (1 H, d, br, $^2J_{\mathrm{PH}}$ = 38.3 Hz, Al–H–Al), 6.63 (4 H, d, $^4J_{\mathrm{PH}}$ = 2.3 Hz, *m*-$\mathrm{H_{Mes}}$), 7.03 (1 H, t, $^3J_{\mathrm{HH}}$ = 7.1 Hz, *p*-$\mathrm{H_{vinylPh}}$), 7.13 (2 H, pseudo-t, *m*-$\mathrm{H_{vinylPh}}$), 7.39 (2 H, d, $^3J_{\mathrm{HH}}$ = 7.5 Hz, *o*-$\mathrm{H_{vinylPh}}$), 7.66 (1 H, d, $^3J_{\mathrm{PH}}$ = 37.5 Hz, PC=CH). ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$, 101 MHz, 300 K): δ 20.7 (s, *p*-$\mathrm{CH_3}$), 25.3 (d, $^3J_{\mathrm{PC}}$ = 8.9 Hz, *o*-$\mathrm{CH_3}$), 31.4 (s br, $\mathrm{PAlCH_2}$), 31.9 (d, $^3J_{\mathrm{PC}}$ = 2.9 Hz, PAl($\mathrm{CH_2CMe_3}$)$_2$), 32.1 (s, CAl($\mathrm{CH_2CMe_3}$)$_2$), 33.0 (s br, $\mathrm{CAlCH_2}$), 35.2 (s, PAl($\mathrm{CH_2C}$*Me*$_3$)$_2$), 35.3 (s, CAl($\mathrm{CH_2C}$*Me*$_3$)$_2$), 127.3 (s, *ipso*-$\mathrm{C_{Mes}}$), 128.6 (s, *m*-$\mathrm{C_{vinylPh}}$), 128.9 (s, o-$\mathrm{C_{vinylPh}}$), 129.1 (s, *p*-$\mathrm{C_{vinylPh}}$), 131.0 (d, $^3J_{\mathrm{PC}}$ = 7.1 Hz, *m*-$\mathrm{C_{Mes}}$), 140.1 (d, $^4J_{\mathrm{PC}}$ = 1.9 Hz, *p*-$\mathrm{C_{Mes}}$), 141.6 (d, $^3J_{\mathrm{PC}}$ = 25.0 Hz, *ipso*-$\mathrm{C_{vinylPh}}$), 142.2 (d, $^2J_{\mathrm{PC}}$ = 8.9 Hz, *o*-$\mathrm{C_{Mes}}$), 159.3 (d, $^2J_{\mathrm{PC}}$ = 10.7 Hz, PC=*C*H); PC=CH not observed. MS (EI, 20 eV, 402 K): m/z (%) 539 (0.2) [$\mathrm{M^+ - 3\ CMe_3}$], 457 (1), 458 (0.5) [$\mathrm{M^+ - 2\ Mes - Me}$], 372 (31), 373 (11) [$\mathrm{Mes_2PC(H){=}C(H)Ph^+}$].

Synthesis of the Diphenyl(phenylethynyl)phosphine Adduct 8. $\mathrm{Ph_2PC{\equiv}CPh}$ (0.328 g, 1.15 mmol) was dissolved in 10 mL of *n*-hexane and treated with a solution of di-*tert*-butylaluminum hydride (0.081 g, 0.57 mmol) in 10 mL of *n*-hexane at room temperature. The solution was stirred for 10 days. The color changed to yellow, and the product started to precipitate. The yellow solid was isolated by filtration. The filtrate was concentrated and cooled to 4 °C to isolate a second fraction of the solid material. Yield: 0.338 g (83%). Mp (argon, sealed capillary): 203 °C dec. Anal. Calcd for $\mathrm{C_{48}H_{49}AlP_2}$ (714.8): C, 80.7; H, 6.9. Found: C, 80.3, H, 6.9. ^{31}P{^{1}H} NMR ($\mathrm{C_6D_6}$, 162 MHz, 300 K): δ 8.9 (d, $^3J_{\mathrm{PP}}$ = 30.4 Hz, endocyclic), 9.8 (d, $^3J_{\mathrm{PP}}$ = 30.4 Hz, exocyclic). ^{1}H NMR ($\mathrm{C_6D_6}$, 400 MHz, 300 K): δ 1.54 (18 H, s, C*Me*$_3$), 6.35 (2 H, d, $^3J_{\mathrm{HH}}$ = 7.8 Hz, *o*-CH, C=C(P)*Ph*), 6.45 (2 H, pseudo-t, *m*-CH, C=C(P)*Ph*), 6.59 (3 H, m, *m*-CH, C=CH*Ph* and *p*-CH, C=C(P)*Ph*), 6.69 (1 H, pseudo-t, *p*-CH, C=CH*Ph*), 6.79 (2 H, d, $^3J_{\mathrm{HH}}$ = 7.3 Hz, *o*-CH, C=CH*Ph*), 6.85 (4 H, m, *m*-CH, (C=C)$_2$P*Ph*$_2$), 6.92 (2 H, m, *p*-CH, (C=C)$_2$P*Ph*$_2$), 6.96 (2 H, m, *p*-CH, (C=C)P*Ph*$_2$), 6.99 (4 H, *m*-CH, (C=C)P*Ph*$_2$), 7.46 (4 H, m, *o*-CH, (C=C)$_2$P*Ph*$_2$), 7.66 (4 H, m, *o*-CH, (C=C)P*Ph*$_2$), 8.71 (1 H, d, $^3J_{\mathrm{PH}}$ = 67.7 Hz, C=C*H*). ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$, 100 MHz, 300 K): δ 17.3 ($\mathrm{CMe_3}$), 33.1 (C*Me*$_3$), 124.9 (dd, $^1J_{\mathrm{PC}}$ = 68.3 Hz, $^4J_{\mathrm{PC}}$ = 4.3 Hz, *i*-C, (C=C)$_2$P*Ph*$_2$), 126.9 (*p*-C, C=C(P)*Ph*), 127.6 (*m*-C, C=C(P)*Ph*), 127.6 (*m*-C and *p*-C, C=CH*Ph*), 127.8 (*m*-C, (C=C)P*Ph*$_2$), 128.4 (*p*-C, (C=C)P*Ph*$_2$), 128.5 (*m*-C, (C=C)$_2$P*Ph*$_2$), 128.7 (d, $^4J_{\mathrm{PC}}$ = 1.4 Hz, *o*-C, C=CH*Ph*), 131.2 (d, $^3J_{\mathrm{PC}}$ = 2.1 Hz, *o*-C, C=C(P)*Ph*), 132.1 (d, $^4J_{\mathrm{PC}}$ = 2.7 Hz, *p*-C, (C=C)$_2$P*Ph*$_2$), 133.5 (d, $^2J_{\mathrm{PC}}$ = 8.8 Hz, *o*-C, (C=C)$_2$P*Ph*$_2$), 136.1 (d, $^2J_{\mathrm{PC}}$ = 21.4 Hz, *o*-C, (C=C)P*Ph*$_2$), 138.5 (dd, $^3J_{\mathrm{PC}}$ = 19.6 Hz, $^2J_{\mathrm{PC}}$ = 11.9 Hz, *i*-C, C=C(P)*Ph*), 138.7 (br., P(Al)*C*=CH), 139.6 (d, $^1J_{\mathrm{PC}}$ = 11.7 Hz, *i*-C, (C=C)P*Ph*$_2$), 139.8 (d, $^3J_{\mathrm{PC}}$ = 16.0 Hz, *i*-C, C=CH*Ph*), 140.9 (dd, $^1J_{\mathrm{PC}}$ = 96.1 Hz, $^2J_{\mathrm{PC}}$ = 8.9 Hz, P(Ph)*C*=C)), 160.9 (d, $^2J_{\mathrm{PC}}$ = 8.2 Hz, C=CH), 199.8 (dd, $^1J_{\mathrm{PC}}$ = 65.0 Hz, $^2J_{\mathrm{PC}}$ = 34.0 Hz, P(Al)*C*=CP). IR (paraffin, CsI, cm^{-1}): 1985 w, 1964 m, 1944 m, 1892 vw, 1861 vw, 1822 w, 1805 w, 1765 vw, 1687 w, 1678 w, 1663 w, 1645 w, 1585 m, 1553 s, 1537 m, 1514 m ν(C=C), phenyl; 1466 vs, 1371 vs (paraffin); 1300 m, 1271 m δ($\mathrm{CH_3}$); 1190 m, 1173 s, 1157 sh, 1101 s, 1069 s, 1022 s, 997 s, 966 m, 932 s, 891 m, 849 s, 806 s, 777 s, 743 s δ(aromatic), ν(CC); 721 s (paraffin); 689 m, 665 m, 635 w phenyl; 615 m, 561 vs, 546 s, 511 m, 490 m, 446 m, 417 m δ(CC), ν(AlC), ν(PC). MS (EI, 20 eV, 393 K): m/z (%) 657 (100), 658 (48) [$\mathrm{M^+ - CMe_3}$], 601 (11), 602 (4) [$\mathrm{M^+ - CMe_3 -}$ butene], 371 (13), 372 (3) [$\mathrm{M^+ - Ph_2PC_2Ph - CMe_3}$].

Synthesis of the Dineopentylaluminum Hydride Adduct 9. A solution of $\mathrm{Ph_2PC{\equiv}CPh}$ (0.380 g, 1.33 mmol) in 10 mL of *n*-hexane was treated with a solution of dineopentylaluminum hydride (0.451 g, 2.65 mmol) in 20 mL of *n*-hexane at room temperature. The mixture adopted a pale yellow color. It was stirred for 19 h at room temperature, concentrated, and cooled to −30 °C. Compound **8** precipitated as a colorless powder. Yield: 0.678 g (81%). Mp (argon, sealed capillary): 123 °C dec. Anal. Calcd for $\mathrm{C_{40}H_{61}Al_2P}$ (626.9): C, 76.6; H, 9.8. Found: C, 77.1; H, 9.9. ^{31}P{^{1}H} NMR (C$_6$D$_6$, 162 MHz, 300 K): δ −17.9. ^{1}H NMR (C$_6$D$_6$, 400 MHz, 300 K): δ 0.72 (4 H, d, $^3J_{PH}$ = 3.4 Hz, PAl(C*H*$_2$CMe$_3$)$_2$), 0.76 and 0.86 (each 2 H, AB spin system, $^2J_{HH}$ = 13.9 Hz, CAl(C*H*$_2$CMe$_3$)$_2$), 1.09 (18 H, s, PAl(CH$_2$C*Me*$_3$)$_2$), 1.39 (18 H, s, CAl(CH$_2$C*Me*$_3$)$_2$), 3.74 (1 H, d, $^2J_{HP}$ = 28.3 Hz, Al−H−Al), 6.55 (2 H, pseudo-t, *m*-CH, C═C*Ph*), 6.66 (1 H, m, *p*-CH, C═C*Ph*), 6.85 (2 H, m, *o*-CH, C═C*Ph*), 6.92 (6 H, m, *p*-CH and *m*-CH, P*Ph*$_2$), 7.45 (4 H, m, *o*-CH, P*Ph*$_2$), 8.26 (1 H, d, $^3J_{PH}$ = 53.9 Hz, C═C*H*). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 100 MHz, 300 K): δ 28.7 (d, $^2J_{PC}$ = 15.7 Hz, PAl(CH$_2$CMe$_3$)$_2$), 31.5 (CAl(CH$_2$CMe$_3$)$_2$), 31.6 (d, $^3J_{CP}$ = 2.3 Hz, PAl(CH$_2$CMe$_3$)$_2$), 35.0 (PAl(CH$_2$C*Me*$_3$)$_2$), 35.7 (CAl(CH$_2$C*Me*$_3$)$_2$), 126.9 (d, $^1J_{PC}$ = 28.9 Hz, *i*-CH, P*Ph*$_2$), 127.4 (*m*-CH, C═C*Ph*), 127.9 (*p*-CH, C═C*Ph*), 128.8 (*o*-CH, C═C*Ph*), 128.8 (d, $^3J_{PC}$ = 9.2 Hz, *m*-CH, P*Ph*$_2$), 130.6 (d, $^4J_{PC}$ = 2.3 Hz, *p*-CH, P*Ph*$_2$), 133.4 (d, $^2J_{PC}$ = 10.6 Hz, *o*-CH, P*Ph*$_2$), 137.9 (d, $^3J_{PC}$ = 16.3 Hz, *i*-CH, C═C*Ph*), 139.4 (d, $^1J_{PC}$ = 36.4 Hz, C═CH), 158.9 (d, $^2J_{PC}$ = 16.9 Hz, C═CH). IR (paraffin, CsI, cm^{-1}): 1950 m, 1894 m, 1803 m phenyl; 1670 m, br ν(AlH); 1582 s, 1551 s ν(C═C), phenyl; 1464 vs, 1377 vs, 1360 vs (paraffin); 1308 s, 1271 m δ(CH$_3$); 1225 vs 1155 w, 1123 s, 1098 s, 1072 m, 1011 s, 997 vs, 968 vs, 930 s, 885 w, 851 s, 741 vs ν(CC), δ(CH), paraffin; 692 vs, 654 s phenyl; 534 s, 509 m, 459 s, 426 w δ(CC), ν(AlC), ν(PC). MS (EI, 20 eV, 373 K): *m*/*z* (%): 441 (2) [M$^+$ − HAl(CH$_2$CMe$_3$)$_2$ − CH$_3$], 287 (100) [PhPC(═CCMe$_3$)AlCH$_2$CMe$_3$$^+$].

Crystal Structure Determinations. Single crystals were obtained by recrystallization from cyclopentane (**3**, dissolved at room temperature, concentrated and stored at room temperature), 1,2-difluorobenzene (**4**, −20 °C; **8** and **9**, +4 °C), and *n*-hexane (**5**, dissolved at 50 °C, slowly cooled to room temperature). The crystallographic data were collected with Bruker Venture (Mo Kα; **3**−**5**) and SMART diffractometers (Cu Kα; **8** and **9**). The structures were solved by direct methods and refined with the program SHELXL-97[19] by a full-matrix least-squares method based on F^2. Hydrogen atoms, with the exception of the hydridic atoms attached to aluminum, were positioned geometrically and allowed to ride on their respective parent atoms. Compounds **4** and **8** crystallized with a molecule of 1,2-difluorobenzene per formula unit. The solvent molecule of **4** was disordered and refined on split positions (0.73:0.27). Both isobutyl groups of **4** at Al2 were disordered (C81, 0.63:0.37; C91, 0.49:0.52). Compound **9** crystallized with two independent molecules; all neopentyl groups of one molecule were disordered and refined on split positions. Further details of the crystal structure determinations are available from the Cambridge Crystallographic Data Center on quoting the depository numbers CCDC-977811 (**3**), −-977810 (**4**), -977809 (**5**), -977813 (**8**), and -977812 (**9**).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

CIF files giving the crystal data for compounds **3**−**5**, **8**, and **9** and figures giving the NMR spectra of compounds **5**−**7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) *Frustrated Lewis Pairs*; Erker, G., Stephan, D. W., Eds.; Springer: Heidelberg, Germany, 2013; Vols. *I* and *II*.

(2) Appelt, C.; Westenberg, H.; Bertini, F.; Ehlers, A. W.; Slootweg, J. C.; Lammertsma, K.; Uhl, W. *Angew. Chem.* **2011**, *123*, 4011−4014; *Angew. Chem., Int. Ed.* **2011**, *50*, 3925−3928.

(3) (a) Ménard, G.; Stephan, D. W. *J. Am. Chem. Soc.* **2010**, *132*, 1796−1797. (b) Ménard, G.; Stephan, D. W. *Angew. Chem.* **2011**, *123*, 8546−8549; *Angew. Chem., Int. Ed.* **2010**, *50*, 8396−8399.

(4) (a) Roters, S.; Appelt, C.; Westenberg, H.; Hepp, A.; Slootweg, J. C.; Lammertsma, K.; Uhl, W. *Dalton Trans.* **2012**, *41*, 9033−9045. See also: (b) Boudreau, J.; Courtemanche, M. A.; Fontaine, F. G. *Chem. Commun.* **2011**, 11131−11133.

(5) (a) Dureen, M. A.; Stephan, D. W. *J. Am. Chem. Soc.* **2009**, *131*, 8396−8397. (b) Dureen, M. A.; Brown, C. C.; Stephan, D. W. *Organometallics* **2010**, *29*, 6594−6607.

(6) Ménard, G.; Stephan, D. W. *Angew. Chem.* **2012**, *124*, 4485−4488; *Angew. Chem., Int. Ed.* **2012**, *51*, 4409−4412.

(7) Ménard, G.; Stephan, D. W. *Angew. Chem.* **2012**, *124*, 8397−8400; *Angew. Chem., Int. Ed.* **2012**, *51*, 8272−8275.

(8) Uhl, W.; Appelt, C. *Organometallics* **2013**, *32*, 5008−5014.

(9) Appelt, C.; Slootweg, J. C.; Lammertsma, K.; Uhl, W. *Angew. Chem.* **2012**, *124*, 6013−6016; *Angew. Chem., Int. Ed.* **2012**, *51*, 5911−5914.

(10) Appelt, C.; Slootweg, J. C.; Lammertsma, K.; Uhl, W. *Angew. Chem.* **2013**, *125*, 4350−4353; *Angew. Chem., Int. Ed.* **2013**, *52*, 4256−4259.

(11) Rosorius, C.; Daniliuc, C. G.; Fröhlich, R.; Kehr, G.; Erker, G. *J. Organomet. Chem.* **2013**, *744*, 149−155.

(12) (a) Sangokoya, S. A.; Pennington, W. T.; Robinson, G. H.; Hrncir, D. C. *J. Organomet. Chem.* **1990**, *385*, 23−31. (b) Wierda, D. A.; Barron, A. R. *Polyhedron* **1989**, *8*, 831−834. (c) McMahon, C. N.; Barron, A. R. *J. Cryst. Chem.* **1997**, *27*, 195−197. (d) Kuczkowski, A.; Schulz, S.; Nieger, M.; Schreiner, P. R. *Organometallics* **2002**, *21*, 1408−1419. (e) Karsch, H. H.; Appelt, A.; Köhler, F. H.; Müller, G. *Organometallics* **1985**, *4*, 231−238. (f) Karsch, H. H.; Zellner, K.; Lachmann, J.; Müller, G. *J. Organomet. Chem.* **1991**, *409*, 109−118.

(13) Uhl, W.; Appelt, C.; Backs, J.; Klöcker, H.; Vinogradov, A.; Westenberg, H. *Z. Anorg. Allg. Chem.* **2014**, *640*, 106−109.

(14) (a) Roters, S.; Hepp, A.; Slootweg, J. C.; Lammertsma, K.; Uhl, W. *Chem. Commun.* **2012**, *48*, 9616−9618. (b) Westenberg, H.; Slootweg, J. C.; Hepp, A.; Kösters, J.; Roters, S.; Ehlers, A. W.; Lammertsma, K.; Uhl, W. *Organometallics* **2010**, *29*, 1323−1330.

(15) Miller, A. D.; Johnson, S. A.; Tupper, K. A.; McBee, J. L.; Don Tilley, T. *Organometallics* **2009**, *28*, 1252−1262.

(16) Downs, A. J.; Greene, T. M.; Collin, S. E.; Whitehurst, L. A. *Organometallics* **2000**, *19*, 527−538.

(17) Uhl, W.; Cuypers, L.; Graupner, R.; Molter, J.; Vester, A.; Neumüller, B. *Z. Anorg. Allg. Chem.* **2001**, *627*, 607−614.

(18) Beachley, O. T., Jr.; Victoriano, L. *Organometallics* **1988**, *7*, 63−67.

(19) (a) *SHELXTL-Plus, REL. 4.1*; Siemens Analytical X-Ray Instruments Inc., Madison, WI, 1990. (b) Sheldrick, G. M. *SHELXL-97, Program for the Refinement of Structures*; Universität Göttingen, Göttingen, Germany, 1997.