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# **Frustrated Lewis Pairs**

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# Paper

Fixation of carbon dioxide and related small molecules by a bifunctional frustrated pyrazolylborane Lewis pair

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# PAPER

# Dimeric aluminum-phosphorus compounds as masked frustrated Lewis pairs for small molecule activation<sup>†</sup>

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Hydroalumination of aryldialkynylphosphines  $RP(C \equiv C^{-t}Bu)_2$  (R = Ph, Mes) with equimolar quantities of diethylaluminum hydride afforded mixed alkenyl–alkynyl cyclic dimers in which the dative aluminum–phosphorus bonds are geminal to the exocyclic alkenyl groups. Addition of triethylaluminum to isolated **1** (R = Ph) or to the *in situ* generated species (R = Mes) caused diethylaluminum ethynide elimination to yield the arylethylphosphorus dimers **2** and **3**. These possess a chair-like  $Al_2C_2P_2$ heterocycle with intermolecular Al–P interactions. The boat conformation (**4**) was obtained by the reaction of  ${}^{t}Bu-P(C \equiv C^{-t}Bu)_2$  with di(*tert*-butyl)aluminum hydride. Despite being dimeric, **2** behaves as a frustrated Lewis pair and activates small molecules. The reaction with carbon dioxide gave *cis/trans* isomeric AlPC<sub>2</sub>O heterocycles that differ only by the configuration of the exocyclic alkenyl unit. Four isomers resulted from the reaction with phenyl isocyanate. This is caused by *cis/trans* isomerization of the initial C=O adduct and subsequent rearrangement to the AlPC<sub>2</sub>N heterocycle, being the C=N adduct.

## Introduction

Frustrated Lewis pairs (FLPs)<sup>1-7</sup> are of enormous interest because of their dipolar activation of small molecules such as dihydrogen, carbon dioxide, and nitrogen oxide. Applications are also directed toward their catalytic activity in hydrogen transfer reactions and the activation of organic substrates. The unprecedented reactivity of FLPs is based on the presence of Lewis acidic and basic centers that interact simultaneously with the substrate. Typically, boron-based Lewis acids, activated by fluorinated aryl groups, are used together with bulky phosphines, being the Lewis base. Other basic centers such as nitrogen or carbene carbon atoms have been applied to a much smaller extent.<sup>3</sup> Metal atoms are also becoming popular as Lewis acidic sites.<sup>7–10</sup> They allow efficient tuning of the FLP's reactivity and limit the need for fluorinated substituents because of the metal's inherently high acidity. In a recent study we reported on the synthesis of an Al-P-based FLP that was generated by hydroaluminating<sup>11</sup> an alkynylphosphine with di(*tert*-butyl)aluminum hydride.<sup>9</sup> This sterically protected FLP proved to be very effective for the reversible dipolar coordination of carbon dioxide and for the activation of the C-H and C=C bonds of terminal alkynes (A to C; Scheme 1).9 Herein we report that with smaller

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substituents FLP dimers result by intermolecular P–Al Lewis pair formation, but they remain capable of activating carbon dioxide and phenyl isocyanate.

## **Results and discussion**

#### Formation of dimeric Al-P Lewis pairs

The starting point of this study are the diethynylarylphosphines (aryl = phenyl, mesityl). Recently, we found their hydroalumination with sterically encumbered  $HAIR_2$  (R = *tert*-butyl or neopentyl) to cause elimination of dialkylaluminum ethynides with concomitant formation of five-membered AlC<sub>2</sub>P<sub>2</sub> heterocycles,<sup>10</sup> which contrasts with the reactions with mono-alkynylphosphines<sup>9</sup> and silicon- and germanium-centered diethynes.<sup>12</sup> We now examine the hydroalumination with a sterically non-congested reagent. Surprisingly, reaction of phenyldi(tert-butylethynyl)phosphine with diethylaluminum hydride at ambient temperature results in the six-membered  $Al_2C_2P_2$  heterocycle 1, which is the dimer of the mixed alkenyl-alkynyl product that is expected from hydroaluminating one C≡C bond, eqn (1). The complex <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of **1** showed four major resonances with different intensities at  $\delta = -8, -28, -34$  and -48. <sup>1</sup>H and <sup>13</sup>C NMR spectra were very complicated with a multitude of partially overlapping resonances and do not allow an unambiguous assignment. The shape of the spectra changed only little at lower temperature and did not depend on concentration or the solvent toluene or benzene. Decomposition occurred at elevated temperatures. We reasoned that the complex spectrum might be due to a change of ring size and conformation, exchange between axial and equatorial groups, partial monomerization,

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and/or the cis- or trans-arrangement of the terminal alkynyl groups. To confirm the purity of the product we added some THF to form the monomeric adduct in which the THF molecules should be coordinated to the aluminum centers, Et<sub>2</sub>Al(THF)-C (=CH-<sup>t</sup>Bu)-P(Ph)-C=C-<sup>t</sup>Bu. Indeed, the spectra simplified with a single <sup>31</sup>P{<sup>1</sup>H} NMR singlet at  $\delta = -44.2$  and <sup>13</sup>C NMR resonances at  $\delta = 79.4$  and 115.4 for the ethynyl carbons and  $\delta =$ 145.1 and 167.4 for those of the ethenyl group. The  ${}^{3}J_{\rm PH}$  coupling constant of 47.2 Hz between the phosphorus and vinylic hydrogen atoms verifies their trans arrangement and thereby the cis-addition of Et<sub>2</sub>Al-H to the alkynyl group.<sup>13</sup> Whereas these observations suggest the formation of a pure product, the spectra obtained in non-coordinating solvents are indicative of the presence of equilibria. We were fortunate that crystalline material was generated from solution that was suitable for a crystal structure determination. The molecular structure (Fig. 1) confirmed the dimeric nature and revealed a chair conformation for the  $Al_2C_2P_2$  heterocycle of 1, having tetracoordinate aluminum and phosphorus atoms and a trans arrangement of the phosphorus and vinylic hydrogens, in accord with the NMR data. The Al-P [250.04(9) pm]<sup>14</sup> and Al–C distances [203.1(2) pm] in the rings are in the normal range and so are the exocyclic C=C [133.9(3) pm] and equatorial C $\equiv$ C bonds [119.2(4) pm];<sup>15</sup> the P–C $\equiv$ C–C group approaches linearity [angles P-C=C 172.2(2)° and C  $\equiv$  C - C 178.5(3)°]. The molecular structure of 1 resembles the Al<sub>2</sub>C<sub>2</sub>P<sub>2</sub> heterocycles reported in the literature.<sup>14</sup>

In solution, 1 decomposed slowly (>one week), presumably by activation of the C $\equiv$ C bonds and formation of heterocycles similar to those described for sterically shielded dialkylaluminum hydrides.<sup>10</sup> To prevent this occurring, we replaced the

alkynyl groups with a less reactive substituent by treating 1 with a slight excess of AlEt<sub>3</sub> in toluene for eleven days, eqn (1). The resulting product 2 was isolated as colorless crystals in 68% yield after concentration and cooling of the reaction mixture to -30 °C. Shorter reaction times could not be achieved by heating of the solutions because 1 decomposes at elevated temperature. The expected byproduct Et<sub>2</sub>Al–C=C-<sup>*t*</sup>Bu, which probably forms dimers,<sup>16</sup> was characterized in solution. In contrast to the ethynyl compound 1, solutions of 2 in benzene or toluene showed simple NMR spectra with the expected resonances at room temperature. A singlet at  $\delta = -14.5$  was observed in the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum. The vinylic hydrogen atoms gave a doublet with the coupling constant <sup>3</sup>J<sub>PH</sub> = 48.0 Hz which is



Fig. 1 Molecular structure of 1. The thermal ellipsoids are drawn at the 40% probability level. Hydrogen atoms are omitted. Important bond lengths (pm) and angles (deg): P(1)–C(2) 176.6(3), C(2)–C(21) 119.2 (4), P(1)–C(3) 180.2(2), C(3)–C(31) 133.9(3), Al(1)–C(3)' 203.1(2), Al (1)–P(1) 250.04(9), P(1)–Al(1)–C(3)' 101.55(7), Al(1)'–C(3)–P(1) 114.8 (1), Al(1)–P(1)–C(3) 114.73(8), P(1)–C(2)–C(21) 172.2(2), C(2)–C (21)–C(22) 178.5(3); Al(1)' and C(3)' generated by -x + 1, -y + 2, -z.



Fig. 2 Molecular structure of 2. The thermal ellipsoids are drawn at the 40% probability level. Hydrogen atoms omitted. Important bond lengths (pm) and angles (deg): P(1)–C(2) 181.7(2), C(2)–C(21) 134.9 (2), Al(1)–C(2) 203.7(2), Al(1)'–P(1) 252.30(5), P(1)'–Al(1)–C(2) 92.55 (4), Al(1)–C(2)–P(1) 118.57(8), Al(1)'–P(1)–C(2) 114.29(5); Al(1)' and P(1)' generated by -x + 1, -y, -z.

characteristic of a *trans*-arrangement of P and H across the C=C double bond. Two different sets of signals resulted for the ethyl groups and two resonances for the vinylic carbon atoms [ $\delta$  = 133.6 and 166.3]. No significant change of the spectra was detected on cooling of a solution of **1** in toluene to 200 K. The data for the THF adduct are given for comparison in the Experimental section. The molecular structure obtained by a crystal structure determination confirmed that **2**, like **1**, had a chair conformation for the Al<sub>2</sub>C<sub>2</sub>P<sub>2</sub> heterocycle (Fig. 2).



Hydroalumination with the more shielded mesityl (instead of phenyl) substituted diethynylphosphine Mes–P(C $\equiv$ C–<sup>*t*</sup>Bu)<sub>2</sub> behaved differently. The reaction with H-AlEt<sub>2</sub> gave a similar complex product mixture as that on stirring 1 for over a week; Et<sub>2</sub>Al-C=C-<sup>t</sup>Bu was identified by NMR as one of the products.<sup>16</sup> Evidently, the initial product decomposes faster than forming a stabilizing dimer akin to 1. To circumvent this, we used an excess of the hydride to accelerate the formation of the addition product and added an equimolar quantity of AlEt<sub>3</sub> after only 10 min to replace the alkynyl for an ethyl substituent, eqn (1). After 18 h colorless crystals of **3** were isolated in 34% yield;  $Et_2Al-C \equiv C-^{t}Bu$  was detected as byproduct. The NMR data of 3 are similar to those of 2 (see experimental part). The molecular structure of 3 is also analogous to that of 2, showing a chair conformation for the  $Al_2C_2P_2$  ring (Fig. 3), while the rather long Al–C bond [204.8(2) pm] may indicate strain in the heterocycle.

Hydroalumination of the *tert*-butyl derivative <sup>*t*</sup>Bu–P ( $C \equiv C$ -<sup>*t*</sup>Bu)<sub>2</sub> with the more bulky H–Al<sup>*t*</sup>Bu<sub>2</sub> reagent (instead of H–AlEt<sub>2</sub>) in n-hexane gave full conversion of the phosphine only in a 1 : 2 ratio of the starting compounds, eqn (2). Colorless crystals of **4** precipitated in 62% yield after concentration and

cooling of the reaction mixture. Because **4** is only sparingly soluble in non-coordinating solvents, the NMR spectra were recorded in THF-d<sub>8</sub>, which should give monomeric units with THF molecules coordinated to the aluminum atoms. Only one resonance was observed in the <sup>31</sup>P{<sup>1</sup>H} ( $\delta = -22.7$ ) and <sup>1</sup>H NMR spectra ( $\delta = 4.04$ , <sup>1</sup>J<sub>PH</sub> = 208.3 Hz) for the P–H group and three <sup>1</sup>H NMR resonances (2 : 1 : 1 ratio) for the four *tert*-butyl groups. The molecular structure of solvent-free **4** in the solid state (Fig. 4) confirmed its dimeric nature and showed bonding characteristics similar to **2** and **3**, but in contrast the molecule is not centrosymmetric and has instead a boat conformation for the Al<sub>2</sub>C<sub>2</sub>P<sub>2</sub> heterocycle. The most remarkable feature is the arrangement of the two P–H groups, one adopting an *endo-* and the



Fig. 3 Molecular structure of 3. The thermal ellipsoids are drawn at the 40% probability level. Hydrogen atoms are omitted. Important bond lengths (pm) and angles (deg): P(1)–C(2) 181.5(2), C(2)–C(21) 135.1 (3), Al(1)'–C(2) 204.8(2), Al(1)–P(1) 255.05(7), P(1)–Al(1)–C(2)' 92.42 (6), Al(1)'–C(2)–P(1) 121.6(1), Al(1)–P(1)–C(2) 101.83(6); Al(1)' and C(2)' generated by -x + 1, -y, -z + 1.



**Fig. 4** Molecular structure of **4**. The thermal ellipsoids are drawn at the 40% probability level. Hydrogen atoms with the exception of P–H are omitted. Important bond lengths (pm) and angles (deg): P(1)–C(71) 185.6(3), C(71)–C(72) 134.9(3), Al(1)–C(81) 203.1(3), Al(1)–P(1) 255.9(2), P(2)–C(81) 179.0(2), C(81)–C(82) 134.2(3), Al(2)–C(71) 203.2(3), Al(2)–P(2) 257.7(1), P(1)–Al(1)–C(81) 103.21(8), Al(1)–C (81)–P(2) 112.7(2), Al(1)–P(1)–C(71) 113.4(1), P(2)–Al(2)–C(71) 94.8 (1), Al(2)–C(71)–P(1) 129.3(1), Al(2)–P(2)–C(81) 113.33(9).

other an *exo*-position, causing the phosphorus atoms to be chemically different and making the eight *tert*-butyl groups diastereotopic.

<sup>t</sup>Bu

+ H-Al<sup>t</sup>Bu<sub>2</sub>

- Al ethynide

x2

`⁺Bu

<sup>t</sup>Bu

+ H-Al<sup>t</sup>Bu<sub>2</sub>

<sup>t</sup>Bu

<sup>t</sup>Bu

<sup>t</sup>Bu

'Bu

<sup>t</sup>Bu

<sup>t</sup>Bu

-<sup>t</sup>Bu

<sup>t</sup>Bu

<sup>t</sup>Bu H

 $^{t}Bu$ 

(2)

<sup>i</sup>Bu

x2

<sup>t</sup>Bu

H-Al<sup>t</sup>Bu<sub>2</sub>

## The mechanism for the formation of 4 may be similar to that elucidated for the reported H-Al<sup>t</sup>Bu<sub>2</sub> hydroalumination of aryl substituted diethynylphosphines $Ar-P(C = C - Bu)_2$ (Ar = Ph, Mes), which rendered five-membered Al<sub>2</sub>C<sub>2</sub>P heterocycles.<sup>10</sup> Thus, following hydroalumination of one C = C bond of the starting material with H-Al<sup>t</sup>Bu<sub>2</sub>, the coordinatively unsaturated aluminum atom of the resulting intermediate may interact with the $\alpha$ -carbon of the remaining C=C bond to form a phosphaallene,<sup>17</sup> ${}^{t}Bu-P = C = C(H) - {}^{t}Bu$ , by eliminating $\int Bu_2 Al C \equiv C - Bu_{2}$ , eqn (2). But instead of undergoing a cycloaddition with the intermediate to give a five-membered heterocycle, the transient phosphaallene undergoes hydroalumination with H-Al<sup>t</sup>Bu<sub>2</sub> to form the Al–P-based FLP that subsequently dimerizes to 4. DFT calculations on phosphaallenes revealed a partial negative charge for the $\alpha$ -carbon atom and a small positive charge for the phosphorus atom,<sup>18</sup> in accord with the regioselectivity of the observed hydroalumination. Evidently, the phosphorus substituent of the starting alkyne determines the course of events with the phenyl and mesityl derivatives giving the five-membered $AlP_2C_2$ and with *tert*-butyl derivative an $Al_2C_2P_2$ heterocycle.

 $1/2 \left[ {}^{t}Bu - Al^{t}Bu_{2} \right]_{2}$ 

# Reaction of dimeric Al-P-based Lewis pair 2 with carbon dioxide

To explore the six-membered  $Al_2C_2P_2$  structures as potential FLPs, we concentrated on the reactivity of 2 toward  $CO_2$ , because 1 is less stable and 4 is difficult to solubilize. As noted, complexation of CO<sub>2</sub> by Al–P-based FLPs are rare.<sup>6,9</sup> Earlier we showed that the monomeric FLP Mes<sub>2</sub>P-C[=C(H)-Ph]-Al<sup>t</sup>Bu<sub>2</sub> complexes CO<sub>2</sub> reversibly. A reduced reactivity might be expected for dimeric 2. While we were conducting the present study, Fontaine and coworkers<sup>7</sup> reported the surprising observation that the dimers  $(R_2PCH_2AlMe_2)_2$  (R = Me, Ph) react readily with  $CO_2$  to monomeric adducts (**D**) that rearrange above -35 °C to yield dimeric aluminum carboxylates (E, Scheme 2). This stimulating finding suggests that also 2 might act as a masked FLP. Indeed, treating a suspension of 2 in n-hexane with CO<sub>2</sub> resulted within seconds in a clear solution of a single adduct (cis-5) that rearranged to trans-5 within 22 h, eqn (3); cis and trans refer to the olefinic positions of the Al and H atoms. *Cis*-5 could not be isolated due to its limited thermal stability, but was characterized by NMR spectroscopy. Trans-5 was isolated in 43% yield by concentrating the reaction mixture under a  $CO_2$  flow with subsequent cooling to -20 °C. After recrystallization, trans-5 could be handled at room temperature in different solvents and in high vacuum without decomposition or rearrangement. The NMR spectra of cis- and trans-5 are similar, respectively showing  ${}^{31}P{}^{1}H$  NMR singlets at  $\delta = -4.6$  and 2.3, characteristic <sup>13</sup>C NMR doublets for the carbonyl carbons at  $\delta = 168.0$  and 165.3,<sup>5,7,9</sup> large  $J_{PC}$  couplings of 120.0 and 109.4 Hz for these carbon atoms that indicate P-C bonding, and two sets of <sup>1</sup>H NMR resonances for the diastereotopic ethyl groups for each isomer. Most distinguishing is the  ${}^{3}J_{\rm PH}$  coupling between the phosphorus and vinylic hydrogen atoms with the larger value of 69.9 Hz assigned to cis-5 and the smaller of 38.3 Hz to trans-5. Cis-5 is the expected kinetic product that subsequently isomerizes. The mechanism for the cis/trans isomerization in hydroalumination and hydrogallation has been discussed recently.<sup>11,13</sup> The molecular structure obtained from an X-ray structure determination confirmed trans-5 (Fig. 5) to be a  $CO_2$  adduct of a monomeric fragment of 2. The P(1)–C(14) bond of 187.4(1) pm between the phosphorus and carbonyl



Scheme 2



O(11)-C(14)-O(12) 127.9(1).

011 012 Fig. 5 Molecular structure of trans-5. The thermal ellipsoids are drawn at the 40% probability level. Hydrogen atoms are omitted. Important bond lengths (pm) and angles (deg): P(1)-C(12) 176.9(1), C(12)-C (121) 134.5(2), P(1)-C(14) 187.4(1), C(14)-O(11) 128.6(2), C(14)-O (12) 121.0(2), Al(1)-C(12) 204.2(1), Al(1)-O(11) 186.9(1), Al(1)-C (12)-P(1) 106.49(6), C(12)-Al(1)-O(11) 92.61(5), Al(1)-O(11)-C(14) 123.26(8), O(11)-C(14)-P(1) 112.17(9), C(12)-P(1)-C(14) 102.45(6),

C14

C12

carbon atoms is relatively long as is the Al(1)-O(11) bond of  $186.9(1) \text{ pm.}^{19}$  The C–O bond lengths of 121.0(2) (C=O) and 128.6(2) pm indicate  $\pi$ -delocalization, whereas the exocyclic C=C bond of 134.5(2) pm is nearly the same as that in 2.





Heating trans-5 in solution at 80 °C for 38 h or at 67 °C as a solid resulted in decomposition to unknown products without evidence for aluminum carboxylates. Clearly, trans-5 has a considerably increased stability as compared to **D** (Scheme 2).



#### Reaction of dimeric Al-P-based Lewis-pair 2 with phenyl isocyanate

Encouraged by the formation of a stable monomeric CO<sub>2</sub> adduct we then decided to explore whether the masked FLP 2 would react likewise with the C=O or C=N bond of phenyl isocyanate. First, we treated a suspension of 2 in n-hexane with one equivalent of the isocyanate at room temperature. Concentrating and cooling of the instantly formed clear solution to -20 °C afforded adduct cis-6 in 60% yield as colorless needles, eqn (4), of which, unfortunately, none was suited for a crystal structure determination, but the NMR data unambiguously revealed the addition of the isocyanate's C=O bond to a monomeric unit of **2.** Characteristic are the two sets of <sup>1</sup>H NMR resonances for the diastereotopic ethyl groups attached to aluminum, the doublet at  $\delta = 7.38$  for the vinylic hydrogen, the <sup>3</sup>J<sub>PH</sub> coupling of 67.8 Hz supporting a *trans* alkenyl arrangement of the P and H atoms (as in **2**), and the <sup>1</sup>J<sub>PC</sub> coupling of 147.3 Hz for the doublet of the former carbonyl carbon ( $\delta = 159.4$ ) that indicates bonding to the phosphorus atom.

*Cis*-**6** has limited stability and rearranges even at room temperature slowly to a mixture of isomers, eqn (4). Heating a toluene solution for 17 h at 85 °C gave a 68:28:3 ratio of *trans*-**6**, *cis*-**7**, and *trans*-**7** and on prolonged heating (7 days at 95 °C) a 37:63 ratio of *trans*-**6** and *trans*-**7** from which only crystals of the *trans*-isomer of **7** could be isolated in 53% yield. *Trans*-**6**, identified in an isomeric mixture, results on C=C bond isomerization of *cis*-**6** and has expectedly nearly identical NMR characteristics, except for the smaller  ${}^{3}J_{PH}$  coupling constant (37.5 Hz) for the vinylic hydrogen atom ( $\delta({}^{1}H) = 6.96$ ).

Most interesting are the isomerizations to *cis*- and *trans*-7 in which the C=N, instead of the C=O bond of the isocyanate, is connected to the dipolar monomeric FLP unit of **2**. *Cis*-7 is the first rearrangement product of *cis*-**6**, as monitored by NMR spectroscopy, in competition with the formation of *trans*-**6**. Whereas *cis/trans* isomerization of the C=C bond is well documented for aluminum or gallium derivatives,<sup>13</sup> this is not the case for the intramolecular rearrangement of the isocyanate group (**6**  $\rightarrow$  7), which is currently topic of further investigation.<sup>4</sup>*e* 

The structural assignments of both isomers of 7 are supported by the NMR spectroscopic data, which differ only slightly from those of 6. The <sup>1</sup>H NMR spectrum showed a  ${}^{3}J_{PH}$  coupling constant of 42.0 Hz for the vinylic hydrogen ( $\delta = 6.96$ ) of trans-7, indicating a trans arrangement with the dialkylaluminum group;  ${}^{3}J_{\rm PH}$  is 69.0 Hz for the vinylic H of *cis*-7 ( $\delta$  = 7.37). The prominent differences between 6 and 7 are the <sup>13</sup>C NMR chemical shifts of the imine versus carbonyl carbon and the  ${}^{1}J_{PC}$  couplings that are respectively  $\delta = 159.4/156.1$  and 147.3/137.5 Hz for *cis/trans*-6 and  $\delta = 167.7/165.7$  and 125.3/114.1 Hz for *cis/* trans-7. As expected, also the <sup>13</sup>C NMR chemical shifts and  ${}^{3}J_{PC}$  couplings differ correspondingly for the *ipso*-carbon of the phenyl group attached to the nitrogen with respective values of  $\delta$ = 147.8/147.4 and 22.9/21.5 Hz for *cis/trans*-6 and  $\delta$  = 144.4/ 144.2 and 12.3/14.1 Hz for *cis/trans*-7 with the  ${}^{3}J_{PC}$  coupling constants being most indicative for the respective structure. The usual mixtures of *cis*-6 and *cis*-7 could not be separated by recrystallization. Only once, upon cooling a solution in nhexane, could solid material be obtained that contained the needles characteristic of cis-6 beside colorless blocks of pure cis-7, allowing its characterization. The crystal structure determinations confirmed the molecular structures of the AIPC<sub>2</sub>N heterocycles cis-7 (Fig. 6) and trans-7 (Fig. 7), corroborating an exocyclic keto group and Al-N [192.8(1) and 196.5(2) pm] and P-C(O) bonds [176.4(1) and 177.3(2) pm] between the isocyanate and the FLP unit; the longer Al-N bond for trans-7 may be due to steric interaction between the substituents. The average ring C-N and exocyclic C=O bond lengths of 133.5 and 123.1 pm, respectively, for the two isomers indicate some  $\pi$ -delocalization.<sup>15</sup>

Because we were unable to obtain crystals for *cis*-**6** and *trans*-**6** to ascertain their molecular structure unequivocally, we decided to use an independent route to eliminate any ambiguity.

![](_page_6_Figure_6.jpeg)

**Fig. 6** Molecular structure of *cis*-7. The thermal ellipsoids are drawn at the 40% probability level. Hydrogen atoms are omitted. Important bond lengths (pm) and angles (deg): P(1)–C(12) 176.4(1), C(12)–C(121) 134.4(2), P(1)–C(14) 187.1(1), C(14)–O(1) 123.0(1), C(14)–N(1) 133.4 (2), Al(1)–C(12) 202.6(1), Al(1)–N(1) 192.8(1), Al(1)–C(12)–P(1) 107.97(6), C(12)–Al(1)–N(1) 92.71(4), Al(1)–N(1)–C(14) 121.10(8), N (1)–C(14)–P(1) 113.10(8), C(12)–P(1)–C(14) 103.96(5), N(1)–C(14)–O (1) 130.2(1), C(14)–N(1)–C(17) 117.39(9).

For this purpose we chose to react phenyl isocyanate with the heavily congested, monomeric FLP Mes<sub>2</sub>P–C[==C(H)–Ph]–Al'Bu<sub>2</sub>, having *trans* alkenyl H and Al substituents, to obtain *trans*-**8** in 99% yield, eqn (5); no rearrangement was observed. A crystal structure determination (Fig. 8) indeed revealed an AlPC<sub>2</sub>O heterocycle with an exocyclic imine bond [127.4(3) pm], a single C–O bond [131.2(3) pm] and an Al–O bond [185.7(2) pm] like those found for CO<sub>2</sub> adduct *trans*-**5**. The NMR characteristics of *trans*-**8** resemble those of *trans*-**6**, particularly the <sup>3</sup>J<sub>PH</sub> of 38.4 Hz for the vinylic hydrogen ( $\delta =$  7.77 ppm) and the <sup>3</sup>J<sub>PC</sub> of 23.8 Hz for the *ipso*-carbon ( $\delta =$  147.5) of the phenyl group attached to nitrogen, albeit that the vinyl hydrogen is more deshielded. With these results we feel that the structural motifs of *cis*-**6** and *trans*-**6** have been confirmed.

![](_page_6_Figure_9.jpeg)

In conclusion, we have shown that the dimeric aluminumphosphorus compound 2 acts as a masked frustrated Lewis pair.

![](_page_7_Figure_1.jpeg)

**Fig.** 7 Molecular structure of *trans*-7. The thermal ellipsoids are drawn at the 40% probability level. Hydrogen atoms are omitted. Important bond lengths (pm) and angles (deg): P(1)–C(12) 177.3(2), C(12)–C (121) 135.0(3), P(1)–C(14) 185.3(2), C(14)–O(2) 123.3(2), C(14)–N(1) 133.6(2), Al(2)–C(12) 202.8(2), Al(2)–N(1) 196.5(2), Al(2)–C(12)–P(1) 107.25(9), C(12)–Al(2)–N(1) 91.80(7), Al(2)–N(1)–C(14) 122.3(1), N (1)–C(14)–P(1) 110.5(1), C(12)–P(1)–C(14) 105.58(8), N(1)–C(14)–O (2) 130.8(2), C(14)–N(1)–C(17) 118.6(1).

It effectively captures  $CO_2$  and isocyanate just like its stable monomeric counterparts that have coordinatively unsaturated aluminum and phosphorus atoms. Because these dimeric Al–P compounds are readily accessible and require less bulky substituents, masked FLPs may lead to broad applicability in activating small molecules.

Isomeric CO<sub>2</sub> and phenyl isocyanate adducts were formed by cis/trans isomerization of the exocyclic olefinic group with the cis Al-H-vinyl form as the kinetically controlled product. The cis-forms originate directly from the starting compounds 1 to 4 and are in accordance with the concerted hydroalumination mechanism.<sup>20</sup> Formation of dimeric formula units and coordinative saturation of the aluminum atoms in 1 to 4 may hinder *cis*/ *trans* isomerisation in these cases.<sup>9,13</sup> The reaction with phenyl isocyanate gives two additional isomers, and all four possible isomers have been assigned unambiguously by NMR spectroscopy in a complicated equilibrium which is not fully understood yet and may include the reversible formation and consumption of intermediates. The first occurrence of the products in the NMR spectra in dependency of reaction time follows the order cis-6, cis-7, trans-6 and trans-7, however, this sequence must not really be representative of the thermodynamically controlled reaction pathway. The initial cis AlPC2O heterocycle (*cis*-6) was isolated in a pure form and results from C=0

![](_page_7_Figure_5.jpeg)

Fig. 8 Molecular structure of 8. The thermal ellipsoids are drawn at the 40% probability level. Hydrogen atoms are omitted. Important bond lengths (pm) and angles (deg): P(1)-C(1) 179.6(2), C(1)-C(2) 134.1(3), P(1)-C(6) 184.2(2), C(6)-O(1) 131.2(3), C(6)-N(1) 127.4(3), Al(1)-C(1) 206.8(2), Al(1)-O(1) 185.7(2), Al(1)-C(1)-P(1) 105.2(1), C(1)-Al (1)-O(1) 91.13(8), Al(1)-O(1)-C(6) 121.7(1), O(1)-C(6)-P(1) 111.9(2), C(1)-P(1)-C(6) 98.7(1), N(1)-C(6)-O(1) 131.5(2), C(6)-N(1)-C(71) 121.8(2).

addition to the monomeric FLP. With longer reaction time and prolonged heating it rearranges to the corresponding *trans*-isomer and to the *cis/trans* isomeric AIPC<sub>2</sub>N heterocycles (*cis/trans*-7), representing the C—N adducts. *Trans*-7 is finally (7 d, 95 °C) enriched in the reaction mixture and was isolated in a pure form after recrystallization. It may represent the most thermodynamically favoured isomer. The structural assignments of the products are in part supported by X-ray crystallographic data and the synthesis and characterization of a related adduct.

## **Experimental section**

#### General considerations

All procedures were carried out under purified argon by use of standard Schlenk methods or within an mBraun Glovebox. Cyclopentane and n-hexane were dried over LiAlH<sub>4</sub>, toluene over Na–benzophenone and 1,2-difluorobenzene over molecular sieves. Diethylaluminum hydride,<sup>21</sup> di(*tert*-butyl)aluminum hydride,<sup>22</sup> (*E*)–Mes<sub>2</sub>P–[C==C(H)–Ph]–Al'Bu<sub>2</sub> (Mes = 2,4,6-Me<sub>3</sub>H<sub>2</sub>C<sub>6</sub>),<sup>9</sup> Ph–P(C==C<sup>-</sup>Bu)<sub>2</sub>,<sup>23</sup> 'Bu–P(C==C<sup>-</sup>Bu)<sub>2</sub>,<sup>24</sup> and Mes–P(C==C<sup>-</sup>Bu)<sub>2</sub>)<sup>10</sup> were synthesized according to literature procedures. Triethylaluminum was used as purchased. Commercially available phenyl isocyanate was distilled and stored over molecular sieves (4 Å). <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H} and <sup>31</sup>P{<sup>1</sup>H} NMR spectra were recorded on Bruker Avance I and III spectrometers. The chemical shifts ( $\delta$ ) were referenced to the residual solvent signals

of  $C_6D_6$  or  $d_8$ -THF. The assignment of the NMR spectra is based on HMBC, HSQC, ROESY, and DEPT135 data. Mass spectra were recorded using a Varian MAT 212 Micromass Quattro LC-Z spectrometer. IR spectra were recorded on a Shimadzu IR Prestige 21 spectrometer. CHN analyses were detected on a Vario EL III CHNS instrument.

#### Synthesis of compound 1

Diethylaluminum hydride, Et<sub>2</sub>AlH, (0.54 g, 6.28 mmol) was added to a solution of phenyldi(tert-butylethynyl)phosphine,  $Ph-P(C \equiv C^{-t}Bu)_2$ , (1.64 g, 6.09 mmol) in n-hexane (15 mL). The mixture was stirred for 2 h at ambient temperature and the dimeric hydroalumination product 1 precipitated as a colorless solid. The suspension was filtered, and the crude product 1 was washed two times with n-hexane (10 mL) and thoroughly evacuated. The filtrate was concentrated and a second fraction of 1 crystallized upon cooling to -30 °C (1.22 g, 1.71 mmol, 56%). Compound 1 is only sparingly soluble in non-coordinating solvents, therefore its THF adduct was characterized by NMR spectroscopy. <sup>1</sup>H NMR (400 MHz,  $d_8$ -THF):  $\delta = 7.47$  (m, 2H, o- $H_{Ph}$ ), 7.23 (m, 2H, *m*- $H_{Ph}$ ), 7.11 (t,  ${}^{2}J_{HH}$  = 7.3 Hz, 1H, *p*- $H_{Ph}$ ), 6.78 (d,  ${}^{3}J_{PH} = 47.2$  Hz, 1H, P–C=C–H), 1.30 (s, 9H, P– C=CH-CMe<sub>3</sub>), 1.28 (s, 9H, P-C=C-CMe<sub>3</sub>), 0.85 (t,  ${}^{3}J_{HH} =$ 8.1 Hz, 6H, Al-CH<sub>2</sub>CH<sub>3</sub>), -0.29 (m, 4H, Al-CH<sub>2</sub>CH<sub>3</sub>); <sup>13</sup>C {<sup>1</sup>H} NMR (126 MHz, d<sub>8</sub>-THF):  $\delta$  = 167.4 (d, <sup>2</sup>J<sub>CP</sub> = 24.8 Hz, P-C=C-H), 145.1 (br., P-C=C-H), 142.4 (d,  ${}^{1}J_{CP} = 9.4$  Hz, *ipso*-C<sub>Ph</sub>), 131.1 (d,  ${}^{2}J_{CP}$  = 16.5 Hz, *m*-C<sub>Ph</sub>), 128.4 (d,  ${}^{3}J_{CP}$  = 4.3 Hz, o-C<sub>Ph</sub>), 126.9 (s, p-C<sub>Ph</sub>), 115.4 (s, P-C≡C-C), 79.4 (d,  ${}^{1}J_{CP} = 13.2$  Hz, P–C=C–C), 38.0 (d,  ${}^{3}J_{CP} = 5.7$  Hz, P–C=CH– *C*Me<sub>3</sub>), 32.6 (d,  ${}^{4}J_{CP} = 10.9$  Hz, P–C=CH–C*Me*<sub>3</sub>), 31.3 (s, P–  $C \equiv C - CMe_3$ ), 29.9 (s, P-C = C-CMe\_3), 10.0 (s, Al-CH<sub>2</sub>CH<sub>3</sub>), 1.1 (s, Al–CH<sub>2</sub>CH<sub>3</sub>); <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, d<sub>8</sub>-THF):  $\delta$  = -44.2; MS (EI, 20 eV, 333 K) m/z (%) = 569 (5) [M<sup>+</sup> - Et-2'Bu], 517 (100) [M<sup>+</sup> – Et–AlEt<sub>2</sub>–C=C–<sup>t</sup>Bu], 327 (8) [1/2 M<sup>+</sup> - Et]; IR (cm<sup>-1</sup>, paraffin, CsI plates): 2200 m, 2156 s (vC $\equiv$ C); 1978 vw, 1957 w, 1907 w, 1888 w, 1811 w, 1699 s, 1666 w, 1573 s br., 1548 s br., 1475 vs (vC=C), phenyl; 1462 vs, 1446 vs (paraffin); 1431 s, 1408 w (δCH<sub>3</sub>); 1377 s (paraffin); 1361 m, 1311 w, 1253 m br. (δCH<sub>3</sub>); 1234 w, 1199 w, 1184 w, 1157 m, 1101 m, 1070 w, 1028 s, 979 s, 952 s, 929 s, 916 s, 850 vs, 796 s, 771 s, 744 s (vCC); 719 m (paraffin); 692 m (Sphenyl); 659 w, 621 vw, 588 w, 559 vw, 524 m, 486 s, 462 m, 435 m (&CC, vAlC, vPC); Anal. Calcd for C<sub>44</sub>H<sub>68</sub>Al<sub>2</sub>P<sub>2</sub>: C, 74.1; H, 9.6. Found: C, 74.4; H, 9.6; MP (sealed capillary, argon): 94 °C (decomposition).

#### Synthesis of compound 2

Triethylaluminum, Et<sub>3</sub>Al, (1.11 g, 9.74 mmol) was added at room temperature to a solution of compound **1**, [(Ph)(<sup>*t*</sup>Bu–C=C)-P–C {==C(H)–'Bu}–AlEt<sub>2</sub>]<sub>2</sub>, (3.16 g, 4.43 mmol) in toluene (150 mL). The mixture was stirred for 11 days at room temperature. The alkynyl compound Et<sub>2</sub>Al–C=C–<sup>*t*</sup>Bu was identified as a byproduct by its characteristic NMR data (<sup>1</sup>H:  $\delta$  = 0.45 (q, AlCH<sub>2</sub>), 1.01 (s, CMe<sub>3</sub>), 1.42 (t, CH<sub>2</sub>CH<sub>3</sub>); <sup>13</sup>C:  $\delta$  = 3.5 (AlCH<sub>2</sub>), 9.7 (CH<sub>2</sub>CH<sub>3</sub>), 29.5 (CMe<sub>3</sub>), 29.8 (CMe<sub>3</sub>), 81.6 (Al–C=C), 149.5 (Al–C=C)). The solution was concentrated and

cooled to -30 °C to obtain colorless crystals of 2 (1.84 g, 3.02 mmol, 68%). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 7.66 (ddd,  ${}^{3}J_{\rm PH} = 9.6$  Hz,  ${}^{3}J_{\rm HH} = 7.5$  Hz,  ${}^{4}J_{\rm HH} = 2.1$  Hz, 2H, o-H<sub>Ph</sub>), 7.10 (d,  ${}^{3}J_{PH} = 48.0$  Hz, 1H, P–C=C–H), 7.05 (m, 2H, m-H<sub>Ph</sub>), 7.04 (m, 1H, *p*-H<sub>Ph</sub>), 2.32 (dq,  ${}^{2}J_{HH} = 14.7$  Hz,  ${}^{3}J_{HH} = 7.4$  Hz, 1H, P-CH<sub>2</sub>CH<sub>3</sub>), 2.04 (dq,  ${}^{2}J_{HH} = 14.8$  Hz,  ${}^{3}J_{HH} = 7.5$  Hz, 1H, P- $CH_2CH_3$ ), 1.64 (t,  ${}^{3}J_{HH} = 6.9$  Hz, 3H, Al- $CH_2CH_3$ ), 1.61 (t,  ${}^{3}J_{\text{HH}} = 6.9$  Hz, 3H, Al–CH<sub>2</sub>CH<sub>3</sub>), 0.89 (s, 9H, P–C=CH–  $CMe_3$ ), 0.75 (dt,  ${}^{3}J_{\rm HH}$  = 7.5 Hz,  ${}^{3}J_{\rm PH}$  = 15.8 Hz, 3H, P-CH<sub>2</sub>CH<sub>3</sub>), 0.66 (m, 2H, Al-CH<sub>2</sub>CH<sub>3</sub>), 0.62 (m, 2H, Al- $CH_2CH_3$ ; <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta = 166.3$  (dd,  ${}^{2}J_{CP} = 2.6 \text{ Hz}, {}^{3}J_{CP} = 1.2 \text{ Hz}, P-C=-C-H), 135.5 \text{ (d, } {}^{1}J_{CP} = 21.1 \text{ Hz}, P-C=-C-H)$ Hz, *ipso*-C<sub>Ph</sub>), 134.0 (t,  ${}^{2}J_{CP} = 5.5$  Hz, *o*-C<sub>Ph</sub>), 133.6 (m, P-C=C-H), 130.0 (s, p-C<sub>Ph</sub>), 128.8 (t,  ${}^{3}J_{CP} = 4.4$  Hz, m-C<sub>Ph</sub>), 38.5 (t,  ${}^{3}J_{CP} = 4.9$  Hz, P–C=CH–CMe<sub>3</sub>), 30.3 (s, P–C=CH– CMe<sub>3</sub>), 23.3 (dd,  ${}^{1}J_{CP} = 36.2$  Hz,  ${}^{4}J_{CP} = 3.0$  Hz, P–CH<sub>2</sub>CH<sub>3</sub>), 11.1 (s, Al-CH<sub>2</sub>CH<sub>3</sub>), 10.5 (s, Al-CH<sub>2</sub>CH<sub>3</sub>), 8.9 (s, P-CH<sub>2</sub>CH<sub>3</sub>), 5.1 (br., Al–CH<sub>2</sub>CH<sub>3</sub>), 3.4 (br., Al–CH<sub>2</sub>CH<sub>3</sub>); <sup>31</sup>P {<sup>1</sup>H} NMR (162 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta = -14.5$ ; MS (EI, 20 eV, 413 K) m/z (%) = 465 (2) [M<sup>+</sup> - 2<sup>t</sup>Bu-Et], 304 (8) [1/2 M<sup>+</sup>], 275 (100)  $[1/2 \text{ M}^+ - \text{Et}]$ , 247 (54)  $[1/2 \text{ M}^+ - \text{Et}-\text{ethene}]$ ; IR (cm<sup>-1</sup>, paraffin, CsI plates): 1973 vw, 1953 w, 1901 vw, 1884 w, 1832 vw, 1813 w, 1762 w, 1658 vw, 1606 m, 1587 w, 1571 w, 1535 s (vC=C, phenyl); 1465 vs, 1454 vs (paraffin); 1436 vs, 1413 m (δCH<sub>3</sub>); 1377 vs (paraffin); 1357 vs, 1325 w, 1305 m, 1273w, 1251 m (δCH<sub>3</sub>); 1240 m, 1190 m, 1159 w, 1101 s, 1070 m, 1028 s, 1001 m, 979 m, 947 m, 921 w, 896 w, 869 m, 844 w, 802 m, 759 w, 740 m (vCC); 719 m (paraffin); 694 m (\deltaphenyl); 646 w, 623 m, 611 m, 576 w, 536 m, 491 m, 455 m, 432 w (δCC, vAlC, vPC); Anal. Calcd for C<sub>36</sub>H<sub>60</sub>Al<sub>2</sub>P<sub>2</sub>: C, 71.0; H, 9.9. Found: C, 71.0; H, 9.8; MP (sealed capillary, argon): 165 °C.

#### Characterization of the THF-adduct of 2

Compound **2** (10 mg) was dissolved in d<sub>8</sub>-THF (1.5 mL). <sup>1</sup>H NMR (500 MHz, d<sub>8</sub>-THF):  $\delta = 7.31$  (m, 2H, *o*-H<sub>Ph</sub>), 7.19 (dd, <sup>2</sup>J<sub>HH</sub> = 7.3 Hz, <sup>2</sup>J<sub>HH</sub> = 6.5 Hz, 2H, *m*-H<sub>Ph</sub>), 7.08 (t, <sup>2</sup>J<sub>HH</sub> = 7.3 Hz, 1H, *p*-H<sub>Ph</sub>), 6.86 (d, <sup>3</sup>J<sub>PH</sub> = 47.2 Hz, 1H, P–C=C–H), 1.95 (m, 1H, P–CH<sub>2</sub>CH<sub>3</sub>), 1.72 (m, 1H, P–CH<sub>2</sub>CH<sub>3</sub>), 1.31 (s, 9H, P–C=CH–CMe<sub>3</sub>), 1.13 (m, 3H, P–CH<sub>2</sub>CH<sub>3</sub>), 0.86 (t, <sup>3</sup>J<sub>HH</sub> = 8.2 Hz, 6H, Al–CH<sub>2</sub>CH<sub>3</sub>), -0.33 (m, 4H, Al–CH<sub>2</sub>CH<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, d<sub>8</sub>-THF):  $\delta = 168.5$  (d, <sup>2</sup>J<sub>CP</sub> = 20.8 Hz, P–C=C-H), 150.2 (br., P–C=C–H), 145.8 (d, <sup>1</sup>J<sub>CP</sub> = 18.2 Hz, *ipso*-C<sub>Ph</sub>), 131.3 (d, <sup>2</sup>J<sub>CP</sub> = 14.2 Hz, *m*-C<sub>Ph</sub>), 128.4 (d, <sup>3</sup>J<sub>CP</sub> = 3.8 Hz, *o*-C<sub>Ph</sub>), 126.6 (s, *p*-C<sub>Ph</sub>), 37.8 (d, <sup>3</sup>J<sub>CP</sub> = 4.9 Hz, P–C=CH–CMe<sub>3</sub>), 32.9 (d, <sup>4</sup>J<sub>CP</sub> = 10.8 Hz, P–C=CH–CMe<sub>3</sub>), 21.0 (d, <sup>1</sup>J<sub>CP</sub> = 10.6 Hz, P–CH<sub>2</sub>CH<sub>3</sub>), 11.7 (d, <sup>2</sup>J<sub>CP</sub> = 21.1 Hz, P–CH<sub>2</sub>CH<sub>3</sub>), 9.9 (s, Al–CH<sub>2</sub>CH<sub>3</sub>), 1.8 (s, Al–CH<sub>2</sub>CH<sub>3</sub>); <sup>31</sup>P {<sup>1</sup>H</sup> NMR (162 MHz, d<sub>8</sub>-THF):  $\delta = -22.9$ .

#### Synthesis of compound 3

Diethylaluminum hydride, Et<sub>2</sub>AlH, (0.36 g, 4.19 mmol) was added at room temperature to a solution of mesityldi(*tert*-butyl-ethynyl)phosphine, Mes–P(C $\equiv$ C'Bu)<sub>2</sub>, (0.66 g, 2.12 mmol) in toluene (25 mL). After stirring for 10 min at room temperature triethylaluminum, AlEt<sub>3</sub>, (0.24 g, 2.11 mmol) was added. The

mixture was stirred for 18 h at room temperature. The solution was concentrated and cooled to -30 °C to obtain colorless crystals of **3** (0.25 g, 0.36 mmol, 34%). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta = 6.92$  (d,  ${}^{3}J_{PH} = 52.6$  Hz, 1H, P–C=C–H), 6.71 (s, 1H, m- $H_{Mes}$ ), 6.68 (d,  ${}^{4}J_{PH}$  = 3.6 Hz, 1H, *m*- $H_{Mes}$ ), 2.71 (m, 1H, P-CH2CH3), 2.67 (s, 3H, o-CH3), 2.53 (s, 3H, o-CH3), 2.24 (m,  ${}^{2}J_{\text{HH}} = 15.2 \text{ Hz}, {}^{3}J_{\text{HH}} = 7.6 \text{ Hz}, 1\text{H}, P-CH_2CH_3), 2.01 \text{ (s, 3H, } p-$ CH<sub>3</sub>), 1.62 (t,  ${}^{3}J_{HH} = 8.1$  Hz, 3H, Al–CH<sub>2</sub>CH<sub>3</sub>), 1.57 (dd,  ${}^{3}J_{HH}$ = 17.4 Hz,  ${}^{3}J_{\rm HH}$  = 9.5 Hz, 3H, Al–CH<sub>2</sub>CH<sub>3</sub>), 0.98 (s, 9H, P– C=CH-CMe<sub>3</sub>), 0.80 (m, 1H, Al-CH<sub>2</sub>CH<sub>3</sub>), 0.78 (m,  ${}^{3}J_{HH} = 7.5$ Hz,  ${}^{3}J_{PH} = 15.4$  Hz, 3H, P-CH<sub>2</sub>CH<sub>3</sub>), 0.70 (m, 1H, Al-CH<sub>2</sub>CH<sub>3</sub>), 0.65 (m, 1H, Al-CH<sub>2</sub>CH<sub>3</sub>), 0.62 (m, 1H, Al- $CH_2CH_3$ ); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta = 164.0$  (coupling constants not resolved, P–C=C–H), 142.7 (d,  ${}^{2}J_{CP} = 5.6$ Hz, o-C<sub>Mes</sub>), 142.6 (d,  ${}^{2}J_{CP}$  = 14.8 Hz, o-C<sub>Mes</sub>), 139.9 (d,  ${}^{4}J_{CP}$  = 1.8 Hz, p-C<sub>Mes</sub>), 134.8 (br., P-C=C-H), 131.4 (d,  ${}^{1}J_{CP} = 19.4$ Hz, *ipso*-C<sub>Mes</sub>), 131.2 (d,  ${}^{3}J_{CP} = 4.9$  Hz, *m*-C<sub>Mes</sub>), 129.4 (d,  ${}^{3}J_{CP}$ = 8.0 Hz, m-C<sub>Mes</sub>), 38.5 (d,  ${}^{3}J_{CP}$  = 8.1 Hz, P-C=CH-CMe<sub>3</sub>), 29.6 (s, P-C=CH-CMe<sub>3</sub>), 26.0 (d,  ${}^{3}J_{CP} = 14.7$  Hz, o-CH<sub>3</sub>), 24.1 (d,  ${}^{3}J_{CP} = 2.9$  Hz, o-CH<sub>3</sub>), 20.9 (s, p-CH<sub>3</sub>), 19.9 (d,  ${}^{1}J_{CP} =$ 32.5 Hz, P-CH<sub>2</sub>CH<sub>3</sub>), 11.2 (s, Al-CH<sub>2</sub>CH<sub>3</sub>), 10.2 (s, Al- $CH_2CH_3$ ), 9.2 (d,  ${}^2J_{CP}$  = 4.4 Hz, P- $CH_2CH_3$ ), 6.7 (br., Al-CH<sub>2</sub>CH<sub>3</sub>), 3.9 (br., Al–CH<sub>2</sub>CH<sub>3</sub>); <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz,  $C_6D_6$ ):  $\delta = -25.5$ ; MS (EI, 20 eV, 333 K) m/z (%) = 346 (7) [1/2  $M^+$ ], 317 (100) [1/2  $M^+$  – Et], 289 (33) [1/2  $M^+$  – Et–ethene]; IR (cm<sup>-1</sup>, paraffin, CsI plates): 1768 vw, 1697 vw, 1653 w, 1633 vw, 1604 m, 1558 w, 1504 w (vC=C, phenyl); 1469 vs, 1454 vs (paraffin); 1448 vs ( $\delta CH_3$ ); 1375 s (paraffin); 1290 w, 1247 m (&CH3); 1188 w br., 1103 vw, 1060 w, 1029 w, 964 w, 954 w, 920 w, 896 vw, 848 m, 754 vw (vCC); 721 m (paraffin); 657 vw, 630 w (δphenyl); 553 vw, 534 w, 514 w, 457 w, 437 w, 414 w (δCC, vAlC, vPC); Anal. Calcd for C<sub>42</sub>H<sub>72</sub>Al<sub>2</sub>P<sub>2</sub>: C, 72.8; H, 10.5. Found: C, 72.7; H, 10.3; MP (sealed capillary, argon): 107 °C (decomposition).

#### Synthesis of compound 4

A solution of *tert*-butyldi(*tert*-butylethynyl)phosphine, <sup>t</sup>Bu-P- $(C \equiv C^{-t}Bu)_2$ , (0.30 g, 1.18 mmol) in 10 mL of n-hexane was cooled to -78 °C and treated with a solution of di(tert-butyl)aluminum hydride, 'Bu<sub>2</sub>AlH, (0.34 g, 2.37 mmol) in 10 mL of n-hexane. The mixture was allowed to warm to room temperature and stirred for 22 h. The alkynyl compound <sup>t</sup>Bu<sub>2</sub>Al-C=C-<sup>t</sup>Bu was identified as a byproduct by its characteristic NMR data<sup>16</sup> (<sup>1</sup>H:  $\delta$  = 1.05 (s, C≡C−CMe<sub>3</sub>), 1.34 (s, AlCMe<sub>3</sub>); <sup>13</sup>C:  $\delta$  = 17.4  $(AlCMe_3)$ , 29.6  $(C \equiv C - CMe_3)$ , 30.1  $(C \equiv C - CMe_3)$ , 31.9 (AlCMe<sub>3</sub>), 79.6 (Al– $C\equiv C$ ), 152.0 (Al– $C\equiv C$ )). The pale orange solution was concentrated until product 4 started to precipitate and subsequently cooled to -45 °C. The solvent was removed, the remaining solid dried in vacuum and recrystallized from toluene (0.23 g, 0.37 mmol, 62%). Once crystallized 4 is almost insoluble in non-coordinating solvents, d8-THF was used as a solvent for the NMR spectroscopic characterization. Hence, the NMR data refers probably to the THF adduct of the monomer. <sup>1</sup>H NMR (200 MHz, 298 K, d<sub>8</sub>-THF):  $\delta = 6.49$  (d, <sup>3</sup> $J_{\text{HP}} = 32.7$ Hz, 1 H, P–C=C–H), 4.04 (d,  ${}^{1}J_{HP} = 208.3$  Hz, 1 H, P–H), 1.20 (s, 9 H, P-C=CH-CMe<sub>3</sub>), 1.20 (d,  ${}^{3}J_{HP} = 11.2$  Hz, 9 H, P- $CMe_3$ ), 0.97 (s, 18 H,  $Al^tBu_2$ );  ${}^{13}C{}^{1}H$  NMR (101 MHz,

298 K, d<sub>8</sub>-THF):  $\delta$  = 161.9 (d, <sup>2</sup>*J*<sub>CP</sub> = 3.0 Hz, C=*C*-CMe<sub>3</sub>), 141.7 (d, <sup>1</sup>*J*<sub>CP</sub> = 53 Hz, *C*=*C*-CMe<sub>3</sub>), 38.3 (d, <sup>3</sup>*J*<sub>CP</sub> = 4.5 Hz, C=*C*-CMe<sub>3</sub>), 32.7 (Al(*CMe*<sub>3</sub>)<sub>2</sub>), 32.2 (d, <sup>2</sup>*J*<sub>CP</sub> = 12.0 Hz, P-*CMe*<sub>3</sub>), 31.9 (d, <sup>4</sup>*J*<sub>CP</sub> = 3.4 Hz, C=*C*-*CMe*<sub>3</sub>), 30.3 (d, <sup>1</sup>*J*<sub>CP</sub> = 11.5 Hz, P-*C*Me<sub>3</sub>), 17.2 (Al(*C*Me<sub>3</sub>)<sub>2</sub>); <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, 298 K, d<sub>8</sub>-THF):  $\delta$  = -22.7; MS (EI, 20 eV, 433 K) *m*/*z* (%) = 624 (0.1) [M<sup>+</sup> - <sup>1</sup>Bu], 255 (100) [1/2 M<sup>+</sup> - <sup>1</sup>Bu], 199 (15) [1/2 M<sup>+</sup> - <sup>1</sup>Bu-butene]; IR (cm<sup>-1</sup>, paraffin, CsI plates): 1568 m, 1553 m, 1533 s (vC=*C*, phenyl); 1452 vs, 1375 vs (paraffin); 1306 w, 1242 m (\deltaCH<sub>3</sub>); 1190 s, 1175 s, 1067 vw, 1028 m, 999 s, 930 s, 893 m, 874 m, 841 m, 804 vs, 781 vs (vCC); 723 m (paraffin); 689 s (phenyl); 650 m, 637 m, 598 w, 561 s, 534 s, 465 s ( $\delta$ CC, vAIC, vPC); Anal. Calcd for C<sub>36</sub>H<sub>76</sub>Al<sub>2</sub>P<sub>2</sub>: C, 69.2; H, 12.3. Found: C, 69.5; H, 12.1; MP (sealed capillary, argon): 118 °C.

#### Synthesis of compound cis-5

 $CO_2$  was bubbled through a solution of compound 2 (ca. 20 mg) in deuterated benzene (4 mL). The suspension adopted immediately a yellow color which disappeared within seconds by the formation of a clear solution. The integration of the resonances in the NMR showed 99% conversion. Although cis-5 was formed almost quantitatively, its relative instability did not allow its purification by recrystallization. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta = 7.43$  (dd,  ${}^{3}J_{\text{HH}} = 7.3$  Hz,  ${}^{3}J_{\text{HP}} = 11.7$  Hz, 2H, o-H<sub>Ph</sub>), 7.29 (d,  ${}^{3}J_{HP} = 69.9$  Hz, 1H, P–C=C–H), 6.90 (m, 1H, p-H<sub>Ph</sub>), 6.87 (m, 2H, m-H<sub>Ph</sub>), 2.58 (m, 1H, P-CH<sub>2</sub>CH<sub>3</sub>), 1.55 (m, 1H, P- $CH_2CH_3$ ), 1.48 (dt,  ${}^2J_{HH} = 15.9$  Hz,  ${}^3J_{HH} = 8.1$  Hz, 6H, Al-CH<sub>2</sub>CH<sub>3</sub>), 0.89 (dt,  ${}^3J_{HH} = 7.6$  Hz,  ${}^3J_{HP} = 20.7$  Hz, 3H, P-CH<sub>2</sub>CH<sub>3</sub>), 0.65 (s, 9H, P-C=CH-CMe<sub>3</sub>), 0.50 (m, 2H, Al- $CH_2CH_3$ ), 0.45 (m, 2H, Al- $CH_2CH_3$ );  ${}^{13}C{}^{1}H$  NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 176.2 (d, <sup>2</sup>J<sub>CP</sub> = 11.7 Hz, P–C=C–H), 168.0 (d,  ${}^{1}J_{CP} = 120.0$  Hz, P–CO<sub>2</sub>), 133.0 (d,  ${}^{4}J_{CP} = 3.1$  Hz, p- $C_{Ph}$ ), 131.5 (d,  ${}^{2}J_{CP} = 8.9$  Hz, o- $C_{Ph}$ ), 129.4 (d,  ${}^{3}J_{CP} = 11.4$  Hz, *m*- $C_{Ph}$ ), 124.2 (d,  ${}^{1}J_{CP} = 64.3$  Hz, *ipso*- $C_{Ph}$ ), 120.38 (br., P-C = C - H), 39.7 (d,  ${}^{3}J_{PC} = 12.5 \text{ Hz}$ , P-C = CH-CMe<sub>3</sub>), 28.6 (s, P-C=CH-CMe<sub>3</sub>), 18.6 (d,  ${}^{1}J_{CP} = 37.7$  Hz, P-CH<sub>2</sub>CH<sub>3</sub>), 10.3 (s, Al-CH<sub>2</sub>CH<sub>3</sub>), 6.7 (s, P-CH<sub>2</sub>CH<sub>3</sub>), 0.7 (br., Al-CH<sub>2</sub>CH<sub>3</sub>), 0.4 (br., Al– $CH_2CH_3$ ); <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta = -4.6$ .

#### Synthesis of compound trans-5

CO<sub>2</sub> was bubbled through a suspension of compound **2** (0.71 g, 1.16 mmol) in n-hexane (45 mL). The suspension adopted a yellow color which disappeared within seconds to give a clear colorless solution. It was concentrated by removal of the solvent under normal pressure in the heat and a constant CO<sub>2</sub> stream. The hot solution was filtered and the crude product precipitated at -20 °C. Recrystallization from 1.2 mL of 1,2-diflourobenzene at -45 °C gave colorless crystals of *trans*-**5** (0.35 g, 1.00 mmol, 43%). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 7.48 (ddd, <sup>3</sup>J<sub>HH</sub> = 7.1 Hz, <sup>3</sup>J<sub>HP</sub> = 11.3 Hz, <sup>3</sup>J<sub>HP</sub> = 1.3 Hz, 2H, *o*-H<sub>Ph</sub>), 6.93 (m, 1H, *p*-C=C-*H*), 1.85 (m, 1H, P-CH<sub>2</sub>CH<sub>3</sub>), 1.49 (t, <sup>3</sup>J<sub>HH</sub> = 8.1 Hz, 3H, Al-CH<sub>2</sub>CH<sub>3</sub>), 1.42 (m, 1H, P-C=CH-CMe<sub>3</sub>), 0.76 (dt, 3H, <sup>3</sup>J<sub>HH</sub> = 7.9 Hz, <sup>3</sup>J<sub>HP</sub> = 15.1 Hz, P-CH<sub>2</sub>CH<sub>3</sub>), 0.59 (m, 1H,

Al-CH2CH3), 0.45 (m, 2H, Al-CH2CH3), 0.33 (m, 1H, Al- $CH_2CH_3$ ); <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta = 176.9$  (d, <sup>2</sup> $J_{CP}$ = 8.2 Hz, P–C=–C–H), 165.3 (d,  ${}^{1}J_{CP}$  = 109.4 Hz, P–CO<sub>2</sub>), 133.1 (d,  ${}^{4}J_{CP}$  = 3.1 Hz, *p*-C<sub>Ph</sub>), 132.1 (d,  ${}^{2}J_{CP}$  = 8.3 Hz, *o*-C<sub>Ph</sub>), 129.5 (d,  ${}^{3}J_{CP} = 11.1$  Hz, *m*-C<sub>Ph</sub>), 126.0 (br., P–C=C–H), 121.9 (d,  ${}^{1}J_{CP} = 63.9$  Hz, *ipso*-C<sub>Ph</sub>), 39.1 (d,  ${}^{3}J_{CP} = 26.4$  Hz, P-C=CH-CMe<sub>3</sub>), 28.5 (s, P-C=CH-CMe<sub>3</sub>), 16.8 (d,  ${}^{1}J_{CP} = 38.7$ Hz, P-CH<sub>2</sub>CH<sub>3</sub>), 10.33 (s, Al-CH<sub>2</sub>CH<sub>3</sub>), 10.27 (s, Al- $CH_2CH_3$ ), 6.4 (d,  ${}^2J_{CP} = 3.2$  Hz, P- $CH_2CH_3$ ), 2.4 (br., Al-CH<sub>2</sub>CH<sub>3</sub>), 1.7 (br., Al–CH<sub>2</sub>CH<sub>3</sub>); <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz,  $C_6D_6$ ):  $\delta = 2.3$ ; MS (EI, 20 eV, 333 K): m/z (%) = 319 (6) [M<sup>4</sup>] - Et], 304 (2) [M<sup>+</sup> - CO<sub>2</sub>], 275 (39) [M<sup>+</sup> - Et-CO<sub>2</sub>], 247 (23)  $[M^+ - Et-CO_2 - ethene], 220 (78) [M^+ - AlEt_2 - CO_2 + H], 205$ (100)  $[(Et)(Ph)P-C(H)=C(H)^{t}Bu^{+}-Me]$ ; IR (cm<sup>-1</sup>, paraffin, CsI plates): 1815 vw; 1695 vs, 1604 vw, 1568 vs, 1535 s (vC=C, vC=O, phenyl); 1460 vs (paraffin); 1404 w (δCH<sub>3</sub>); 1377 vs (paraffin); 1332 w, 1305 vw, 1255 s (δCH<sub>3</sub>); 1199 vw, 1184 vw, 1159 w, 1103 m, 981 m, 943 w, 914 w, 850 m, 817 w, 763 m, 736 vs (vCC, vCO); 723 vs (paraffin); 694 vs (ophenyl); 634 w, 596 m, 542 m, 489 w, 460 w, 447 w, 418 vw (δCC, vAlC, vAlO, vPC); Anal. Calcd for C<sub>19</sub>H<sub>30</sub>AlO<sub>2</sub>P: C, 65.5; H, 8.7. Found: C, 65.3; H, 8.6; MP (sealed capillary, argon): 67 °C.

#### Synthesis of compound cis-6

Phenyl isocyanate (0.08 mL, 0.088 g, 0.739 mmol) was added to a suspension of compound 2 (0.225 g, 0.370 mmol) in n-hexane (20 mL). The color of the suspension changed to colorless within seconds. A clear solution resulted, which was concentrated and stored at -20 °C. Compound cis-6 crystallized as colorless needles (0.189 g, 0.446 mmol, 60%). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 7.75 (d, <sup>3</sup>J<sub>HH</sub> = 7.27 Hz, 2H, *o*-H<sub>PhIso</sub>), 7.62 (m, 2H, o-H<sub>Ph</sub>), 7.38 (d,  ${}^{3}J_{HP}$  = 67.8 Hz, 1H, P–C=C–H), 7.19 (t,  ${}^{3}J_{HH}$  = 7.8 Hz, 2H, m-H<sub>PhIso</sub>), 6.95 (m, 2H, p-H<sub>Ph</sub>), 6.93 (m, 1H, *p*-H<sub>PhIso</sub>), 6.93 (m, 2H, *m*-H<sub>Ph</sub>), 3.00 (m,  ${}^{2}J_{HH} = 14.9$ Hz,  ${}^{3}J_{HH} = 7.5$  Hz, 1H, P–CH<sub>2</sub>CH<sub>3</sub>), 1.80 (m,  ${}^{2}J_{HH} = 14.9$  Hz,  ${}^{3}J_{\text{HH}} = 7.5 \text{ Hz}, 1\text{H}, P-CH_2CH_3), 1.48 (t, {}^{3}J_{\text{HH}} = 8.1 \text{ Hz}, 6\text{H}, \text{Al} CH_2CH_3$ ), 1.04 (dt,  ${}^{3}J_{HH} = 7.5$  Hz,  ${}^{3}J_{HP} = 20.3$  Hz, 3H, P-CH<sub>2</sub>CH<sub>3</sub>), 0.74 (s, 9H, P-C=CH-CMe<sub>3</sub>), 0.46 (m, 2H, Al- $CH_2CH_3$ ), 0.46 (m, 2H, Al- $CH_2CH_3$ ); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 175.0 (d, <sup>2</sup>J<sub>CP</sub> = 8.8 Hz, P–C=C–H), 159.4 (d,  ${}^{1}J_{CP} = 147.3$  Hz, P–CON), 147.8 (d,  ${}^{3}J_{CP} = 22.9$  Hz, *ipso*-C<sub>PhIso</sub>), 132.7 (d,  ${}^{2}J_{CP}$  = 3.0 Hz, *p*-C<sub>Ph</sub>), 131.6 (d,  ${}^{4}J_{CP}$  = 9.1 Hz, o-C<sub>Ph</sub>), 129.2 (d,  ${}^{3}J_{CP} = 11.4$  Hz, m-C<sub>Ph</sub>), 128.8 (m- $C_{PhIso}$ ), 126.5 (d,  ${}^{1}J_{CP} = 68.7$  Hz, *ipso*- $C_{Ph}$ ), 125.1 (*o*- $C_{PhIso}$ ), 124.8 (*p*-C<sub>PhIso</sub>), 121.0 (br., d,  ${}^{1}J_{CP} = 7.8$  Hz, P–C=C–H), 38.8 (d,  ${}^{3}J_{CP} = 11.7$  Hz, P–C=CH–CMe<sub>3</sub>), 28.8 (d,  ${}^{4}J_{CP} = 1.4$  Hz, P–C==CH–CMe<sub>3</sub>), 20.2 (d,  ${}^{1}J_{CP}$  = 41.6 Hz, P–CH<sub>2</sub>CH<sub>3</sub>), 10.48 (s, Al–CH<sub>2</sub>CH<sub>3</sub>), 10.46 (s, Al–CH<sub>2</sub>CH<sub>3</sub>), 6.6 (d,  ${}^{2}J_{CP} = 1.5$  Hz, P-CH<sub>2</sub>CH<sub>3</sub>), 1.2 (br., Al-CH<sub>2</sub>CH<sub>3</sub>), 0.9 (br., Al-CH<sub>2</sub>CH<sub>3</sub>); <sup>31</sup>P {<sup>1</sup>H} NMR (162 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 1.4; MS (EI, 20 eV, 298 K) m/z (%) = 394 (100) [M<sup>+</sup> - Et], 275 (44) [M<sup>+</sup> - Et-ethene-NPh]; IR (cm<sup>-1</sup>, paraffin, CsI plates): 1683 vw, 1653 w, 1628 vs, 1589 s, 1576 s, 1570 s, 1558 s, 1539 vw, 1506 vw (vC=C, vC=N, phenyl); 1458 vs (paraffin); 1406 vw ( $\delta$ CH<sub>3</sub>); 1375 vs (paraffin); 1298 m, 1259 m (δCH<sub>3</sub>); 1182 w, 1153 w, 1107 m, 1072 w, 1034 w, 1026 w, 1009 w, 998 w, 941 w, 918 vw, 891 w, 853 w, 822 w, 802 w, 795 m, 773 w, 766 m, 745 m, 731 s (vCC,

#### Synthesis of compound cis-7

Cis-7 was generally obtained as a mixture with cis-6 and trans-6 when solutions of cis-6 were stirred at room temperature for several days. In only a single case colorless crystals of *cis*-7 were obtained in an irreproducible procedure by repeated recrystallization from n-hexane and 1,2-difluorobenzene over several weeks. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 7.77 (m, <sup>3</sup>J<sub>HH</sub> = 7.8 Hz, 2H, o- $H_{PhIso}$ ), 7.63 (m, 2H, o- $H_{Ph}$ ), 7.37 (d,  ${}^{3}J_{HP}$  = 69.0 Hz, 1H, P-C==C-H), 7.18 (m, 2H, m-H<sub>PhIso</sub>), 6.96 (m, 1H, p-H<sub>PhIso</sub>), 6.95 (m, 2H, *m*-H<sub>Ph</sub>), 6.95 (m, 1H, *p*-H<sub>Ph</sub>), 2.87 (m,  ${}^{2}J_{HH} = 14.5$  Hz,  ${}^{3}J_{\rm HH} = 7.5$  Hz, 1H, P–CH<sub>2</sub>CH<sub>3</sub>), 1.62 (m, 1H, P–CH<sub>2</sub>CH<sub>3</sub>), 1. 45 (dt,  ${}^{3}J_{\text{HH}} = 8.0$  Hz, 3H, Al–CH<sub>2</sub>CH<sub>3</sub>), 1.04 (dt, 3H,  ${}^{3}J_{\text{HH}} =$ 7.6 Hz,  ${}^{3}J_{\text{HP}} = 20.4$  Hz, P–CH<sub>2</sub>CH<sub>3</sub>), 0.74 (s, 9H, P–C=CH–  $CMe_3$ ), 0.46–0.53 (m, 4H, Al– $CH_2CH_3$ ); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz,  $C_6D_6$ ):  $\delta = 175.2$  (d,  ${}^2J_{CP} = 12.9$  Hz, P–C=C–H), 167.7 (d,  ${}^{1}J_{CP} = 125.3$  Hz, P–CN), 144.4 (d,  ${}^{3}J_{CP} = 12.3$  Hz, *ipso*-C<sub>PhIso</sub>), 132.9 (d,  ${}^{4}J_{CP} = 3.1$  Hz, *p*-C<sub>Ph</sub>), 131.8 (d,  ${}^{2}J_{CP} =$ 8.8 Hz, o-C<sub>Ph</sub>), 129.3 (d,  ${}^{3}J_{CP} = 11.6$  Hz, m-C<sub>Ph</sub>), 129.0 (m- $C_{PhIso}$ ), 125.5 (d,  ${}^{1}J_{CP} = 66.6$  Hz, *ipso*- $C_{Ph}$ ), 125.1 (*p*- $C_{PhIso}$ ), 125.1 (o-C<sub>PhIso</sub>), 118.5 (br., P-C=C-H), 39.6 (d,  ${}^{3}J_{CP} = 12.8$ Hz, P-C=CH-CMe<sub>3</sub>), 28.8 (d,  ${}^{4}J_{CP} = 1.3$  Hz, P-C=CH- $CMe_3$ ), 18.4 (d,  ${}^{1}J_{CP} = 41.7$  Hz, P- $CH_2CH_3$ ), 10.7 (s, Al-CH<sub>2</sub>CH<sub>3</sub>), 10.6 (s, Al-CH<sub>2</sub>CH<sub>3</sub>), 6.8 (s, P-CH<sub>2</sub>CH<sub>3</sub>), 1.8 (br., Al-CH<sub>2</sub>CH<sub>3</sub>), 1.6 (br., Al-CH<sub>2</sub>CH<sub>3</sub>); <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta = -0.7$ ; MS (EI, 20 eV, 333 K) m/z (%) = 422 (1) [M<sup>+</sup> - H], 394 (100) [M<sup>+</sup> – Et], 275 (12) [M<sup>+</sup> – Et–ethene–NPh]; IR (cm-1, paraffin, CsI plates): 1977 vw, 1958 vw, 1938 vw, 1896 w, 1870 vw, 1849 w, 1820 vw, 1790 vw, 1769 vw, 1724 vw, 1689 vw, 1630 vs, 1576 vs (vC=O, vC=C, phenyl); 1450 vs (paraffin); 1406 s ( $\delta$ CH<sub>3</sub>); 1375 s (paraffin); 1360 s, 1331 w, 1298 s, 1254 w (&CH3); 1234 vw, 1223 vw, 1184 s, 1155 m, 1107 s, 1070 m, 1026 s, 980 s, 941 s, 924 w, 895 s, 847 vw, 822 m, 795 s, 766 w, 750 vs (vCC, vCN); 723 s (paraffin); 691 s, 675 w, 646 s, 633 s, 596 s, 581 s, 550 m, 536 m, 507 s, 494 s, 459 s, 432 s (&CC, vAlC, vAlN, vPC); Anal. Calcd for C<sub>25</sub>H<sub>35</sub>AlNOP: C, 70.9; H, 8.3; N, 3.3. Found: C, 70.6; H, 7.9; N, 3.2; MP (sealed capillary, argon): 108 °C.

#### Synthesis of compound trans-6

Phenyl isocyanate (0.04 mL, 0.043 g, 0.361 mmol) was added to a suspension of compound **2** (0.109 g, 0.179 mmol) in toluene (10 mL) and stirred for 5 min at ambient temperature. A clear solution was formed. Heating for 17 h at 85 °C gave a mixture of 68% of *trans*-**6**, 28% of compound *cis*-**7** and 3% of *trans*-**7**, which was used for the NMR spectroscopic characterization of *trans*-**6**. Attempts for further purification by recrystallization remained unsuccessful. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 7.94 (dd, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz, <sup>5</sup>J<sub>HP</sub> = 0.8 Hz, 2H, *o*-H<sub>PhIso</sub>), 7.68 (m, 2H, *o*-H<sub>Ph</sub>), 7.25 (t, <sup>3</sup>J<sub>HH</sub> = 7.8 Hz, 2H, *m*-H<sub>PhIso</sub>), 6.95 (m, 1H, *p*-H<sub>Ph</sub>), 6.95 (m, 2H, *m*-H<sub>Ph</sub>), 6.95 (m, 1H, *p*-H<sub>PhIso</sub>), 6.95 (d, <sup>3</sup>J<sub>HP</sub>

= 37.5 Hz, 1H, P-C=C-H), 2.17 (m, 1H, P-CH<sub>2</sub>CH<sub>3</sub>), 1.62 (m, 1H, P– $CH_2CH_3$ ), 1.51 (t,  ${}^{3}J_{HH} = 8.1$  Hz, 3H, Al– $CH_2CH_3$ ), 1.33 (t,  ${}^{3}J_{HH} = 8.1$  Hz, 3H, Al–CH<sub>2</sub>CH<sub>3</sub>), 1.15 (s, 9H, P–C=CH– CMe<sub>3</sub>), 0.91 (dt, 3H,  ${}^{3}J_{HH} = 7.5$  Hz,  ${}^{3}J_{HP} = 18.5$  Hz, P-CH<sub>2</sub>CH<sub>3</sub>), 0.58 (m, 1H, Al-CH<sub>2</sub>CH<sub>3</sub>), 0.38 (m, 1H, Al- $CH_2CH_3$ ; <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta = 175.7$  (d, <sup>2</sup> $J_{CP}$ = 6.1 Hz, P–C=C–H), 156.1 (d,  ${}^{1}J_{CP}$  = 137.5 Hz, P–CNO), 147.4 (d,  ${}^{3}J_{CP} = 21.5$  Hz, *ipso*-C<sub>PhIso</sub>), 132.9 (d,  ${}^{4}J_{CP} = 3.1$  Hz,  $p-C_{Ph}$ ), 132.2 (d,  ${}^{2}J_{CP} = 8.4$  Hz,  $o-C_{Ph}$ ), 129.3 (d,  ${}^{3}J_{CP} = 11.1$ Hz, m-C<sub>Ph</sub>), 128.9 (m-C<sub>PhIso</sub>), 126.5 (br., P-C=C-H), 125.6 (o- $C_{PhIso}$ ), 125.1 (*p*- $C_{PhIso}$ ), 123.9 (d,  ${}^{1}J_{CP} = 68.0$  Hz, *ipso*- $C_{Ph}$ ), 39.1 (d,  ${}^{3}J_{CP} = 25.9$  Hz, P–C=CH–CMe<sub>3</sub>), 28.7 (d,  ${}^{4}J_{CP} = 1.4$ Hz, P–C=CH–CMe<sub>3</sub>), 17.9 (d,  ${}^{1}J_{CP} = 43.0$  Hz, P–CH<sub>2</sub>CH<sub>3</sub>), 10.54 (s, Al-CH<sub>2</sub>CH<sub>3</sub>), 10.48 (s, Al-CH<sub>2</sub>CH<sub>3</sub>), 6.4 (d,  ${}^{2}J_{CP}$  = 3.5 Hz, P-CH<sub>2</sub>CH<sub>3</sub>), 2.9 (br., Al-CH<sub>2</sub>CH<sub>3</sub>), 2.0 (br., Al- $CH_2CH_3$ ); <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta = 10.4$ .

#### Synthesis of compound trans-7

Phenyl isocyanate (0.09 mL, 0.102 g, 0.857 mmol) was added to a suspension of compound 2 (0.26 g, 0.427 mmol) in toluene (10 mL). A clear solution was obtained after stirring at ambient temperature for 5 min. Heating to 95 °C for 7 d gave a mixture of trans-6 (37%) and trans-7 (63%). The solvent was removed in vacuum, and the residue was dissolved in 6 mL of n-hexane. trans-7 crystallized as a colorless solid upon cooling to -30 °C (0.191 g, 0.45 mmol, 53%). <sup>1</sup>H NMR (400 MHz,  $C_6D_6$ ):  $\delta =$ 7.71 (m,  ${}^{3}J_{HH} = 5.7$  Hz, 2H, o-H<sub>Ph</sub>), 7.62 (d,  ${}^{3}J_{HH} = 8.2$  Hz, 2H,  $o-H_{PhIso}$ ), 7.20 (t,  ${}^{3}J_{HH} = 7.8$  Hz, 2H,  $m-H_{PhIso}$ ), 7.00 (m, 2H, p- $H_{Ph}$ ), 6.98 (m, 2H, *m*- $H_{Ph}$ ), 6.96 (m, 1H, *p*- $H_{PhIso}$ ), 6.96 (d,  ${}^{3}J_{HP}$ = 42.0 Hz, 1H, P-C=C-H), 2.19 (m, 1H, P-CH<sub>2</sub>CH<sub>3</sub>), 1.57 (m, 1H, P–C $H_2$ CH<sub>3</sub>), 1.35 (t,  ${}^{3}J_{HH} = 8.1$  Hz, 3H, Al–CH<sub>2</sub>C $H_3$ ), 1.26  $(t, {}^{3}J_{HH} = 8.1 \text{ Hz}, 3H, \text{Al-CH}_{2}CH_{3}), 1.17 \text{ (s, 9H, P-C=CH-}$  $CMe_3$ ), 0.96 (dt,  ${}^3J_{\rm HH}$  = 7.5 Hz,  ${}^3J_{\rm HP}$  = 18.4 Hz, 3H, P- $CH_2CH_3$ ), 0.40 (m, 4H, Al- $CH_2CH_3$ );  ${}^{13}C{}^{1}H$  NMR (101 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 176.8 (d, <sup>2</sup>J<sub>CP</sub> = 9.4 Hz, P–C=C–H), 165.7 (d,  ${}^{1}J_{CP} = 114.1$  Hz, P–CN), 144.2 (d,  ${}^{3}J_{CP} = 14.1$  Hz, *ipso*-C<sub>PhIso</sub>), 133.2 (d,  ${}^{2}J_{CP} = 8.0$  Hz, o-C<sub>Ph</sub>), 133.0 (d,  ${}^{1}J_{CP} = 3.1$  Hz, p-C<sub>Ph</sub>), 129.3 (d,  ${}^{3}J_{CP} = 11.1$  Hz, m-C<sub>Ph</sub>), 128.9 (m- $C_{PhIso}$ ), 126.0 (*o*- $C_{PhIso}$ ), 125.4 (*p*- $C_{PhIso}$ ), 123.4 (d,  ${}^{1}J_{CP} = 67.1$ Hz, *ipso*-C<sub>Ph</sub>), 123.3 (br., P–C=C–H), 39.1 (d,  ${}^{3}J_{CP} = 26.4$  Hz, P-C=CH-CMe<sub>3</sub>, 28.7 (d,  ${}^{4}J_{CP} = 1.17$  Hz, P-C=CH-CMe<sub>3</sub>), 16.7 (d,  ${}^{1}J_{CP} = 43.2$  Hz, P–CH<sub>2</sub>CH<sub>3</sub>), 10.5 (s, Al–CH<sub>2</sub>CH<sub>3</sub>), 10.26 (s, Al–CH<sub>2</sub>CH<sub>3</sub>), 6.6 (d,  ${}^{2}J_{CP} = 2.8$  Hz, P–CH<sub>2</sub>CH<sub>3</sub>), 2.6 (br., Al–*C*H<sub>2</sub>CH<sub>3</sub>); <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta = 6.1$ ; MS (EI, 20 eV, 333 K) m/z (%) = 422 (0.1) [M<sup>+</sup> – H], 394 (100)  $[M^+ - Et]$ , 275 (38)  $[M^+ - Et$ -ethene-NPh]; IR (cm<sup>-1</sup>, paraffin, CsI plates): 1953 w, 1938 w, 1901 vw, 1875 vw, 1852 w, 1825 vw, 1802 w, 1788 w, 1755 vw, 1715 m, 1678 vw, 1659 w, 1641 m, 1622 s, 1575 m, 1564 m, 1555 m, 1500 m, 1485 s (vC=C, vC=O, phenyl); 1454 vs (paraffin); 1410 w ( $\delta$ CH<sub>3</sub>); 1375 m (paraffin); 1348 w, 1302 s, 1261 w (δCH<sub>3</sub>); 1240 vw, 1225 vw, 1184 m, 1134 vw, 1109 s, 1098 m, 1070 s, 1030 s, 1013 m, 999 w, 984 w, 966 m, 941 w, 910 m, 893 w, 860 s, 821 m, 812 s, 766 vs, 754 vs (vCC, vCN); 731 vs (paraffin); 692 s (δphenyl); 623 vs, 596 vs, 581 vs, 538 m, 513 m, 492 m, 463 m, 430 m, 409 vw (\deltaCC, vAlC, vAlN, vPC); Anal. Calcd

for  $C_{25}H_{35}AINOP$ : C, 70.9; H, 8.3; N, 3.3. Found: C, 70.8; H, 8.3; N, 3.2; MP (sealed capillary, argon): 126 °C.

#### Synthesis of compound 8

Phenyl isocyanate (0.10 mL, 0.114 g, 0.96 mmol) was added to a solution of (E)-Mes<sub>2</sub>P-[C=C(H)-Ph]-Al'Bu<sub>2</sub> (0.49 g, 0.96 mmol) in toluene (15 mL). The mixture was stirred for 3 h at room temperature. All volatiles were removed in vacuum. Crystallization from cyclopentane afforded the pure product 8 as vellow crystals (0.60 g, 0.95 mmol, 99%). <sup>1</sup>H NMR (200 MHz,  $C_6D_6$ ):  $\delta = 7.90$  (d,  ${}^{3}J_{HH} = 8.1$  Hz, 2 H, *o*-H<sub>PhIso</sub>), 7.77 (d,  ${}^{3}J_{HP}$ = 38.4 Hz, 1 H, P–C=C–H), 7.49 (d,  ${}^{3}J_{HH}$  = 7.5 Hz, 2 H, o- $H_{Ph}$ ), 7.24 (t,  ${}^{3}J_{HH} = 7.8$  Hz, 2 H, m- $H_{PhIso}$ ), 7.18 (t,  ${}^{3}J_{HH} = 7.5$ Hz, 2 H, *m*-H<sub>Ph</sub>), 7.06 (t,  ${}^{3}J_{HH} = 7.4$  Hz, 1 H, *p*-H<sub>Ph</sub>), 6.96 (t,  ${}^{3}J_{\text{HH}} = 7.4 \text{ Hz}, 1 \text{ H}, p-\text{H}_{\text{PhIso}}), 6.62 \text{ (d, } {}^{4}J_{\text{HP}} = 3.8 \text{ Hz}, 4 \text{ H}, m-$ H<sub>Mes</sub>), 2.38 (s, 12 H, o-CH<sub>3</sub>), 1.95 (s, 6 H, p-CH<sub>3</sub>), 1.16 (s, 18 H, AlCMe<sub>3</sub>);  ${}^{13}C{}^{1}H{}$  NMR (101 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta = 158.3$  (d,  ${}^{2}J_{CP} = 4.5$  Hz, P–C=C–H), 158.0 (d,  ${}^{1}J_{CP} = 141.0$  Hz, P–CN), 147.5 (d,  ${}^{3}J_{CP} = 23.8$  Hz, *ipso*-C<sub>PhIso</sub>), 144.8 (d,  ${}^{2}J_{CP} = 9.2$  Hz, o-C<sub>Mes</sub>), 143.2 (d,  ${}^{4}J_{CP}$  = 3.0 Hz, p-C<sub>Mes</sub>), 140.6 (d,  ${}^{3}J_{CP}$  = 32.1 Hz, *ipso*-C<sub>Ph</sub>), 139.4 (d,  ${}^{1}J_{CP} = 5,0$  Hz, P–C=C–H), 132.4 (d,  ${}^{3}J_{\rm CP} = 10.7$  Hz, m-C<sub>Mes</sub>), 129.9 (p-C<sub>Ph</sub>), 129.3 (m-C<sub>Ph</sub>), 128.9 (m-C<sub>PhIso</sub>), 128.2 (o-C<sub>Ph</sub>), 125.7 (o-C<sub>PhIso</sub>), 125.4 (p-C<sub>PhIso</sub>), 119.4 (d,  ${}^{1}J_{CP} = 67.8$  Hz, *ipso*-C<sub>Mes</sub>), 32.0 (Al(CMe<sub>3</sub>)<sub>2</sub>), 25.0 (d,  ${}^{3}J_{CP} = 4.5$  Hz, *o*-CH<sub>3</sub>), 20.8 (d,  ${}^{5}J_{CP} = 1.0$  Hz, *p*-CH<sub>3</sub>), 16.7 br.  $(Al(CMe_3)_2); {}^{31}P{}^{1}H$  NMR (162 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta = 15.2$ ; MS (EI, 20 eV, 403 K): m/z = 574 (7) [M<sup>+</sup> - <sup>t</sup>Bu], 512 (10) [M<sup>+</sup> -Ph–NCO], 455 (52) [M<sup>+</sup> – Ph–NCO–<sup>*t*</sup>Bu], 399 (18) [M<sup>+</sup> – <sup>*t*</sup>Bu– butane-Ph-NCO], 372 (71)  $[M^+ - Ph-NCO-Al(CMe_3)_2 + H];$ IR (cm<sup>-1</sup>, paraffin, CsI plates): 1931 vw, 1888 vw, 1865 vw, 1775 vw, 1736 vw, 1628 m, 1582 w, 1553 w, 1503 vw (vC=C, vC=0, phenyl); 1449 s, 1375 m (paraffin); 1294 w, 1271 w, 1248 w (δCH<sub>3</sub>); 1153 w, 1101 vw, 1067 vw, 1028 vw, 1003 vw, 934 vw, 885 vw, 853 w, 806 w, 783 w, 746 m (vCC, vCN); 723 s (paraffin); 689 w, 673 vw (ophenyl); 638 w, 625 w, 548 w, 503 vw, 471 vw, 453 vw, 438 vw, 403 vw, 365 vw, 341 vw (8CC, vAlC, vAlO, vPC); Anal. Calc. for C<sub>41</sub>H<sub>51</sub>PAlNO: C, 77.9; H, 8.1; N, 2.2. Found: C, 77.0; H, 7.7; N, 1.9; MP (sealed capillary, argon): 154 °C (decomposition).

#### Crystal structure determinations

Single crystals were obtained as described above with the synthetic procedures. The crystallographic data were collected with Bruker SMART 6000 (Cu) and STOE IPDS II (Mo) diffract-ometers. The crystals were coated with a perfluoropolyether, picked up with a glass fiber and immediately mounted in the cooled nitrogen stream of the diffractometer. The structures were solved by direct methods and refined with the program SHELXL-97<sup>25</sup> by a full-matrix least-squares method based on  $F^2$ . Crystal data, data collection parameters and structure refinement details are given in Table 1. The molecules of **1**, **2** and **3** are located on crystallographic inversion centers. Compound **4** crystallizes as twinned crystals with three independent domains. Reflections were separated by applying the diffractometer software, those of the main domain were used for structure solution and refinement. The P–H groups of **4** are disordered. Their

	1	2	3	4	trans-5	cis-7	trans-7	$\textbf{8}{\cdot}0.5C_6F_2H_4$
Formula F	C <sub>44</sub> H <sub>68</sub> Al <sub>2</sub> P <sub>2</sub> 712 9	C <sub>36</sub> H <sub>60</sub> Al <sub>2</sub> P <sub>2</sub> 608 7	C <sub>42</sub> H <sub>72</sub> Al <sub>2</sub> P <sub>2</sub>	$C_{36}H_{76}Al_2P_2$	C <sub>19</sub> H <sub>30</sub> AlO <sub>2</sub> P 348 4	C <sub>25</sub> H <sub>35</sub> AlNOP	C <sub>25</sub> H <sub>35</sub> AlNOP	C <sub>44</sub> H <sub>52.5</sub> AlFNOP
Crystal	Monoclinic	Monoclinic	Monoclinic	Triclinic	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)	$P2_1/n$ (no. 14)	<i>P</i> 1 (no. 2)	<i>P</i> 1 (no. 2)	<i>P</i> 1 (no. 2)	$P2_1/n$ (no. 14)	<i>C</i> 2/ <i>c</i> (no. 15)
a (pm)	1083.70 (2)	1022.66 (1)	1044.90 (1)	992.85 (3)	777.90 (3)	835.16 (5)	1285.46 (5)	3821.57 (4)
b (pm)	1252.41 (2)	1949.00 (2)	1539.75 (2)	1077.38 (4)	912.98 (3)	897.67 (5)	1239.67 (9)	1410.78 (1)
$\alpha$ (°)	1722.99 (3) 90	900.15 (1) 90	1300.43 ( <i>2</i> ) 90	79.662 (2)	91.206 (3)	81.019 (4)	1644.03 (7) 90	1363.68 (2) 90
β(°)	108.281 (1)	109.275 (1)	106.326 (1)	84.097 (2)	91.247 (3)	76.329 (4)	110.714 (3)	112.305 (1)
$\gamma$ (°) V (nm <sup>3</sup> )	90	90	90	66.108(1)	114.460 (3)	80.138 (4)	90	90 7 8006 (1)
$T(\mathbf{K})$	2.22048(7)	1.81775(3) 153(2)	2.10978(3) 153(2)	2.0343(1) 153(2)	1.03038(0) 153(2)	1.2300(1) 153(2)	2.4303(2)	7.8090(1) 153(2)
$\mu (mm^{-1})$	1.459 (Cu	1.703 (Cu	1.519 (Cu	1.508 (Cu	0.183 (Mo	0.162 (Mo	0.163 (Mo	1.133 (Cu Kα)
	Κα)	Κα)	Κα)	Κα)	Κα)	Κα)	Κα)	
Unique rflns	3839	3315	3099 (0.1896)	5997	4907	5896 (0.0230)	5885 (0.0893)	6803 (0.0383)
$(R_{\rm int})$	(0.0931)	(0.0423)		(0.0183)	(0.0394)			
$R_1$ (reflns I	0.0549	0.0376	0.0527 (2673)	0.0488	0.0353	0.0314 (4711)	0.0513 (4263)	0.0544 (5961)
$> 2\sigma(I)$	(3000)	(2966)	0.1005	(54/4)	(3990)	0.0014	0.1.150	0.1(10
$WR_2$ (all data)	0.1542	0.1080	0.1335	0.1208	0.0932	0.0814	0.1459	0.1610
CCDC	861398	861399	861400	861401	861402	861403	861404	861405

Table 1 Crystal data, data collection parameters, and structure refinement details for 1 to 4, trans-5, cis- and trans-7, and 8

phosphorus atoms were refined on split positions (0.70:0.30); the hydrogen atoms are on fixed positions with artificial displacement parameters. **8** crystallizes with half a molecule of difluorobenzene per formula unit. The solvent molecule is disordered across a twofold rotational axis. In addition a fluorine atom occupies two positions. Only three hydrogen atoms of the difluorobenzene molecule were considered.

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