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Published in:
 Dalton Transactions

DOI:
[10.1039/c7dt00318h](https://doi.org/10.1039/c7dt00318h)

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Document Version
 Publisher's PDF, also known as Version of record

Publication date:
 2017

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Zijlstra, H. S., Pahl, J., Penafiel, J., & Harder, S. (2017). "Masked" Lewis-acidity of an aluminum alpha-phosphinoamide complex. *Dalton Transactions*, 46(11), 3601-3610. <https://doi.org/10.1039/c7dt00318h>

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Cite this: *Dalton Trans.*, 2017, **46**, 3601

“Masked” Lewis-acidity of an aluminum α -phosphinoamide complex†

Harmen S. Zijlstra,^{a,b,c} Jürgen Pahl,^a Johanne Penafiel^{a,c} and Sjoerd Harder^{*a}

The reaction of $\text{Ph}_2\text{P}(\text{DIPP})\text{NH}$ with AlMe_3 cleanly gives an aluminum amide complex that crystallizes as a centrosymmetric dimer with a six-membered Al-N-P-Al-N-P ring. In aromatic solvents the dimer remains intact but the Al-P bond is readily broken upon addition of THF to form $\text{Ph}_2\text{P}(\text{DIPP})\text{NAlMe}_2 \cdot \text{THF}$. Efforts to use $[\text{Ph}_2\text{P}(\text{DIPP})\text{NAlMe}_2]_2$ as a “masked” Lewis acidic activator for olefin polymerization catalysts were unsuccessful but the complex showed a Frustrated Lewis pair reactivity instead. The P/Al complex reacts with isocyanates to give the C=O inserted product that crystallizes as a five-membered ring system Al-O-C(NR)-P-N . The reaction of $[\text{Ph}_2\text{P}(\text{DIPP})\text{NAlMe}_2]_2$ with CO_2 , however, gave an insertion in the N-Al bond and the dimeric product $[\text{Ph}_2\text{P}(\text{DIPP})\text{NCO}_2\text{AlMe}_2]_2$ was isolated. The dimer $[\text{Ph}_2\text{P}(\text{DIPP})\text{NAlMe}_2]_2$ is one of the few Al/P FLPs that can activate C=C double bonds irreversibly. A reaction with allyl methyl sulfide and 1-hexene led to the clean formation of the structurally similar activated alkene products $[(\text{DIPP})\text{N-Ph}_2\text{P-CH}(\text{CH}_2\text{SMe})\text{CH}_2]\text{AlMe}_2$ and $[(\text{DIPP})\text{N-Ph}_2\text{P-CH}(\text{C}_4\text{H}_9)\text{CH}_2]\text{AlMe}_2$.

Received 26th January 2017,
Accepted 13th February 2017

DOI: 10.1039/c7dt00318h

rsc.li/dalton

Introduction

Frustrated Lewis pair (FLP) chemistry is one of the most rapidly growing fields in main group chemistry.¹ This is in part due to the activation^{1a,2} of a wide variety of small molecules and functional groups and exciting applications in metal-free catalysis.³ Although the majority of systems consist of P/B or N/B pairs, variations in which Al is used as the Lewis acid are becoming increasingly popular. Inter- and intra-molecular Al -based FLPs are capable of solubilizing saline alkali metal hydrides,⁴ chelating $\text{Au}(\text{I})$ atoms,⁵ forming dialkylaluminum hydride adducts,⁶ dehydrogenating amine-boranes⁷ and activating small molecules like CO_2 ,^{8–16} isocyanates,^{8,11,12} carbonyls,¹⁷ terminal alkynes,^{15,18} H_2 ,¹⁹ and alkenes.²⁰

By definition a FLP is formed when the Lewis acid and Lewis base cannot interact with one another due to steric or electronic hindrance. If the steric demands around the Al center could be decreased, it should be possible to obtain a highly reactive species that could potentially exceed the aforementioned FLPs in reactivity. A system fulfilling these requirements is the dimeric $(\text{R}_2\text{PCH}_2\text{AlMe}_2)_2$ ($\text{R} = \text{Me}$, Ph , or $t\text{Bu}$)

which was introduced by the research groups of Uhl, Lammertsma, and Fontaine a few years ago.^{11,14} These complexes form stable Lewis adducts in both solution and a solid state but undergo FLP type reactivity upon exposure to CO_2 and $t\text{Bu-N=C=O}$. This “masked” FLP reactivity is based on the fact that the Al-P bond in these dimers is not very strong on account of the mismatch between the hard Lewis acid (Al) and soft Lewis base (P). In the presence of a substrate the Al-P bond is readily broken leaving a highly reactive three-coordinate Al center. This feature might enable other types of Lewis acid enhanced reactivity as well.

We are particularly interested in the activation of group 4 metallocene catalysts for olefin polymerization catalysis. Generally, such catalysts are activated by a highly Lewis acidic Al site in methylalumoxane (MAO):²¹ e.g. Me -abstraction from $\text{Cp}^*_2\text{ZrMe}_2$ gives the highly active ion-pair $[\text{Cp}^*_2\text{ZrMe}]^+[\text{MAO-Me}]^-$. Since the use of MAO has many disadvantages, among which its instability over time and the extremely high excess needed to achieve optimal polymerization activities,²² we actively pursue the goal to develop simple, well-defined activators. In this context, we became interested in Al complexes containing ligands with soft, weakly intramolecular coordinating, phosphine groups. Our target compound is the amide- AlMe_2 complex $\text{Ph}_2\text{P}(\text{DIPP})\text{NAlMe}_2$ in which an α - Ph_2P -substituent potentially blocks a coordination site on the Al center and a large bulky DIPP -substituent prevents oligomerization (Scheme 1, $\text{DIPP} = 2,6\text{-iPr}_2\text{-C}_6\text{H}_3$). Due to a hard-soft mismatch of the $\text{Al}\cdots\text{P}$ contacts such bonds are labile and therefore these complexes could be considered to be “masked” Lewis acids. Investigations towards the activation of

^aInorganic and Organometallic Chemistry, University of Erlangen-Nürnberg, Egerlandstrasse 1, 91058 Erlangen, Germany. E-mail: sjoerd.harder@fau.de

^bDutch Polymer Institute (DPI), P. O. Box 902, 5600 AX Eindhoven, Netherlands

^cStratingh Institute, University of Groningen, Nijenborgh 4, 9747 AG Groningen, Netherlands

† Electronic supplementary information (ESI) available: Crystallographic details and selected ^1H spectra. CCDC 1528561–1528566. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c7dt00318h

Scheme 1 Proposed structures of the amide- AlMe_2 complex and activation of $\text{Cp}^*_2\text{ZrMe}_2$.

$\text{Cp}^*_2\text{ZrMe}_2$ as a polymerization catalyst unexpectedly showed a completely different course. The complex showed FLP-type reactivity and is one of the few Al/P FLPs that can activate $\text{C}=\text{C}$ double bonds irreversibly. We here report the synthesis and structure of Al-amide reagents with phosphine substituents, evaluate initial efforts to use them as olefin polymerization catalyst activators and subsequently discuss their application in small molecule activation by FLP-type reactivity.

Results and discussion

We chose to use the readily synthesized, oxidation stable, and the literature known²³ phosphinoamine ligand $\text{Ph}_2\text{P(DIPP)NH}$ as the precursor for Al complexes with a “masked” Lewis-acidity. The reaction of $\text{Ph}_2\text{P(DIPP)NH}$ with Me_3Al in toluene at 100 °C over three hours cleanly gave the expected $\text{Ph}_2\text{P(DIPP)NAlMe}_2$ complex in 92% yield. The ^{31}P NMR spectrum shows one singlet signal at $\delta = 35.8$ ppm whereas its ^1H NMR reveals the Al–Me signal as a doublet at $\delta = -0.12$ ppm ($^3J_{\text{PH}} = 3.4$ Hz). The occurrence of magnetic coupling between the (Me)H and P nuclei suggests P–Al coordination either through a strained three-membered P–N–Al ring or a larger six-membered ring (Scheme 1).

X-ray analysis of $\text{Ph}_2\text{P(DIPP)NAlMe}_2$ revealed its dimeric nature (Fig. 1). The centrosymmetric dimer contains a central six-membered heterocyclic $\text{Al}_2\text{N}_2\text{P}_2$ ring in chair conformation. The valence bond angles around N add up to $359.2(7)^\circ$, indicating a planar conformation. The DIPP substituents are oriented perpendicular to the ring. The Al–P' distance is $2.5080(5)$ Å and falls within the range of those reported for similar complexes such as $[\text{Et}_2\text{AlC}(\text{CHtBu})\text{P}(\text{Ph})\text{Et}]_2$ or $(\text{R}_2\text{PCH}_2\text{AlMe}_2)_2$ (R = Me or Ph).^{12,14} The P–N–Al angle at the trigonal N atom and the N–Al–P' angle at the tetrahedral Al center are $124.09(5)^\circ$ and $109.63(3)^\circ$, respectively.

Attempts to obtain a monomeric complex by increasing the bulk around the Al metal failed. Reactions of $i\text{Bu}_3\text{Al}$ or $t\text{Bu}_3\text{Al}$ with $\text{Ph}_2\text{P(DIPP)NH}$ gave a variety of unidentified products. This is most likely due to the fact that deprotonation of $\text{Ph}_2\text{P(DIPP)NH}$ with these bulkier reagents requires harsher reac-

Fig. 1 Molecular structure of $[\text{Ph}_2\text{P(DIPP)NAlMe}_2]_2$. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles ($^\circ$): Al–P' $2.5080(5)$, Al–N $1.9097(10)$, P–N $1.6746(10)$, Al–Me1 $1.9662(12)$, Al–Me2 $1.9952(12)$, $\text{C}_{\text{Ar}}\text{–N–Al}$ $114.39(7)$, P–N–Al $124.09(5)$, P'–Al–N $109.69(3)$, N–Al–Me1 $109.35(5)$, N–Al–Me2 $115.62(5)$, Me1–Al–P' $102.44(4)$, Me2–Al–P' $100.47(4)$, Me1–Al–Me2 $117.76(5)$.

tion conditions (120 °C for up to 2 weeks), which leads to undesired side reactions and decomposition.

The “masked” Lewis-acidity of the phosphino-coordinated Al center was tested by the addition of THF as a Lewis base. The complex readily reacts with minor amounts of THF and selectively forms the $\text{Ph}_2\text{P(DIPP)NAlMe}_2\cdot\text{THF}$ adduct. The formation of a monomeric complex can be conveniently observed by NMR as the Al–Me signal goes from a doublet with $\text{P}\cdots\text{Me}$ coupling at $\delta = -0.12$ ppm to a singlet at $\delta = -0.41$ ppm. This high field shift is in agreement with the stronger electron donating properties of THF compared to phosphine. Crystals of the THF adduct were grown from a benzene solution at 5 °C and the structure was determined by X-ray analysis (Fig. 2).

The structure has no crystallographic symmetry and contains the Al center in a distorted tetrahedral environment with valence angles varying from $108.06(10)^\circ$ to $118.93(13)^\circ$. The Al–N bond length is $1.856(2)$ Å and is shorter than that of

Fig. 2 Molecular structure of the monomeric aluminum complex $\text{Ph}_2\text{P}(\text{DIPP})\text{NAlMe}_2\cdot\text{THF}$. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Al–N 1.856(2), P–N 1.703(2), Al–Me1 1.965(3), Al–Me2 1.971(3), Al...P 3.0396(12), P–N–Al 117.25(12), P–N–C1 123.43(17), C1–N–Al 119.13(17), N–Al–Me1 110.18(12), N–Al–Me2 114.44(12), N–Al–O 108.06(10), Me1–Al–Me2 118.93(13), Me1–Al–O 102.82(11), Me2–Al–O 100.67(11).

1.9097(19) Å in the dimer. The P–N bond, on the contrary, is elongated as compared to $[\text{Ph}_2\text{P}(\text{DIPP})\text{NAlMe}_2]_2$ (1.703(2) Å vs. 1.6746(10) Å). This is likely the result of differences in the charge distribution in the P–N fragment: the P–Al contact in the dimer results in increased negative hyperconjugation of negative charge from N^- to PPh_2 . This explains why the dimer displays a longer Al–N and a shorter P–N bond when compared to the monomer. The Al...P distance of 3.0396(12) Å is too long to be considered a bonding contact. This conclusion is supported by the close to trigonal coordination sphere around N: C1–N–Al 119.13(17)°, P1–N–Al 117.25(12)°, and C1–N–P1 123.43(17)° ($\Sigma_{\text{bond angles}} = 359.81(26)^\circ$).

In order to evaluate the potential application of $[\text{Ph}_2\text{P}(\text{DIPP})\text{NAlMe}_2]_2$ as a Me^- abstracting agent we studied its reactivity towards $\text{Cp}^*_2\text{ZrMe}_2$. A mixture of both complexes was dissolved in C_6D_6 and allowed to react while the reaction progress

was monitored by ^1H NMR spectroscopy. At room temperature, no reaction was observed even after several days. Attempts to force reactivity by heating the sample led in all cases to decomposition into unidentified products. It is likely that the anticipated highly reactive $[\text{Cp}^*_2\text{ZrMe}]^+$ cation is not stable under these forced conditions. In order to trap the potentially formed complex $[\text{Cp}^*_2\text{ZrMe}]^+ [\text{Ph}_2\text{P}(\text{DIPP})\text{NAlMe}_3]^-$ we introduced allyl methyl sulfide as a trapping agent. This method has been previously used by Hessen and coworkers who successfully trapped highly reactive cationic metallocene species.²⁴ The unsaturated alkene part of the thioether mimics the first alkene during polymerization and could insert into the Zr–Me bond. Subsequent intramolecular coordination of the thioether function would form a stable cationic complex that shows no further polymerization activity (Scheme 2, pathway a). Addition of the thioether to a solution of $[\text{Ph}_2\text{P}(\text{DIPP})\text{NAlMe}_2]_2$ and $\text{Cp}^*_2\text{ZrMe}_2$ in C_6D_6 at room temperature, however, led to the formation of a new complex which, over the course of three days at 55 °C, became the predominant species. Cooling of the C_6D_6 solution led to the formation of single crystals suitable for X-ray analysis. A crystal structure determination (Fig. 3) surprisingly showed a completely different product that contains no Zr but instead the alkenyl thioether has been activated by an Al/P FLP (Scheme 2, pathway b).

The product has no crystallographic symmetry and crystallizes with two independent molecules in the asymmetric part of the unit cell. Both molecules are structurally similar, the only difference being a slight disorder in the S–Me group of one of the molecules. The Al–N bond of 1.969(3) Å is much longer than that in the dimer and the THF adduct (1.908(1) Å and 1.856(2) Å, respectively). The Al–Me bonds (avg. 1.985(5) Å) are slightly longer than those in the dimer or the THF adduct (avg. 1.9806(13) Å and 1.968(3) Å, respectively). This underscores the zwitterionic character of the product in which there is a formal negative charge on Al and positive charge on P. The P–C2 bond and the P–C(aryl) bond are 1.820(4) Å and 1.810(5) Å comparable in length and significantly shorter than the P–C(aryl) bonds in the dimer and THF-adduct (1.8359(11) Å and 1.844(3) Å, respectively). This underscores the phosphonium character of the P center (for comparison, P–C distances

Scheme 2 Proposed (a) vs. observed (b) reactivity of $[\text{Ph}_2\text{P}(\text{DIPP})\text{NAlMe}_2]_2$ with $\text{Cp}^*_2\text{ZrMe}_2$ in the presence of allyl methyl sulfide.

Fig. 3 Molecular structure of $[(\text{DIPP})\text{N}-\text{Ph}_2\text{P}-\text{CH}(\text{CH}_2\text{SMe})\text{CH}_2]\text{AlMe}_2$. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles ($^\circ$), values given are the average of both molecules: Al–N 1.968(3), Al–C1 2.016(5), Al–Me1 1.983(5), Al–Me2 1.986(5), P–C2 1.820(4), P–N 1.623(3), C1–C2 1.537(6), P–N–Al 111.9(2), N–Al–C1 91.4(2), N–Al–Me1 112.9(2), N–Al–Me2 112.9(2), Me1–Al–C1 115.3(2), Me2–Al–C1 113.2(2), Me1–Al–Me2 110.3(2).

Fig. 4 Molecular structure of the $[(\text{DIPP})\text{N}-\text{Ph}_2\text{P}-\text{CH}(\text{C}_4\text{H}_9)\text{CH}_2]\text{AlMe}_2$. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles ($^\circ$), average values: Al–N 1.974(3), Al–C1 2.015(3), Al–Me1 1.990(3), Al–Me2 1.976(4), P–C2 1.821(3), P–N 1.622(2), C1–C2 1.545(4), P–N–Al 111.24(13), N–Al–C1 92.29(11), N–Al–Me1 113.36(14), N–Al–Me2 108.56(13), Me1–Al–C1 118.55(15), Me2–Al–C1 107.07(15), Me1–Al–Me2 115.00(15).

in Ph_4P^+ and Ph_3P are 1.792(2) Å²⁵ and 1.828(5) Å,²⁶ respectively).

This reactivity indicates that the Al–P bond in $[\text{Ph}_2\text{P}(\text{DIPP})\text{NAlMe}_2]_2$ indeed can be readily split to form a Lewis-acidic monomer. The dimer is not able to abstract a Me group from Cp^*ZrMe_2 but can in the presence of an alkene reacting as a FLP reagent.

Whereas C=C bond activation by P/B FLPs is well-documented,²⁷ there are only a few examples of P/Al FLPs for alkene activation by Stephan and coworkers.²⁰ While $t\text{Bu}_3\text{P}/\text{Al}(\text{C}_6\text{F}_5)_3$ reacts with ethylene to form the addition product $t\text{Bu}_3\text{P}^+-\text{CH}_2\text{CH}_2-\text{Al}^-(\text{C}_6\text{F}_5)_3$, addition of ethylene to the FLP combination $\text{Me}_3\text{P}/\text{Al}(\text{C}_6\text{F}_5)_3$ is reversible. Reactions with substituted alkenes (propene, 1-butene) led to deprotonation and formation of allylic species that C–C couple by subsequent alkene insertion. We recently reported an example of addition of 1-hexene to an FLP containing a highly Lewis-acidic cationic Al species $[(\text{DIPPn}(\text{nacnac}))\text{AlMe}]^+$ and the weak Lewis base Ph_3P .²⁸ The herein observed addition of a substituted alkene to an FLP containing a weak arylphosphine Lewis base and a neutral Al center is remarkable. This urged us to investigate the FLP reactivity of $[\text{Ph}_2\text{P}(\text{DIPP})\text{NAlMe}_2]_2$ in more depth.

The alkene-activation product $[(\text{DIPP})\text{N}-\text{Ph}_2\text{P}-\text{CH}(\text{CH}_2\text{SMe})\text{CH}_2]\text{AlMe}_2$ can be directly obtained in much higher yields (up to 77%) upon a reaction of $[\text{Ph}_2\text{P}(\text{DIPP})\text{NAlMe}_2]_2$ with allyl methyl sulfide at 70 °C. Its ¹H NMR spectrum is complicated as a stereocenter is formed upon activation of the double bond. This leads to diastereotopicity for groups like AlMe_2 , Ph_2P and CHMe_2 (see ESI Fig. S3†). The Al–Me doublet (−0.12 ppm) from $[\text{Ph}_2\text{P}(\text{DIPP})\text{NAlMe}_2]_2$ disappears and two Al–Me singlets show up at 0.07 and −0.17 ppm. The *i*Pr groups show four different doublets (Me) and two septets (CH). The proton at C2 shows up as a broad multiplet around 3.43 ppm

due to the stereocenter (coupling to different H nuclei at neighboring CH_2) and coupling to the P nucleus. The two CH_2 groups originating from the thioether display four individual multiplets at 2.61, 1.83, 1.60, and 0.42 ppm. The ³¹P signals shift only slightly from 36.3 to 35.8 ppm.

The “masked” FLP $[\text{Ph}_2\text{P}(\text{DIPP})\text{NAlMe}_2]_2$ also smoothly reacts with the unactivated alkene 1-hexene. A similar insertion product is obtained in good yields (up to 79%) after briefly heating (70 °C) a toluene solution (Fig. 4).

The molecular structure contains no crystallographic symmetry and is very similar to that of $[(\text{DIPP})\text{N}-\text{Ph}_2\text{P}-\text{CH}(\text{CH}_2\text{SMe})\text{CH}_2]\text{AlMe}_2$. The Al–N, Al–Me, Al–C1, P–C2, and P–N bond lengths are within error of those for the thioether complex. Also, the NMR spectra of the 1-hexene insertion product show similarities to those of $[(\text{DIPP})\text{N}-\text{Ph}_2\text{P}-\text{CH}(\text{CH}_2\text{SMe})\text{CH}_2]\text{AlMe}_2$ (see the ESI†).

The smooth reaction of $[\text{Ph}_2\text{P}(\text{DIPP})\text{NAlMe}_2]_2$ with alkenes prompted us to study its reactivity towards other small molecules. Placing a suspension of $[\text{Ph}_2\text{P}(\text{DIPP})\text{NAlMe}_2]_2$ in benzene under a CO_2 atmosphere at room temperature led to a clear solution after 30 minutes. The product was directly crystallized from the reaction mixture at 5 °C and a crystal structure determination revealed a centrosymmetric dimeric complex (Fig. 5). The structure shows that two CO_2 molecules are inserted into the Al–N bonds, resulting in an eight-membered heterocycle $\text{Al}_2\text{C}_2\text{O}_4$. The ring is made of two carboxylate units that bridge two AlMe_2 moieties. The coordination geometries around C and N are trigonal planar with $\Sigma_{\text{bond angles}} = 359.9(3)^\circ$ and $\Sigma_{\text{bond angles}} = 359.4(3)^\circ$, respectively. Thus C and N can be considered sp^2 -hybridized. Additionally, the substructure NCO_2 is almost planar suggesting an extended delocalized system. The C–N bond distance is shorter than a typical C–N single bond (around 1.47 Å) but longer than a typical C=N

Fig. 5 Molecular structure of the C_{2h} isomer of $[\text{Ph}_2\text{P}(\text{DIPP})\text{N}(\text{CO}_2)\text{AlMe}_2]_2$. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Al–O1 1.8279(9), Al–O2' 1.8571(9), Al–Me1 1.9532(14), Al–Me2 1.9547(13), C–O1 1.2866(13), C–O2 1.2701(14), C–N 1.3580(14), P–N 1.7849(10), O1–C–O2 122.18(10), N–C–O1–O2 177.5(2), O1–Al–O2' 100.56(4), O1–Al–Me1 111.35(5), O1–Al–Me2 106.73(5), O2'–Al–Me1 107.86(6), O2'–Al–Me2 104.48(5), Me1–Al–Me2 123.31(6).

double bond (around 1.28 Å) indicating some delocalization of the N lone-pair over the carboxylate unit: $\text{Ph}_2\text{P}(\text{DIPP})\text{N}^+=\text{C}(\text{O})^-_2$. The P atom is not part of the delocalized structure as the lone-pair of the P lies approximately in the NCO_2 -plane. As for the C–O bond distances, they are between a single (*circa* 1.43 Å) and a double bond (*circa* 1.21 Å).²⁹

The ^{31}P NMR spectrum displays a singlet at $\delta = 65.6$ ppm. The ^1H NMR spectrum, however, revealed that in solution two stereoisomers coexist. This observation is similar to that in earlier reported work on FLP reactivity in an aluminum hydrazine complex.⁸ On account of a C–N double bond character either a C_{2h} or C_{2v} isomer could be formed (Scheme 3). Assuming a solution structure in which the $\text{Al}_2\text{C}_2\text{O}_4$ ring is on average planar, the C_{2h} isomer has a C_2 axis perpendicular to the ring whereas the C_{2v} isomer has a C_2 axis through both Al centers (in both cases the $\text{Al}_2\text{C}_2\text{O}_4$ ring is a mirror plane).

In the C_{2h} -isomer, only one signal for the methyl substituents on the aluminum at $\delta = -0.56$ ppm is observed. In the C_{2v} -isomer, however, two different signals ($\delta = -0.55$ ppm and $\delta = -0.30$ ppm) in a ratio 1 : 1 are observed: two Me groups face the DIPP substituents whereas the others face the Ph_2P -substituents. At room temperature the two isomers coexist in a ratio of 3 : 4 (C_{2h} : C_{2v}). The ^{13}C spectra show the carbon atom of the inserted CO_2 molecule at $\delta = 162.7$ ppm and $\delta = 162.8$ ppm for

the two isomers. Fontaine and coworkers described a similar insertion of CO_2 into the CH_2 –Al bond in $\text{R}_2\text{PCH}_2\text{AlMe}_2$ and obtained the product $\text{R}_2\text{PCH}_2\text{CO}_2\text{AlMe}_2$ (R = Me or Ph).¹⁴ Prior to product formation, however, FLP reactivity led to the expected cyclic product with a five-membered P–C–Al–C(O)–O ring that rearranged to $\text{R}_2\text{PCH}_2\text{CO}_2\text{AlMe}_2$.

To gain more insight into the insertion mechanism, the reaction was followed by ^{31}P NMR spectroscopy. The dimer $[\text{Ph}_2\text{P}(\text{DIPP})\text{NAlMe}_2]_2$ is poorly soluble in aromatic solvents. Addition of CO_2 , however, gave after shaking rapid dissolution of the substrate. The first ^{31}P NMR spectrum was measured ten minutes after the addition of CO_2 and further ^{31}P NMR spectra were recorded every two hours over the course of 18 hours without stirring. Two main intermediates could be identified. The first one appeared immediately at the start and disappeared after 8 hours. The signal of the second intermediate species with a ^{31}P chemical shift of 4.5 ppm increased along with the vanishing of the first intermediate and disappeared in less than two hours after its formation to give rise to the product. Unfortunately, this species could not be isolated and the NMR spectroscopic data obtained could not give clear structural information. Hence, the CO_2 insertion mechanism was a subject of further study. In order to get a better understanding of the rearrangement and insertion of CO_2 into the Al–N bond, the complex was reacted with isocyanates. Two possible adducts can be expected from the reaction of isocyanates with FLPs.³⁰ Addition to the C=O bond gives an Al-alkoxide whereas addition to the C=N bond results in an Al-amide as the product.

One equivalent of the isocyanate $\text{DIPP-N}=\text{C}=\text{O}$ was added to a suspension of $[\text{Ph}_2\text{P}(\text{DIPP})\text{NAlMe}_2]_2$ in benzene and stirred at room temperature until a clear solution was obtained. Formation of the Al-alkoxide was observed after one day (Scheme 4). After two days the solvent was removed and the white solid was washed with hexane. Crystals suitable for X-ray diffraction were obtained from a benzene solution of the product upon storage at room temperature. The crystal structure determination revealed addition to the C=O bond resulting in the formation of an Al-alkoxide product (Fig. 6).

The crystal structure of $[(\text{DIPP})\text{N-Ph}_2\text{P-C(N-DIPP)O}]\text{AlMe}_2$ displays an Al–N–P–C–O cycle that is nearly planar. The phosphorus atom lies 0.3164(3) Å outside the N–Al–O–C least-squares-plane. The P–N1 distance of 1.6259(10) is significantly shorter than that in the dimeric CO_2 complex (1.7849(10) Å) but comparable to those in the alkene insertion products. The P–C bond length of 1.8350(12) Å is similar to those reported

Scheme 3 Reaction of $\text{Ph}_2\text{P}(\text{DIPP})\text{NAlMe}_2$ with CO_2 giving two stereoisomers with C_{2h} and C_{2v} symmetry.

Scheme 4 Reaction of $\text{Ph}_2\text{P}(\text{DIPP})\text{NAlMe}_2$ with $\text{DIPP-N}=\text{C}=\text{O}$.

Fig. 6 Molecular structure of $[(\text{DIPP})\text{N}-\text{Ph}_2\text{P}-\text{C}(\text{N-DIPP})\text{O}]\text{AlMe}_2$. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Al–O 1.8324(10), Al–Me1 1.9727(16), Al–Me2 1.9459(17), Al–N1 1.9424(11), C1–O 1.3120(14), C1–N2 1.2725(17), P–C1 1.8350(12), P–N1 1.6259(10), O–C1–P 112.58(9), O–Al–N1 90.93(4), O–Al–Me1 112.73(6), O–Al–Me2 107.55(7), N1–Al–Me1 112.00(6), N1–Al–Me2 117.84(6), Me1–Al–Me2 113.56(8), N1–P–C1–O 18.3616(7), C1–P–N1–Al 16.8630(9).

for other $\text{C}=\text{O}$ isocyanate FLP complexes.^{31,32} The C1–O has a single bond character which is expected as similar observations have been reported.⁸ The C1–N2 bond of 1.2725(17) Å is close to that in similar complexes (*circa* 1.26 Å)^{8,31–33} and has a double bond character.

The ^1H NMR spectrum of $[(\text{DIPP})\text{N}-\text{Ph}_2\text{P}-\text{C}(\text{N-DIPP})\text{O}]\text{AlMe}_2$ shows one doublet for the *i*Pr signals of the inserted isocyanate at $\delta = 1.27$ ppm due to unhindered rotation around the N2–C_{ipso} axis. In contrast, the *i*Pr substituents of the Al-bound anilide give two doublets at $\delta = 0.32$ ppm and $\delta = 1.21$ ppm which indicates that free rotation around the N1–C_{ipso} axis is hindered by sterics. The large difference in chemical shifts (*circa* 0.9 ppm) is likely due to the ring current effects of neighboring Ph-substituents, which cause an unusually low chemical shift of 0.32 ppm. The ^{13}C spectra display a characteristic doublet for the carbon atom of the heterocycle at $\delta = 156.8$ ppm with a large $^1J_{\text{CP}}$ of 160 Hz. Important to mention is the chemical shift in the ^{31}P NMR spectroscopy with a singlet at $\delta = 7.1$ ppm. This value is quite similar to the ^{31}P chemical shift observed for the second intermediate species for the CO_2 insertion ($\delta = 4.5$ ppm). This is an indication that the CO_2 insertion might go through a similar five-membered ring with an exo-cyclic $\text{C}=\text{O}$ bond instead of a $\text{C}=\text{N}(\text{DIPP})$ moiety.

A tentative mechanism for the reaction of $[\text{Ph}_2\text{P}(\text{DIPP})\text{NAlMe}_2]_2$ with CO_2 is shown in Scheme 5. Addition of CO_2 to

Scheme 5 Hypothetical mechanism for CO_2 insertion.

the dimer may result in cleavage in two monomers. We assume the first intermediate to be $\text{Ph}_2\text{P}(\text{DIPP})\text{NAlMe}_2\text{-O}=\text{C}=\text{O}$ in which CO_2 coordinates to the monomeric species. We have not been able to isolate such an unknown Al/ CO_2 adduct by crystallization and assume the $\text{Al}\cdots\text{O}=\text{C}=\text{O}$ contact at most to be weak and highly dynamic. Some observations, however, are in favor of its existence: (i) $[\text{Ph}_2\text{P}(\text{DIPP})\text{NAlMe}_2]_2$ is insoluble in C_6D_6 but addition of CO_2 immediately results in a clear solution. (ii) The ^{31}P NMR spectrum shows a singlet at 51.7 ppm, very similar to the one of the monomeric species $\text{Ph}_2\text{P}(\text{DIPP})\text{NAlMe}_2\cdot\text{THF}$ ($\delta = 51.1$ ppm). (iii) The ^1H NMR spectrum of the dimer displays a characteristic doublet for the Me–Al groups that is due to coupling with P. This coupling disappears after CO_2 addition. (iv) The possible existence of such intermediates is based on a calculational study by Uhl *et al.*¹¹ Any hard claims for such an Al/ CO_2 adduct, however, can only be made by providing crystal structure evidence which is part of our future work.

Coordination of CO_2 to the Al center activates the $\text{C}=\text{O}$ bond and is followed by a phosphine nucleophilic attack. The heteroatom-cycle Al–N–P–C–O is similar to that in the product obtained in reaction with $\text{DIPP-N}=\text{C}=\text{O}$. The rather acute bond angle O–Al–N of 90.93(4)° at the tetrahedral Al center indicates ring strain. Since Al–N bonds are generally weaker than Al–O bonds (bond dissociation energies in diatomic molecules at 298 K: Al–N: $\leq 368 \pm 15$ kJ mol^{−1}; Al–O: 501.9 ± 10.6 kJ mol^{−1})^{29b} there is a higher probability for ring opening by breaking the Al–N bond. This is followed by rearrangement to the final product $[\text{Ph}_2\text{P}(\text{DIPP})\text{N}(\text{CO}_2)\text{AlMe}_2]_2$ in which the CO_2 reagent is formally inserted into the N–Al bond. Alternatively, a second CO_2 molecule first inserts into the N–Al

bond and this is followed by elimination of the CO₂ molecule captured by the P/Al FLP (similar as reported by Uhl and coworkers).¹¹

Conclusions

We have reported a simple high yielding route to the phosphino-amide AlMe₂ complex, [Ph₂P(DIPP)NAlMe₂]₂. The complex is dimeric but the weak Al–P interaction is broken upon addition of THF to form Ph₂P(DIPP)NAlMe₂·THF showing the “masked” Lewis acidity of this complex. Investigations towards the activation of Cp*₂ZrMe₂ as a polymerization catalyst were unsuccessful and instead showed unexpected FLP reactivity. [Ph₂P(DIPP)NAlMe₂]₂ can activate alkenes to irreversibly form the Al/P insertion product. Activation of C=C bonds by Al/P FLPs is rare and this complex is one of the few complexes capable of doing so. Further investigations into its FLP reactivity showed that it also undergoes insertion reactions with CO₂ and DIPP–N=C=O. This gives either CO₂ insertion into the N–Al bond leading to the product [Ph₂P(DIPP)N(CO₂)Al(Me)₂]₂ or C=O insertion into the P–Al bond giving [(DIPP)N–Ph₂P–C(N–DIPP)O]AlMe₂. The facile synthetic accessibility and high reactivity of [Ph₂P(DIPP)NAlMe₂]₂ towards a range of substrates (especially alkenes) makes this complex an interesting target for further reactivity studies or potential applications in catalysis.

Experimental

General considerations

All experiments were carried out under an inert atmosphere using standard Schlenk and glove box techniques. Benzene and THF were dried over sodium, distilled and stored under a nitrogen atmosphere. Toluene, pentane, hexane and Et₂O were degassed by bubbling nitrogen through the solvent reservoir, dried over activated alumina columns and stored under an inert atmosphere. Starting materials were purchased from Sigma-Aldrich, ACROS, and ABCR and were used as received. Chlorodiphenylphosphine was freshly distilled prior to use. DIPP–N=C=O and DIPPNH₂ were dried over CaH₂ and freshly distilled prior to use. Methylallyl thioether and 1-hexene were stored over activated 4 Å molecular sieves prior to use and Ph₂P(DIPP)NH was synthesized according to the literature procedure.²³ CO₂ (N55) was purchased from Air Liquid and used without further purification. NMR spectra have been measured on Bruker Avance DPX-300 MHz or Avance III HD 400 MHz and HD 600 MHz spectrometers. Elemental analysis was performed with a Hekatech Eurovector EA3000 analyzer. All crystal structures have been measured on a Bruker Smart diffractometer with a CCD detector or a SuperNova (Agilent) diffractometer with dual Cu and Mo microfocus sources and an Atlas S2 detector. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 1528561 [Ph₂P(DIPP)

NAlMe₂]₂, 1528562 Ph₂P(DIPP)NAlMe₂·THF, 1528563 [(DIPP)N–Ph₂P–CH(CH₂SMe)CH₂]AlMe₂, 1528564 [(DIPP)N–Ph₂P–CH(C₄H₉)CH₂]AlMe₂, 1528565 [Ph₂P(DIPP)N(CO₂)Al(Me)₂]₂, 1528566 [(DIPP)N–Ph₂P–C(N–DIPP)O]AlMe₂.

Synthesis of [Ph₂P(DIPP)NAlMe₂]₂. Ph₂P(DIPP)NH (3.08 g, 8.52 mmol) was dissolved in toluene (20 mL) and AlMe₃ (4.5 mL, 2 M in hexanes, 9.0 mmol) was added. The resulting solution was stirred at 100 °C for 3 h. The solvent was removed under vacuum and the remaining solid was washed with hexane (3 × 5 mL) and dried under vacuum to give [Ph₂P(DIPP)NAlMe₂]₂ as a white solid (3.23 g, 3.91 mmol, 92%). Crystals for X-ray analysis were grown in hot toluene.

¹H NMR (400 MHz, C₆D₆, 25 °C): δ (ppm) = –0.12 (d, ³J_{HP} = 3.4 Hz, 6H, Al(CH₃)₂), 0.45 (d, ³J_{HH} = 6.7 Hz, 6H, *i*Pr–CH₃), 1.30 (d, ³J_{HH} = 6.7 Hz, 6H, *i*Pr–CH₃), 3.87 (sept., ³J_{HH} = 6.7 Hz, 2H, *i*Pr–CH), 6.92–6.99 (m, 6H, Ar), 7.02–7.06 (m, 2H, Ar), 7.11–7.14 (m, 1H, Ar), 7.51–7.59 (m, 4H, Ar).

³¹P NMR (162 MHz, C₆D₆): δ = 35.8 (s) ppm.

Elemental analysis, formula C₅₂H₆₆Al₂N₂P₂ (834.44): calcd C 74.80, H 7.97, N 3.35; found C 75.09, H 7.98, N 3.18.

Due to the very low solubility in aromatic solvents, no assignable ¹³C spectrum could be obtained. Addition of polar solvents to increase solubility led to dimer cleavage (*vide infra*).

Synthesis of Ph₂P(DIPP)NAlMe₂·THF. [Ph₂P(DIPP)NAlMe₂]₂ (50.0 mg, 60.0 μmol) was suspended in C₆D₆ (0.6 mL) and a few drops of THF-*d*₈ were added. This led to the immediate formation of a clear solution of Ph₂P(DIPP)NAlMe₂·THF. Full conversion was determined by ¹H-NMR analysis. Dropwise addition of hexanes to the solution led to the immediate formation of crystalline material suitable for X-ray analysis.

¹H NMR (400 MHz, C₆D₆, 25 °C): δ (ppm) = –0.41 (s, 6H, Al(CH₃)₂), 0.77 (d, ³J_{HH} = 6.9 Hz, 6H, *i*Pr–CH₃), 1.25 (d, ³J_{HH} = 6.9 Hz, 6H, *i*Pr–CH₃), 3.72 (sept., ³J_{HH} = 6.9 Hz, 2H, *i*Pr–CH), 6.92–6.99 (m, 6H, Ar), 7.02–7.07 (m, 2H, Ar), 7.08–7.14 (m, 7H, Ar), 7.64–7.70 (m, 4H, Ar).

¹³C NMR (75 MHz, C₆D₆, 25 °C): δ (ppm) = –7.3 (Al–CH₃), 24.4 (*i*Pr–CH₃), 24.9 (s, THF), 25.6 (*i*Pr–CH₃), 28.7 (*i*Pr–CH), 71.8 (s, THF), 124.0 (d, ³J_{CP} = 2.26, Ar), 124.5 (d, ⁴J_{CP} = 2.26, Ar), 127.9 (s, Ar), 128.4 (s, Ar), 135.0 (d, ²J_{CP} = 23.40, Ar), 143.1 (d, ¹J_{CP} = 24.91 Ar), 146.5 (*ortho*-Ar), 147.4 (d, ²J_{CP} = 3.02, *ipso*-Ar).

³¹P NMR (162 MHz, C₆D₆, 25 °C): δ (ppm) = 51.1 (s).

Elemental analysis, formula C₃₀H₄₁AlNOP (489.27): calcd C 73.59, H 8.44, N 2.86; found C 73.27, H 8.44, N 2.67.

Reaction of [Ph₂P(DIPP)NAlMe₂]₂ with Cp*₂ZrMe₂ in the absence or presence of methylallyl thioether. [Ph₂P(DIPP)NAlMe₂]₂ (29.4 mg, 35.3 μmol) and Cp*₂ZrMe₂ (29.9 mg, 76.3 μmol) were dissolved in C₆D₆ (0.6 mL). The sample was shaken for 30 seconds and the reaction progress was monitored *via* ¹H NMR spectroscopy by recording spectra every hour for the first four hours and then the next day. No reaction was observed. Methylallyl thioether was added to trap and stabilize a potential cationic complex. Reaction progress was again monitored by ¹H NMR spectroscopy and the sample was stored for two days at room temperature: no reaction was observed. Heating the complex to 55 °C overnight resulted in conversion. Cooling the solution yielded colorless crystals

which upon X-ray analysis proved to be [(DIPP)N-Ph₂P-CH(CH₂SMe)CH₂][AlMe₂]. The ¹H NMR spectrum matches this product as well.

Synthesis of [(DIPP)N-Ph₂P-CH(CH₂SMe)CH₂][AlMe₂]. [Ph₂P(DIPP)NAlMe₂]₂ (0.244 g, 293 μmol) was suspended in toluene (10 mL) and methylallyl thioether (80.0 μL, 731 μmol) was added at once. The resulting mixture was heated at 70 °C for 30 minutes, after which a clear solution was formed. The solution was cooled to room temperature and stirred for another three hours. The mixture was concentrated to 1/3 of its original volume and cooled to give a colorless powder that was isolated by centrifugation. Concentration of the mother liquor yielded a second crop of crystalline material. Both solids were combined and washed with pentane (2 × 2 mL) to give [(DIPP)N-Ph₂P-CH(CH₂SMe)CH₂][AlMe₂] as a colorless solid (277 mg, 449 μmol, 77%).

¹H NMR (300 MHz, C₆D₆, 25 °C) δ (ppm) = −0.17 (s, 3H, Al-CH₃), −0.07 (d, ³J_{HH} = 6.7 Hz, 3H, *i*Pr-CH₃), 0.07 (s, 3H, Al-CH₃), 0.37–0.48 (m, 1H, Al-CH₂), 0.45 (d, ³J_{HH} = 6.8 Hz, 3H, *i*Pr-CH₃), 1.24 (d, ³J_{HH} = 6.5 Hz, 3H, *i*Pr-CH₃), 1.34 (d, ³J_{HH} = 6.7 Hz, 3H, *i*Pr-CH₃), 1.50–1.70 (m, 1H, Al-CH₂), 1.73 (s, 3H, S-CH₃), 1.82 (m, 1H, S-CH₂), 2.61 (m, 1H, S-CH₂), 3.12 (hept, ³J_{HH} = 7.0 Hz, 1H, *i*Pr-CH), 3.33–3.53 (m, 1H, (P)CH), 3.92 (sept., ³J_{HH} = 6.5 Hz, 1H, *i*Pr-CH), 6.72–7.13 (m, 11H, Ar), 7.58–7.69 (m, 2H, Ar).

³¹P NMR (121 MHz, C₆D₆, 25 °C) δ (ppm) = 36.3 (s).

¹³C NMR (75 MHz, C₆D₆, 25 °C) δ (ppm) = −6.0 (s, Al-CH₃), −5.5 (s, Al-CH₃), 10.3 (s, Al-CH₂), 16.8 (s, S-CH₃), 23.3 (s, *i*Pr-CH₃), 24.5 (s, *i*Pr-CH₃), 25.9 (s, *i*Pr-CH₃), 27.7 (s, *i*Pr-CH₃), 28.1 (s, *i*Pr-CH), 28.4 (s, *i*Pr-CH), 37.6 (d, ¹J_{CP} = 73.5 Hz, PCH), 41.0 (d, ²J_{CP} = 10.2 Hz, S-CH₂), 122.8 (s, Ar), 123.9 (s, Ar), 124.7 (d, ⁴J_{CP} = 3.0 Hz, Ar), 125.0 (d, ⁴J_{CP} = 2.9 Hz, Ar), 125.6 (d, ⁴J_{CP} = 3.2 Hz, Ar), 128.6 (s, Ar), 128.8 (s, Ar), 129.0 (d, ²J_{CP} = 10.6 Hz, Ar), 129.9 (s, Ar), 132.4 (d, ³J_{CP} = 3.1 Hz, Ar), 132.8 (d, ⁴J_{CP} = 2.6 Hz, Ar), 133.2 (d, ³J_{CP} = 7.2 Hz, Ar), 133.6 (d, ³J_{CP} = 8.7 Hz, Ar), 137.7 (d, ³J_{CP} = 7.0 Hz, Ar), 147.5 (d, ³J_{CP} = 4.5 Hz, Ar), 147.9 (d, ³J_{CP} = 5.6 Hz, Ar).

³¹P NMR (121 MHz, C₆D₆): δ = 36.3 (s) ppm.

Elemental analysis, formula C₃₀H₄₁AlNPS (505.25): calcd C 71.26, H 8.17, N 2.77; found C 70.69, H 7.99, N 2.46.

Synthesis of [(DIPP)N-Ph₂P-CH(C₄H₉)CH₂][AlMe₂]. [Ph₂P(DIPP)NAlMe₂]₂ (0.231 g, 0.277 mmol) was suspended in toluene (10 mL) and 1-hexene (0.10 mL, 0.798 mmol) was added. The mixture was heated to 70 °C for 30 min after which a clear solution was obtained. The solution was stirred at room temperature for 3 hours and all of the solvent was evaporated under high vacuum. The resulting white powder was washed with pentane (3 × 2 mL). After drying under high vacuum the product was obtained as a white powder (0.218 g, 0.435 mmol, 79%).

¹H NMR (300 MHz, C₆D₆, 25 °C) δ (ppm) = −0.13 (s, 3H, Al-CH₃), 0.03 (d, ³J_{HH} = 6.7 Hz, 3H, *i*Pr-CH₃), 0.10 (s, 3H, Al-CH₃), 0.31–0.18 (m, 1H, Al-CH₂), 0.47 (d, ³J_{HH} = 6.8 Hz, 3H, *i*Pr-CH₃), 0.50–0.63 (m, 1H, Al-CH₂), 0.76 (t, ³J_{HH} = 7.2 Hz, 3H, CH₃), 0.92–1.25 (m, 4H, CH₂), 1.29 (d, ³J_{HH} = 6.6 Hz, 3H, *i*Pr-CH₃), 1.36 (d, ³J_{HH} = 6.7 Hz, 3H, *i*Pr-CH₃), 1.41–1.67 (m,

2H, CH₂), 3.05 (m, 1H, (P)CH), 3.24 (hept, ³J_{HH} = 6.9 Hz, 1H, *i*Pr-CH), 3.97 (hept, ³J_{HH} = 6.9 Hz, 1H, *i*Pr-CH), 6.80–7.13 (m, 11H, Ar), 7.60–7.71 (m, 2H, Ar).

¹³C NMR (75 MHz, C₆D₆, 25 °C) δ (ppm) = −6.0 (s, Al-CH₃), −5.4 (s, Al-CH₃), 8.2–8.5 (m, Al-CH₂), 14.3 (s, CH₂CH₃), 23.0 (s, CH₂CH₂CH₃), 24.2 (s, *i*Pr-CH₃), 24.5 (s, *i*Pr-CH₃), 26.0 (s, *i*Pr-CH₃), 27.7 (s, *i*Pr-CH₃), 28.1 (s, *i*Pr-CH), 28.4 (s, *i*Pr-CH), 29.4 (d, ²J_{CP} = 17.0 Hz, CH₂CH₂CH₂), 35.4 (d, ³J_{CP} = 5.3 Hz, CH₂CH₂CH₂), 36.3 (d, ¹J_{CP} = 75.6 Hz, PCH), 123.2 (s, Ar), 124.3 (s, Ar), 124.7 (d, ⁴J_{CP} = 2.9 Hz, Ar), 124.9 (d, ⁴J_{CP} = 2.8 Hz, Ar), 125.5 (d, ⁴J_{CP} = 3.1 Hz, Ar), 127.9 (s, Ar), 128.2 (s, Ar), 129.0 (d, ²J_{CP} = 10.4 Hz, Ar), 129.5 (s, Ar), 130.5 (s, Ar), 132.2 (d, ³J_{CP} = 3.0 Hz, Ar), 132.6 (d, ⁴J_{CP} = 2.7 Hz, Ar), 133.3 (d, ³J_{CP} = 7.1 Hz, Ar), 133.6 (d, ³J_{CP} = 8.8 Hz, Ar), 138.1 (d, ³J_{CP} = 7.0 Hz, Ar), 147.6 (d, ³J_{CP} = 4.4 Hz, Ar), 147.9 (d, ³J_{CP} = 5.4 Hz, Ar).

³¹P NMR (121 MHz, C₆D₆, 25 °C) δ (ppm) = 37.8 (s).

Elemental analysis of crystals with one co-crystallized C₆H₆, formula C₃₈H₅₁AlNP (579.79): calcd C 78.72, H 8.87, N 2.42; found C 79.07, H 9.29, N 2.79.

Synthesis of [Ph₂P(DIPP)N(CO₂)AlMe₂]₂. [Ph₂P(DIPP)NAlMe₂]₂ (0.50 g, 0.60 mmol) was suspended in benzene (5 mL). The suspension was degassed 3 times before CO₂ (0.8 bar) was added. The suspension was stirred for 30 min at room temperature after which a clear solution was obtained. Crystals were grown upon cooling (5 °C) of this solution (0.41 g, 0.89 mmol, 75%).

C_{2v}-isomer:

¹H NMR (400 MHz, C₆D₆, 25 °C): δ (ppm) = −0.55 (s, 6H, Al(CH₃)₂), −0.30 (s, 6H, Al(CH₃)₂), 0.76 (d, ³J_{HH} = 6.7 Hz, 6H, *i*Pr-CH₃), 1.26 (d, ³J_{HH} = 6.8 Hz, 6H, *i*Pr-CH₃), 3.15 (m, 2H, *i*Pr-CH), 6.92 (s, 1H, Ar), 6.97–7.06 (m, 7H, Ar), 7.09–7.15 (m, 1H, Ar), 7.52–7.61 (m, 4H, Ar).

¹³C NMR (75 MHz, C₆D₆, 25 °C): δ (ppm) = −11.0 (Al-CH₃), −10.5 (Al-CH₃), 23.2 (*i*Pr-CH₃), 25.2 (*i*Pr-CH₃), 29.4 (*i*Pr-CH), 124.4 (Ar), 128.6 (d, ³J_{CP} = 3.8 Hz, Ar), 128.9 (Ar), 130.3 (Ar), 134.8 (d, ¹J_{CP} = 25.7 Hz, Ar), 135.9 (d, ²J_{CP} = 21.1 Hz, Ar), 137.2 (d, ²J_{CP} = 6.0 Hz, *ipso*-Ar), 146.2 (*ortho*-Ar), 162.8 (d, ²J_{CP} = 110.2 Hz, O-C-O).

³¹P NMR (162 MHz, C₆D₆, 25 °C): δ (ppm) = 65.6 (s).

C_{2h}-isomer:

¹H NMR (400 MHz, C₆D₆, 25 °C): δ (ppm) = −0.56 (s, 12H, Al(CH₃)₂), 0.84 (d, ³J_{HH} = 6.7 Hz, 6H, *i*Pr-CH₃), 1.36 (d, ³J_{HH} = 6.7 Hz, 6H, *i*Pr-CH₃), 3.21 (m, 2H, *i*Pr-CH), 6.92 (s, 1H, Ar), 6.97–7.06 (m, 7H, Ar), 7.09–7.15 (m, 1H, Ar), 7.52–7.61 (m, 4H, Ar).

¹³C NMR (75 MHz, C₆D₆, 25 °C): δ (ppm) = −10.3 (Al-CH₃), 23.4 (*i*Pr-CH₃), 25.2 (*i*Pr-CH₃), 29.3 (*i*Pr-CH), 124.6 (Ar), 128.5 (d, ³J_{CP} = 3.77, Ar), 129.0 (Ar), 130.2 (Ar), 134.6 (d, ¹J_{CP} = 24.2 Hz, Ar), 136.1 (d, ²J_{CP} = 21.9 Hz, Ar), 136.8 (d, ²J_{CP} = 3.0 Hz, *ipso*-Ar), 146.2 (*ortho*-Ar), 162.7 (d, ²J_{CP} = 104.9 Hz, O-C-O).

³¹P NMR (162 MHz, C₆D₆, 25 °C): δ (ppm) = 65.6 (s).

Elemental analysis, formula C₅₄H₆₆Al₂N₂O₄P₂ (923.02): calcd C 70.27, H 7.21, N 3.03; found C 70.83, H 7.27, N 3.00.

Synthesis of [(DIPP)N-Ph₂P-C(N-DIPP)O]AlMe₂. Benzene (5 mL) was added to a mixture of [Ph₂P(DIPP)NAlMe₂]₂ (0.50 mg, 0.60 mmol) and DIPP-N=C=O (0.26 g, 1.26 mmol). The suspension was stirred over the weekend at room tempera-

ture. The solvent was removed in a vacuum and the remaining solid was washed with hexane (5 × 3 mL). The product was obtained as a white powder (0.53 g, 0.85 mmol, 71%). Suitable crystals for X-ray diffraction could be grown from a solution of the product (50 mg) in benzene (1 mL).

¹H NMR (400 MHz, C₆D₆, 25 °C): δ (ppm) = −0.17 (s, 6H, Al(CH₃)₂), 0.31 (d, ³J_{HH} = 6.7 Hz, 6H, *i*Pr-CH₃), 1.20 (d, ³J_{HH} = 6.7 Hz, 6H, *i*Pr-CH₃), 1.26 (d, ³J_{HH} = 6.9 Hz, 12H, *i*Pr-CH₃), 3.09 (sept., ³J_{HH} = 6.9 Hz, 2H, *i*Pr-CH), 3.53 (sept., ³J_{HH} = 6.7 Hz, 2H, *i*Pr-CH), 6.81–7.02 (m, 8H, Ar), 7.05–7.12 (m, 1H, Ar), 7.17–7.26 (m, 3H, Ar), 7.79–7.91 (m, 4H, Ar).

¹³C NMR (75 MHz, C₆D₆, 25 °C): δ (ppm) = −7.4 (Al-CH₃), 23.4 (*i*Pr-CH₃), 23.8 (*i*Pr-CH₃), 26.6 (*i*Pr-CH₃), 28.7 (*i*Pr-CH), 29.2 (*i*Pr-CH), 123.2 (Ar), 124.4 (Ar), 125.1 (d, ⁴J_{CP} = 2.25 Hz, Ar), 126.4 (d, ⁴J_{CP} = 3.00 Hz, Ar), 126.6 (Ar), 128.9 (d, ³J_{CP} = 12.08 Hz, Ar), 133.1 (d, ³J_{CP} = 2.25 Hz, Ar), 133.8 (d, ²J_{CP} = 9.06 Hz, Ar), 135.3 (d, ³J_{CP} = 7.45 Hz, *ortho*-Ar), 138.7 (*ortho*-Ar), 143.9 (d, ¹J_{CP} = 21.89 Hz, Ar-C-P), 147.6 (d, ²J_{CP} = 4.53 Hz, *ipso*-Ar), 156.8 (d, ¹J_{CP} = 160.02 Hz, P-C-(O)N).

³¹P NMR (162 MHz, C₆D₆, 25 °C): δ (ppm) = 7.1 (s).

Elemental analysis, formula C₃₉H₅₀AlN₂OP (620.78): calcd C 75.46, H 8.12, N 4.51; found C 74.87, H 8.12, N 4.66.

Conflict of interest

The authors declare no competing financial interest.

Acknowledgements

This research forms part of the research program of the Dutch Polymer Institute (DPI), project #728. We like to acknowledge Dr F. Heinemann (University Erlangen-Nürnberg) for measurement of part of the X-ray data.

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