Mysterious MAO

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Chapter 4

aza-MAO and Other Amine Based Al Alkyl Complexes

Chapter 4 presents the synthesis and reactivity of several *aza*-MAO and amide based three-coordinate Al complexes. Isolobal substitution of O for NR leads to well defined $(MeAlNR)_n$ clusters which are tested as potential cocatalysts. This is followed by the synthesis, characterization, and reactivity of aryl and phosphine stabilized masked three-coordinate Al complexes. Ligands containing weakly coordinating R_2P or aryl moieties allow for the isolation and characterization of highly reactive Lewis acidic Al complexes. These complexes are studied for their reactivity towards Lewis bases and zirconocenes and their cocatalytic potential is investigated.

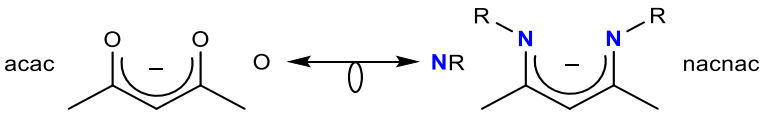
Parts of this chapter will be submitted for publication:

H. S. Zijlstra, J. Pahl, J. Penafiel, S. Harder, *to be submitted*.

4.1 Introduction

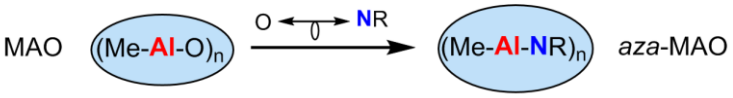
Aza-MAO, isolobal exchange of O for NR

The isolobal substitution of O for NR is a widely used concept in ligand design. Exchange of the *oxo* group O for an *imino* NR substituent allows for steric and electronic control through variation of the organic R group. A good example of this substitution is the conversion of acac (acetylacetonate) ligands into nacnac (ß-diketiminate) ligands, which has led to a versatile ligand system in which electronic and steric parameters can be tuned conveniently (Scheme 4.1).[1]



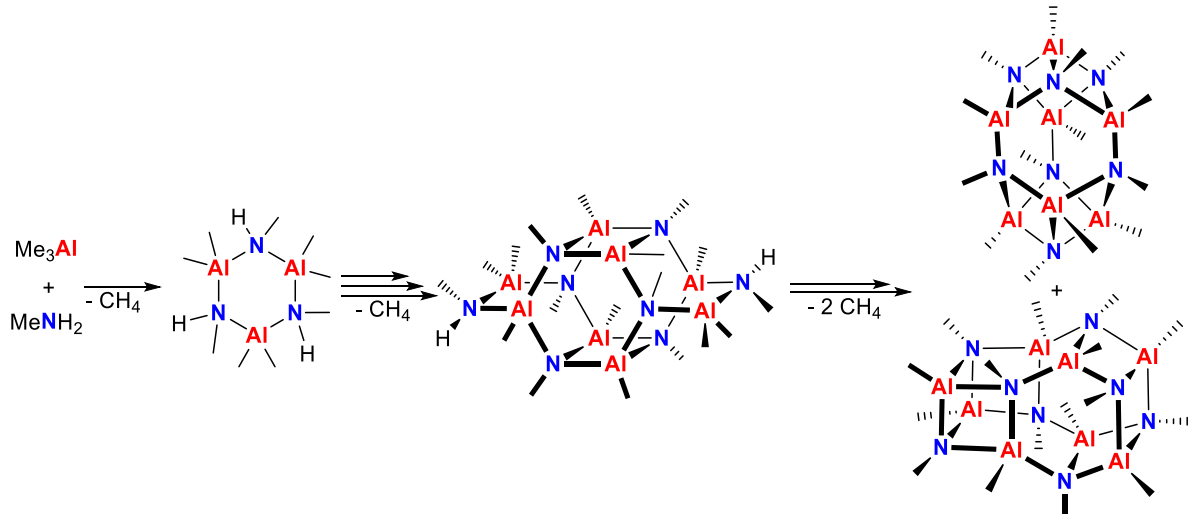
Scheme 4.1 Isolobal O for NR substitution; illustration of the conversion of acac into nacnac.

Similarly, substitution of the O group in MAO for a NR moiety leads to the conversion of $(MeAlO)_n$ into $(MeAlNR)_n$ (Scheme 4.2). Introduction of the organic R substituent allows for control over the steric and electronic properties of the formed complex.



Scheme 4.2 Isolobal conversion of $(MeAlO)_n$ into $(MeAlNR)_n$.

Such "*aza*-MAO" complexes can be synthesized by the reaction of Me_3Al with RNH_2 in which the R groups control aggregate size and structure. Small substituents such as Me undergo stepwise condensation, leading to the release of CH_4 and the formation of large cages such as $(MeAlNMe)_n$ (n = 7 or 8; Scheme 4.3).[2,3]



Scheme 4.3 Synthesis of $(MeAlNMe)_n$ (n = 7 and 8) and its observed intermediates

Reaction of Me_3Al with $MeNH_2$ initially leads to the formation of a $AlMe_3{\cdot}NH_2Me$ adduct which releases CH_4 to give $(Me_2AlNHMe)_3$.[4] This trimer decomposes at 215°C to eventually give a mixture of $(MeAlNMe)_7$ and $(MeAlNMe)_8$. Both species interconvert into each other and their ratio is strongly temperature dependent. $(MeAlNMe)_7$ was crystalographically characterized whereas $(MeAlNMe)_8$ was assigned its structure based on NMR data and a comparison with the structure of the analogues $(HAlN\textit{n}Pr)_8$ complex.[6] Attempts to clarify the reaction pathway through which these cages are formed were only partially successful. The formation necessarily involves different $(Me_2AlNHMe)_m(MeAlNMe)_n$ intermediates, but only the $(Me_2AlNHMe)_2(MeAlNMe)_6$ complex could be characterized.[7] It is interesting to note that the $(MeAlNMe)_n$ cages are isostructural to $(\textit{t}BuAlO)_n$ (n = 7 and 8) reported by Barron *et al.*[5]

Increasing the size of the R substituent leads to the formation of smaller *aza*-MAO aggregates. For example, usage of Mes- (Mes = 2,4,6-*tri*-Me-C_6H_2) and C_6F_5-NH_2 leads to the formation of the cube-like $(MeAlNR)_4$ whereas $PhNH_2$ gives a hexameric $(MeAlNPh)_6$ cage (Figure 4.1).[7-9] This cage is structurally identical to the $(\textit{t}BuAlO)_6$ analogue reported by Barron *et al.*[5a]

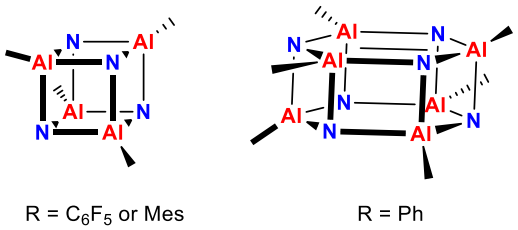
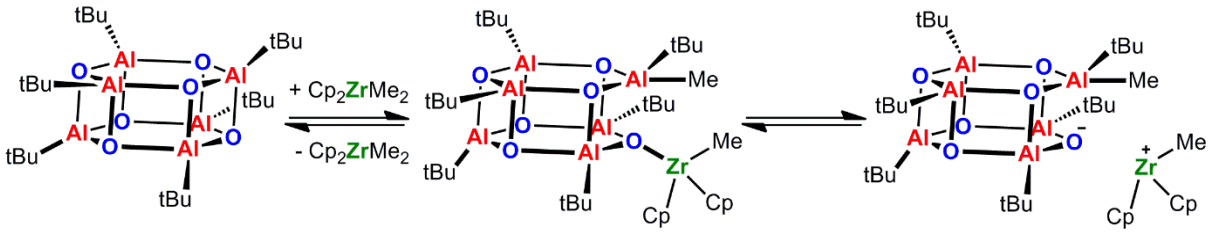


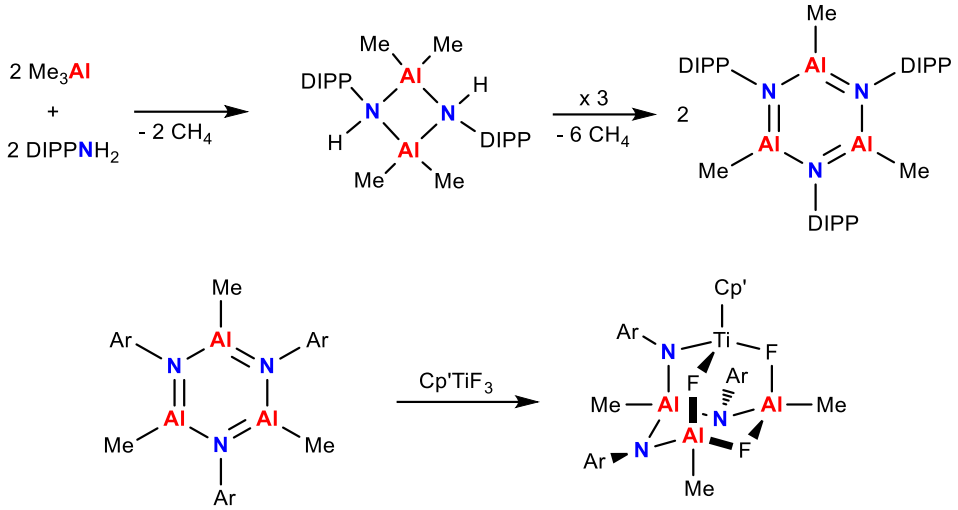
Figure 4.1 Structural motifs of reported *aza*-MAO clusters (R groups on N omitted for clarity).

Depending on the substituent, reaction conditions can also influence the structure of the product. Reaction of Me_3Al with $\textit{i}PrNH_2$ can lead to the formation of either a tetramer or hexamer.[10,11] Other small changes such as the exchange of Al-Me for Al-Ph gives $(phAlNPh)_4$ instead of $(MeAlNPh)_6$ whereas the usage of *n*Pr instead of *i*Pr leads to the formation of a tetramer instead of a hexamer.[9,12,13] All these examples clearly show that small changes in the NR or alkyl group on the Al lead to distinct variations in the obtained structure. It should, however, be noted that all the Al centers in these clusters are four-coordinate and less Lewis acidic than three-coordinate Al centers. To the best of our knowledge, none of these complexes have been studied as potential co-catalysts. Even though they do not possess Lewis acidic Al centers the *aza*-MAO clusters could react through Latent Lewis acidity. This reactivity was first proposed by Barron *et al.* based on the reactivity of their $(\textit{t}BuAlO)_n$ (n = 6-9, 12) cages (Scheme 4.4).[5c] Dissociation of an Al-O bond breaks up the cluster and provides a three-coordinate Lewis acidic Al site that possesses co-catalytic activities (see Chapter 1).



Scheme 4.4 Latent Lewis acidity as proposed by Barron *et al.*[5c]

The only known *aza*-MAO cluster containing three-coordinate Al centers is obtained from the reaction of Me_3Al with $DIPPNH_2$ (DIPP = 2,6-di-*i*Pr-C_6H_3) and was reported by Powers *et al.* (Scheme 4.5).[6] The formed alumazene, $(MeAlNDIPP)_3$, is a borazine analogue with restricted aromaticity that contains only Lewis acidic three-coordinate Al centers.

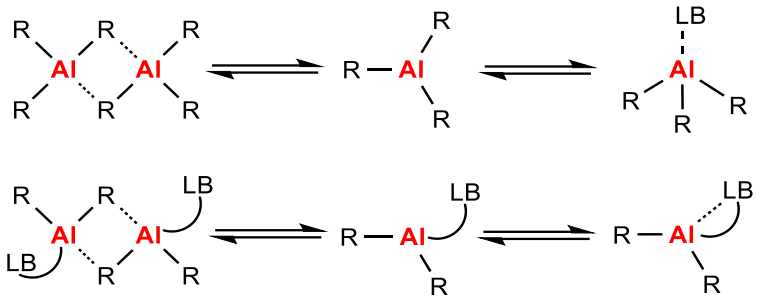


Scheme 4.5 Synthesis of alumazene and its reactivity towards $Cp'TiF_3$ (Ar = DIPP).

The increased reactivity of this complex as compared to the earlier discussed four-coordinate *aza*-MAO clusters can be seen upon mixing it with titanocene fluorides ($Cp'TiF_3$). Reaction of $(MeAlNDIPP)_3$ and $Cp'TiF_3$ leads to adamantane-like cages that are formed through fluorine/nitrogen metathesis (Scheme 4.5).[14] This reactivity makes alumazene an efficient and good precursor for the synthesis of fluoride containing imidotitanium complexes.

Complexes with a masked three-coordinate Al center

With the exception of the alumazene, all previously discussed *aza*-MAO complexes form cage structures containing only four-coordinate Al centers. These cages may or may not be able to act as cocatalysts through latent Lewis acidity (*vide supra*). Therefore related three-coordinate Al containing complexes should also be considered. However, it is challenging to obtain reactive monomeric AlR_3 complexes, since small R substituents lead to dimerization and formation of Al_2R_6 (Scheme 4.6).



Scheme 4.6 Different potential equilibria between internal and external Lewis base stabilized three-coordinate Al complexes.

Large R substituents can lead to the formation of monomeric AlR_3 complexes, but decrease the reactivity of the formed complexes; rendering them inert for applications in polymerization catalysis. The addition of a Lewis base can lead to the splitting of the R_6Al_2 dimer and the formation of a monomeric Lewis adduct. Depending on the Lewis base used, there is an equilibrium between the coordinated and non-coordinated form; this leads to a highly reactive three-coordinate Al center which will, once again, form a dimer. In order to drive this equilibrium towards the adduct side, the Lewis basic site can be included in the substituent. Now the base is always in the proximity of the Al center, which thereby constantly prevents the formation of dimers. Upon the introduction of a substrate, the Lewis base detaches from the Al center, which reveals a reactive three-coordinate Al center. Several different synthetic strategies can be used to obtain such a "masked" three-coordinate Al complex. Examples of this include the introduction of a P atom or aromatic aryl rings in the ligand core (Figure 4.2).

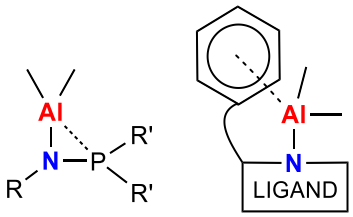
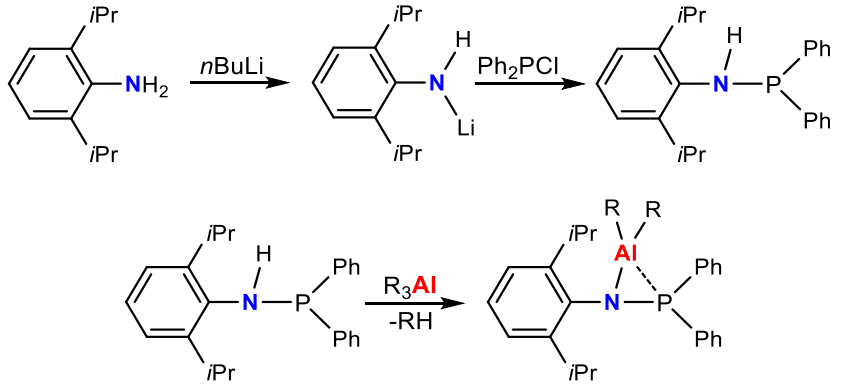


Figure 4.2 Masked three-coordinate Al amide complexes with weakly coordinating R_2P or aryl ligands.

Here both P and the aryl ring are soft donors and act as internal stabilizers of the reactive Al center. As Al is a hard acceptor a hard-soft mismatch is created, therefore only a weak bonding interaction between both donor and acceptor is anticipated. This interaction should be strong enough to stabilize the three-coordinate Al when no other substrates are around but weak enough to be readiliy broken in the presence of reactive substrates thus creating a stable but reactive highly Lewis acidic Al center. Variations of both ligand systems and their Al complexes have been synthesized and seem to possess the desired characteristics (*vide infra*).

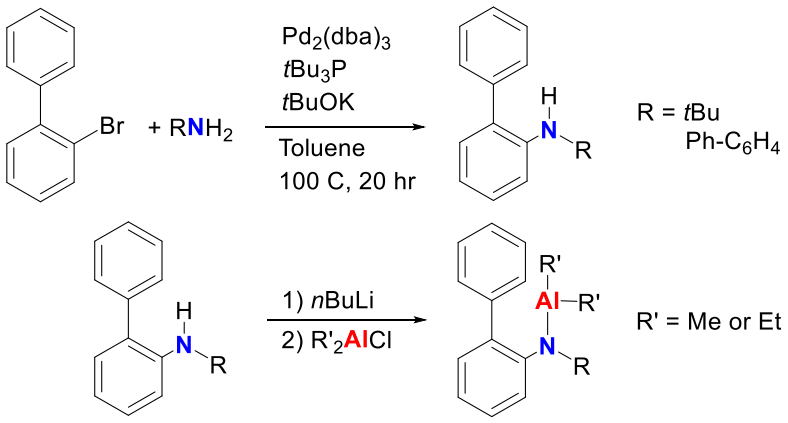
Phosphino amines have been known for many years and can be used for a wide variety of metal complexes.[15] They are easily synthesized via the reaction of lithium amide (R'NHLi) with a chlorophospine (R_2PCl; Scheme 4.7).[16]



Scheme 4.7 Synthesis of $Ph_2PNH(DIPP)$ and its proposed complexation with R_3Al (R = Me or Et).

The straightforward reaction of the $R_2PNH(R')$ with Al alkyls leads to the formation of their respective Al alkyl complexes.[17] The wide range of commercially available amines and the possibility to vary the substituents on the phosphine allow for tuning of the ligand system. This way the reactivity of different Al complexes as potential cocatalysts can be tested.

As mentioned previously, aromatic π-systems can also be used to stabilize a highly reactive three-coordinate Al species. This approach has been used before by Stephan *et al.* who used the (Ph-C_6H_4)N(R)H ligand as a suitable precursor (Scheme 4.8).[18] This ligand can be obtained easily through a palladium catalyzed Buchwald-Hartwig coupling of 2-bromobiphenyl with RNH_2.[19]



Scheme 4.8 Synthesis of (Ph-C_6H_4)N(R)H ligands and their Al alkyl complexes.[18,19]

The obtained amine is then reacted with *n*BuLi and R'_2AlCl to give the respective Al alkyl complex. Similarly to the phosphine amines, these ligands are synthesized in a one pot reaction and can be conveniently adapted by varying the amine (RNH_2) used in the reaction.

Stephan *et al.* demonstrated that upon metalation a monomeric (Ph-C_6H_4)$_2$NAlMe$_2$ complex was formed (Figure 4.3).[18] This species contains a three-coordinate Al center which is stabilized through interaction with the aromatic π-system of the Ph-C_6H_4 moiety both in solid state as well as in solution. Upon addition of THF or $Ph_3P{=}CH_2$, the ligand-Al interaction is broken and the Lewis base readily coordinates to the "naked" Al center to form the respective adducts.

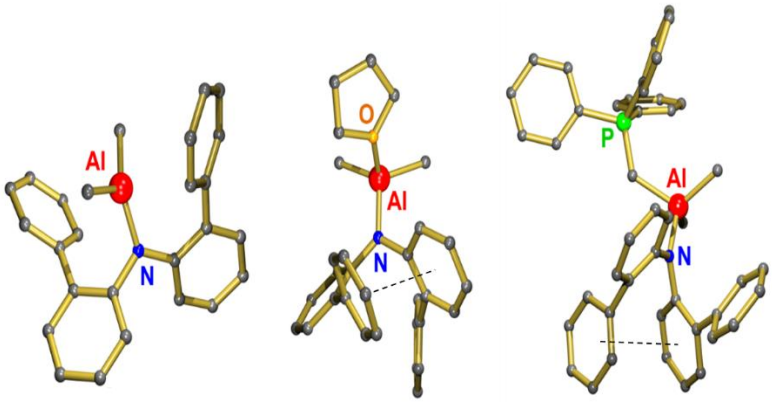


Figure 4.3 X-ray structure of (Ph-C_6H_4)$_2$NAlMe$_2$ and its THF and $Ph_3P{=}CH_2$ adducts.[18]

Upon coordination, both biphenyl arms bend backward and stabilize each other through π-stacking. This leaves the Al center exposed and allows for an easy and clean formation of the respective adducts. This indicates that the Al center has the desired Lewis acidity and therefore our goal was to obtain similar systems and study their interaction towards metallocene polymerization catalysts.

Both proposed ligand systems are readily prepared and can easily be modified to optimize their steric demand and electronic properties. The respective Al alkyl complexes are also easily obtained and have been reported in the literature to possess a Lewis acidic three-coordinate Al center. Together with the earlier described *aza*-MAO derivatives, these compounds are an interesting class of nitrogen based Al alkyl complexes that have potential as cocatalyst in alkene polymerization.

In this chapter, the synthesis and reactivity of a variety of *aza*-MAO clusters will be described. Particular focus will be put on their interaction with Lewis bases and metallocene catalysts. Furthermore, the simple and internally stabilized three-coordinate Al complexes discussed previously will be described and also investigated for their reactivity toward metallocenes and their potential applicability as cocatalysts.

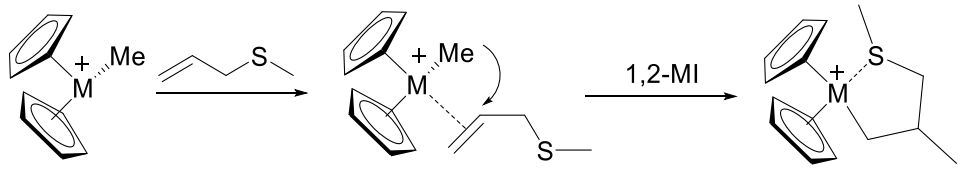
4.2 Results and Discussion

4.2.1 Aza-MAO isolobal exchange of O for NR

We chose to synthesize and study the reactivity of several previously reported $(MeAlNR)_n$ derivatives (R = Me, *i*Pr, Ph, C_6F_5, and DIPP). Almost all can be obtained by following the literature procedures starting from Me_3Al and common RNH_2 precursors.[2,6,8-10] The complexes $(MeAlNPh)_6$, $(MeAlNC_6F_5)_4$, and $(MeAlNDIPP)_3$ could be reproduced following these routes but the synthesis of $(MeAlNMe)_7$ and $(MeAlNiPr)_4$ proved more problematic. Multiple species were observed for the Me derivative which are most likely a combination of the desired $(MeAlNMe)_n$ (n = 7 and 8) clusters and different $(Me_2AlNHMe)_m(MeAlNMe)_n$ species. Despite several attempts and temperature modifications to the reported procedures, no single defined product could be obtained and further investigations on these compounds were discontinued. Release of the second equivalent of CH_4 for the *i*Pr derivative proved difficult and even after 18 hours of reflux in toluene, $(Me_2AlNHiPr)_2$ was the major product isolated and it was therefore not used for further investigations.

A drop of pyridine was added to C_6D_6 solutions of the well-defined $(MeAlNPh)_6$, $(MeAlNC_6F_5)_4$, and $(MeAlNDIPP)_3$ complexes to study their interaction with Lewis bases. No reactivity of $(MeAlNC_6F_5)_4$ and $(MeAlNDIPP)_3$ with pyridine was observed whereas some very minor (< 1%) new products could be seen in the ^1H NMR spectrum upon reaction of $(MeAlNPh)_6$. These could not be isolated and thus remain unknown. This lack of reactivity is surprising as it was anticipated that addition of a strong Lewis base like pyridine should lead to Al-N bond cleavage and formation of the respective adducts.

Similarly no reaction was observed upon the addition of the isolated *aza*-MAO clusters to $Cp^*_2ZrMe_2$ mixtures. Several different solvents, reaction temperatures and Al:M ratios were tested without success. Due to the fact that Me abstraction by an $(MeAlNR)_n$ cluster could be slow, inefficient, or incomplete we added allyl methyl sulfide to the mixture to trap any polymerization active intermediates. This method uses a thioether to mimic the first polymerization insertion, leading to a sulfur stabilized cationic complex and has been described previously by Hessen *et al*. (Scheme 4.9).[20]



Scheme 4.9. $[Cp^*_2MMe]^+$ trapping with allyl methyl sulfide (anion omitted for clarity, 1,2-MI = 1,2 migratory insertion).

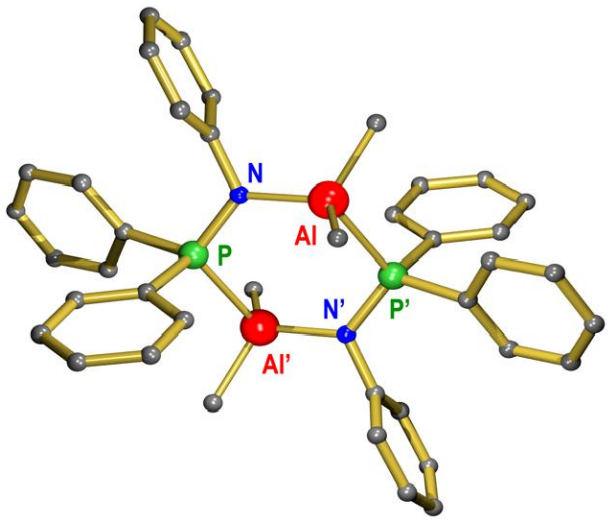
Upon the formation of the cation, the allyl methyl sulfide acts as a regular olefin, it coordinates to the M center and the first insertion takes place. After this, the S immediately coordinates to the metal center rendering it unreactive and producing a stabilized cation-anion pair.

As the addition of the thioether did not lead to any change in the reactants, it can be safely concluded that the *aza*-MAO clusters tested do not react with metallocene precatalysts. Although they are structurally similar to Barron's $(t\text{BuAlO})_n$ clusters they are much less reactive. The biggest difference between both systems is the binding environment of the O and N, respectively. The O connects three Al centers whereas the N is connected to three Al centers and one R substituent. The introduction of a R group leads to well-defined clusters, but also decreases the reactivity, rendering the formed structures inert towards Lewis bases and metallocene precatalysts.

4.2.2 Complexes with a masked three-coordinate Al center

Phosphino amines

In order to obtain more reactive Al complexes, phosphine amine based ligands were studied (Scheme 4.7). We chose to work with the $Ph_2PNH(DIPP)$ derivative as it is readily prepared following the route described in Scheme 4.7. The respective Al alkyl complexes can be obtained in good yields upon refluxing of the ligand with Me_3Al or Et_3Al in toluene (92% and 84% yield, respectively). The ^1H NMR of the Al-Me complex shows a doublet at – 0.12 ppm for the Al-Me protons, indicating a ^1H-^{31}P coupling and therefore P is likely coordinated to Al. Therefore a complex with internal or external P-Al coordination is assumed. Both the Me and Et complexes are poorly soluble in non-coordinating solvents but the Me derivative could be crystallized from hot toluene (Figure 4.4).



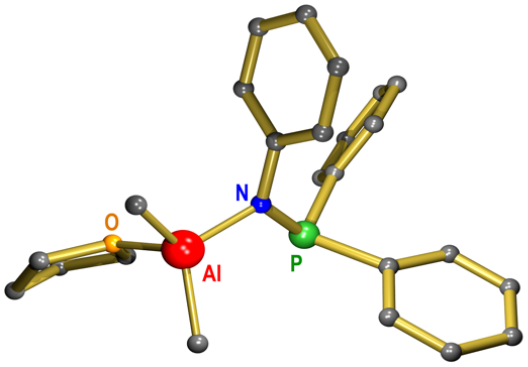
Bond length (Å)	
Al-P'	2.508(6)
Al-N	1.910(1)
P-N	1.675(1)
Bond angle (°)	
P-N-Al	124.09(5)
N-P-Al'	111.30(3)
N-Al-P'	109.69(3)

Figure 4.4 X-ray structure of $[Ph_2PN(DIPP)AlMe_2]_2$ (*i*Pr groups omitted for clarity) and selected bond lengths and angles.

X-ray analysis of $Ph_2PN(DIPP)AlMe_2$ confirmed the formation of a dimeric complex. It seems that the dimer with a central 6-membered $(AlNP)_2$ rings is more stable than a monomer with a highly strained 3-membered AlNP ring. The structure has crystallographic C_i axis with the DIPP substituents perpendicular to the ring. The six-membered ring shows a chair-like formation with bond angles around N adding up to almost 360°, indicating a planar moiety. The Al-P' and Al-N distances are 2.508(6) Å and 1.910(1) Å and fall within the range of those reported for similar complexes.[21] The P-N distance is 1.675(1) Å which is commonly observed for N-P single bonds.[22] The P-N-Al at trigonal N and N-Al-P' angles at tetrahedral Al are 124.09(5)° and 109.69(3)°, respectively.

As similar dimeric structures have been proposed for Et derivatives of phosphine amide complexes, it seems reasonable to assume that $[Ph_2PN(DIPP)AlEt_2]_2$ also exists as a dimer.[17] Attempts to obtain monomeric complexes through the introduction of *i*Bu or *t*Bu groups on the Al center gave a variety of unidentified products. This is most likely due to the high temperatures required in the amine deprotonation step which led to unwanted side reactions and decomposition.

Both the Me- and Et-complexes readily react with THF to form the respective $Ph_2PN(DIPP)AlR_2{\cdot}THF$ adducts. Upon addition of just a few drops of THF to a solution of $[Ph_2PN(DIPP)AlMe_2]_2$, only the monomeric adduct is observed. This reaction can be monitored conveniently by ^1H NMR spectroscopy as the Al-Me signal goes from a doublet to a singlet and shifts from – 0.12 to – 0.41 ppm. Mismatch between a hard acceptor (Al) and a soft donor (P) as observed in the Al-P bond in the dimer leads to cleavage and formation of a monomer with the hard-hard combination Al-O (Figure 4.5).



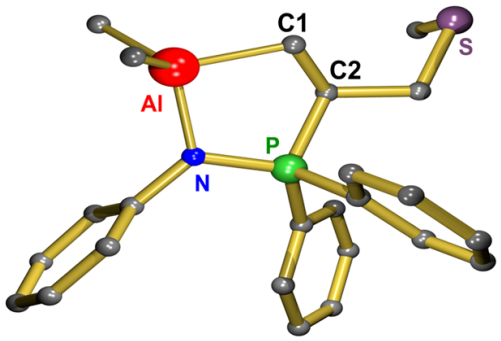
Bond length (Å)	
Al-N	1.856(2)
Al-O	1.934(2)
P-N	1.703(2)
Bond angle (°)	
P-N-Al	117.25(12)
N-Al-O	108.06(10)

Figure 4.5 X-ray structure of $Ph_2PN(DIPP)AlMe_2{\cdot}THF$ (*i*Pr groups omitted for clarity) and selected bond lengths and angles.

The compound has no crystallographic symmetry and contains the Al center in a distorted tetrahedral environment. The Al-N bond length is 1.856(2) Å, which is shorter than the one reported for the dimer (1.908(1) Å). The P-N bond in the complex is 1.703(2) Å, which is significantly larger than that observed for $[Ph_2PN(DIPP)AlMe_2]_2$ (1.674(1) Å).

Due to the low solubility of the $[Ph_2PN(DIPP)AlR_2]_2$ (R = Et or Me) complexes in polar solvents, the related $[Ph_2PN(tBu)AlMe_2]_2$ compound was synthesized. Exchange of the DIPP group for *t*Bu gives a complex that is highly soluble in non-aromatic solvents while still having similar reactivity as the DIPP compound. As could be shown by ^{1}H NMR, pyridine also readily cleaves the Al-P bond to give the monomeric adducts as can be seen by the lost of P-H coupling in the Al-Me signal (s, – 0.17 ppm).

In order to study the potential of these complexes as cocatalysts, they were reacted with $Cp^*_2ZrMe_2$ and the reaction was monitored by ^{1}H NMR spectroscopy. Initially no reaction was observed, therefore allyl methyl sulfide was added in an attempt to trap any potentially formed active catalyst (Scheme 4.9). After addition of the thioether, the formation of a new product was observed in the ^{1}H NMR spectrum. Over the course of a three days, this became the predominant species. Cooling of the solution led to the formation of single crystals suitable for X-ray analysis (Figure 4.6).



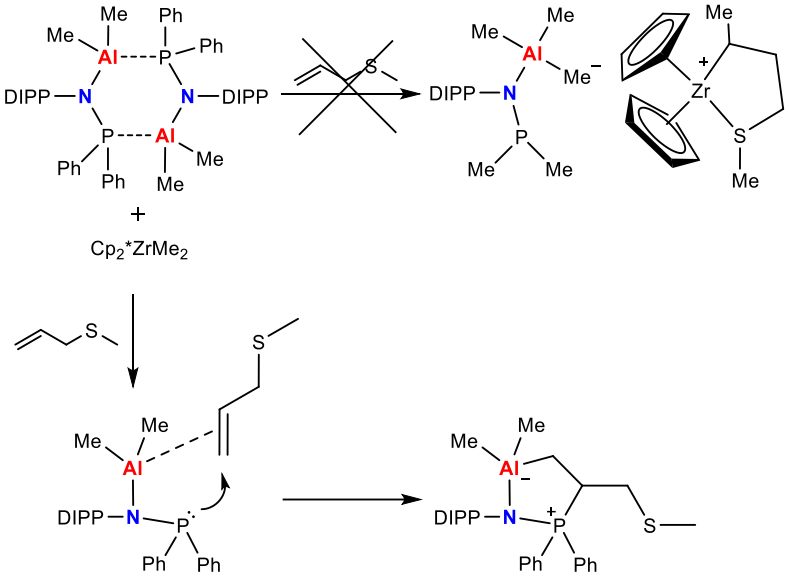
Bond length (Å)	
Al-N	1.969(3)
Al-C1	2.018(5)
P-C2	1.820(4)
P-N	1.621(3)
Bond angle (°)	
P-N-Al	111.99(17)

Figure 4.6 X-ray structure of $[(DIPPN)PPh_2(C_4H_8S)]AlMe_2$ (*i*Pr groups omitted for clarity) and selected bond lengths and distances.

The molecular structure contained no Zr and showed instead the formation of alkene addition to the $[(DIPPN)PPh_2(C_4H_8S)]AlMe_2$ complex (Figure 4.6).The complex has no crystallographic symmetry and crystallizes with two independent molecules in the asymmetric part of the unit cell. Both molecules are structurally identical as all bond lengths and angles are within standard deviation of each other. The only difference between them being that one has disorder in the SMe group. The Al-N bond is 1.969(3) Å and is much larger than that in the dimer or in the monomeric THF adduct (1.908(1) Å and 1.856(2) Å, respectively). The P-N distance is 1.621(3) Å, which is shorter than that observed for the previously discussed derivatives. The P-C2 bond and the P-C(aryl) bond are comparable with 1.820(4) Å and 1.806(4) Å. This is similar for the Al-C bonds which are 1.984(2) Å for the Al-Me and 2.018(5) Å for the Al-C1 interaction.

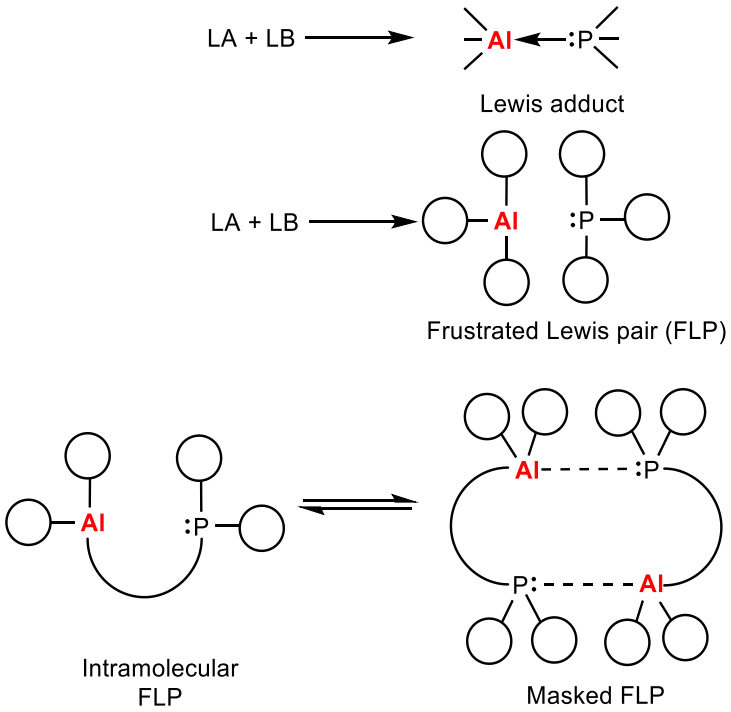
$[(DIPPN)PPh_2(C_4H_8S)]AlMe_2$ can also be obtained directly upon reaction of $[Ph_2PN(DIPP)AlMe_2]_2$ with allyl methyl sulfide. This reaction proceeds smoothly upon brief heating of the substrates and gives the product in good yields (77%). The observed reactivity of $[Ph_2PN(DIPP)AlMe_2]_2$ shows that even though the dimer can be split very easily, the Al center is not able to abstract a Me group from Cp_2*ZrMe_2

(Scheme 4.10). It is unclear if there is really no reactivity toward the metallocene or if the alkene insertion occurs much faster and therefore it is not observed. As, however, no major change in product distribution is observed upon combination of $[Ph_2PN(DIPP)AlMe_2]_2$ with $Cp^*_2ZrMe_2$ it can be assumed that the amido phosphines studied are unsuitable as potential cocatalysts.



Scheme 4.10 Proposed vs. observed reactivity of $[Ph_2PN(DIPP)AlMe_2]_2$ with $Cp^*_2ZrMe_2$ in the presence of allyl methyl sulfide.

This observed reactivity could be described as Frustrated Lewis Pair (FLP) chemistry.[23] This rapidly growing area is based on a Lewis acids and Lewis bases that are very bulky and for steric reasons do not form classical Lewis adducts (Scheme 4.11). As $[Ph_2PN(DIPP)AlMe_2]_2$ is a dimeric complex with weak P-Al bonds it can be considered as a masked intramolecular FLP.



Scheme 4.11 Frustrated Lewis Pairs.

Although the observed FLP reactivity is undesired, it should be noted that the addition of an unactivated alkene to a FLP is rather unusual and only few examples with B/P FLP's have been reported.[24] To the best of our knowledge, this is the first intramolecular Al/P FLP that readily reacts with unactivated alkenes. Further studies, indeed, showed that $[Ph_2PN(DIPP)AlMe_2]_2$ reacts with a variety of small molecules in an FLP fashion (Figure 4.7). Discussion of these results are outside the scope of this chapter and can be found elsewhere.[25]

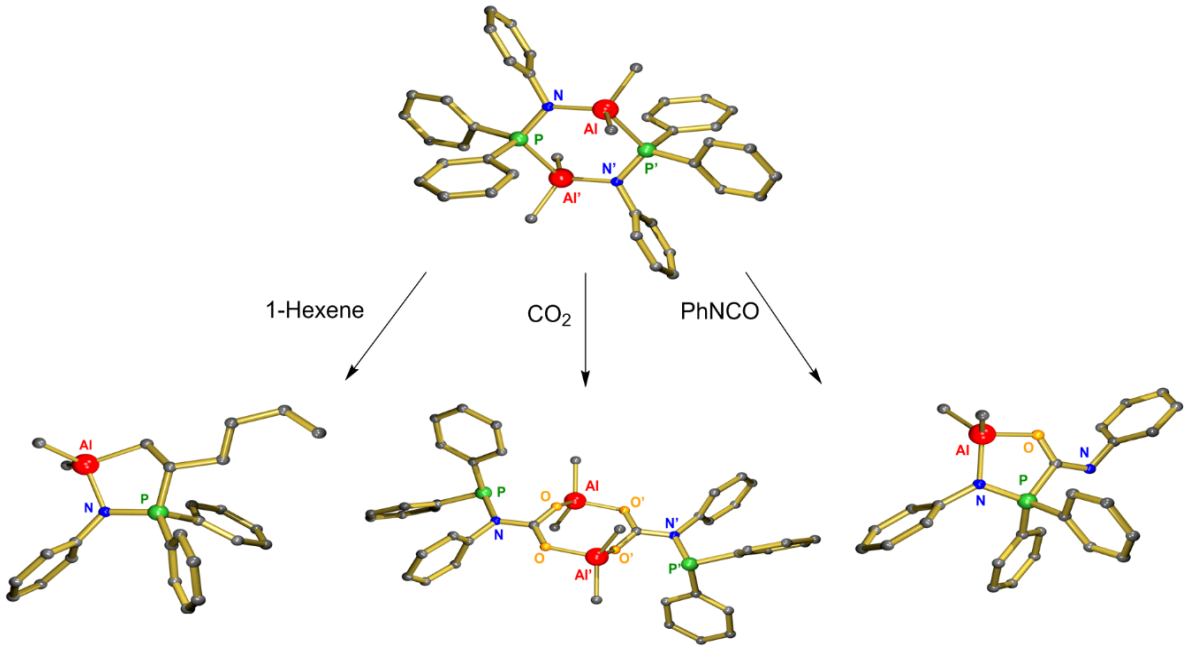


Figure 4.7 Reactivity of $[Ph_2PN(DIPP)AlMe_2]_2$ with selected small molecules.

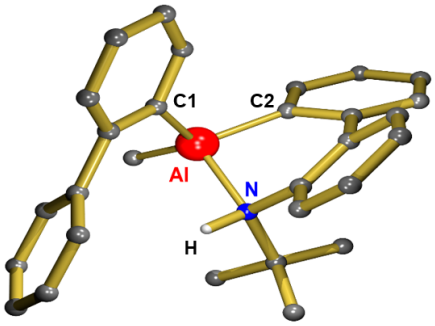
Biphenyl amines

In order to avoid FLP reactivity of the stabilized Al complex, complexes with the phosphine-free ligands (Ph-C_6H_4)N(R) were investigated (Scheme 4.8). As discussed previously (*vide supra*), the Al center is stabilized through π-interaction with the aryl ring. Stephan *et al.* already showed that if R = (Ph-C_6H_4) a stable monomeric complex could be obtained.[18] These internally stabilized three-coordinate Al complexes react smoothly with Lewis bases to give the respective adducts. In these adducts, the Ph-C_6H_4 arms bend away from the Al center, a configuration which is stabilized by π-interaction between both aryl rings (Figure 4.3). Using these results as our starting point, we set out to study the reactivity the (Ph-C_6H_4)$_2$N$AlMe_2$ with Cp*$_2$ZrMe_2. Upon mixing both complexes, no reaction was observed. No results were produced even after prolonged reaction times (3 days), careful heating (up to 50°C) and the addition of allyl methyl sulfide.

This lack of reactivity could potentially be due to the steric hindrance of the Ph-C_6H_4 arms. This prevents the Lewis acidic Al center from coming close enough to the Zr center to abstract a Me group. As the work of Stephan *et al*. showed that the arms can bend backward relatively easily this lack of reactivity could also be due to the electronic properties of the Al center.[18] Therefore the ligand was modified to change the steric and electronic properties of the backbone. The assymetric (Ph-C_6H_4)NH(*t*Bu) derivative had already been reported by Stephan *et al*.[18] and the bulky (Ph-C_6H_4)NH(DIPP) derivative could also be obtained using a similar route. Synthesis of (Ph-C_6H_4)NH(C_6F_5) was also attempted but the ligand decomposed during distillation and no successful milder purification procedures could be

found. The (Ph-C_6H_4)N(R)$AlMe_2$ (R = *t*Bu or DIPP) can be obtained by reacting the Li salt (Ph-C_6H_4)NLi(R) with Me_2AlCl. It should, however, be noted that despite many attempts, minor decomposition resulting in the formation of (Ph-C_6H_4)NH(R) could not be avoided. Due to this ever persistent contamination, both complexes could only be isolated as oils and all crystallization attempts have proven unsuccessful thus far. Interestingly, the (Ph-C_6H_4)N(*t*Bu)$AlMe_2$ derivative shows two Al-Me signals (– 0.01 and – 0.84 ppm) which could indicate formation of a dimer. The (Ph-C_6H_4)N(DIPP)$AlMe_2$ on the other hand only shows one Al-Me signal (– 0.83 ppm), indicating a monomeric species. Due to difficulties in getting the pure products no further evidence could be obtained but seemingly the size of the NR group does influence the structure of the resulting Al complex.

In order to ensure that the observed ligand did not originate from impurities in the Li-salt, the preparation method was altered. The (Ph-C_6H_4)NH(*t*Bu) ligand was purified by vacuum distillation, reacted with an excess of *n*BuLi, and allowed to stir overnight to ensure reaction completeness. Reaction of the isolated Li salt with Me_2AlCl led to the formation of crystalline material (10% yield). X-ray analysis showed that this was not the expected (Ph-C_6H_4)N(*t*Bu)$AlMe_2$ complex but [(Ph-C_6H_4)NH(*t*Bu)](Ph-C_6H_4)AlMe (Figure 4.8).



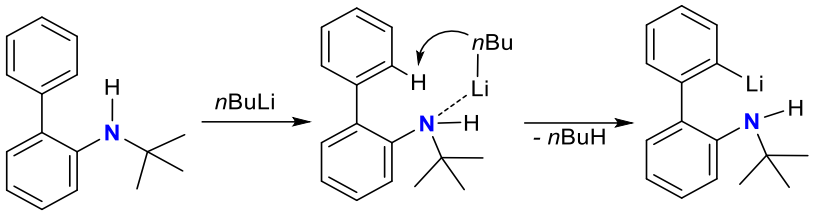
Bond length (Å)	
Al-N	2.045(2)
Al-C1	2.004(3)
Al-C2	1.976(4)
Bond angle (°)	
N-Al-C1	97.06(10)
N-Al-C2	94.60(10)

Figure 4.8 X-ray structure of [(Ph-C_6H_4)NH(*t*Bu)](Ph-C_6H_4)AlMe and selected bond lengths and angles.

The complex contains one (Ph-C_6H_4)NH(*t*Bu) ligand, which is deprotonated at the *ortho*-position of the Ph ring, and a *ortho*-deprotonated Ph-C_6H_5 fragment which are both bound to an Al center with one remaining Me group. The ligand still has its NH and is deprotonated on the *ortho*-position of the phenyl ring. The complex has no crystallographic symmetry and contains Al in a distorted tetrahedral coordination environment with C-Al-C angles varying from 112.9(1)° to 119.1(1)°. The Al-C distances vary from 1.975(3) Å to 2.004(3) Å and are within the range of those observed for the earlier discussed complexes. The Al-N distance is long with 2.004(3) Å, which is expected for the relatively weak bonding interaction of a bulky neutral amine.

It is unclear what the exact mechanism for the formation of this complex is, but it can be speculated that deprotonation of the *ortho*-position of the phenyl could be due to a proximity effect. This allows

the amino substituent to act as a directing metalating group, giving for the respective lithiated compound which upon reaction with Me_2AlCl, forms the observed naphtyl aluminum complex (Scheme 4.12).



Scheme 4.12 Directed lithiation of (Ph-C_6H_4)NH(*t*Bu).

The other substituent on the Al, Ph-C_6H_4 could originate from unreacted diphenylbromide that is left in the ligand after distillation or could be formed upon the decomposition of the ligand. Subsequent batches were synthesized and characterized to investigate potential contamination but from ^1H and ^{13}C analysis no remaining Ph-C_6H_4Br could be observed. Given the observed product, however, it seems likely there was Ph-C_6H_4Br present in the batch from which the crystals were isolated. It is unclear how exactly this can react with the (Ph-C_6H_4)NH(*t*Bu)$AlMe_2$ but it might undergo ligand exchange with a (Ph-C_6H_5)$AlMe_2$ that forms from the reaction of Ph-C_6H_4Li with Me_2AlCl. This exchange then leads to the formation of the isolated [(Ph-C_6H_4)NH(*t*Bu)](Ph-C_6H_4)AlMe. The formed complex is extremely air sensitive and the full characterization has proven difficult as only the decomposition products are observed in the ^1H NMR spectra. As this unexpected product is not relevant for cocatalytic studies, its exact formation and characterization were not pursued. It nonetheless shows that minor changes in the reaction conditions can lead to unexpected products.

Despite minor ligand contamination in the (Ph-C_6H_4)N(R)$AlMe_2$ (R = *t*Bu or DIPP) complexes and lack of concrete structural information, we decided to further study their reactivity towards Lewis bases and Cp_2*$ZrMe_2$. THF readily coordinates to (Ph-C_6H_4)N(DIPP)$AlMe_2$ to give its THF adduct. X-ray characterization shows a monomeric THF adduct similar to that of (Ph-C_6H_4)$_2$N$AlMe_2$·THF (Figure 4.9).[18]

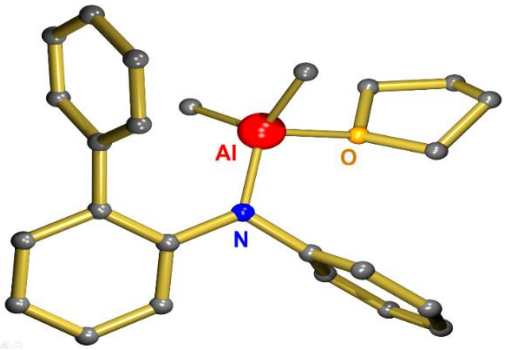


Figure 4.9 X-ray structure of (Ph-C_6H_4)N(DIPP)$AlMe_2$·THF (*i*Pr groups omitted for clarity).

Due to poor crystal quality a poor data set was obtained and only connectivity can be established. From the structure it can be observed that initially the exchange of one of the Ph-C_6H_4 arms for a DIPP moiety leads to a more accessible Al center. However, lack of a second Ph-C_6H_4 arm does not allow for the stabilizing π-π stacking as observed for the symmetric (Ph-C_6H_4)$_2$NAlMe$_2$ derivative. Therefore the arm does not bend backwards and remains in the proximity of the Al center giving for a more sterically crowded Al center upon adduct formation.

4.3 Conclusions and Outlook

A range of different *aza*-MAO complexes with the general formula (MeAlNR)$_n$ (n = 3, 4 and 6) have been synthesized according to literature procedures and tested for its reactivity towards Lewis bases and metallocene catalysts. Despite their structural similarities to the (*t*BuAlO)$_n$ cages, very limited reactivity towards pyridine and no reactivity towards Cp*$_2$ZrMe$_2$ was observed. This shows that although the isolobal substitution of O for NR leads to well-defined clusters, it also renders the complex inactive as a potential cocatalyst.

Ligands with soft Lewis basic sites such as phosphines or aryl groups can be used to obtain masked three-coordinate Al complexes. These compounds are much more Lewis acidic than the studied *aza*-MAO derivatives in this study and readily coordinate to Lewis bases. Unfortunately the reactivity of these complexes towards metallocene catalysts seems limited.

The Ph$_2$PN(R)AlMe$_2$ complexes (R = *t*Bu, DIPP) exist as dimeric structures but can be easily obtained as their monomeric adduct upon the addition of a variety of reactants. Despite their easy reactivity with Lewis bases, no reactivity with Cp*$_2$ZrMe$_2$ was observed. Instead Ph$_2$PN(DIPP)AlMe$_2$ was found to react in an FLP manner and readily activated a variety of small molecules. Even the highly uncommon addition of an unsaturated alkene across the Al and P could be observed.

Weak intramolecular Ar···Al coordination could also mask a three-coordinate Al center. No reactivity towards Cp*$_2$ZrMe$_2$ was observed using (Ph-C_6H_4)$_2$NAlMe$_2$. Substitution of one of the Ph-C_6H_4 arms for a *t*Bu or DIPP substituents did not lead to an increase in reactivity. Due to the extreme sensitivity of both complexes no detailed investigations on their reactivity could be carried out. It does seem, however, that the size and nature of the substituent influences the structure and stability of the Al complex and its respective adduct with THF. Substitution of Ph-C_6H_4 for *t*Bu leads to a species with asymmetric Al-Me groups wheras for the DIPP derivative only one Al-Me signal was observed. Seemingly, both Ph-C_6H_4 arms are necessarily to obtain an open and accessible Al center. Upon coordination of a substituent such as THF a stable conformation in which both ligand arms are stabilized by π-π stacking and bent away from the Al center is observed for the symmetric (Ph-C_6H_4)$_2$NAlMe$_2$. Upon the exchange of one of these arms, this function is lost resulting in the formation

of complexes in which the ligand substituent remains in the proximity of the Al center making it more sterically crowded and decreasing its accesibility.

4.4 Experimental Section

General considerations

All experiments were performed under a nitrogen atmosphere by using standard Schlenk line and glove box techniques. The solvents were dried on alumina columns and were degassed by bubbling nitrogen through the solvent reservoir. Chemicals were purchased in reagent grade from commercial suppliers (ABCR, Acros Organics, Alfa Aesar, and Sigma Aldrich) and used, unless noted otherwise, without further purification. $(MeAlNMe)_7$,[2] $(MeAlNPh)_6$,[9] $(MeAlNC_6F_5)_4$,[8] $(MeAlNiPr)_4$,[10] $(MeAlNDIPP)_3$,[6] $Ph_2PNH(DIPP)$,[16] $[Ph_2PN(tBu)AlMe_2]_2$,[17b] $(Ph\text{-}C_6H_4)_2NAlMe_2$,[18] $(Ph\text{-}C_6H_4)N(tBu)Li$,[18] and Cp_2*ZrMe_2[26] were prepared according to their reported procedures. ^1H and ^{13}C NMR were recorded on Bruker Avance 300, 400, and 600 MHz spectrometers (specified at individual experiments). Crystal structure determinations were carried out on a Bruker Nonius Kappa CCD (Mo). Single crystals were coated with perfluoro-polyether and immediately mounted in the cold nitrogen stream of the diffractometer. Elemental analysis was carried out using a Eurovector EA 3000 analyzer.

Reactivity of aza-MAO complexes

Reaction of $(MeAlNR)_n$ complexes with pyridine

$(MeAlNR)_n$ (150 mg) was dissolved in pyridine (5 mL) and the resulting solution was stirred for 30 minutes. All volatiles were removed under reduced pressure and the conversion into stable $(MeAlNR)_n$·pyridine complexes was measured by ^1H NMR spectroscopy. None to very limited $(MeAlNPH)_6$ conversion was observed, even after prolonged reaction times and heating.

Reaction of $(MeAlNR)_n$ complexes with $Cp*_2ZrMe_2$

Two equivalents of a given $(MeAlNR)_n$ cluster were combined with $Cp*_2ZrMe_2$ and dissolved in C_6D_6 (0.6 mL). The sample was shaken for 30 seconds and the reaction progress was monitored by ^1H NMR spectroscopy. As no reaction could be observed, methylallyl thioether was added to trap a potential cationic complex. Reaction progress was monitored by ^1H NMR spectroscopy and the sample was kept for two days at room temperature and then gradually heated, which resulted only in the decomposition of $Cp*_2ZrMe_2$.

Synthesis and reactivity of phospino-amines

Synthesis of $[Ph_2PN(DIPP)AlMe_2]_2$

$Ph_2PNH(DIPP)$ (3.08 g, 8.52 mmol) was dissolved in toluene (20 mL) and Me_3Al (4.5 mL (2M in hexanes), 9.0 mmol) was added dropwise after which the solution was heated at 90°C for 18 hours. The

suspension was cooled and all volatiles were removed under reduced pressure. Washing with pentane (3 x 5 mL) gave $[Ph_2PN(DIPP)AlMe_2]_2$ as a colorless powder (3.23 g, 3.91 mmol, 92%). Suitable crystals for X-ray analysis were grown from hot toluene.

^{1}H NMR (400 MHz, C_6D_6): δ = 7.59-7.51 (m, 4H, *Ar*), 7.14-7.11 (m, 1H, *Ar*), 7.06-7.02 (m, 2H, *Ar*), 6.99-6.92 (m, 6H, *Ar*), 3.87 (m, 2H, C*H*$(CH_3)_2$), 1.30 (d, $^3J_{HH}$ = 6.9 Hz, 6H, CH(C*H*$_3)_2$), 0.45 (d, $^3J_{HH}$ = 6.9 Hz, 6H, CH(C*H*$_3)_2$), − 0.12 (d, $^3J_{HP}$ = 4.0 Hz, 6H, Al-*Me*) ppm.
^{31}P NMR (162 MHz, C_6D_6): δ = 35.8 (s) ppm.
$C_{52}H_{66}Al_2N_2P_2$ (834.44): calcd. C 74.80, H 7.97, N 3.35; found C 74.33, H 7.86, N 3.11.

Synthesis of $[Ph_2PN(DIPP)AlEt_2]_2$

$Ph_2PNH(DIPP)$ (400 mg, 1.10 mmol) was dissolved in toluene (10 mL) and Et_3Al (0.85 mL, 6.2 mmol) was added dropwise after which the solution was heated at 100°C overnight. The suspension was cooled and all volatiles were removed under reduced pressure. Washing with pentane (2 x 5 mL) gave $[Ph_2PN(DIPP)AlEt_2]_2$ as a colorless powder (0.41 g, 0.46 mmol, 84%).

^{1}H NMR (400 MHz, C_6D_6): δ = 7.90-7.40 (m, 4H, *Ar*), 7.14-7.10 (m, 1H, *Ar*), 7.07-7.02 (m, 2H, *Ar*), 7.01-6.93 (m, 6H, *Ar*), 3.81 (m, 2H, C*H*$(CH_3)_2$), 1.43 (d, $^3J_{HH}$ = 6.9 Hz, 6H, CH(C*H*$_3)_2$), 0.95 (t, $^3J_{HH}$ = 8.0 Hz, 6H, Al-CH_2-C*H*$_3$), 0.76 (m, 4H, Al-CH_2-C*H*$_3$), 0.29 (d, $^3J_{HH}$ = 6.9 Hz, 6H, CH(C*H*$_3)_2$) ppm.
^{31}P NMR (162 MHz, C_6D_6): δ = 35.9 (s) ppm.

Synthesis of $Ph_2PN(DIPP)AlMe_2$·THF

$[Ph_2PN(DIPP)AlMe_2]_2$ (50.0 mg, 60.0 μmol) was dissolved in C_6D_6 (0.6 mL) and a few drops of THF-d_8 were added to give a clear solution of $Ph_2PN(DIPP)AlMe_2$·THF (quantitative, 29.4 mg, 60.0 μmol). Dropwise addition of hexanes to this mixture led to the immediate formation of crystalline material suitable for X-ray analysis.

^{1}H NMR (400 MHz, C_6D_6): δ = 7.70-7.64 (m, 4H, *Ar*), 7.14-7.08 (m, 1H, *Ar*), 7.07-7.02 (m, 2H, *Ar*), 6.99-6.92 (m, 6H, *Ar*), 3.72 (m, 2H, C*H*$(CH_3)_2$), 1.25 (d, $^3J_{HH}$ = 6.9 Hz, 6H, CH(C*H*$_3)_2$), 0.77 (d, $^3J_{HH}$ = 6.9 Hz, 6H, CH(C*H*$_3)_2$), − 0.41 (s, 6H, Al-*Me*) ppm.
^{13}C NMR (75 MHz, C_6D_6): δ = 147.4 (d, $^2J_{CP}$ = 3.0, Ar), 146.5 (Ar), 143.1 (d, $^1J_{CP}$ = 24.9, Ar), 135.0 (d, $^2J_{CP}$ = 23.4, Ar), 128.4 (Ar), 127.9 (Ar), 124.5 (d, $^4J_{CP}$ = 2.3, Ar), 124.0 (d, $^3J_{CP}$ = 2.3, Ar), 71.8 (THF), 28.7 (*C*H$(CH_3)_2$), 25.6 (CH(*C*H$_3)_2$), 24.9 (THF), 24.4 (CH(*C*H$_3)_2$), − 7.28 (Al-Me) ppm.
^{31}P NMR (162 MHz, C_6D_6): δ = 51.1 (s) ppm.
$C_{30}H_{41}AlNOP$ (489.27): calcd. C 73.59, H 8.44, N 2.86; found C 73.27, H 8.44, N 2.67.

Synthesis of $Ph_2PN(DIPP)AlEt_2$·THF

$[Ph_2PN(DIPP)AlEt_2]_2$ (50.0 mg, 57.0 μmol) was dissolved in C_6D_6 (0.6 mL) and a few drops of THF-d_8 were added to give a clear solution of $Ph_2PN(DIPP)AlEt_2$·THF (quantitative, 29.5 mg, 57.0 μmol) .

^{1}H NMR (400 MHz, C_6D_6): δ = 7.60-7.52 (m, 4H, *Ar*), 7.14-6.98 (m, 9H, *Ar*), 3.61 (m, 2H, C*H*$(CH_3)_2$), 1.33 (t, $^{3}J_{HH}$ = 8.0 Hz, 6H, Al-CH_2C*H*$_3$), 1.24 (d, $^{3}J_{HH}$ = 6.9 Hz, 6H, CH(C*H*$_3)_2$), 0.65 (d, $^{3}J_{HH}$ = 6.9 Hz, 6H, CH(C*H*$_3)_2$), 0.28 (m, 4H, Al-CH_2C*H*$_3$) ppm.

^{13}C NMR (75 MHz, C_6D_6): δ = 147.2 (d, $^{2}J_{CP}$ = 3.0, Ar), 146.2 (Ar), 143.1 (d, $^{1}J_{CP}$ = 24.9, Ar), 135.0 (d, $^{2}J_{CP}$ = 23.4, Ar), 128.4 (Ar), 128.0 (Ar), 124.5 (d, $^{4}J_{CP}$ = 2.3, Ar), 124.1 (d, $^{3}J_{CP}$ = 2.3, Ar), 69.4 (THF), 28.7 (*C*H$(CH_3)_2$), 25.9 (CH(*C*H$_3)_2$), 22.4 (THF), 24.2 (CH(*C*H$_3)_2$), 10.38 (Al–CH_2*C*H$_3$), 2.05 (Al– *C*H_2CH_3) ppm.

^{31}P NMR (162 MHz, C_6D_6): δ = 50.1 (s) ppm.

Synthesis of $Ph_2PN(DIPP)AlMe_2$·Pyr

$[Ph_2PN(DIPP)AlMe_2]_2$ (32 mg, 0.40 mmol) was dissolved in pyridine (0.6 mL) to give a clear solution. The solvent was removed under reduced pressure and the solid was washed with pentane (3 x 0.5 mL) to give $Ph_2PN(DIPP)AlMe_2$·Pyr as a colorless solid (28.0 mg, 60.0 μmol, 73%).

^{1}H NMR (400 MHz, C_6D_6): δ = 8.46 (d, $^{3}J_{HH}$ = 5.2 Hz, 2H, *Py*), 7.51-7.46 (m, 4H, *Ar*), 7.17-7.00 (m, 9H, *Ar*), 6.75 (tt, $^{3}J_{HH}$ = 7.5 Hz, $^{4}J_{HH}$ = 1.5 Hz, 1H, *Py*), 6.41 (dd, $^{3}J_{HH}$ = 7.5 Hz, $^{3}J_{HH}$ = 5.2 Hz, 2H, *Py*), 3.67 (m, 2H, C*H*$(CH_3)_2$), 1.17 (d, $^{3}J_{HH}$ = 6.9 Hz, 6H, CH(C*H*$_3)_2$), (d, $^{3}J_{HH}$ = 6.9 Hz, 6H, CH(C*H*$_3)_2$), − 0.17 (s, 6H, Al-*Me*) ppm.

^{31}P NMR (162 MHz, C_6D_6): δ = 51.3 (s) ppm.

Synthesis of $Ph_2PN(tBu)AlMe_2$·Pyr

$[Ph_2PN(tBu)AlMe_2]_2$ (44.0 mg, 70.5 μmol) was dissolved in pyridine (0.6 mL) to give a clear solution. The solvent was removed under reduced pressure and the solid was washed with pentane (3 x 0.5 mL) to give $Ph_2PN(tBu)AlMe_2$·Pyr as a colorless solid (38.7 mg, 99.0 μmol, 70%).

^{1}H NMR (400 MHz, C_6D_6): δ = 8.26 (dd, $^{3}J_{HH}$ = 5.3 Hz, $^{4}J_{HH}$ = 1.6Hz, 2H, *Py*), 7.48-7.44 (m, 4H, *Ar*), 7.14-7.06 (m, 6H, *Ar*), 6.79 (tt, $^{3}J_{HH}$ = 7.7 HH, $^{4}J_{HH}$ = 1.5 Hz, 1H, *Py*), 6.45 (dd, $^{3}J_{HH}$ = 7.7 Hz, $^{3}J_{HH}$ = 5.3 Hz, 2H, *Py*), 1.17 (s, 9H, C(C*H*$_3)_3$), − 0.20 (s, 6H, Al-*Me*) ppm.

^{31}P NMR (162 MHz, C_6D_6): δ = 50.8 (s) ppm.

Reaction of $Ph_2PN(DIPP)AlMe_2$ with $Cp^*_2ZrMe_2$

$[Ph_2PN(DIPP)AlMe_2]_2$ (29.4 mg, 35.3 μmol) and $Cp^*_2ZrMe_2$ (29.9 mg, 76.3 μmol) were dissolved in C_6D_6 (0.6 mL). The sample was shaken for 30 seconds and the reaction progress was monitored by ^{1}H NMR spectroscopy. As no reaction could be observed, methylallyl thioether was added to trap a potential cationic complex. Reaction progress was monitored by ^{1}H NMR spectroscopy and the sample was kept for two days at room temperature and then heated at 55°C overnight. Cooling the solution yielded colorless crystals which upon X-ray analysis proved to be $[(DIPPN)PPh_2(C_4H_8S)]AlMe_2$.

Synthesis of [(DIPPN)PPh$_2$(C$_4$H$_8$S)]AlMe$_2$

[Ph$_2$PN(DIPP)AlMe$_2$]$_2$ (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 had 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 x 2 mL) to give [(DIPPN)PPh$_2$(C$_4$H$_8$S)]AlMe$_2$ as a colorless solid (277 mg, 449 μmol, 77%).

^{1}H NMR (300 MHz, C$_6$D$_6$): δ = 7.69-7.58 (m, 2H, *Ar*), 7.13-6.72 (m, 11H, *Ar*), 3.92 (sept, $^3J_{HH}$ = 6.9 Hz, 1H, C*H*(CH$_3$)$_2$), 3.53-3.33 (m, 1H, P-C*H*), 3.12 (sept, $^3J_{HH}$ = 6.9 Hz, 1H, C*H*(CH$_3$)$_2$), 2.61 (m, 1H, S-C*H*H-CH), 1.88-1.78 (m, 1H, S-CH*H*-CH), 1.73 (s, 3H, S-*Me*), 1.70-1.50 (m, 1H, Al-CH*H*-CH), 1.34 (d, $^3J_{HH}$ = 6.9 Hz, CH(C*H*$_3$)$_2$), 1.24 (d, $^3J_{HH}$ = 6.9 Hz, 3H, CH(C*H*$_3$)$_2$), 0.45 (d, $^3J_{HH}$ = 6.9 Hz, 3H, CH(C*H*$_3$)$_2$), 0.48-0.37 (m, 1H, Al-CH*H*-CH), 0.07 (s, 3H, Al-*Me*), − 0.05 (d, $^3J_{HH}$ = 6.9 Hz, 3H, CH(C*H*$_3$)$_2$), − 0.17 (s, 3H, Al-*Me*) ppm.
^{13}C NMR (75 MHz, C$_6$D$_6$): δ = 147.9 (d, $^3J_{CP}$ = 5.6 Hz, Ar), 147.5 (d, $^3J_{CP}$ = 4.5 Hz, Ar), 137.7 (d, $^3J_{CP}$ = 7.0 Hz, Ar), 133.6 (d, $^3J_{CP}$ = 8.7 Hz, Ar), 133.2 (d, $^3J_{CP}$ = 7.2 Hz, Ar), 132.8 (d, $^4J_{CP}$ = 2.6 Hz, Ar), 132.4 (d, $^4J_{CP}$ = 3.1 Hz, Ar), 129.9 (Ar), 129.0 (d, $^2J_{CP}$ = 10.6 Hz, Ar), 128.8 (s, Ar), 128.6 (Ar), 125.6 (d, $^4J_{CP}$ = 3.2 Hz, Ar), 125.0 (d, $^4J_{CP}$ = 2.9 Hz, Ar), 124.7 (d, $^4J_{CP}$ = 3.0 Hz, Ar), 122.8 (Ar), 123.9 (Ar), 41.0 (d, $^2J_{CP}$ = 10.2 Hz, (CH)*C*H$_2$S), 37.6 (d, $^1J_{CP}$ = 73.5 Hz, P*C*H), 28.4 (*C*H(CH$_3$)$_2$), 28.1 (*C*H(CH$_3$)$_2$), 23.3 (CH(*C*H$_3$)$_2$), 24.5 (CH(*C*H$_3$)$_2$), 25.9 (CH(*C*H$_3$)$_2$), 27.7 (CH(*C*H$_3$)$_2$), 16.8 (S-Me), 10.3 (Al-*C*H$_2$), − 5.5 (Al-Me), − 6.0 (Al-Me).
^{31}P NMR (121 MHz, C$_6$D$_6$): δ = 36.3 (s) ppm.
C$_{30}$H$_{41}$AlNPS (505.25): calcd. C 71.26, H 8.17, N 2.77, S 6.34; found C 70.69, H 7.99, N 2.46 S 5.62.

Synthesis and reactivity of biphenyl amines

Synthesis of (Ph-C$_6$H$_4$)N(DIPP)H

*t*Bu$_3$P (56.0 mg, 0.278 mmol) and Pd$_2$(dba)$_3$ (159 mg, 0.174 mmol) were dissolved in degassed toluene (30 mL) and the solution was stirred for 20 minutes. 2-Bromobiphenyl (1.00 mL, 5.80 mmol), *t*BuOK (720 mg, 6.40 mmol), and 2,6-di-*i*Pr-aniline (1.10 mL, 5.80 mmol) were added and the mixture was heated at 105°C for 19 hours. The suspension was cooled and filtered through a plug of silica and the remaining solid was washed with diethylether (3 x 20 mL). All organic phases were combined and all volatiles were evaporated under reduced pressure to give a sticky solid. This was extracted with hexanes (3 x 10 mL) and gave an oil upon evaporation of the solvent. Vacuum distillation of the oil (3 mbar, 300°C) yielded (Ph-C$_6$H$_4$)N(DIPP)H as a yellow oil (1.65 g, 5.01 mmol, 86%).

^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.60 (d, $^3J_{HH}$ = 8.1 Hz, 2H, *Ar*), 7.52 (t, $^3J_{HH}$ = 7.5 Hz, 2H, *Ar*), 7.41 (t, *J* = 7.5 Hz, 1H), 7.33-7.26 (br m, 2H, *Ar*), 7.25-7.17 (br m, 2H, *Ar*), 7.09 (t, $^3J_{HH}$ = 7.5 Hz, 1H, *Ar*), 6.80 (t, *J* =

7.5 Hz, 1H), 6.23 (d, $^3J_{HH}$ = 8.1 Hz, 1H, *Ar*), 5.24 (s, 1H, N-*H*), 3.15 (s, 2H, C*H*$(CH_3)_2$), 1.17 (d, $^3J_{HH}$ = 6.9 Hz, 6H, CH(C*H*$_3)_2$), 1.09 (d, $^3J_{HH}$ = 6.9 Hz, 6H, CH(C*H*$_3)_2$) ppm.

^{13}C NMR (75 MHz, C_6D_6): δ = 147.5 (Ar), 144.8 (Ar), 139.5 (Ar), 135.4 (Ar), 130.1 (Ar), 129.3 (Ar), 129.0 (Ar), 128.5 (Ar), 127.4 (Ar), 127.2 (Ar), 126.9 (Ar), 123.8 (Ar), 117.3 (Ar), 111.4 (Ar), 110.9 (Ar), 28.4 (*C*H$(CH_3)_2$), 24.5 (CH(*C*H$_3)_2$), 22.9 (CH(*C*H$_3)_2$), ppm.

$C_{24}H_{27}N$ (329.49): calcd. C 87.49, H 8.26, N 4.25; found C 87.06, H 8.36, N 3.84.

Synthesis of (Ph-C_6H_4)N(DIPP)Li

(Ph-C_6H_4)N(DIPP)H (1.65 g, 5.01 mmol) was dissolved in hexanes (15 mL) and cooled to – 70°C. *n*BuLi (2.7 mL (2M in hexanes), 5.4 mmol) was added slowly and the mixture was allowed to stir for one hour. The mixture was warmed to room temperature and separated by centrifugation. The obtained solid was washed with pentane (2 x 5 mL) to give (Ph-C_6H_4)N(DIPP)Li as a yellow solid (1.58 g, 4.70 mmol, 94%).

^{1}H NMR (300 MHz, C_6D_6): δ = 8.11 (dd, $^3J_{HH}$ = 7.6 Hz, $^5J_{HH}$ = 1.2 Hz, 2H, *Ar*), 7.32 (br m, 3H, *Ar*), 7.20-7.07 (br m, 4H, *Ar*), 6.92 (tt, $^3J_{HH}$ = 7.6 Hz, $^5J_{HH}$ = 1.2 Hz, 1H, *Ar*), 6.52 (td, $^3J_{HH}$ = 7.6 Hz, $^5J_{HH}$ = 1.2 Hz, 1H, *Ar*), 6.37 (dd, $^3J_{HH}$ = 7.6 Hz, $^5J_{HH}$ = 1.2 Hz, 1H, *Ar*), 3.71 (m, 2H, C*H*$(CH_3)_2$), 1.37 (d, $^3J_{HH}$ = 6.9 Hz, 6H, CH(C*H*$_3)_2$), 1.20 (d, $^3J_{HH}$ = 6.9 Hz, 6H, CH(C*H*$_3)_2$) ppm.

^{13}C NMR (75 MHz, C_6D_6): δ = 147.7 (Ar), 145.4 (Ar), 140.2 (Ar), 136.1 (Ar), 130.7 (Ar), 129.7 (Ar), 129.4 (Ar), 124.2 (Ar), 123.9 (Ar), 118.2 (Ar), 112.1 (Ar), 28.8 (*C*H$(CH_3)_2$), 24.6 (CH(*C*H$_3)_2$), 23.1 ((CH(*C*H$_3)_2$)) ppm.

Synthesis of (Ph-C_6H_4)N(DIPP)AlMe_2

(Ph-C_6H_4)N(DIPP)Li (200 mg, 0.594 mmol) was suspended in pentane (10 mL) and cooled to – 35°C. Me_2AlCl (0.653 mL (1M in hexanes), 0.653 mmol) was added slowly and the reaction mixture was stirred for 30 minutes. The mixture was warmed to room temperature and separated by centrifugation. The solid was dried under reduced pressure and subsequently extracted with dichloromethane (2 x 5 mL). Evaporation of the solvent and washing with hexanes (3 x 4 mL) gave (Ph-C_6H_4)N(DIPP)AlMe_2 as a sticky orange solid (48.1 mg, 0.125 mmol, 21%). Despite several attempts to exclude all air and moisture the obtained product always contained minor amounts of the ligand (Ph-C_6H_4)NH(DIPP) (min. 3%).

^{1}H NMR (300 MHz, C_6D_6): δ = 7.81 (d, $^3J_{HH}$ = 8.0 Hz, 2H, *Ar*), 7.30-7.10 (br m, 6H, *Ar*), 7.05 (d, $^3J_{HH}$ = 7.5 Hz, 1H, *Ar*), 7.00-6.91 (br m, 1H, *Ar*), 6.81 (t, $^3J_{HH}$ = 7.5 Hz, 1H, *Ar*), 6.68 (t, $^3J_{HH}$ = 7.4 Hz, 1H, *Ar*), 6.28 (d, $^3J_{HH}$ = 8.0 Hz, 1H), 3.51 (m, 2H, C*H*$(CH_3)_2$), 1.28 (d, $^3J_{HH}$ = 6.9 Hz, 6H, CH(C*H*$_3)_2$), 1.15 (d, $^3J_{HH}$ = 6.9 Hz, 6H, CH(C*H*$_3)_2$), − 0.83 (s, 6H, Al-*Me*) ppm.

^{13}C NMR (75 MHz, C_6D_6): δ = 151.6 (Ar), 147.9 (Ar), 146.8 (Ar), 140.6 (Ar), 135.6 (Ar), 130.4 (Ar), 129.0 (Ar), 125.8 (Ar), 125.0 (Ar), 117.2 (Ar), 117.0 (Ar), 28.6 (*C*H(CH_3)$_2$), 25.2 (CH(*C*H$_3$)$_2$), 25.0 (CH(*C*H$_3$)$_2$), − 8.71 (Al-Me) ppm.

Synthesis of (Ph-C_6H_4)N(DIPP)$AlMe_2$·THF

(Ph-C_6H_4)N(DIPP)$AlMe_2$ (40.0 mg, 0.104 mmol) was dissolved in THF (5 mL). Slow evaporation of the solvent gave a brown solid. The solid was dried under reduced pressure and washed with pentane (2 x 2 mL) to give (Ph-C_6H_4)N(DIPP)$AlMe_2$·THF as a colorless solid (25.0 mg, 547 μmol, 53%).

^{1}H NMR (300 MHz, C_6D_6): δ = 7.80 (dd, $^3J_{HH}$ = 8.2 Hz, $^5J_{HH}$ = 1.2 Hz, 2 H, *Ar*), 7.30-7.19 (br m, 5H, *Ar*), 7.11-6.93 (br m, 3H, *Ar*), 6.70 (td, $^3J_{HH}$ 7.3 Hz, $^5J_{HH}$ = 1.2 Hz, 1H, *Ar*), 6.42 (dd, $^3J_{HH}$ = 8.2 Hz, $^5J_{HH}$ = 1.2 Hz, 1H, *Ar*), 3.65 (m, 2H, C*H*(CH_3)$_2$), 3.25 (m, 4H, THF), 1.23 (dd, $^3J_{HH}$ = 9.4 Hz, $^5J_{HH}$ = 6.8 Hz, 12H, (CH(C*H*$_3$)$_2$), 1.11 (m, 4H, THF), − 0.84 (s, 6H, Al-*Me*) ppm.

Synthesis of (Ph-C_6H_4)N(*t*Bu)$AlMe_2$

(Ph-C_6H_4)N(*t*Bu)Li (200 mg, 0.865 mmol) was suspended in pentane (10 mL) and cooled to – 35°C. Me_2AlCl (0.952 mL (1M in hexanes), 0.952 mmol) was added slowly and the reaction mixture was stirred for 30 minutes. The mixture was warmed to room temperature, separated by centrifugation and the solid was extracted with dichloromethane (2 x 5 mL) to give a brown oil. Washing with hexanes (3 x 4 mL) gave (Ph-C_6H_4)N(*t*Bu)$AlMe_2$ as a sticky, oily brown solid (86.1 mg, 0.242 mmol, 28%). Despite several attempts to exclude all air and moisture the obtained product always contained ligand and another unidentified species (min. 20%).

^{1}H NMR (300 MHz, C_6D_6): δ = 8.01-7.94 (br m, 1H, *Ar*), 7.46-7.27 (br m, 5H, *Ar*), 7.02 (td, $^3J_{HH}$ = 7.6 Hz, $^5J_{HH}$ = 1.4 Hz, 1H, *Ar*), 6.84 (td, $^3J_{HH}$ = 7.6 Hz, $^5J_{HH}$ = 1.4 Hz, 1H, *Ar*), 6.23 (dd, $^3J_{HH}$ = 7.6 Hz, $^5J_{HH}$ = 1.4 Hz, 1H, *Ar*), 0.62 (s, 9H, C(C*H*$_3$)$_3$), − 0.01 (s, 3H, Al-*Me*), − 0.84 (s, 3H, Al-*Me*) ppm.
Due to unavoidable impurities it was not possible to obtain an interpretable ^{13}C spectrum.

Note: for the following synthetic description the reaction were modified and will therefore be described.

Attempted alternative synthesis of (Ph-C_6H_4)N(*t*Bu)$AlMe_2$

tBu_3P (112 mg, 0.554 mmol) and $Pd_2(dba)_3$ (350 mg, 0.382 mmol) were dissolved in degassed toluene (40 mL) and the mixture was allowed to stir for 20 minutes. 2-bromobiphenyl (2.00 mL, 11.6 mmol), *t*BuOK (1.44 g, 12.8 mmol), and *t*$BuNH_2$ (1.22 mL, 11.60 mmol) were added and the mixture was heated at 105°C for 48 hours. The suspension was cooled and filtered through a plug of silica and the remaining solid was washed with diethylether (3 x 50 ml). All organic phases were combined and all volatiles were evaporated under reduced pressure to give a sticky solid. This was extracted with hexanes (3 x 10 mL)

and gave an oil upon evaporation of the solvent. Vacuum distillation of the oil (3 mbar, 280°C) yielded (Ph-C_6H_4)N(*t*Bu)NH as a yellow oil (1.65 g, 5.01 mmol, 86%). (see ref. 18 for the NMR data)

(Ph-C_6H_4)N(*t*Bu)NH (1.52 g, 6.75 mmol) was dissolved in hexanes (15 mL) and cooled to – 35°C. *n*BuLi (3.24 ml (2.5 M in hexanes) was added and the suspension was warmed to room temperature and stirred for 24 hours. The mixture was separated by centrifugation and the solid was washed with pentane (3 x 5 mL) to give (Ph-C_6H_4)N(*t*Bu)NLi as a pale yellow solid (1.25 g, 5.4 mmol, 80%). (see ref. 18 for the NMR data)

(Ph-C_6H_4)N(*t*Bu)NLi (200 mg, 0.865 mmol) was dissolved in hexanes (10 mL) and cooled to – 35°C and Me_2AlCl was added slowly (0.952 mL (1M in hexanes), 0.952 mmol). The mixture was warmed to room temperature and stirred for 24 hours. The solution was concentrated to 1/3 of its original volume and stored in the freezer. After several days colorless crystals were obtained and isolated by filtration (20.6 mg, 86.5 μmol, 10%). X-ray analysis revealed this to be [(Ph-C_6H_4)N(*t*Bu)H](Ph-C_6H_4)AlMe instead of the desired (Ph-C_6H_4)N(*t*Bu)$AlMe_2$.
All attempts to characterize the product by NMR led to decomposition and non-interpretable NMR spectra.

Reaction of (Ph-C_6H_4)$_2$N$AlMe_2$ with Cp*$_2$$ZrMe_2$

(Ph-C_6H_4)$_2$N$AlMe_2$ (25.0 mg, 66.3 μmol) and Cp*$_2$$ZrMe_2$ (16.0 mg, 40.8 μmol) were combined in an NMR tube and dissolved in C_6D_6 (0.6 mL). The mixture was shaken for one minute, ^{1}H NMR analysis showed only the respective starting materials.
Addition of methylallyl thioether to trap a potential cationic complex did not lead to a reaction and heating of subsequent samples led to decomposition.

Crystal structure determination

All crystal structures were solved using direct methods (SHELXT-2014)[27] and refined with SHELXL-2014[28] using OLEX2.[29] All geometry calculations and graphics were performed with PLATON.[30] The hydrogen atoms were places on calculated positions and were refined isotropically in a riding mode. Special features of the refinement are noted below. The crystal data have been summarized in Table 4.1.

Structural determination of Ph_2PN(DIPP)$AlMe_2$·THF:

The structure of Ph_2PN(DIPP)$AlMe_2$·THF crystallizes in the chiral space group $P2_12_12_1$ and the Flack parameter refined to 0.023(26).

Structural determination of [(DIPPN)$PPh_2(C_4H_8S)$]$AlMe_2$:

[(DIPPN)$PPh_2(C_4H_8S)$]$AlMe_2$ crystallizes with two molecules in the asymmetric part of the unit cell. On one of them the thioether molecule is disordered in the S and terminal CH_3 atoms. This disorder was modeled and the atoms were refined anisotropically.

Structural determination of (Ph-C_6H_4)N(DIPP)$AlMe_2$·THF:

Due to the poor data quality, all aromatic rings have been constrained with the AFIX 66 command.

Table 4.1 Crystal structure data

Sample	$[Ph_2PN(DIPP)AlMe_2]_2$	$Ph_2PN(DIPP)AlMe_2$·THF	$[Ph_2PN(DIPP)](C_4H_8S)AlMe_2$
Moiety Formula	$C_{52}H_{66}Al_2N_2P_2$	$C_{30}H_{41}AlNOP$	$C_{30}H_{41}AlNPS$
Empirical Formula	$C_{52}H_{66}Al_2N_2P_2$	$C_{30}H_{41}AlNOP$	$C_{30}H_{41}AlNPS$
M_w (g/mol)	834.97	489.59	505.65
Color/Appearance	Colorless blocks	Colorless blocks	Colorless blocks
Crystal Size (mm)	0.22 x 0.11 x 0.10	0.26 x 0.20 x 0.15	0.18 x 0.15 x 0.11
Crystal System	triclinic	orthorhombic	triclinic
Space Group	$P\bar{1}$	$P2_12_12_1$	$P\bar{1}$
a, b, c (Å)	9.7257(15) 10.3432(17) 12.758(2)	9.8330(12) 10.0370(6) 28.666(6)	9.296(2) 16.751(3) 18.941(5)
α, β, γ (°)	96.545(3) 99.302(3) 109.982(3)	90 90 90	88.25(2) 89.542(16) 80.584(16)
V(Å^3)	1170.3(3)	2829.7(7)	2908.3(11)
Z	2	4	4
ρ (g/cm^3)	1.185	1.149	1.155
μ (mm^{-1})	0.164 (Mo K_α)	0.150 (Mo K_α)	0.215(Mo K_α)
Temperature (K)	150	150	150
$\theta_{min-max}$ (°)	1.6-29.6	2.9-27.5	2.7-26.5
Dataset (h, k, l)	−13:13, −14:14, −17:17	−12:12, −12:13, −33:37	−11:11, −21:21, −23:23
Total Reflexes	24513	37996	63838
Unique Reflexes	6532	6328	12047
R(int)	0.0244	0.0379	0.0951
Parameter	268	313	646
Observed Reflexes [I > 2.0 σ (I)]	5753	5757	7292
R_1	0.0341	0.0400	0.0743
ωR2	0.0834	0.1013	0.1364
GooF	1.034	1.131	1.039
$\Delta\rho_{fin}$ (min/max) (e/Å^3)	−0.25, 0.42	−0.38, 0.35	−0.40, 0.51

Sample	(Ph-C_6H_4)N(DIPP)$AlMe_2$·THF	[(Ph-C_6H_4)N(*t*Bu)H](Ph-C_6H_4)AlMe
Moiety Formula	$C_{30}H_{40}AlNO$	$C_{29}H_{30}AlN$
Empirical Formula	$C_{30}H_{40}AlNO$	$C_{29}H_{30}AlN$
M_w (g/mol)	457.61	419.52
Color/Appearance	Colorless blocks	Colorless blocks
Crystal Size (mm)	0.28 x 0.05 x 0.04	0.18 x 0.11 x 0.07
Crystal System	orthorhombic	triclinic
Space Group	*Pbca*	$P\bar{1}$
a, b, c (Å)	17.7180(9) 15.5260(13) 19.5910(11)	11.283(2) 12.611(3) 16.478(4)
α, β, γ (°)	90 90 90	90.35(3) 90.27(2) 92.17(2)
V(Å^3)	5389.3(6)	2342.9(9)
Z	8	6
ρ (g/cm^3)	1.128	1.196
μ (mm^{-1})	0.097 (Mo K_α)	0.121 (Mo K_α)
Temperature (K)	150	150
$\theta_{min-max}$ (°)	2.7-26.0	2.7-27.5
Dataset (h, k, l)	−21:21, −19:19, −24:24	−14:14, −16:16, −21:21
Total Reflexes	57077	69625
Unique Reflexes	5285	10551
R(int)	0.2406	0.1357
Parameter	268	567
Observed Reflexes [I > 2.0 σ (I)]	2642	6546
R_1	0.0960	0.0613
ωR2	0.2248	0.1282
GooF	1.065	1.079
$\Delta\rho_{fin}$ (min/max) (e/Å^3)	−0.61, 0.48	−0.32, 0.28

4.5 References

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