Flexible Coordination of N,P-Donor Ligands in Aluminum Dimethyl and Dihydride Complexes

Citation for published version:
Falconer, RL, Nichol, GS & Cowley, MJ 2019, 'Flexible Coordination of N,P-Donor Ligands in Aluminum Dimethyl and Dihydride Complexes', Inorganic Chemistry. https://doi.org/10.1021/acs.inorgchem.9b01061

Digital Object Identifier (DOI):
10.1021/acs.inorgchem.9b01061

Link:
Link to publication record in Edinburgh Research Explorer

Document Version:
Peer reviewed version

Published In:
Inorganic Chemistry

General rights
Copyright for the publications made accessible via the Edinburgh Research Explorer is retained by the author(s) and / or other copyright owners and it is a condition of accessing these publications that users recognise and abide by the legal requirements associated with these rights.

Take down policy
The University of Edinburgh has made every reasonable effort to ensure that Edinburgh Research Explorer content complies with UK legislation. If you believe that the public display of this file breaches copyright please contact openaccess@ed.ac.uk providing details, and we will remove access to the work immediately and investigate your claim.
Flexible coordination of N,P-Donor Ligands in Aluminum Dimethyl and Dihydride Complexes

Rosalyn L. Falconer, Gary S. Nichol, Michael J. Cowley*

School of Chemistry, University of Edinburgh, Joseph Black Building, David Brewster Road, Edinburgh, EH9 3FJ, UK

ABSTRACT.

Aluminum hydrides, once a simple class of stoichiometric reductants, are now emerging as powerful catalysts for organic transformations such as the hydroboration or hydrogenation of unsaturated bonds. The coordination chemistry of aluminum hydrides supported by phosphorus donors is relatively underexplored. Here, we report aluminum dihydride and dimethyl complexes supported by amido-phosphine ligands, and study their coordination behavior in solution and in the solid state. All complexes exist as κ²-N,P complexes in the solid state. However, we find that for amidophosphine ligands bearing bulky aminophosphine donors, aluminum dihydride and dimethyl complexes undergo a ‘ligand-slip’ rearrangement in solution to generate κ²-N,N complexes. Thus, importantly for catalytic activity, we find that the coordination behavior of the phosphorus donor can be modulated by controlling its steric bulk. We show that the reported aluminum hydrides catalyze the hydroboration of alkynes by HBPin, and that the variable coordination mode exhibited by the amidophosphine ligand modulates catalytic activity.
Introduction

Aluminum hydrides such as LiAlH$_4$, RedAl (sodium bis(2-methoxyethoxy)aluminum hydride) and AlH$_3$ are ubiquitous in synthetic chemistry for their use as reducing agents.\textsuperscript{1} Recently, the scope of reactivity of these simple aluminum hydrides has been expanded into the catalytic hydroboration of alkenes and alkynes; a development of significant environmental and economic importance due to the high abundance and relatively low toxicity of aluminum compared to platinum group metals.\textsuperscript{2-3} Numerous other uncomplicated aluminum hydride compounds are also capable of the hydroboration or even hydrogenation of unsaturated polar bonds such as aldehydes, ketones or imines.\textsuperscript{4-5} Aluminum hydride compounds with more complex ligands have also been investigated. For example, $N$-heterocyclic imine-coordinated aluminum hydrides catalyze carbonyl hydroboration\textsuperscript{6} whilst the $\beta$-diketiminate stabilized aluminum dihydride I (Figure 1), also catalyzes the hydroboration of alkynes.\textsuperscript{7} The dihydride I is also a precursor to $\beta$-diketiminate stabilized Al(I) species (at least within the coordination sphere of a transition metal).\textsuperscript{8}

Reported aluminum dihydride complexes overwhelmingly use nitrogen donor ligands (e.g. I-III, Figure 1).\textsuperscript{9-13} Typically, these ligands are also multi-dentate (to stabilize the intrinsically electron poor aluminum center) and sterically hindered, in order to prevent dimerization or oligimerization by bridging interactions. In coordination chemistry, ligands greatly influence the chemistry at the metal center. Thus, the investigation and development of aluminum hydride chemistry using a diverse array of ligand classes is essential for the expansion of aluminum hydride chemistry and catalysis.

Aluminum dihydrides or related species with phosphorus-based ligands are much rarer. A few examples of dimethyl aluminum complexes with mixed-donor ligands are known, in which
bidentate ligands having one nitrogen donor also contain a “soft” donor, such as sulfur or phosphorus (IV and V, Figure 1).\textsuperscript{14-18} The likely more labile aluminum-phosphorus interaction offers the possibility of hemilability, which can be useful in the stabilization of catalytic transition or resting states.\textsuperscript{19} Indeed, Fryzuk \textit{et al.} used NMR spectroscopy to demonstrate the fluxional coordination of the phosphorus donor atoms in V, resulting in an equilibrium between 4- and 5-coordinate aluminum centers.\textsuperscript{20}

![Figure 1: Literature examples of aluminum dihydride and dimethyl complexes stabilized by nitrogen based ligands (I-III) or mixed donor ligands (IV-VI).\textsuperscript{9-11, 15, 20-21} (I, IV: Ar = 2,6-C\textsubscript{6}H\textsubscript{3}Pr\textsubscript{2}, VI: R = R’ = Ph, \textsuperscript{1}Pr or R = Ph, R’ = \textsuperscript{1}Pr).}

In comparison to mixed-donor methyl complexes, mixed-donor aluminum dihydride complexes are scarce, with only a single example.\textsuperscript{21} Most phosphorus-coordinated aluminum hydrides are limited to simple adducts between phosphines and alane, with the exception of VI (Figure 1), reported by Liang \textit{et al.} in 2009, which was synthesized \textit{via} the reduction of the corresponding aluminum dichloride using LiAlH\textsubscript{4}.\textsuperscript{21-22} Hemilability of the phosphorus donors was not found in this example, likely due to the rigidity of the ligand backbone.

Herein, we describe novel aluminum dimethyl and dihydride species stabilized by mixed \textit{N,P}-donor ligands that display flexible coordination modes based on a ‘ligand-slip’ phenomenon.
Results and discussion

The amido-phosphine ligands 1a-c\textsuperscript{23} (Figure 2) have previously been used to prepare nickel and palladium complexes, as well as to support reactive Si(II) compounds\textsuperscript{24-27}. The steric bulk around both nitrogen and phosphorus centers of 1a-c has not only enabled the isolation of reactive species such as Si(II) hydrides, but also modulates reversible Si(II)/Si(IV) oxidative additions/reductive eliminations. At the phosphorus donor in particular, both steric bulk and electron donating ability are readily tunable. We were interested whether this class of ligands could be employed to support aluminum centers and whether they could be used to modulate their structure and reactivity.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure2.png}
\caption{Mixed donor ligands 1a-c}
\end{figure}

\textbf{Synthesis and solid-state structures of dimethyl aluminum complexes.} Dimethylaluminum complexes are a broad class of compounds that have been reported as catalysts or cocatalysts in alkene polymerisation\textsuperscript{28-30}. Complexes of dimethyl aluminum stabilized by many nitrogen or mixed donor ligands have been reported, rendering this class of compounds ideal for benchmarking the coordination abilities of ligands 1a-c. We decided to first investigate the coordination of ligands 1 to dimethyl aluminum moieties.

The coordination of 1b and 1c to silicon(IV) centers has been reported and was achieved by deprotonation before treatment with the appropriate silicon halide\textsuperscript{27}. Accordingly, ligands 1a-c were deprotonated with \textsuperscript{6}BuLi at -78 °C to afford yellow solutions of 2a-c (Scheme 1). A characteristic resonance is observed in \textsuperscript{31}P{\textsuperscript{1}H} NMR spectra of these solutions in the form of a 1:1:1:1 quartet upfield compared to the free ligand. The 1:1:1:1 multiplicity indicates coordination
to lithium (e.g. 2a $^{31}$P$^{1}$H NMR: $\delta$ 10.9 ppm, $J$$_{PLi}$ = 54 Hz). Similarly, in the $^7$Li NMR spectra, doublets are observed due to coupling with phosphorus (e.g. 2a $^7$Li NMR: $\delta$ 1.3 ppm, $J$$_{LiP}$ = 54 Hz).

Scheme 1: Lithiation of ligands 1 to form 2 followed by reaction with dimethylaluminum chloride to form dimethyl aluminum complexes 3a-c.

The dimethyl aluminum complexes 3a-c were obtained by reaction of the in-situ generated lithiated ligands 2 with 1 equivalent of dimethylaluminum chloride. Extraction of the products in pentane, followed by filtration and evaporation of the solvent afforded 3a-c as yellow air-sensitive solids. Complexes 3a and 3c could be isolated as analytically pure solids by crystallization, whilst 3b was clearly identified but resisted purification attempts. All three complexes 3a-c were extremely sensitive to air and moisture.
Figure 3: Molecular structure of 3a (left) and 3c (right) with thermal ellipsoids drawn at 50% probability level. Hydrogen atoms and disordered ligand atoms are omitted for clarity. Selected bond distances (Å) and angles (°) for 3a: N(1)-Al(1) 1.895(14), P(1)-Al(1) 2.4800(6), Al(1)-C(1) 1.9652(19), Al(1)-C(2) 1.970(2), N(1)-Al(1)-P(1) 86.67(4), N(1)-Al(1)-C(1) 116.12(8), N(1)-Al(1)-C(2) 115.25(8), P(1)-Al(1)-C(1) 114.53(7), P(1)-Al(1)-C(2) 114.00(7), C(1)-Al(1)-C(2) 109.00(9); 3c: N(1)-Al(1) 1.917(3), P(1)-Al(1) 2.5304(9), Al(1)-C(1) 1.967(4), Al(1)-C(2) 1.964(4), N(1)-Al(1)-P(1) 85.59(8), N(1)-Al(1)-C(1) 116.14(19), N(1)-Al(1)-C(2) 116.19(19), P(1)-Al(1)-C(1) 115.98(13), P(1)-Al(1)-C(2) 115.99(14), C(1)-Al(1)-C(2) 106.4(2).

The solid-state structures of 3a and 3c were determined by X-ray crystallography (Figure 3). Both compounds have a tetrahedral aluminum center with coordinated nitrogen and phosphorus donors forming a planar ring. The ring is heavily skewed with (as might be expected) a substantially shorter interaction between aluminum and the N-donor than with the phosphine (e.g.
3a, Al(1)–N(1) 1.8985(14) Å vs Al(1)–P(1) 2.4800(6) Å. Both Al–N and Al–P distances are comparable to those previously reported, for example the N,P-coordinated dimethyl aluminum complex IV (Al–N 1.894(6) Å, Al–P 2.477(3) Å).\textsuperscript{15}

The Al–N bond distances of 3a and 3c are indistinguishable, but the Al–P bond length is slightly longer in the latter at 2.5304(8) Å, indicating the phosphorus is less strongly bound to the aluminum center. The aminophosphine donor of 3c is more electron donating than the dialkylphosphine of 3a, which would be expected to give rise to the opposite trend.\textsuperscript{31} The origin of the difference is likely due to steric effects: the greater steric bulk in 3c prevents the close approach of the phosphine to the aluminum center. Indeed, this can be observed in the C(1)–Al(1)–C(2) angle, which is smaller in the case of 3c (106.4(2)°) than 3a (109.00(9)°) despite the similar bite angles of the two (3a, 86.67(4)°; 3c, 85.59(8)°).

**Solution behavior of 3a-c.** Despite their similar solid-state structures, in the solution phase NMR spectroscopy revealed differences in coordination behavior between the dimethylaluminum complexes 3a-c. No signals were observed for any of the compounds by $^{27}$Al NMR spectroscopy. NMR spectroscopy of dimethylaluminum complexes 3a and 3b was consistent with the solid-state structure determined for 3a. $^{31}$P{$^{1}$H} NMR spectroscopy revealed a single resonance for each (3a: 1.6 ppm, 3b: 64.0 ppm) shifted upfield compared to the respective free ligand resonances ($\Delta\delta$(3a) = -54.4 ppm; $\Delta\delta$(3b) = -83.3 ppm). The $^{31}$P{$^{1}$H} resonances for 3a and 3b were also significantly broadened in comparison to free ligands 1a and 1b, presumably as a result of coordination of the phosphorus to the quadrupolar (I = 5/2) aluminum nucleus (3a full width at half maximum ($\Delta\nu_{1/2}$) = 21.1 Hz, 1a = 2.7 Hz).
In the $^1$H NMR spectra of $3a$ and $3b$, resonances corresponding to the aluminum methyl groups appear as doublets arising from coupling to phosphorus ($3a$: -0.33 and -0.19 ppm, $^2J_{HP} = 2.5$ Hz). The $^1$H NMR spectrum also shows that each CH$_3$ group in the Dipp substituent is inequivalent, indicating restricted rotation likely due to steric constraints.

Crystalline $3c$ was also characterized by solution phase NMR spectroscopy. Surprisingly, the $^{31}$P{$^1$H} NMR spectrum contained two resonances, at 99.9 ppm and 49.7 ppm in a ratio of 3:2 (the same ratio was observed by $^1$H NMR spectroscopy). The resonance at 49.7 ppm is broadened ($\Delta \nu_{1/2} = 47.5$ Hz) and downfield ($\Delta \delta = -40.9$ ppm) from that of $1c$, so is consistent with coordination of the phosphorus to the aluminum center as in $3a$ and $3b$. Conversely, the resonance at 99.9 ppm is sharp ($\Delta \nu_{1/2} = 5.3$ Hz) and close in chemical shift to that of the free ligand $1c$ ($\Delta \delta = +9.3$ ppm), which indicates the phosphorus in this environment is not coordinated to the aluminum center.

Scheme 2: Proposed structures of $\kappa^2$-$N,P$ and $\kappa^2$-$N,N$ $3c$. In the solid state, only $\kappa^2$-$N,P$ $3c$ is observed, whilst in solution, both $\kappa^2$-$N,P$ and $\kappa^2$-$N,N$ isomers are observed.

On the basis of the $^{31}$P NMR spectroscopic data, and by analogy with the behavior more fully studied in the hydride analogue $5c$ (see below), we propose that $3c$ exists in two forms in solution, in which the ligand exhibits a variable coordination mode, having either $\kappa^2$-$N,P$ or $\kappa^2$-$N,N$ coordination. In the solid state, $\kappa^2$-coordination is exclusively observed. In solution, however, the two isomers are present as a result of the flexible coordination mode of the ligand.
The $^1$H NMR spectrum of 3c is consistent with both $\kappa^2$-N,P and $\kappa^2$-N,N isomers existing in solution, with two sets of resonances present in a ratio of 57:43 (consistent with the 3:2 ratio observed by $^{31}$P NMR). Multinuclear 2-D NMR spectroscopic experiments verified that in both isomers the ligand backbone was intact and undisturbed. The possibility of a dimeric $\kappa^1$-N isomer of 3c (with e.g. bridging methyl ligands) was excluded based on an analysis of the $^1$H DOSY NMR spectrum, which indicated that both the observed isomers diffused at the same rate in solution. Similarly, high resolution mass spectrometry also identified the product as 3c with no evidence of a dimeric species observed.

**Synthesis of aluminum dihydride complexes.** Following the preparation of the dimethyl aluminum complexes 3a-c, we turned our attention to the preparation of aluminum dihydride complexes. Ligands 1a-c do not react with Me$_2$EtN·AlH$_3$, in contrast to the observed reactivity of amidine ligands which evolve H$_2$ and form aminidinato aluminum dihydrides. Treatment with LiAlH$_4$ also had no effect. Thus, we used the lithiated ligands 2a-c as precursors instead.

Treatment of 2b with a single equivalent of Me$_2$EtN·AlH$_3$ resulted in a yellow solution, the $^{31}$P NMR spectrum of which revealed a quartet (110.8 ppm, $^2J_{PH} = 34$ Hz) which collapsed to a singlet in the $^{31}$P{$^1$H} spectrum. This evidence, as well as further characterization by multinuclear NMR spectroscopy and mass spectrometry, confirmed the formation of aluminate complex 4b (Scheme 3).

The addition of a second equivalent of Me$_2$EtN·AlH$_3$ to solutions of 4b was monitored by $^{31}$P{$^1$H} NMR spectroscopy, which revealed complete consumption of 4b and formation of a new species represented by a broad singlet (61.3 ppm, $\Delta\nu_\delta = 55.7$ Hz), indicating phosphorus coordination to aluminum. Analysis of the $^{27}$Al NMR spectrum revealed the formation of LiAlH$_4$. Based on this evidence, the reaction pathway shown in Scheme 3 is proposed: reaction of 2b with
Me₂EtN·AlH₃ proceeds by forming 4b by displacement of the amine from Me₂EtN·AlH₃. The second equivalent of Me₂EtN·AlH₃ abstracts a hydride from 4b, generating 5b, LiAlH₄, and eliminating the amine.

Scheme 3: Proposed mechanism for the reaction of 2 with Me₂EtN·AlH₃ (NR₃ = NMe₃ or NMe₂Et) to form aluminum dihydride 5 via charged intermediate 4.

When 2a was treated with 1 equivalent of Me₂EtN·AlH₃, the resulting pale yellow solution was revealed to contain a mixture of compounds by ³¹P{¹H} NMR spectroscopy. In addition to residual lithiated ligand 2a, equal quantities of the aluminate intermediate 4a (8.0 ppm) and the neutral aluminum dihydride 5a (-10.1 ppm) were observed. LiAlH₄ was also observed by ²⁷Al NMR spectroscopy. The 2:1:1 ratio of the three species reveals that the lithiated ligand 2a and the intermediate aluminate 4a react at comparable rates with Me₂EtN·AlH₃ to generate the statistical mixture. This contrasts to the situation for 4b, where hydride abstraction by Me₂EtN·AlH₃ is much slower than its coordination to lithiated ligand 2b. Upon addition of a second equivalent of Me₂EtN·AlH₃ to 4a, the reaction mixture turned colorless and the ³¹P{¹H} NMR spectrum showed complete conversion to 5a (7.5 ppm).

Preparatively, the dihydride complexes 5a-c were obtained in multi-gram quantities from treatment of the lithiated ligands 2a-c with 2 equivalents of Me₃N·AlH₃ or Me₂EtN·AlH₃. All three
compounds could be isolated as colorless solids in excellent yields of 80-90 %. Dihydrides 5b and 5c could be further purified by crystallization from hexane.

In the \textsuperscript{1}H NMR spectra of 5a and 5b, Al-H resonances are visible as very broad singlets at 4.6 ppm (5a, $\Delta \nu_{\text{b}} = 71.6$ Hz; 5b $\Delta \nu_{\text{b}} = 125.3$ Hz), due to the influence of the quadrupolar aluminum atom. Despite the lower steric influence of the hydride ligands compared to the methyl ligands of 3a and 3b, the methyl groups of the Dipp-substituent remain inequivalent, indicating continued restricted rotation. Compound 5c has more complex solution behavior that will be discussed below.

IR spectroscopy of solid-state samples of 5a-c revealed the expected symmetric and antisymmetric Al-H stretches (5a: 1810, 1786; 5b 1831, 1816; 5c 1825, 1801 cm$^{-1}$) for a four coordinate aluminum dihydride center.$^{33-34}$

**Solid state structures of 5b and 5c.** The structures of 5b and 5c were verified by X-ray diffraction (Figure 4). Broadly, the structures are analogous to those of 3a and 3c. The amido-phosphine ligand in each compound is $\kappa^2$-$\text{N,P}$ coordinated, which together with the hydride ligands (located using a difference map and allowed to refine freely) results in a tetrahedral environment at the aluminum center. The two structures have statistically identical N–Al bond distances (5b: 1.8972(15) Å; 5c: 1.892(2) Å) which are essentially identical to those observed for the dimethyl analogues 3a and 3c. A more substantial difference is observed in the P–Al bond distances, which for the dihydride 5c is shorter than in the corresponding dimethyl complex 3c (Al(1)–P(1) 5c 2.4791(10) Å, 3c 2.5304(8) Å). The contraction of this bond can be explained by the smaller size of the hydride substituents. Similarly, a comparison between the two dihydrides 5b and 5c reveals a shorter Al(1)–P(1) distance for 5b as a result of reduced bulk at the phosphorus center in comparison to 5c (5b 2.4442(7) Å, 5c 2.4791(10) Å). The larger bite angles for the dihydrides 5b
and 5c [5b (87.47(5)°), 5c (86.60(6)°)] compared to the dimethyl compounds is also due to the smaller hydride substituents compared to methyl groups.

Figure 4: Molecular structures of 5b (left) and 5c (right). The aluminum hydride atoms were located using a difference map and allowed to refine freely. Ligand hydrogen atoms and disorder omitted for clarity. Selected bond lengths (Å) and angles (deg.) 5b: N(1)-Al(1) 1.8972(15), P(1)-Al(1) 2.4442(7), N(1)-Al(1)-P(1) 87.47(5); 5c: N(1)-Al(1) 1.892(2), P(1)-Al(1) 2.4790(10), N(1)-Al(1)-P(1) 86.60(6)
**Solution Phase NMR Characterization of 5c.** Like its dimethyl analogue 3c, the dihydride 5c exhibits variable coordination modes in solution. Upon dissolution of crystalline 5c, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum revealed the presence of two broad singlets at 96.9 ppm ($\Delta\nu_\delta = 137.9$ Hz) and 47.8 ppm ($\Delta\nu_\delta = 96.6$ Hz) in a ratio of 1:2. By $^1\text{H}$ NMR, two sets of resonances were also observed for all proton environments, including the dihydride ligands (signals at $\kappa^2$-$N,N$ $5c$ 4.3 ppm, $\kappa^2$-$N,P$ $5c$ 4.6 ppm. The ratio of the two species as measured by $^1\text{H}$ NMR in a ratio of 35:65, consistent with that observed in the $^{31}\text{P}$ NMR spectrum).

![Diagram of proposed structures of $\kappa^2$-$N,P$ and $\kappa^2$-$N,N$ 5c.](image)

Scheme 4: Proposed structures of $\kappa^2$-$N,P$ and $\kappa^2$-$N,N$ 5c. In the solid state, only $\kappa^2$-$N,P$ 5c is observed, whilst in solution both $\kappa^2$-$N,P$ and $\kappa^2$-$N,N$ isomers are observed.

The two solution-phase isomers of 5c were determined to be $\kappa^2$-$N,P$ 5c, as observed in the solid state, and a $\kappa^2$-$N,N$ isomer in which the phosphine ligand has ‘slipped’ and coordinates through one of the phosphorus-bound nitrogen atoms (Scheme 4). Evidence for the $\kappa^2$-$N,N$ coordination mode is as follows:

1. The two isomers are both monomeric species, as revealed by $^1\text{H}$-DOSY measurements which indicate similar diffusion coefficients. Thus, we were able to rule out the presence of a dimeric species with bridging hydrides (consistent with solution- and solid-phase IR spectroscopy which did not reveal evidence of bridging hydride ligands).

2. In the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum, the resonance at 96.9 ppm is assigned to the $\kappa^2$-$N,N$ isomer due to its similarity to that observed for the free ligand 1c (90.6 ppm), which indicates the
phosphorus center is not coordinated to aluminum. The resonance at 47.8 ppm is assigned to
the \( \kappa^2-N,P \) isomer observed in the solid state (confirmed by solid-state NMR measurements
– see below).

3. The aluminum-hydride stretching frequencies recorded for 5c in solution (1823 cm\(^{-1}\)) and in
the solid-state (1825, 1801 cm\(^{-1}\)) are consistent with a four-coordinate aluminum dihydride
species in both phases, ruling out a \( \kappa^1-N \) isomer in which the phosphine is uncoordinated.

4. Using DFT we performed geometry optimization and frequency calculations on \( \kappa^2-N,P \)
isomers of 5a-5c at the and M062X/Def2SVPP and M062X/6,31G+(d,p)/Lanl2DZ levels
(table S1). Following the lead of Crimmin et al., we found that calculations using the split
basis set were essential to replicate experimentally observed Al–H stretching frequencies.\(^{33}\)
The calculations accurately reproduced the experimentally observed geometries and IR
stretching frequencies for 5a-c, enabling us to use this computational methodology to assign
the identity of the solution-phase isomer of 5c.

5. A relaxed potential energy surface (PES) scan of 5c in which the Al–P distance was increased
systematically starting from the \( \kappa^2-N,P \) geometry revealed two potential minima (Figure S1),
which were reoptimized at the M062X/6,31G+(d,p)/Lanl2DZ level (Figure 5, Table S2). A
\( \kappa^1-N \) isomer was found to be 22.6 kcal mol\(^{-1}\) higher in energy than the \( \kappa^2-N,P \) isomer (the
calculated Al–H stretching frequencies for this three-coordinate aluminum dihydride of 1934
and 1922 cm\(^{-1}\) were also inconsistent with experimental values). However, the \( \kappa^2-N,N \) isomer
located in the PES scan was found to be very close in energy to \( \kappa^2-N,P \) 5c (–0.8 kcal mol\(^{-1}\)
more stable – DFT does not replicate the experimentally observed order of stability, though
it does correctly place the two species very close in energy). Calculated Al–H stretching
frequencies for \( \kappa^2-N,P \) and \( \kappa^2-N,N \) 5c (1863, 1845 and 1860 and 1813 cm\(^{-1}\) respectively) are
sufficiently close to explain the single peak observed in the experimental solution-phase spectrum (1829 cm\(^{-1}\)).

Figure 5: Computed energies of \(\kappa^2-N,P\), \(\kappa^2-N,N\) and \(\kappa^1-N\) 5c (M062X/6,31G+(d,p)/Lanl2DZ)

The ligand-slip rearrangement of 5c from \(\kappa^2-N,P\) to \(\kappa^2-N,N\) is likely driven by a preference for the ‘hard’ nitrogen donor functionality of the diaminophosphine donor over the ‘softer’ phosphorus center. The increased proportion of the \(\kappa^2-N,N\) isomer for the dimethyl-complex 3c compared to the dihydride 5c suggests that the ring-expansion that occurs as a consequence of the isomerization from \(\kappa^2-N,P\) to \(\kappa^2-N,N\) may also be favorable as a route to relieve steric strain. The more restrained, sterically crowded, and less basic (due to the silyl substituent) tert-butyl amino groups of 3b and 5b cannot favorably participate in the same isomerization as 3c and 5c.

Interconversion between \(\kappa^2-N,P\) and \(\kappa^2-N,N\) 3c or 5c in solution was not observable, and we were thus unable to determine activation barriers for this process. Although resonances for the coordinated and free phosphine centers in both isomers of 5c are broad, using NMR spectroscopy, we could find no evidence for exchange between the two sites, even at elevated temperatures. The variable coordination mode of the ligand in both 3c and 5c appears to provide them with higher reactivity and renders them the most sensitive derivatives in these series. Indeed, 3c was found to be extremely challenging to handle due to its high sensitivity to air and moisture.
Solid State NMR Spectroscopy. To further confirm our assignment of $^{31}$P resonances for the $\kappa^2$-$N,P$ and $\kappa^2$-$N,N$ isomers of $3c$ and $5c$, we undertook solid-state NMR spectroscopy, since from crystallographic studies $\kappa^2$-$N,P$-coordination is exclusively observed. The MAS $^{31}$P{$^1$H} NMR spectra of $3c$ and $5c$ are consistent with X-ray crystallography, revealing only a single phosphorus environment for each compound (Figure 5). In both cases the solid-state chemical shift is almost identical to the solution phase signal assigned to the $\kappa^2$-$N,P$ isomers (e.g. $3c$ solid phase: 47.8 ppm, solution: 49.7 ppm; $5c$ solid phase: 47.5 ppm, solution: 47.8 ppm). Furthermore, the lineshapes observed in the $^{31}$P{$^1$H} NMR spectra indicate quadrupolar coupling between aluminum and phosphorus, explaining the observed variation from the expected 1:1:1:1:1:1 sextet. No other resonances were observed in the $^{31}$P{$^1$H} MAS NMR spectra, ruling out the presence of the $\kappa^2$-$N,N$-isomer in the solid state.

For $3a$-$b$ and $5a$-$b$, which all display exclusive $\kappa^2$-$N,P$ coordination in solution, the observed MAS $^{31}$P{$^1$H} NMR spectra each contain a single resonance extremely close in chemical shift to that observed in solution (e.g. $5a$ solution phase: 8.0 ppm, solid phase: 8.9 ppm). Although we were unable to observe any resonances for any of the compounds reported here by solution-phase $^{27}$Al NMR spectroscopy, solid-state experiments were more successful. Details of $^{27}$Al{$^1$H} CPMG NMR spectra for $3a$-$c$ and $5a$-$c$ are provided in the Supporting Information.
Conclusions

In summary, we have synthesized aluminum dimethyl and dihydride complexes with a series of amido-phosphine ligands of varying steric bulk. The bulky bidentate ligands 1a-c enable the isolation of reactive aluminum dihydrides, the synthesis of which was observed to proceed through five-coordinate aluminate intermediates (4a-c). Evidence from X-ray crystallography and solid state NMR spectroscopy indicates that for all dimethyl and dihydride complexes, both nitrogen and phosphorus donor atoms are bound to the aluminum centers in the solid state. In solution, however, altering the steric bulk of the ligand enables control over coordination mode at the aluminum center: for the bulkiest ligand employed – 1c – both the dimethyl and dihydride complexes 3c and 5c exist as a mixture of κ²-N,P and κ²-N,N isomers.

Scheme 5: Catalytic hydroboration of phenylacetylene and 2-cyclooctyne using 5a-c.

The variable coordination mode of the ligand is encouraging as a potential route to control the stoichiometric or catalytic reactivity of the aluminum dihydride centers. For example, preliminary results indicate that 5a-5c are active catalysts for the hydroboration of alkyl- and aryl-alkynes with
HBPin (see SI). The accessibility of the κ²-N,N coordination mode for 5c has a clear effect on reactivity. Whilst all three dihydrides catalyze the hydroboration of phenylacetylene with HBPin, 5a and 5b are significantly more efficient, with conversions of 79 and 83 % after 2 hours at 110 °C compared to 53 % for 5c. We are now further exploring the coordination chemistry, reactivity and catalytic applications of the dihydrides 5a-c.

Experimental Section

General Procedures. All manipulations were carried out under an argon atmosphere using standard Schlenk or glovebox techniques. Reactions were carried out in glass Schlenk tubes, which were dried for 16 hours at 110 °C before use. Solvents were obtained from an inert solvent purification system and stored over 4 Å molecular sieves. C₆D₆ and d₈-THF were dried over potassium then vacuum distilled and stored over 4 Å molecular sieves.

Ligands 1b and 1c²³, their precursors (imine²⁴, chlorophosphines PCl(NᵗBu)₂SiMe₂²³ and PCl(NᵗBuCH₂)₂³⁵) and [H₃Al·NMe₃]³⁶ were synthesised according to literature procedures. SiMe₂(NHᵗBu)₂ was synthesised according to a modified literature procedure (See Supporting Information). Tert-butylamine was dried over calcium hydride and vacuum distilled prior to use. LiAlH₄ was purified by extraction with diethyl ether and filtration to afford a white solid, which was stored under an inert atmosphere. Trimethylammonium chloride was dried under vacuum at 50 °C for 3 hours prior to use. All other reagents were purchased from commercial suppliers and used without further purification.
General Synthesis of 2. To a solution of 1 in THF cooled to -78 °C, nBuLi (2.5M in hexanes, 1 equivalent) was added dropwise. The cold bath was removed and the resultant yellow solution was stirred at room temperature for 1 hour. Monitoring by $^{31}$P{$^1$H} NMR spectroscopy revealed the presence of lithiated ligand 2, which was characterised in situ.

2a. $^{31}$P{$^1$H} (C$_4$H$_8$O, 202.5 MHz, 300 K): $\delta$ 10.9 (1:1:1:1 quartet, $J_{P-Li} = 54$ Hz); $^7$Li (C$_4$H$_8$O, 194.4 MHz, 300 K): $\delta$ 1.3 (d, $J_{Li-P} = 54$ Hz)

2b. $^{31}$P{$^1$H} (C$_4$H$_8$O, 202.5 MHz, 300 K): $\delta$ 96.4 (1:1:1:1 quartet, $J_{P-Li} = 63$ Hz); $^7$Li (C$_4$H$_8$O, 194.4 MHz, 300 K): $\delta$ 1.1 (d, $J_{Li-P} = 63$ Hz)

2c. $^{31}$P{$^1$H} (C$_4$H$_8$O, 202.5 MHz, 300 K): $\delta$ 68.6 (1:1:1:1 quartet, $J_{P-Li} = 54$ Hz); $^7$Li (C$_4$H$_8$O, 194.4 MHz, 300 K): $\delta$ 1.5 (d, $J_{Li-P} = 54$ Hz)

General Syntheses of 3. To a solution of 1 in THF cooled to -78 °C, nBuLi (2.5M in hexanes, 1 equivalent) was added dropwise. The cold bath was removed and the resultant yellow solution was stirred at room temperature for 1 hour. The reaction mixture was cooled to -78 °C and Me$_2$AlCl (1.0 M in hexanes) was added dropwise. The cold bath was removed and the resultant solution was stirred at room temperature for 1 hour. The solvent was removed in vacuo, the product extracted in hexane and dried to afford 3a-c.

3a: 1a (0.40 g, 0.97 mmol), THF (20 mL), nBuLi (0.39 mL, 0.97 mmol, 1.0 eq), Me$_2$AlCl (0.97 mL, 0.97 mmol, 1.0 eq) yielded 3a (0.34 g, 75%) as a pale yellow solid. Colourless crystals suitable for X-ray crystallography were grown from a saturated diethyl ether solution at 4 °C.

$^1$H (C$_6$D$_6$, 500 MHz, 300 K): $\delta$ -0.33 (d, $^3J_{HP} = 2.5$ Hz, 3H, AlCH$_3$), -0.19 (d, $^3J_{HP} = 2.5$ Hz, 3H, AlCH$_3$), 1.10 (m, 1H, $\eta^5$CH$_{2}$Nor), 1.19 (d, $^3J_{HP} = 8.6$ Hz, 9H, CH$_{3}$Bu), 1.22 (d, $^3J_{HP} = 8.6$ Hz, 9H,
CH₃Bu), 1.24 (d, ³JHH = 6.8 Hz, 3H, CH₃iPr), 1.26 (d, ³JHH = 6.8 Hz, 3H, CH₃iPr), 1.37 (d, ³JHH =
6.8 Hz, 6H, CH₃iPr), 1.43 (m, 2H, CH₂CbridgeheadCp), 1.55 (m, 1H, ½CH₂CbridgeheadCN), 1.61 (m, 1H,
½CH₂Norb), 1.66 (m, 1H, ½CH₂CbridgeheadCN), 2.50 (br s, 1H, PCCHbridgehead), 2.95 (br s, 1H,
NCCHbridgehead), 3.44 (sept, ³JHH = 6.8 Hz, 1H, CHiPr), 3.61 (sept, ³JHH = 6.8 Hz, 1H, CHiPr), 7.17-
7.19 (m, 3H, H aromatic); ¹³C (C₆D₆, 126 MHz, 300 K): δ -5.7 (br s, AlCH₃), -4.3 (br s, AlCH₃), 25.2
(s, CH₃iPr), 25.4 (s, CH₃iPr), 25.7 (s, CH₃iPr), 25.8 (s, CH₃iPr), 25.9 (d, JCP = 2 Hz, CH₂CbridgeheadCP),
27.6 (s, CH₃iPr), 27.7 (s, CH₃iPr), 30.0 (s, CH₂CbridgeheadCN), 30.1 (d, JCP = 5 Hz, CH₃Bu), 30.5 (d, JCP
= 5 Hz, CH₃Bu), 34.4 (d, JCP = 30 Hz, C₆Bu), 34.8 (d, JCP = 31 Hz, C₆Bu), 43.8 (d, JCP = 9 Hz,
PCCH), 44.1 (d, JCP = 2 Hz, NCCH), 48.3 (d, JCP = 3 Hz, CH₂Norb), 80.2 (d, JCP = 42 Hz, PCCH),
124.2 (s, C meta), 124.3 (s, C meta), 126.1 (s, C para), 141.7 (d, JCP = 3 Hz, NC₆Ar), 147.1 (s, CCHiPr),
147.4 (s, CCHiPr), 185.1 (d, JCP = 21 Hz, NCCH); ³¹P{¹H} (C₆D₆, 162 MHz, 300 K): δ 1.6 (s, Δν/₅
= 21.1 Hz); High Resolution Mass Spec (APPI): m/z = 469.341919 [C₂₉H₄₉AlNP]⁺ (theoretical
= 469.341252); Elemental Analysis: Found (%): C, 74.13; H, 10.38; N, 2.85. Calc. for
C₂₉H₄₉AlNP: C, 74.16; H, 10.52; N, 2.98.

3b: 1b (0.3 g, 0.60 mmol), THF (20 mL), nBuLi (0.24 mL, 0.60 mmol, 1.0 eq), Me₂AlCl (0.60
mL, 0.60 mmol, 1.0 eq) yielded 3b (0.17 g, 56%) as a yellow solid. Some impurities (less than
10%) were observed by NMR spectroscopy due to reaction with water, but could not be separated
since crystallisation of 3b was not possible.

¹H NMR (C₆D₆, 500 MHz, 300 K): δ -0.26 (d, ³JHP = 3.9 Hz, 3H, AlCH₃), -0.12 (d, ³JHP = 3.9
Hz, 3H, AlCH₃), 0.27 (s, 3H, SiCH₃), 0.32 (s, 3H, SiCH₃), 1.12 (d, ²JHH = 8.1 Hz, 1H, ½CH₂Norb),
1.25 (s, 9H, CH₃Bu), 1.26 (s, 9H, CH₃Bu), 1.25 (d, ³JHH = 6.8 Hz, 3H, CH₃iPr), 1.26 (d, ³JHH = 6.8
Hz, 3H, CH₃iPr), 1.32 (d, ³JHH = 6.8 Hz, 3H, CH₃iPr), 1.41 (d, ³JHH = 6.8 Hz, 3H, CH₃iPr), 1.42 (m,
2H, CH₂CbridgeheadCP), 1.60 (d, ²JHH = 8.1 Hz, 1H, ½CH₂Norb), 1.69 (m, 2H, CH₂CbridgeheadCN), 2.53
(br s, 1H, CH\textsubscript{bridgeheadCP}), 3.13 (br s, 1H, CH\textsubscript{bridgeheadCN}), 3.51 (sept, $^3J_{HH} = 6.8$ Hz, CH$_{iPr}$), 3.70 (sept, $^3J_{HH} = 6.8$ Hz, CH$_{iPr}$), 7.11 - 7.21 (m, 3H, H\textsubscript{aromatic}); $^{13}$C NMR (C$_6$D$_6$, 126 MHz, 300 K): $\delta$ -6.3 (br d, $J_{CP} = 24.8$ Hz, AlCH$_3$), -5.4 (br d, $J_{CP} = 19.9$ Hz, AlCH$_3$), 4.6 (d, $J_{CP} = 1.4$ Hz, SiCH$_3$), 6.7 (s, 3H, tBu), 25.3 (s, CH$_3$), 25.4 (s, CH$_3$), 25.6 (s, CH$_3$), 26.0 (s, CH$_3$), 26.3 (s, CH$_2$), 27.6 (s, CH$_3$), 27.8 (s, CH$_3$), 29.4 (s, CH$_2$), 32.3 (d, $J_{CP} = 5.4$ Hz, tBu), 32.6 (s, 1H, CH$_2$), 32.9 (d, $J_{CP} = 4.9$ Hz, CH$_2$), 46.6 (d, $J_{CP} = 4.7$ Hz, CH$_2$), 50.8 (d, $J_{CP} = 3.9$ Hz, C'Bu), 50.9 (d, $J_{CP} = 2.8$ Hz, C'Bu), 99.1 (d, $J_{CP} = 29.2$ Hz, P'C), 124.3 (s), 124.3 (s), 126.3 (s), 141.2 (d, $J_{CP} = 3.1$ Hz, NC), 146.6 (s, C'I), 147.0 (s, C'I), 186.8 (d, $J_{CP} = 33.9$ Hz, NC); $^{31}$P{$^1$H} (C$_6$D$_6$, 162 MHz, 300 K): $\delta$ 46.0 (s, $\Delta v/2 = 35.8$ Hz); High Resolution Mass Spec (APPI): m/z = 555.371654 [C$_{31}$H$_{55}$AlN$_3$PSi]$^+$ (theoretical = 555.371277).

3c: 1c (0.43 g, 0.92 mmol), THF (20 mL), $^n$BuLi (0.37 mL, 0.92 mmol, 1.0 eq), Me$_2$AlCl (0.92 mL, 0.60 mmol, 1.0 eq). To gain analytically pure material, 3c was further purified by recrystallization from hexanes at -20 °C to yield colourless crystals (0.23 g, 48%). Two isomers were identified in the NMR spectra of approximate ratio of 4:3 of $\kappa^2$-N,N 3c to $\kappa^2$-N,P 3c at 300 K (determined from the $^1$H NMR spectrum). Due to the high air-sensitivity of this species, some impurities were observed in solution NMR spectra ($^{31}$P{$^1$H} NMR spectrum, 10% unidentified impurity at 75.1 ppm).

$\kappa^2$-N,N 3c: $^1$H (C$_6$D$_6$, 500 MHz, 300 K): $\delta$ -0.67 (s, 3H, AlMe), -0.13 (s, 3H, AlMe), 0.89 (m, 1H, CH$_2$), 1.18 (m, 1H, CH$_2$), 1.21 (s, 18H, CH$_3$), 1.24 (d, $^3J_{HH} = 6.8$ Hz, 6H, CH$_3$), 1.27 (d, $^3J_{HH} = 6.8$ Hz, 3H, CH$_3$), 1.45 (m, 2H, CH$_2$), 1.47 (d, $^3J_{HH} = 6.8$ Hz, 3H, CH$_3$), 1.63 (m, 1H, CH$_2$), 1.72 (m, 1H, CH$_2$), 2.49 (br s, 1H, CH$_2$), 2.82 (m, 1H, CH$_2$), 2.83 (m, 1H, CH$_2$), 2.97 (m, CH$_2$), 3.15 (m, 1H, CH$_2$).
\(\frac{1}{2}\text{NCH}_2\), 3.73 (sept, \(J_{HH} = 6.8\text{ Hz}, 1\text{H}, \text{CH}_{iPr}\)), 3.85 (sept, \(J_{HH} = 6.8\text{ Hz}, 1\text{H}, \text{CH}_{iPr}\)), 3.88 (m, 1H, \\
\(\text{AlMe}\)), 24.3 (s, CH\(_{3iPr}\)), 24.8 (s, CH\(_{3iPr}\)), 25.75 (s, CH\(_{3iPr}\)), 25.97 (s, CH\(_{2\text{CbridgeheadCP}}\)), 26.1 (s, \\
\(\text{CH}_{3iPr}\)), 27.0 (s, CH\(_{iPr}\)), 28.2 (s, CH\(_{iPr}\)), 29.3 (s, CH\(_{2\text{CbridgeheadCN}}\)), 29.7 (d, \(J_{CP} = 9.5\text{ Hz}, \text{CH}_{3\text{Bu}}\)), \\
29.73 (d, \(J_{CP} = 7.7\text{ Hz}, \text{CH}_{3\text{Bu}}\)), 29.8 (d, \(J_{CP} = 5.6\text{ Hz}, \text{CH}_{3\text{Bu}}\)), 43.84 (s, CH\(_{2\text{Norb}}\)), 43.88 (d, \(J_{CP} = \\
12.6\text{ Hz}, \text{NCH}\)), 45.3 (s, CH\(_{\text{bridgeheadCP}}\)), 45.7 (d, \(J_{CP} = 42.0\text{ Hz}, \text{CH}_{\text{bridgeheadCN}}\)), 48.8 (d, \(J_{CP} = \\
2.8\text{ Hz}, \text{NCH}\)), 53.2 (d, \(J_{CP} = 6.0\text{ Hz}, \text{C}^6\text{Bu}\)), 63.7 (d, \(J_{CP} = 11.7\text{ Hz}, \text{C}^6\text{Bu}\)), 103.5 (d, \(J_{CP} = 37.7\text{ Hz}, \\
\text{PCCH}\)), 123.9 (s, C\(_{\text{meta}}\)), 124.5 (s, C\(_{\text{meta}}\)), 125.2 (s, C\(_{\text{para}}\)), 144.1 (s, \(\text{NC}_{\text{Ar}}\)), 146.5 (s, \(\text{CCHiPr}\)), 147.0 \\
(s, \(\text{CCHiPr}\)), 165.0 (d, \(J_{CP} = 5.0\text{ Hz}, \text{NCCH}\)); \(^{31}\text{P}\{\text{\textsuperscript{1}H}\} (\text{C}_6\text{D}_6, 162\text{ MHz}, 300\text{ K}): \delta 99.9 (s, \Delta \nu_{\delta} = \\
5.3\text{ Hz}).

\(\kappa^{2-N,P}\text{ 3c}\): \(\text{\textsuperscript{1}H} (\text{C}_6\text{D}_6, 500\text{ MHz}, 300\text{ K}): \delta -0.27 (d, \(J_{\text{HP}} = 3.1\text{ Hz}, 3\text{H}, \text{AlMe}\)), -0.14 (d, \(J_{\text{HP}} = \\
3.1\text{ Hz}, 3\text{H}, \text{AlMe}\)), 1.06 (dm, \(J_{HH} = 8.1\text{ Hz}, 1\text{H}, \frac{1}{2}\text{CH}_{2\text{Norb}}\)), 1.25 (d, \(J_{HH} = 6.8\text{ Hz}, 3\text{H}, \text{CH}_{3\text{Pr}}\)), \\
1.26 (d, \(J_{HH} = 6.8\text{ Hz}, 3\text{H}, \text{CH}_{3\text{Pr}}\)), 1.30 (s, 9H, \text{CH}_{3\text{Bu}})), 1.32 (s, 9H, \text{CH}_{3\text{Bu}})), 1.33 (m, 1H, \\
\(\frac{1}{2}\text{CH}_{2\text{CbridgeheadCP}}\)), 1.38 (m, 1H, \(\frac{1}{2}\text{CH}_{2\text{CbridgeheadCP}}\)), 1.40 (d, \(J_{HH} = 6.8\text{ Hz}, 3\text{H}, \text{CH}_{3\text{Pr}}\)), 1.42 (d, \\
\(J_{HH} = 6.8\text{ Hz}, 3\text{H}, \text{CH}_{3\text{Pr}}\)), 1.56 (m, \(J_{HH} = 8.1\text{ Hz}, 1\text{H}, \frac{1}{2}\text{CH}_{2\text{Norb}}\)), 1.63 (m, 2H, \text{CH}_{2\text{CbridgeheadCN}}), \\
2.48 (br s, 1H, \text{CH}_{\text{bridgeheadCP}}), 2.59 (m, 1H, \(\frac{1}{2}\text{NCH}_2\)), 2.66 (m, 1H, \(\frac{1}{2}\text{NCH}_2\)), 2.82 (m, 1H, \(\frac{1}{2}\text{NCH}_2\), \\
2.89 (m, 1H, \text{NCH}_2), 3.05 (br s, 1H, \text{CH}_{\text{bridgeheadCN}}), 3.52 (sept, \(J_{HH} = 6.8\text{ Hz}, 1\text{H}, \text{CH}_{iPr}\)), 3.74 \\
(sept, \(J_{HH} = 6.8\text{ Hz}, 1\text{H}, \text{CH}_{iPr}\)), 7.15-7.20 (m, 3H, H\(_{\text{aromatic}}\)); \(^{13}\text{C} (\text{C}_6\text{D}_6, 126\text{ MHz}, 300\text{ K}): \delta -4.2 \\
(s, \text{AlMe}), -3.5 (s, \text{AlMe}), 25.2 (s, \text{CH}_{3\text{Pr}}), 25.4 (s, \text{CH}_{3\text{Pr}}), 25.68 (s, \text{CH}_{3\text{Pr}}), 25.84 (s, \\
\text{CH}_{2\text{CbridgeheadCP}}), 27.4 (s, \text{CH}_{iPr}), 27.6 (s, \text{CH}_{iPr}), 29.2 (s, \text{CH}_{3\text{Bu}}), 29.4 (d, \(J_{CP} = 2.2\text{ Hz}, \\
\text{CH}_{2\text{CbridgeheadCN}}), 29.7 (d, \(J_{CP} = 7.6\text{ Hz}, \text{CH}_{3\text{Bu}})), 42.0 (d, \(J_{CP} = 4.2\text{ Hz}, \text{CH}_{\text{bridgeheadCN}}), 43.6 (s, \\
\text{NCH}_2), 44.2 (d, \(J_{CP} = 9.9\text{ Hz}, \text{CH}_{\text{bridgeheadCP}}), 44.3 (s, \text{NCH}_2), 46.6 (d, \(J_{CP} = 5.3\text{ Hz}, \text{CH}_{2\text{Norb}}), 52.5 \\
(d, \(J_{CP} = 11.7\text{ Hz}, \text{C}^6\text{Bu}), 52.8 (d, \(J_{CP} = 8.8\text{ Hz}, \text{C}^6\text{Bu}), 95.5 (d, \(J_{CP} = 33.5\text{ Hz}, \text{PCCH}), 124.29 (s,
C_{meta}, 124.32 (C_{meta}), 126.2 (s, C_{para}), 142.0 (d, J_{CP} = 3.9 Hz, NCAr), 146.7 (s, CCH_{3iPr}), 148.0 (s, CCH_{3iPr}), 185.3 (d, J_{CP} = 34.1 Hz, NCCH); $^{31}$P{$^1$H} (C$_6$D$_6$, 162 MHz, 300 K): δ 49.7 (s, Δν$_{y1}$ = 47.5 Hz); **High Resolution Mass Spec (EI):** m/z = 525.37703 [C$_{31}$H$_{53}$AlN$_3$P]$^+$ (theoretical = 525.37871); **Elemental Analysis:** Found (%): C, 70.71; H, 10.18; N, 8.03. Calc. for C$_{31}$H$_{53}$AlN$_3$P: C, 70.82; H, 10.16; N, 7.99.

**Synthesis of 4b.** To a solution of 1b (0.10 g, 0.2 mmol) in THF (20 mL) at -78 °C, nBuLi (2.5 M in hexanes, 0.08 mL, 0.2 mmol, 1 eq) was added dropwise. The cold bath was removed and the resultant yellow solution was stirred at room temperature for 1 hour. The reaction mixture was cooled to -78 °C and H$_3$Al·NMe$_2$Et (0.5M in toluene, 0.4 mL, 1 eq) was added dropwise. The cold bath was removed and the resultant yellow solution was stirred at room temperature for 20 minutes and the solvent removed in vacuo to afford the product as a yellow oil. No further purification was attempted.

$^1$H NMR (C$_4$D$_8$O, 500 MHz, 300 K): δ 0.29 (s, 3H, SiCH$_3$), 0.33 (s, 3H, SiCH$_3$), 0.84 (m, 1H, ½CH$_2$Norb), 1.07 (d, 3J$_{HH} = 6.8$ Hz, 3H, CH$_3$iPr), 1.08 (d, 3J$_{HH} = 6.8$ Hz, 3H, CH$_3$iPr), 1.12 (d, 3J$_{HH} = 6.8$ Hz, 3H, CH$_3$iPr), 1.14 (d, 3J$_{HH} = 6.8$ Hz, 3H, CH$_3$iPr), 1.18 (m, 2H, CH$_2$CbridgeheadCP), 1.19 (s, 9H, CH$_3$Bu), 1.21 (s, 9H, CH$_3$Bu), 1.25 (m, 1H, ½CH$_2$Norb), 1.54 (m, 1H, ½CH$_2$CbridgeheadCN), 1.62 (m, 1H, ½CH$_2$CbridgeheadCN), 2.19 (br s, 1H, CHbridgeheadCP), 3.35 (br s, 1H, CHbridgeheadCN), 3.54 (sept, 3J$_{HH} = 6.8$ Hz, 1H, CH$_3$Pri), 6.83-6.90 (m, 3H, H$_{aromatic}$). Note: It was not possible to locate the Al-H resonances even with the use of $^1$H{$^{31}$P} NMR experiments, likely due to extremely high linewidth.

$^{13}$C NMR (C$_4$D$_8$O, 126 MHz, 300 K): δ 6.5 (s, SiCH$_3$), 8.3 (d, J$_{CP} = 5.7$ Hz, SiCH$_3$), 24.3 (d, J$_{CP} = 10.2$ Hz, CH$_3$iPr), 26.0 (d, J$_{CP} = 15.2$ Hz, CH$_3$iPr), 27.2 (s, CH$_2$CbridgeheadCP), 28.11 (s, CH$_3$Pri), 28.13 (s, CH$_3$Pri), 30.1 (s, CH$_2$CbridgeheadCN), 32.9 (d, J$_{CP} = 5.4$ Hz, CH$_3$Bu), 33.4 (d, J$_{CP} = 4.8$ Hz, CH$_3$Bu), 42.1 (d, J$_{CP} = 1.5$ Hz, CHbridgeheadCN), 46.5 (s, CH$_2$Norb),
47.2 (d, $J_{CP} = 5.5$ Hz, CH$_{bridgeheadCP}$), 51.4 (d, $J_{CP} = 11.5$ Hz, C$^t$Bu), 51.6 (d, $J_{CP} = 14.6$ Hz, C$^t$Bu), 111.2 (d, $J_{CP} = 43.1$ Hz, PCCH), 123.1 (d, $J_{CP} = 10.0$ Hz, C$_{meta}$), 124.2 (s, C$_{para}$), 146.7 (s, CCH$_{iPr}$), 148.0 (s, CCH$_{iPr}$), 150.7 (s, NCAr), 174.2 (d, $J_{CP} = 33.2$ Hz, NCCH); $^{31}$P (C$_4$D$_8$O, 162 MHz, 300 K): $\delta$ 110.8 (q, $^2J_{PH} = 34$ Hz); $^7$Li (C$_4$D$_8$O, 194.4 MHz, 300 K): $\delta$ -0.43 (s); High Resolution Mass Spec (EI): m/z = 528.34912 [C$_{29}$H$_{52}$N$_3$AlPSi]$^+$ (theoretical = 528.34891).

**General Synthesis of 5.** To a solution of ligand 1a-c in THF cooled to -78 °C, nBuLi (2.5M in hexanes) was added dropwise. The cold bath was removed and the resultant yellow solution was stirred at room temperature for 1 hour. The reaction mixture was cooled to -78 °C and a solution of H$_3$Al·NMe$_3$ in THF was added dropwise. The cold bath was removed and the resultant colourless solution was stirred at room temperature for 1 hour. The solvent was removed in vacuo, the product extracted in hexane and dried to afford a white solid. H$_3$Al·NMe$_2$Et (0.5 M in toluene) can be used in place of H$_3$Al·NMe$_3$. In this work, H$_3$Al·NMe$_2$Et was used for initial test reactions to synthesise up to 0.2 g of 5 using an identical procedure to that described above.

**5a:** 1a (1.63 g, 0.0039 mol), THF (50 mL), nBuLi (1.6 mL, 0.0039 mol, 1.0 eq), H$_3$Al·NMe$_3$ (0.84 g, 0.0037 mol, 2.4 eq) in THF (20 mL) yielded 5a (1.57 g, 91%).

$^1$H (C$_6$D$_6$, 500 MHz, 300 K): $\delta$ 1.11 (dm, $^2J_{HH} = 8.1$ Hz, 1H, $\frac{1}{2}$CH$_{2Norb}$), 1.19 (d, $^3J_{HP} = 14.2$ Hz, 9H, CH$_{3iPr}$), 1.22 (d, $^3J_{HP} = 14.2$ Hz, 9H, CH$_{3iPr}$), 1.28 (d, $^3J_{HH} = 6.8$ Hz, 3H, CH$_{3iPr}$), 1.31 (m, 2H, CH$_2$CbridgeheadCP), 1.42 (d, $^3J_{HH} = 6.8$ Hz, 3H, CH$_{3iPr}$), 1.44 (d, $^3J_{HH} = 6.8$ Hz, 3H, CH$_{3iPr}$), 1.51 (m, 1H, $\frac{1}{2}$CH$_2$CbridgeheadCN), 1.62 (dm, $^2J_{HH} = 8.1$ Hz, 1H, $\frac{1}{2}$CH$_{2Norb}$), 1.67 (m, 1H, $\frac{1}{2}$CH$_2$CbridgeheadCN), 2.53 (br s, 1H, PCCH$_{bridgehead}$), 2.94 (br s, 1H, NCCH$_{bridgehead}$), 3.42 (sept, $^3J_{HH} = 6.8$ Hz, CH$_{iPr}$), 3.63 (sept, $^3J_{HH} = 6.8$ Hz, 1H, CH$_{iPr}$), 4.6 (br s, 2H, AlH$_2$), 7.16-7.22 (m, 3H, H$_{aromatic}$); $^{13}$C (C$_6$D$_6$, 126 MHz, 300 K): $\delta$ 24.0 (s, CH$_{3iPr}$), 24.7 (s,
CH$_3$iPr), 25.2 (d, $J_{CP} = 1.8$ Hz, CH$_2$CbridgeheadCP), 25.8 (s, CH$_3$iPr), 25.9 (s, CH$_3$iPr), 28.0 (s, CH$iP$),
28.1 (s, CH$iP$), 29.6 (d, $J_{CP} = 4.5$ Hz, CH$_3$Bu), 30.1 (s, CH$_2$CbridgeheadCN), 30.1 (d, $J_{CP} = 4.0$ Hz, CH$_3$Bu), 34.1 (d, $J_{CP} = 18.2$ Hz, C'Bu), 34.3 (d, $J_{CP} = 18.9$ Hz, C'Bu), 43.6 (d, $J_{CP} = 9.1$ Hz, CHbridgeheadCP), 44.1 (d, $J_{CP} = 2.1$ Hz, CHbridgeheadCN), 48.6 (d, $J_{CP} = 3.9$ Hz, CH$_2$Norb), 81.0 (d, $J_{CP} = 44.5$ Hz, PCCH), 124.1 (s, C$_{meta}$), 124.2 (s, C$_{meta}$), 126.3 (s, C$_{para}$), 141.4 (d, $J_{CP} = 3.0$ Hz, NC$_{Ar}$), 146.8 (s, CCH$iP$), 147.1 (s, CCH$iP$), 185.1 (d, $J_{CP} = 20.1$ Hz, NCCH); $^{31}$P($^1$H) (C$_6$D$_6$, 162 MHz, 300 K): $\delta$ 8.0 (s, $\Delta$N$_{3/2}$ = 34.7 Hz);
High Resolution Mass Spec (EI): m/z = 441.30855 $[C$_{27}$H$_{45}$AlNP]$+$ (theoretical = 441.30996);
Elemental Analysis: Found (%): C, 73.11; H, 10.39; N, 3.13. Calc. for C$_{27}$H$_{45}$AlNP: C, 73.43; H, 10.27; N, 3.17;
IR (solution, cm$^{-1}$): 1810, 1786; IR (solid, cm$^{-1}$): 1811.

5b: 1b (3.00 g, 0.0060 mol), THF (80 mL), $^n$BuLi (2.4 mL, 0.0060 mol, 1.0 eq), H$_3$Al·NMe$_3$
(1.28 g, 0.014 mol, 2.4 eq) in THF (15 mL) yielded 5b (2.95 g, 93%). Colourless crystals suitable
for X-ray crystallography were grown from a saturated hexane solution at -20 °C.

$^1$H NMR (C$_6$D$_6$, 500 MHz, 300 K): $\delta$ 0.24 (s, 3H, SiCH$_3$), 0.29 (s, 3H, SiCH$_3$), 1.13 (d, $^2$J$_{HH} = 8.1$ Hz, 1H, $^{1/2}$CH$_2$Norb), 1.28 (d, $^4$J$_{HP} = 0.8$ Hz, 9H, CH$_3$Bu), 1.29 (d, $^4$J$_{HP} = 0.8$ Hz, 9H, CH$_3$Bu),
1.30 (d, $^3$J$_{HH} = 6.8$ Hz, 3H, CH$_3$iPr), 1.31 (d, $^3$J$_{HH} = 6.8$ Hz, 3H, CH$_3$iPr), 1.38 (m, 2H, CH$_2$CbridgeheadCP), 1.44 (d, $^3$J$_{HH} = 6.8$ Hz, 3H, CH$_3$iPr), 1.45 (d, $^3$J$_{HH} = 6.8$ Hz, 3H, CH$_3$iPr), 1.62 (d, $^2$J$_{HH} = 8.1$ Hz, $^{1/2}$CH$_2$Norb), 1.67 (m, 2H, CH$_2$CbridgeheadCN), 2.57 (br s, 1H, CHbridgeheadCP), 3.12 (br s, 1H, CHbridgeheadCN), 3.53 (sept, $^3$J$_{HH} = 6.8$ Hz, 1H, CH$iP$), 3.74 (sept, $^3$J$_{HH} = 6.8$ Hz, 1H, CH$iP$), 4.6
(br s, 2H, Al-H), 7.17-7.23 (m, 3H, H aromatic); $^{13}$C NMR (C$_6$D$_6$, 126 MHz, 300 K): $\delta$ 4.4 (d, $J_{CP} =$ 1.6 Hz, SiCH$_3$), 6.3 (d, $J_{CP} = 3.2$ Hz, SiCH$_3$), 24.1 (s, CH$_3$iPr), 24.6 (s, CH$_3$iPr), 25.6 (d, $J_{CP} = 1.0$
Hz, CH$_2$CbridgeheadCP), 25.8 (s, CH$_3$iPr), 25.9 (s, CH$_3$iPr), 28.0 (s, CH$iP$), 28.3 (s, CH$iP$), 29.3 (s, CH$_2$CbridgeheadCN), 32.3 (d, $J_{CP} = 5.4$ Hz, CH$_3$Bu), 32.7 (d, $J_{CP} = 5.2$, CH$_3$Bu), 40.7 (d, $J_{CP} = 3.9$ Hz,
CH_{bridgeheadCN}, 43.9 (d, J_{CP} = 9.7 Hz, CH_{bridgeheadCP}), 46.8 (d, J_{CP} = 4.9 Hz, CH_{2Norb}), 51.4 (d, J_{CP} = 2.5 Hz, C^{tBu}), 51.5 (d, J_{CP} = 3.6 Hz, C^{tBu}), 99.7 (d, J_{CP} = 32.6 Hz, PCCCH), 124.1 (s, C_{meta}), 124.2 (s, C_{meta}), 126.5 (s, C_{para}), 140.8 (d, J_{CP} = 3.5 Hz, NC_{Ar}), 146.4 (s, C_{tBu}), 146.5 (s, C_{tBu}), 187.6 (d, J_{CP} = 33.9 Hz, NCCH); \textit{^31P}[^1H] NMR (C_{6}D_{6}, 162 MHz, 300 K): \delta 61.3 (s, J_{\nu_{31p}} = 65.4 Hz);

High Resolution Mass Spec (EI): m/z = 527.33886 [C_{29}H_{51}AlN_{3}PSi]^+ (theoretical = 527.33998);

Elemental Analysis: Found (%): C, 65.95; H, 9.66; N, 7.83. Calc. for C_{29}H_{51}AlN_{3}PSi: C, 66.00; H, 9.74; N, 7.96; IR (solid, cm\textsuperscript{-1}): 1831, 1816; IR (solution, cm\textsuperscript{-1}): 71820.

\textbf{5c}: 1c (2.00 g, 0.0043 mol), THF (100 mL), \textit{n}BuLi (1.7 mL, 0.0043 mol, 1.0 eq), H_{3}Al·NMe_{3} (0.91 g, 0.010 mol, 2.4 eq) in THF (15 mL). The final product was further purified by recrystallization from hexanes at -20 °C to yield 5c as colourless crystals (1.68 g, 79%). Two isomers were identifiable in the solution phase NMR spectra in a ratio of 4:7 for \kappa^2-N,N 5c to \kappa^2-N,P 5c at 300 K (determined from the \textit{^1H} NMR spectrum).

\textbf{\kappa^2-N,N 5c}: \textit{^1H} (C_{6}D_{6}, 500 MHz, 300 K): \delta 0.91 (m, 1H, \textit{\textfrac{1}{2}}CH_{2Norb}), 1.18 (d, J_{HP} = 1.3 Hz, 9H, CH_{3Bu}), 1.23 (d, J_{HH} = 6.8 Hz, 3H, CH_{3iPr}), 1.25 (m, 1H, \textit{\textfrac{1}{2}}CH_{2Norb}), 1.31 (d, J_{HH} = 6.8 Hz, 6H, CH_{3iPr}), 1.32 (s, 9H, CH_{3Bu}), 1.43 (m, 2H, CH_{2BridgeheadCP}), 1.60 (d, J_{HH} = 6.8 Hz, 3H, CH_{3iPr}), 1.65 (m, 1H, \textit{\textfrac{1}{2}}CH_{2BridgeheadCN}), 1.71 (m, 1H, \textit{\textfrac{1}{2}}CH_{2BridgeheadCN}), 2.56 (m, 1H, CH_{BridgeheadCP}), 2.70 (m, 1H, \textit{\textfrac{1}{2}}NCH_{2}), 2.78 (m, 1H, \textit{\textfrac{1}{2}}NCH_{2}), 2.97 (m, 1H, CH_{BridgeheadCN}), 3.33 (m, 1H, \textit{\textfrac{1}{2}}NCH_{2}), 3.56 (m, 1H, \textit{\textfrac{1}{2}}NCH_{2}), 3.85 (sept, J_{HH} = 6.8 Hz, 1H, CH_{iPr}), 3.98 (sept, J_{HH} = 6.8 Hz, 1H, CH_{iPr}), 4.3 (br s, 2H, AlH_{2}) 7.18-7.21 (m, 3H, Haromatic); \textit{^13C} (C_{6}D_{6}, 126 MHz, 300 K): \delta 25.4 (s, CH_{2BridgeheadCP}), 25.6 (s, CH_{3iPr}), 25.7 (s, CH_{3iPr}), 25.92 (s, CH_{3iPr}), 27.5 (s, CH_{iPr}), 28.9 (s, CH_{iPr}), 29.0 (d, J_{CP} = 4.6 Hz, CH_{3Bu}), 29.6 (d, J_{CP} = 10.7 Hz, CH_{3Bu}), 29.8 (d, J_{CP} = 1.8 Hz, CH_{2BridgeheadCN}), 44.2 (s, CH_{2Norb}), 45.1 (s, CH_{BridgeheadCN}), 45.7 (s, NCH_{2}), 45.8 (d, J_{CP} = 39.1 Hz, CH_{2BridgeheadCN})
CH\(\text{bridgeheadCP}\), 48.8 (d, \(J_{\text{CP}} = 3.3\) Hz, NCH\(_2\)), 53.5 (d, \(J_{\text{CP}} = 5.0\) Hz, C\(^3\)Bu), 53.8 (d, \(J_{\text{CP}} = 3.9\) Hz, C\(^3\)Bu), 104.8 (d, \(J_{\text{CP}} = 36.9\) Hz, PCC\(_{\text{CH}}\)), 123.9 (s, C\(_{\text{meta}}\)), 124.6 (s, C\(_{\text{meta}}\)), 125.2 (s, C\(_{\text{para}}\)), 143.22 (s, N\(_{\text{C\(_6\)}}\)), 145.8 (C\(_{\text{CH\(_{iPr}\)}}\)), 146.53 (s, C\(_{\text{CH\(_{iPr}\)}}\)), 167.4 (d, \(J_{\text{CP}} = 2.7\) Hz, NCC\(_{\text{CH}}\)); \(^{31}\text{P}^{1}\text{H}\) (C\(_6\)D\(_6\), 162 MHz, 300 K): \(\delta\) 96.9 (s, \(\Delta\nu_{1/2} = 137.9\) Hz).

\(^{2}\text{N,P} \text{5c: } ^{1}\text{H} (\text{C}_6\text{D}_6, 500 \text{ MHz}, 300 \text{ K}): \delta 1.07 (\text{dm}, \(J_{\text{HH}} = 8.4\) Hz, 1H, \(\text{CH}_{2\text{Norb}}\)), 1.29 (d, \(J_{\text{HH}} = 6.8\) Hz, 3H, \(\text{CH}_{3\text{iPr}}\)), 1.30 (d, \(J_{\text{HH}} = 6.8\) Hz, 3H, \(\text{CH}_{3\text{iPr}}\)), 1.32 (s, 9H, C\(_{\text{CH\(_{iPr}\)}}\)), 1.35 (s, 9H, \(\text{CH}_{3\text{tBu}}\)), 1.39 (m, 2H, CH\(_{2\text{bridgeheadCP}}\)), 1.42 (d, \(J_{\text{HH}} = 6.8\) Hz, 3H, \(\text{CH}_{3\text{iPr}}\)), 1.45 (d, \(J_{\text{HH}} = 6.8\) Hz, 3H, \(\text{CH}_{3\text{iPr}}\)), 1.56 (m, 1H, \(\text{CH}_{2\text{Norb}}\)), 1.63 (m, 2H, CH\(_{2\text{bridgeheadCN}}\)), 2.52 (m, 1H, CH\(_{\text{bridgeheadCP}}\)), 2.60 (m, 1H, \(\text{CH}_{2\text{Norb}}\)), 2.72 (m, 1H, \(\text{CH}_{2\text{Norb}}\)), 2.79 (m, 1H, \(\text{CH}_{2\text{Norb}}\)), 2.88 (m, 1H, NCH\(_2\)), 3.02 (m, 1H, \(\text{CH}_{2\text{bridgeheadCN}}\)), 3.54 (sept, \(J_{\text{HH}} = 6.8\) Hz, 1H, C\(_{\text{CH\(_{iPr}\)}}\)), 3.76 (sept, \(J_{\text{HH}} = 6.8\) Hz, 1H, C\(_{\text{CH\(_{iPr}\)}}\)), 4.6 (br s, 2H, AlH\(_2\)) 7.18-7.21 (m, 3H, H\(_{\text{aromatic}}\)); \(^{13}\text{C} (\text{C}_6\text{D}_6, 126 \text{ MHz}, 300 \text{ K}): \delta 24.0 (s, \text{CH}_{3\text{iPr}}), 24.7 (s, \text{CH}_{3\text{iPr}}), 25.3 (s, \text{CH}_{2\text{bridgeheadCP}}), 25.8 (s, \text{CH}_{3\text{iPr}}), 25.86 (s, \text{CH}_{3\text{iPr}}), 27.9 (s, \text{CH}_{2\text{iPr}}), 28.1 (s, \text{CH}_{2\text{iPr}}), 29.0 (d, \(J_{\text{CP}} = 4.6\) Hz, C\(_{\text{3tBu}}\)), 29.3 (s, C\(_{\text{CH\(_{2\text{bridgeheadCN}}\)}}\)), 29.9 (d, \(J_{\text{CP}} = 4.6\) Hz, C\(_{\text{3tBu}}\)), 42.7 (d, \(J_{\text{CP}} = 4.4\) Hz, C\(_{\text{bridgeheadCN}}\)), 43.6 (d, \(J_{\text{CP}} = 9.9\) Hz, C\(_{\text{bridgeheadCP}}\)), 43.9 (s, NCH\(_2\)), 44.2 (s, NCH\(_2\)), 46.6 (d, \(J_{\text{CP}} = 4.9\) Hz, CH\(_{2\text{Norb}}\)), 53.4 (d, \(J_{\text{CP}} = 9.8\) Hz, C\(^3\)Bu), 53.6 (d, \(J_{\text{CP}} = 5.4\) Hz, C\(^3\)Bu), 97.0 (d, \(J_{\text{CP}} = 35.3\) Hz, PCC\(_{\text{CH}}\)), 124.1 (s, C\(_{\text{meta}}\)), 124.3 (s, C\(_{\text{meta}}\)), 126.4 (s, C\(_{\text{para}}\)), 141.0 (d, \(J_{\text{CP}} = 4.0\) Hz, NCA\(_{\text{r}}\)), 146.51 (s, C\(_{\text{CH\(_{iPr}\)}}\)), 146.8 (s, C\(_{\text{CH\(_{iPr}\)}}\)), 185.4 (d, \(J_{\text{CP}} = 34.0\) Hz, NCC\(_{\text{CH}}\)); \(^{31}\text{P}^{1}\text{H}\) (C\(_6\)D\(_6\), 162 MHz, 300 K): \(\delta\) 47.8 (s, \(\Delta\nu_{1/2} = 96.6\) Hz); High Resolution Mass Spec (EI): \(m/z = 497.35079 \ [\text{C}_{29}\text{H}_{49}\text{AlN}_{3}\text{P}]^{+}\) (theoretical = 497.34741); Elemental Analysis: Found (%): C, 69.80; H, 9.80; N, 8.33. Calc. for C\(_{29}\)H\(_{51}\)AlN\(_3\)PSi: C, 69.99; H, 9.92; N, 8.44; IR (solid, \text{cm}^{-1}): 1825, 1801; IR (solution, \text{cm}^{-1}): 1823.
ASSOCIATED CONTENT

Supporting Information.

The following files are available free of charge.

Supporting Information (Experimental procedures, full characterization of compounds, crystallographic details, solid state NMR details, solution phase NMR spectra; PDF)

AUTHOR INFORMATION

Corresponding Author

*Michael J. Cowley, michael.cowley@ed.ac.uk

Author Contributions

RLF conceived and performed experiments and co-wrote the manuscript, GSN contributed to crystallographic studies, MJC designed and coordinated the study and co-wrote the manuscript.

Funding Sources

This project has received funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme (grant agreement no. ERC-2016-STG-716315).

ACKNOWLEDGMENT

Mass spectrometry was performed at SIRCAMS at the University of Edinburgh by Faye Cruikshank (APPI) and Alan Taylor (EI).

REFERENCES

1. Cox, L. R., Science of Synthesis. Thieme Chemistry: 2008; Vol. 36, p 55.
2. Bismuto, A.; Thomas, S. P.; Cowley, M. J., Aluminum Hydride Catalyzed Hydroboration of Alkynes. *Angew. Chem., Int. Ed.* **2016**, *55* (49), 15356-15359.

3. Bismuto, A.; Cowley, M. J.; Thomas, S. P., Aluminum-Catalyzed Hydroboration of Alkenes. *ACS Catal.* **2018**, *8* (3), 2001-2005.

4. Elsen, H.; Färber, C.; Ballmann, G.; Harder, S., LiAlH4: From Stoichiometric Reduction to Imine Hydrogenation Catalysis. *Angew. Chem., Int. Ed.* **2018**, *57* (24), 7156-7160.

5. Pollard, V. A.; Orr, S. A.; McLellan, R.; Kennedy, A. R.; Hevia, E.; Mulvey, R. E., Lithium diamidodihydridoaluminates: bimetallic cooperativity in catalytic hydroboration and metallation applications. *Chem. Commun.* **2018**, *54* (10), 1233-1236.

6. Franz, D.; Sirtl, L.; Pöthig, A.; Inoue, S., Aluminum Hydrides Stabilized by N-Heterocyclic Imines as Catalysts for Hydroborations with Pinacolborane. *Z Anorg Allg Chem* **2016**, *642* (22), 1245-1250.

7. Yang, Z.; Zhong, M.; Ma, X.; Nijesh, K.; De, S.; Parameswaran, P.; Roesky, H. W., An Aluminum Dihydride Working as a Catalyst in Hydroboration and Dehydrocoupling. *J. Am. Chem. Soc.* **2016**, *138* (8), 2548-2551.

8. Hooper, T. N.; Garçon, M.; White, A. J. P.; Crimmin, M. R., Room temperature catalytic carbon–hydrogen bond alumination of unactivated arenes: mechanism and selectivity. *Chem. Sci.* **2018**, *9* (24), 5435-5440.

9. Chang, J.-C.; Hung, C.-H.; Huang, J.-H., An Unusual Hydride-Bridged Aluminum Complex with a Square-Planar Tetraaluminum Core Stabilized by 2,5-Bis((Dimethylamino)methyl)pyrrole Ligands. *Organometallics* **2001**, *20* (22), 4445-4447.
10. Chu, T.; Korobkov, I.; Nikonov, G. I., Oxidative Addition of σ Bonds to an Al(I) Center. *J. Am. Chem. Soc.* **2014**, *136* (25), 9195-9202.

11. Cowley, A. H.; Gabbai, F. P.; Isom, H. S.; Decken, A., New developments in the chemistry of organoaluminum and organogallium hydrides. *J. Organomet. Chem.* **1995**, *500* (1), 81-88.

12. Luo, B.; Kucera, B. E.; Gladfelter, W. L., Hydrido and chloro gallium and aluminium complexes with the tridentate bis(2-dimethylaminoethyl)amide ligand. *Dalton Trans.* **2006**, *37*, 4491-4498.

13. Atwood, J. L.; Robinson, K. D.; Jones, C.; Raston, C. L., Cationic aluminium hydrides: \([\text{H}_2\text{Al}]^+\text{[AlH}_4^-]\) , \(\text{L } = \text{N,N,N',N",N"-pentamethyldiethylenetriamine}\) and 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane. *Journal of the Chemical Society, Chemical Communications* **1991**, *23*, 1697-1699.

14. Coles, M. P.; Swenson, D. C.; Jordan, R. F.; Young, V. G., Aluminum Complexes Incorporating Bulky Nitrogen and Sulfur Donor Ligands. *Organometallics* **1998**, *17* (18), 4042-4048.

15. Liang, L.-C.; Huang, M.-H.; Hung, C.-H., Aluminum Complexes Incorporating Bidentate Amido Phosphine Ligands. *Inorg. Chem.* **2004**, *43* (6), 2166-2174.

16. DeMott, J. C.; Guo, C.; Foxman, B. M.; Yandulov, D. V.; Ozerov, O. V., Five-coordinate aluminum complexes of a PNP ligand. *Mendeleev Commun.* **2007**, *17* (2), 63-65.

17. Lee, W.-Y.; Liang, L.-C., Organoaluminium complexes incorporating an amido phosphine chelate with a pendant amine arm. *Dalton Trans.* **2005**, *11*, 1952-1956.
18. Liang, L.-C., Metal complexes of chelating diarylamido phosphine ligands. *Coord. Chem. Rev.* **2006**, *250* (9), 1152-1177.

19. Slone, C. S.; Weinberger, D. A.; Mirkin, C. A., The Transition Metal Coordination Chemistry of Hemilabile Ligands. In *Progress in Inorganic Chemistry*, Karlin, K. D., Ed. John Wiley & Sons, Inc.: 1999; Vol. 48, pp 233-350.

20. Fryzuk, M. D.; Giesbrecht, G. R.; Olovsson, G.; Rettig, S. J., Synthesis and Characterization of Four- and Five-Coordinate Organoaluminum Complexes Incorporating the Amido Diphosphine Ligand System N(SiMe$_2$CH$_2$PPr$_2$)$_2$. *Organometallics* **1996**, *15* (22), 4832-4841.

21. Lee, P.-Y.; Liang, L.-C., Synthesis and Structural Characterization of Five-Coordinate Aluminum Complexes Containing Diarylamido Diphosphine Ligands. *Inorg. Chem.* **2009**, *48* (12), 5480-5487.

22. Jones, C.; Koutsantonis, G. A.; Raston, C. L., Lewis base adducts of alane and gallane. *Polyhedron* **1993**, *12* (15), 1829-1848.

23. Baceiredo, A.; Kato, T.; Mao, Y.; Berthe, J.; Bousquié, M. Method of Hydrosilylation Implementing an Organic Catalyst Derived from Germylene. US2017313729 (A1), 2017/11/02, 2017.

24. Guan, Z.; Marshall, W. J., Synthesis of New Phosphine Imine Ligands and Their Effects on the Thermal Stability of Late-Transition-Metal Olefin Polymerization Catalysts. *Organometallics* **2002**, *21* (17), 3580-3586.
25. Gau, D.; Kato, T.; Saffon-Merceron, N.; Cossio, F. P.; Baceiredo, A., Stable Phosphonium Sila-ylide with Reactivity as a Sila-Wittig Reagent. *J. Am. Chem. Soc.* 2009, 131 (25), 8762-8763.

26. Gau, D.; Kato, T.; Saffon-Merceron, N.; De Cózar, A.; Cossío, F. P.; Baceiredo, A., Synthesis and Structure of a Base-Stabilized C-Phosphino-Si-Amino Silyne. *Angew. Chem., Int. Ed.* 2010, 49 (37), 6585-6588.

27. Rodriguez, R.; Gau, D.; Contie, Y.; Kato, T.; Saffon-Merceron, N.; Baceiredo, A., Synthesis of a Phosphine-Stabilized Silicon(II) Hydride and Its Addition to Olefins: A Catalyst-Free Hydrosilylation Reaction. *Angew. Chem., Int. Ed.* 2011, 50 (48), 11492-11495.

28. Coles, M. P.; Jordan, R. F., Cationic Aluminum Alkyl Complexes Incorporating Amidinate Ligands. Transition-Metal-Free Ethylene Polymerization Catalysts. *J. Am. Chem. Soc.* 1997, 119 (34), 8125-8126.

29. Malpass, D. B., Commercially Available Metal Alkyls and Their Use in Polyolefin Catalysts. *Handbook of Transition Metal Polymerization Catalysts* 2010.

30. Budzelaar, P. H. M.; Talarico, G., Insertion and β-Hydrogen Transfer at Aluminium. In *Group 13 Chemistry III: Industrial Applications*, Roesky, H. W.; Atwood, D. A., Eds. Springer Berlin Heidelberg: Berlin, Heidelberg, 2003; pp 141-165.

31. Clarke, M. L.; Cole-Hamilton, D. J.; Slawin, A. M. Z.; Woollins, J. D., P–N bond formation as a route to highly electron rich phosphine ligands. *Chem. Commun.* 2000, (20), 2065-2066.

32. Cole, M. L.; Jones, C.; Junk, P. C.; Kloth, M.; Stasch, A., Synthesis and Characterization of Thermally Robust Amidinato Group 13 Hydride Complexes. *Chem. - Eur. J.* 2005, 11 (15), 4482-4491.
33. Nako, A. E.; Gates, S. J.; White, A. J. P.; Crimmin, M. R., Preparation and properties of a series of structurally diverse aluminium hydrides supported by β-diketiminate and bis(amide) ligands. *Dalton Trans.* **2013**, *42* (42), 15199-15206.

34. Cui, C.; Roesky, H. W.; Schmidt, H.-G.; Noltemeyer, M.; Hao, H.; Cimpoesu, F., Synthesis and Structure of a Monomeric Aluminum(I) Compound [{HC(CMeNAr)₂}Al] (Ar=2,6-iPr₂C₆H₃): A Stable Aluminum Analogue of a Carbene. *Angew. Chem., Int. Ed.* **2000**, *39* (23), 4274-4276.

35. Krysiak, J.; Lyon, C.; Baceiredo, A.; Gornitzka, H.; Mikolajczyk, M.; Bertrand, G., Stable Optically Pure Phosphino(silyl)carbenes: Reagents for Highly Enantioselective Cyclopropanation Reactions. *Chem. - Eur. J.* **2004**, *10* (8), 1982-1986.

36. Jouet, R. J.; Warren, A. D.; Rosenberg, D. M.; Bellitto, V. J.; Park, K.; Zachariah, M. R., Surface Passivation of Bare Aluminum Nanoparticles Using Perfluoroalkyl Carboxylic Acids. *Chem. Mater.* **2005**, *17* (11), 2987-2996.
Mixed $N,P$-donor stabilized aluminum dimethyl and dihydride complexes were synthesized.

Variation of the ligand’s phosphine donor group enables control over the coordination mode at aluminum.