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

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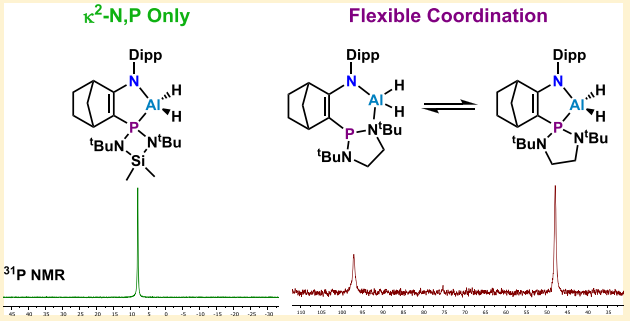
Supporting Information

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 P donors is relatively underexplored. Here, we report aluminum dihydride and dimethyl complexes supported by amidophosphine ligands and study their coordination behavior in solution and in the solid state. All complexes exist as κ^2-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 κ^2-N,N complexes. Thus, importantly for catalytic activity, we find that the coordination behavior of the P 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 the catalytic activity.



INTRODUCTION

Aluminum hydrides such as $LiAlH_4$, sodium bis(2-methoxyethoxy)aluminum hydride (RedAl), and AlH_3 are ubiquitous in synthetic chemistry for their use as reducing agents.[1] Recently, the scope of the reactivity of these simple aluminum hydrides has been expanded into catalytic hydroboration of alkenes and alkynes, a development of significant environmental and economic importance because of the high abundance and relatively low toxicity of aluminum compared to platinum group metals.[2,3] Numerous other uncomplicated aluminum hydride compounds are also capable of hydroboration or even hydrogenation of unsaturated polar bonds such as aldehydes, ketones, or imines.[4,5] Aluminum hydride compounds with more complex ligands have also been investigated. For example, N-heterocyclic imine-coordinated aluminum hydrides catalyze carbonyl hydroboration[6] while the β-diketiminate-stabilized aluminum dihydride **I** (Figure 1) also catalyzes the hydroboration of alkynes.[7] The dihydride **I** is also a precursor to β-diketiminate-stabilized aluminum(I) species (at least within the coordination sphere of a transition metal).[8]

Reported aluminum dihydride complexes overwhelmingly use N-donor ligands (e.g., **I**−**III**; Figure 1).[9−13] Typically, these ligands are also multidentate (to stabilize the intrinsically electron-poor Al 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.

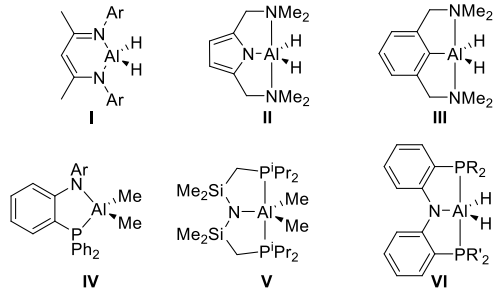


Figure 1. Literature examples of aluminum dihydride and dimethyl complexes stabilized by N-based ligands (**I**−**III**) or mixed donor ligands (**IV**−**VI**).[9−11,15,20,21] (**I** and **IV** have Ar = 2,6-$C_6H_3{}^iPr_2$, and **VI** has R = R′ = Ph, ^{i}Pr or R = Ph and R′ = ^{i}Pr).

Aluminum dihydrides or related species with P-based ligands are much rarer. A few examples of dimethylaluminum complexes with mixed-donor ligands are known, in which bidentate ligands having one N donor also contain a "soft" donor, such as S or P (**IV** and **V**; Figure 1).[14−18] The likely more labile Al−P interaction offers the possibility of hemilability, which can be useful in the stabilization of catalytic transition or resting states.[19] Indeed, Fryzuk et al. used NMR spectroscopy to demonstrate the fluxional

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coordination of P-donor atoms in **V**, resulting in an equilibrium between four- and five-coordinate Al centers.[20]

In comparison to mixed-donor methyl complexes, mixed-donor aluminum dihydride complexes are scarce, with only a single example.[21] Most P-coordinated aluminum hydrides are limited to simple adducts between phosphines and alane, with the exception of **VI** (Figure 1), reported by Liang et al. in 2009, which was synthesized via the reduction of the corresponding aluminum dichloride using $LiAlH_4$.[21,22] Hemilability of the P donors was not found in this example, likely because of the rigidity of the ligand backbone.

Herein, we describe novel aluminum dimethyl and dihydride species stabilized by mixed N,P-donor ligands that display flexible coordination modes based on a "ligand-slip" phenomenon.

RESULTS AND DISCUSSION

The amidophosphine ligands **1a**–**1c**[23] (Figure 2) have previously been used to prepare nickel and palladium

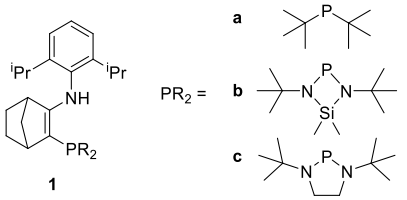


Figure 2. Mixed-donor ligands **1a**–**1c**.

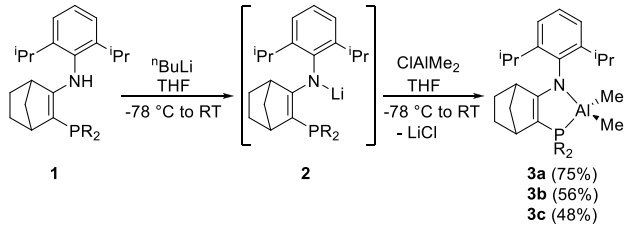
complexes, as well as to support reactive silicon(II) compounds.[24−27] The steric bulk around both the N and P centers of **1a**–**1c** has not only enabled the isolation of reactive species such as silicon(II) hydrides but also modulates reversible Si^{II}/Si^{IV} oxidative additions/reductive eliminations. At the P donor in particular, both steric bulk and electron-donating ability are readily tunable. We were interested in whether this class of ligands could be employed to support Al centers and whether they could be used to modulate their structure and reactivity.

Synthesis and Solid-State Structures of Aluminum Dimethyl Complexes. Dimethylaluminum complexes are a broad class of compounds that have been reported as catalysts or cocatalysts in alkene polymerization.[28−30] Complexes of dimethylaluminum stabilized by many N- or mixed-donor ligands have been reported, rendering this class of compounds ideal for benchmarking the coordination abilities of ligands **1a**–**1c**. We decided to first investigate the coordination of ligand **1** to dimethylaluminum moieties.

The coordination of **1b** and **1c** to Si^{IV} centers has been reported and was achieved by deprotonation before treatment with the appropriate silicon halide.[27] Accordingly, ligands **1a**–**1c** were deprotonated with nBuLi at −78 °C to afford yellow solutions of **2a**–**2c** (Scheme 1). A characteristic resonance is observed in the $^{31}P\{^{1}H\}$ 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 Li (e.g., **2a**, $^{31}P\{^{1}H\}$ NMR δ 10.9, J_{PLi} = 54 Hz). Similarly, in the ^{7}Li NMR spectra, doublets are observed because of coupling with P (e.g., **2a**, ^{7}Li NMR δ 1.3, J_{LiP} = 54 Hz).

The dimethylaluminum complexes **3a**–**3c** were obtained by reaction of the in situ generated lithiated ligand **2** with 1 equiv of dimethylaluminum chloride. Extraction of the products in

Scheme 1. Lithiation of Ligand 1 To Form 2 Followed by Reaction with Dimethylaluminum Chloride To Form Dimethylaluminum Complexes 3a–3c



pentane, followed by filtration and evaporation of the solvent afforded **3a**–**3c** as yellow air-sensitive solids. Complexes **3a** and **3c** could be isolated as analytically pure solids by crystallization, while **3b** was clearly identified but resisted purification attempts. All three complexes **3a**–**3c** were extremely sensitive to air and moisture.

The solid-state structures of **3a** and **3c** were determined by X-ray crystallography (Figure 3). Both compounds have a tetrahedral Al center with coordinated N and P donors, forming a planar ring. The ring is heavily skewed with (as might be expected) a substantially shorter interaction between Al and the N donor than with the phosphine [e.g., **3a**, Al1−N1 1.8985(14) Å vs Al1−P1 2.4800(6) Å]. Both the Al−N and Al−P distances are comparable to those previously reported, for example the N,P-coordinated dimethylaluminum complex **IV** [Al−N 1.894(6) Å; Al−P 2.477(3) Å].[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 that P is less strongly bound to the Al center. The aminophosphine donor of **3c** is more electron-donating than the dialkylphosphine donor of **3a**, which would be expected to give rise to the opposite trend.[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 Al center. Indeed, this can be observed in the C1−Al1−C2 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–3c. Despite their similar solid-state structures, solution-phase NMR spectroscopy revealed differences in the coordination behavior among the dimethylaluminum complexes **3a**–**3c**. 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 [$\Delta\partial$(**3a**) = −54.4 ppm; $\Delta\partial$(**3b**) = −83.3 ppm]. The $^{31}P\{^{1}H\}$ NMR resonances for **3a** and **3b** were also significantly broadened in comparison to the free ligands **1a** and **1b**, presumably as a result of coordination of the P to the quadrupolar ($I = {}^{5}/_{2}$) Al nucleus [**3a**, full width at half-maximum ($\Delta\nu_{1/2}$) = 21.1 Hz; **1a**, $\Delta\nu_{1/2}$ = 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 P (**3a**, δ −0.33 and −0.19, $^{2}J_{HP}$ = 2.5 Hz). The ^{1}H NMR spectrum also shows that each CH_3 group in the 2,6-diisopropylphenyl (Dipp) substituent is inequivalent, indicating restricted rotation likely because of steric constraints.

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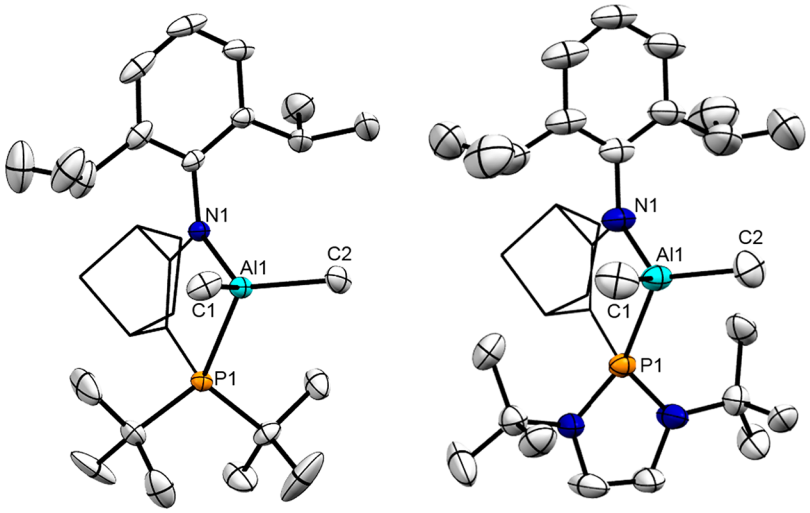


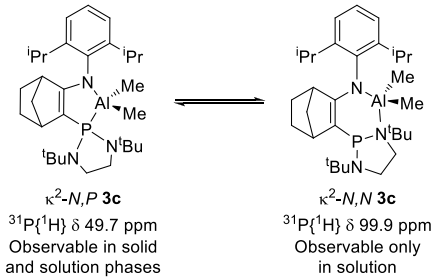
Figure 3. Molecular structures of **3a** (left) and **3c** (right) with thermal ellipsoids drawn at the 50% probability level. H and disordered ligand atoms are omitted for clarity. Selected bond distances (Å) and angles (deg) for **3a**: N1−Al1 1.895(14), P1−Al1 2.4800(6), Al1−C1 1.9652(19), Al1−C2 1.970(2); N1−Al1−P1 86.67(4), N1−Al1−C1 116.12(8), N1−Al1−C2 115.25(8), P1−Al1−C1 114.53(7), P1−Al1−C2 114.00(7), C1−Al1−C2 109.00(9). Selected bond distances (Å) and angles (deg) for **3c**: N1−Al1 1.917(3), P1−Al1 2.5304(9), Al1−C1 1.967(4), Al1−C2 1.964(4); N1−Al1−P1 85.59(8), N1−Al1−C1 116.14(19), N1−Al1−C2 116.19(19), P1−Al1−C1 115.98(13), P1−Al1−C2 115.99(14), C1−Al1−C2 106.4(2).

Crystalline **3c** was also characterized by solution-phase NMR spectroscopy. Surprisingly, the $^{31}P\{^{1}H\}$ NMR spectrum contained two resonances, at 99.9 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 ($\Delta\partial$ = −40.9 ppm) from that of **1c** and so is consistent with coordination of P to the Al 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** ($\Delta\partial$ = +9.3 ppm), which indicates that P in this environment is not coordinated to the Al center.

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 κ^2-N,P or κ^2-N,N coordination (Scheme 2). In the solid state, κ^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 the κ^2-N,P and κ^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 2D NMR spectroscopic experiments verified that in both isomers the ligand backbone was intact and undisturbed. The possibility of a dimeric κ^1-N isomer of **3c** (with, e.g., bridging methyl ligands) was excluded based on analysis of the ^{1}H DOSY NMR spectrum, which indicated that both of the observed isomers diffused at the same rate in solution. Similarly, high-resolution mass spectrometry (HRMS) also identified the product as **3c**, with no evidence of a dimeric species observed.

Scheme 2. Proposed Structures of κ^2-*N,P*- and κ^2-*N,N*-3c[a]



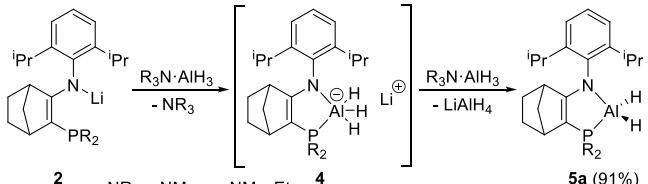
[a]In the solid state, only κ^2-*N,P*-**3c** is observed, while in solution, both the κ^2-N,P- and κ^2-N,N isomers are observed.

Synthesis of Aluminum Dihydride Complexes. Following the preparation of the dimethylaluminum complexes **3a**−**3c**, we turned our attention to the preparation of aluminum dihydride complexes. Ligands **1a**−**1c** do not react with $Me_2EtN{\cdot}AlH_3$, in contrast to the observed reactivity of amidine ligands, which evolve H_2 and form aminidinatoaluminum dihydrides.[32] Treatment with $LiAlH_4$ also had no effect. Thus, we used the lithiated ligands **2a**−**2c** as precursors instead.

Treatment of **2b** with a single equivalent of $Me_2EtN{\cdot}AlH_3$ resulted in a yellow solution, the ^{31}P NMR spectrum of which revealed a quartet (δ 110.8, $^{2}J_{PH}$ = 34 Hz), which collapsed to a singlet in the $^{31}P\{^{1}H\}$ NMR spectrum. This evidence, as well as further characterization by multinuclear NMR spectroscopy and mass spectrometry, confirmed formation of the aluminate complex **4b** (Scheme 3).

The addition of a second equivalent of $Me_2EtN{\cdot}AlH_3$ to solutions of **4b** was monitored by $^{31}P\{^{1}H\}$ NMR spectroscopy, which revealed complete consumption of **4b** and the formation

Scheme 3. Proposed Mechanism for the Reaction of 2 with $Me_2EtN{\cdot}AlH_3$ (NR_3 = NMe_3 or NMe_2Et) To Form the Aluminum Dihydride 5 via the Charged Intermediate 4



NR_3 = NMe_3 or NMe_2Et

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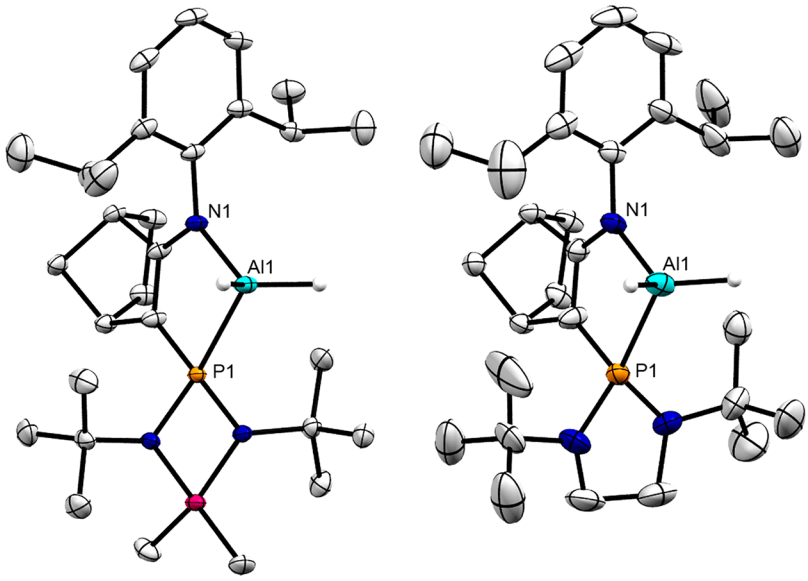

Figure 4. Molecular structures of **5b** (left) and **5c** (right). The aluminum hydride atoms were located using a difference map and allowed to refine freely. H and disordered ligand atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) for **5b**: N1−Al1 1.8972(15), P1−Al1 2.4442(7); N1−Al1−P1 87.47(5). Selected bond lengths (Å) and angles (deg) for **5c**: N1−Al1 1.892(2), P1−Al1 2.4790(10); N1−Al1−P1 86.60(6).

of a new species represented by a broad singlet (61.3 ppm, $\Delta\nu_{1/2}$ = 55.7 Hz), indicating P coordination to Al. Analysis of the ^{27}Al NMR spectrum revealed the formation of $LiAlH_4$. On the basis of this evidence, the reaction pathway shown in Scheme 3 is proposed: the reaction of **2b** with $Me_2EtN{\cdot}AlH_3$ proceeds by forming **4b** by displacement of the amine from $Me_2EtN{\cdot}AlH_3$. The second 1 equivalent of $Me_2EtN{\cdot}AlH_3$ abstracts a hydride from **4b**, generating **5b** and $LiAlH_4$ and eliminating the amine.

When **2a** was treated with 1 equiv of $Me_2EtN{\cdot}AlH_3$, the resulting pale-yellow solution was revealed to contain a mixture of compounds by $^{31}P\{^1H\}$ 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. $LiAlH_4$ was also observed by ^{27}Al 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 $Me_2EtN{\cdot}AlH_3$ to generate a statistical mixture. This contrasts to the situation for **4b**, where hydride abstraction by $Me_2EtN{\cdot}AlH_3$ is much slower than its coordination to the lithiated ligand **2b**. Upon the addition of a second equivalent of $Me_2EtN{\cdot}AlH_3$ to **4a**, the reaction mixture turned colorless and the $^{31}P\{^1H\}$ NMR spectrum showed complete conversion to **5a** (7.5 ppm).

Preparatively, the dihydride complexes **5a**−**5c** were obtained in multigram quantities from treatment of the lithiated ligands **2a**−**2c** with 2 equiv of $Me_3N{\cdot}AlH_3$ or $Me_2EtN{\cdot}AlH_3$. 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 ^{1}H NMR spectra of **5a** and **5b**, Al−H resonances are visible as very broad singlets at 4.6 ppm (**5a**, $\Delta\nu_{1/2}$ = 71.6 Hz; **5b**, $\Delta\nu_{1/2}$ = 125.3 Hz) because of the influence of the quadrupolar Al 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 the solid-state samples of **5a**−**5c** revealed the expected symmetric and antisymmetric Al−H stretches (**5a**, 1810 and 1786 cm^{-1}; **5b**, 1831 and 1816 cm^{-1}; **5c**, 1825 and 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 amidophosphine ligand in each compound is κ^2-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 Al 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 with 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 that in the corresponding dimethyl complex **3c** [Al1−P1: **5c**, 2.4791(10) Å; **3c**, 2.5304(8) Å]. 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 Al1−P1 distance for **5b** as a result of reduced bulk at the P 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 those of the dimethyl compounds are also due to the smaller hydride substituents compared to the methyl groups.

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 $^{31}P\{^1H\}$ NMR spectrum revealed the presence of two broad singlets at 96.9 ppm ($\Delta\nu_{1/2}$ = 137.9 Hz) and 47.8 ppm ($\Delta\nu_{1/2}$ = 96.6 Hz) in a ratio of 1:2. By ^{1}H NMR, two sets of resonances were also observed for all proton environments, including the dihydride ligands (signals at κ^2-*N,N*-**5c**, 4.3 ppm, κ^2-*N,P*-**5c**, 4.6 ppm; the ratio of the two species as measured by

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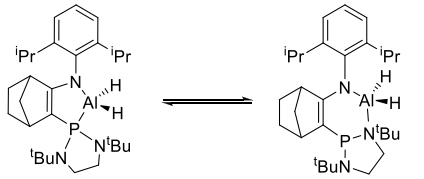
^{1}H NMR in a ratio of 35:65, consistent with that observed in the ^{31}P NMR spectrum).

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

Scheme 4. Proposed Structures of κ^2-*N,P*- and κ^2-*N,N*-5c[a]



[a]In the solid state, only κ^2-*N,P*-**5c** is observed, while in solution, both the κ^2-N,P and κ^2-N,N isomers are observed.

(1) The two isomers are both monomeric species, as revealed by ^{1}H DOSY NMR 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}P{^{1}H} NMR spectrum, the resonance at 96.9 ppm is assigned to the κ^2-N,N isomer because of its similarity to that observed for the free ligand **1c** (90.6 ppm), which indicates that the P center is not coordinated to Al. The resonance at 47.8 ppm is assigned to the κ^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 and 1801 cm^{-1}) are consistent with a four-coordinate aluminum dihydride species in both phases, ruling out a κ^1-N isomer in which the phosphine is uncoordinated.

(4) Using density functional theory (DFT), we performed geometry optimization and frequency calculations on κ^2-N,P isomers of **5a**−**5c** at the 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 replicating experimentally observed Al−H stretching frequencies.[33] The calculations accurately reproduced the experimentally observed geometries and IR stretching frequencies for **5a**−**5c**, 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 κ^2-N,P geometry revealed two potential minima (Figure S1), which were reoptimized at the M062X/6,31G+(d,p)/Lanl2DZ level (Figure 5 and Table S2). A κ^1-N isomer was found to be 22.6 kcal mol^{-1} higher in energy than the κ^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 the experimental values). However, the κ^2-N,N isomer located in the PES scan was found to be very close in energy to κ^2-*N,P*-**5c** (−0.8 kcal mol^{-1}

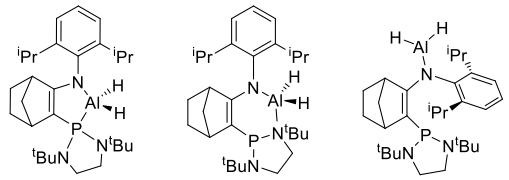


Figure 5. Computed energies of κ^2-*N,P*-, κ^2-*N,N*-, and κ^1-*N*-**5c** [M062X/6,31G+(d,p)/Lanl2DZ].

more stable; DFT does not replicate the experimentally observed order of stability, although it does correctly place the two species very close in energy). Calculated Al−H stretching frequencies for κ^2-*N,P*- and κ^2-*N,N*-**5c** (1863, 1845, and 1860, 1813 cm^{-1}, respectively) are sufficiently close in order to explain the single peak observed in the experimental solution-phase spectrum (1829 cm^{-1}).

The ligand-slip rearrangement of **5c** from κ^2-N,P to κ^2-N,N is likely driven by a preference for the "hard" N-donor functionality of the diaminophosphine donor over the "softer" P center. The increased proportion of the κ^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 isomerization from κ^2-N,P to κ^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*-butylamino groups of **3b** and **5b** cannot favorably participate in the same isomerization as **3c** and **5c**.

Interconversion between κ^2-*N,P*- and κ^2-*N,N*-**3c** or -**5c** in solution was not observable, and we were thus unable to determine the 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 because of its high sensitivity to air and moisture.

Solid-State NMR Spectroscopy. To further confirm our assignment of ^{31}P resonances for the κ^2-N,P and κ^2-N,N isomers of **3c** and **5c**, we undertook solid-state NMR spectroscopy because from crystallographic studies κ^2-N,P-coordination is exclusively observed. The ^{31}P{^{1}H} MAS NMR spectra of **3c** and **5c** are consistent with X-ray crystallography, revealing only a single-P environment for each compound (Figure 6). In both cases, the solid-state chemical shift is almost identical with the solution-phase signal assigned to the κ^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 line shapes observed in the ^{31}P{^{1}H} NMR spectra indicate quadrupolar coupling between Al and P, 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 κ^2-N,N isomer in the solid state.

For **3a**, **3b**, **5a**, and **5b**, which all display exclusive κ^2-N,P coordination in solution, the observed ^{31}P{^{1}H} MAS NMR spectra each contain a single resonance extremely close in chemical shift to that observed in solution (e.g., **5a**, solution

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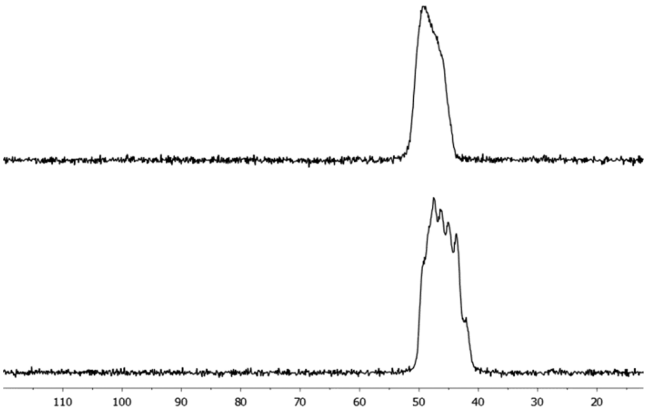


Figure 6. $^{31}P\{^{1}H\}$ (9.4 T, 14 kHz, MAS) NMR spectra for **3c** (top) and **5c** (bottom).

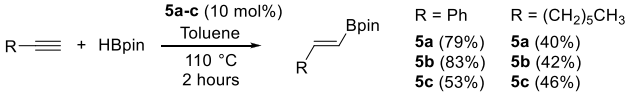
phase, 8.0 ppm, solid phase, 8.9 ppm). Although we were unable to observe any resonances for any of the compounds reported here by solution-phase ^{27}Al NMR spectroscopy, solid-state experiments were more successful. Details of the $^{27}Al\{^{1}H\}$ CPMG NMR spectra for **3a**−**3c** and **5a**−**5c** are provided in the Supporting Information.

CONCLUSIONS

In summary, we have synthesized aluminum dimethyl and dihydride complexes with a series of amidophosphine ligands of varying steric bulk. The bulky bidentate ligands **1a**−**1c** enable the isolation of reactive aluminum dihydrides, the synthesis of which was observed to proceed through five-coordinate aluminate intermediates (**4a**−**4c**). Evidence from X-ray crystallography and solid-state NMR spectroscopy indicates that, for all dimethyl and dihydride complexes, both N- and P-donor atoms are bound to the Al centers in the solid state. In solution, however, altering the steric bulk of the ligand enables control over the coordination mode at the Al center: for the bulkiest ligand employed, **1c**, both the dimethyl and dihydride complexes **3c** and **5c** exist as a mixture of κ^2-N,P and κ^2-N,N isomers.

The variable coordination mode of the ligand is encouraging as a potential route to controlling 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 arylalkynes with HBPin (see the SI). The accessibility of the κ^2-N,N coordination mode for **5c** has a clear effect on the reactivity. While 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 h at 110 °C compared to 53% for **5c**. We are now further exploring the coordination chemistry, reactivity, and catalytic applications of the dihydrides **5a**−**5c** (Scheme 5).

Scheme 5. Catalytic Hydroboration of Phenylacetylene and 2-Cyclooctyne Using 5a−5c



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 h at 110 °C before use. Solvents were obtained from an inert solvent purification system and stored over 4 Å molecular sieves. C_6D_6 and tetrahydrofuran (THF)-d_8 were dried over potassium, then vacuum-distilled, and stored over 4 Å molecular sieves.

Ligands **1b** and **1c**,[23] their precursors [imine[24] and chlorophosphines $PCl(N^tBu)_2SiMe_2$[23] and $PCl(N^tBuCH_2)_2$[35]], and [$H_3Al\cdot NMe_3$][36] were synthesized according to literature procedures. $SiMe_2(NH^tBu)_2$ was synthesized according to a modified literature procedure (see the SI). *tert*-Butylamine was dried over calcium hydride and vacuum-distilled prior to use. $LiAlH_4$ 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 h 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 was added dropwise nBuLi (2.5 M in hexanes, 1 equiv). The cold bath was removed, and the resultant yellow solution was stirred at room temperature for 1 h. Monitoring by $^{31}P\{^{1}H\}$ NMR spectroscopy revealed the presence of the lithiated ligand **2**, which was characterized in situ.

2a. $^{31}P\{^{1}H\}$ NMR (C_4H_8O, 202.5 MHz, 300 K): δ 10.9 (1:1:1:1 quartet, J_{P-Li} = 54 Hz). ^{7}Li NMR (C_4H_8O, 194.4 MHz, 300 K): δ 1.3 (d, J_{Li-P} = 54 Hz).

2b. $^{31}P\{^{1}H\}$ NMR (C_4H_8O, 202.5 MHz, 300 K): δ 96.4 (1:1:1:1 quartet, J_{P-Li} = 63 Hz). ^{7}Li NMR (C_4H_8O, 194.4 MHz, 300 K): δ 1.1 (d, J_{Li-P} = 63 Hz).

2c. $^{31}P\{^{1}H\}$ NMR (C_4H_8O, 202.5 MHz, 300 K): δ 68.6 (1:1:1:1 quartet, J_{P-Li} = 54 Hz). ^{7}Li NMR (C_4H_8O, 194.4 MHz, 300 K): δ 1.5 (d, J_{Li-P} = 54 Hz).

General Synthesis of 3. To a solution of **1** in THF cooled to −78 °C was added dropwise nBuLi (2.5 M in hexanes, 1 equiv). The cold bath was removed, and the resultant yellow solution was stirred at room temperature for 1 h. The reaction mixture was cooled to −78 °C, and Me_2AlCl (1.0 M in hexanes) was added dropwise. The cold bath was removed, and the resultant solution was stirred at room temperature for 1 h. The solvent was removed in vacuo, and the product was extracted in hexane and dried to afford **3a**−**3c**.

3a. **1a** (0.40 g, 0.97 mmol), THF (20 mL), nBuLi (0.39 mL, 0.97 mmol, 1.0 equiv), and Me_2AlCl (0.97 mL, 0.97 mmol, 1.0 equiv) yielded **3a** (0.34 g, 75%) as a pale-yellow solid. Colorless crystals suitable for X-ray crystallography were grown from a saturated diethyl ether solution at 4 °C. ^{1}H (C_6D_6, 500 MHz, 300 K): δ −0.33 (d, $^{3}J_{HP}$ = 2.5 Hz, 3H, $AlCH_3$), −0.19 (d, $^{3}J_{HP}$ = 2.5 Hz, 3H, $AlCH_3$), 1.10 (m, 1H, $^{1}/_{2}CH_{2Norb}$), 1.19 (d, $^{3}J_{HP}$ = 8.6 Hz, 9H, CH_{3tBu}), 1.22 (d, $^{3}J_{HP}$ = 8.6 Hz, 9H, CH_{3tBu}), 1.24 (d, $^{3}J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.26 (d, $^{3}J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.37 (d, $^{3}J_{HH}$ = 6.8 Hz, 6H, CH_{3iPr}), 1.43 (m, 2H, $CH_{2CbridgeheadCP}$), 1.55 (m, 1H, $^{1}/_{2}CH_{2CbridgeheadCN}$), 1.61 (m, 1H, $^{1}/_{2}CH_{2Norb}$), 1.66 (m, 1H, $^{1}/_{2}CH_{2CbridgeheadCN}$), 2.50 (br s, 1H, $PCCH_{bridgehead}$), 2.95 (br s, 1H, $NCCH_{bridgehead}$), 3.44 (sept, $^{3}J_{HH}$ = 6.8 Hz, 1H, CH_{iPr}), 3.61 (sept, $^{3}J_{HH}$ = 6.8 Hz, 1H, CH_{iPr}), 7.17−7.19 (m, 3H, $H_{aromatic}$). ^{13}C NMR (C_6D_6, 126 MHz, 300 K): δ −5.7 (br s, $AlCH_3$), −4.3 (br s, $AlCH_3$), 25.2 (s, CH_{3iPr}), 25.4 (s, CH_{3iPr}), 25.7 (s, CH_{3iPr}), 25.8 (s, CH_{3iPr}), 25.9 (d, J_{CP} = 2 Hz, $CH_{2CbridgeheadCP}$), 27.6 (s, CH_{iPr}), 27.7 (s, CH_{iPr}), 30.0 (s, $CH_{2CbridgeheadCN}$), 30.1 (d, J_{CP} = 5 Hz, CH_{3tBu}), 30.5 (d, J_{CP} = 5 Hz, CH_{3tBu}), 34.4 (d, J_{CP} = 30 Hz, CtBu), 34.8 (d, J_{CP} = 31 Hz, CtBu), 43.8 (d, J_{CP} = 9 Hz, PCCH), 44.1 (d, J_{CP} = 2 Hz, NCCH), 48.3 (d, J_{CP} = 3 Hz, CH_{2Norb}), 80.2 (d, J_{CP} = 42 Hz, PCCH), 124.2 (s, C_{meta}), 124.3 (s, C_{meta}), 126.1 (s, C_{para}), 141.7 (d, J_{CP} = 3 Hz, NC_{Ar}), 147.1 (s, CCH_{iPr}), 147.4 (s, CCH_{iPr}), 185.1 (d, J_{CP} = 21 Hz, NCCH). $^{31}P\{^{1}H\}$ NMR (C_6D_6, 162 MHz, 300 K): δ 1.6 (s, $\Delta\nu_{1/2}$ = 21.1 Hz). HRMS (APPI): m/z 469.341919 ($[C_{29}H_{49}AlNP]^+$; theoretical m/z 469.341252). Elem anal. Found: C, 74.13; H, 10.38; N, 2.85. Calcd for $C_{29}H_{49}AlNP$: C, 74.16; H, 10.52; N, 2.98.

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3b. **1b** (0.3 g, 0.60 mmol), THF (20 mL), nBuLi (0.24 mL, 0.60 mmol, 1.0 equiv), and Me_2AlCl (0.60 mL, 0.60 mmol, 1.0 equiv) yielded **3b** (0.17 g, 56%) as a yellow solid. Some impurities (less than 10%) were observed by NMR spectroscopy because of reaction with water but could not be separated because crystallization of **3b** was not possible.

^{1}H NMR (C_6D_6, 500 MHz, 300 K): δ −0.26 (d, $^3J_{HP}$ = 3.9 Hz, 3H, $AlCH_3$), −0.12 (d, $^3J_{HP}$ = 3.9 Hz, 3H, $AlCH_3$), 0.27 (s, 3H, $SiCH_3$), 0.32 (s, 3H, $SiCH_3$), 1.12 (d, $^2J_{HH}$ = 8.1 Hz, 1H, $^1/_2CH_{2Norb}$), 1.25 (s, 9H, CH_{3tBu}), 1.26 (s, 9H, CH_{3tBu}), 1.25 (d, $^3J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.26 (d, $^3J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.32 (d, $^3J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.41 (d, $^3J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.42 (m, 2H, $CH_{2CbridgebeadCP}$), 1.60 (d, $^2J_{HH}$ = 8.1 Hz, 1H, $^1/_2CH_{2Norb}$), 1.69 (m, 2H, $CH_{2CbridgeheadCN}$), 2.53 (br s, 1H, $CH_{bridgeheadCP}$), 3.13 (br s, 1H, $CH_{bridgeheadCN}$), 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, $H_{aromatic}$). ^{13}C NMR (C_6D_6, 126 MHz, 300 K): δ −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 (d, J_{CP} = 3.7 Hz, $SiCH_3$), 25.3 (s, CH_{3iPr}), 25.4 (s, CH_{3iPr}), 25.6 (s, CH_{3iPr}), 26.0 (s, CH_{3iPr}), 26.3 (s, $CH_{2CbridgeheadCP}$), 27.6 (s, CH_{iPr}), 27.8 (s, CH_{iPr}), 29.4 (s, $CH_{2CbridgeheadCN}$), 32.3 (d, J_{CP} = 5.4 Hz, CH_{3tBu}), 32.7 (d, J_{CP} = 4.9 Hz, CH_{3tBu}), 40.6 (d, J_{CP} = 3.5, CHCN), 44.3 (d, J_{CP} = 43.9, CHCP), 46.6 (d, J_{CP} = 4.7 Hz, CH_{2Norb}), 50.8 (d, J_{CP} = 3.9 Hz, C^tBu), 50.9 (d, J_{CP} = 2.8 Hz, C^tBu), 99.1 (d, J_{CP} = 29.2 Hz, PCCH), 124.3 (s, C_{meta}), 124.3 (s, C_{meta}), 126.3 (s, C_{para}), 141.2 (d, J_{CP} = 3.1 Hz, NC_{Ar}), 146.6 (s, CCH_{iPr}), 147.0 (s, CCH_{iPr}), 186.8 (d, J_{CP} = 33.9 Hz, NCCH). ^{31}P{^{1}H} (C_6D_6, 162 MHz, 300 K): δ 64.0 (s, $\Delta\nu_{1/2}$ = 35.8 Hz). HRMS (APPI): m/z 555.371654 ($[C_{31}H_{55}AlN_3PSi]^+$; theoretical m/z 555.371277).

3c. **1c** (0.43 g, 0.92 mmol), THF (20 mL), nBuLi (0.37 mL, 0.92 mmol, 1.0 equiv), and Me_2AlCl (0.92 mL, 0.60 mmol, 1.0 equiv) were mixed. To gain analytically pure material, **3c** was further purified by recrystallization from hexanes at −20 °C to yield colorless crystals (0.23 g, 48%). Two isomers were identified in the NMR spectra with an approximate ratio of 4:3 of κ^2-*N,N*-**3c** to κ^2-*N,P*-**3c** at 300 K (determined from the ^{1}H NMR spectrum). Because of 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).

κ^2-*N,N*-**3c**. ^{1}H NMR (C_6D_6, 500 MHz, 300 K): δ −0.67 (s, 3H, AlMe), −0.13 (s, 3H, AlMe), 0.89 (m, 1H, $^1/_2CH_{2Norb}$), 1.18 (m, 1H, $^1/_2CH_{2Norb}$), 1.21 (s, 18H, CH_{3tBu}), 1.24 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH_{3iPr}), 1.27 (d, $^3J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.45 (m, 2H, $CH_{2CbridgeheadCP}$), 1.47 (d, $^3J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.63 (m, 1H, $^1/_2CH_{2CbridgeheadCN}$), 1.72 (m, 1H, $^1/_2CH_{2CbridgeheadCN}$), 2.49 (br s, 1H, $CH_{bridgeheadCP}$), 2.82 (m, 1H, $^1/_2NCH_2$), 2.83 (m, 1H, $^1/_2NCH_2$), 2.97 (m, $CH_{bridgeheadCN}$), 3.15 (m, 1H, $^1/_2NCH_2$), 3.73 (sept, $^3J_{HH}$ = 6.8 Hz, 1H, CH_{iPr}), 3.85 (sept, $^3J_{HH}$ = 6.8 Hz, 1H, CH_{iPr}), 3.88 (m, 1H, $^1/_2NCH_2$), 7.15−7.20 (m, 3H, $H_{aromatic}$). ^{13}C NMR (C_6D_6, 126 MHz, 300 K): δ −5.5 (s, AlMe), −4.7 (s, AlMe), 24.3 (s, CH_{3iPr}), 24.8 (s, CH_{3iPr}), 25.75 (s, CH_{3iPr}), 25.97 (s, $CH_{2CHbridgeheadCP}$), 26.1 (s, CH_{3iPr}), 27.0 (s, CH_{iPr}), 28.2 (s, CH_{iPr}), 29.3 (s, $CH_{2CbridgeheadCN}$), 29.7 (d, J_{CP} = 9.5 Hz, CH_{3tBu}), 29.73 (d, J_{CP} = 7.7 Hz, CH_{3tBu}), 29.8 (d, J_{CP} = 5.6 Hz, CH_{3tBu}), 43.84 (s, CH_{2Norb}), 43.88 (d, J_{CP} = 12.6 Hz, NCH_2), 45.3 (s, $CH_{bridgeheadCP}$), 45.7 (d, J_{CP} = 42.0 Hz, $CH_{bridgeheadCN}$), 48.8 (d, J_{CP} = 2.8 Hz, NCH_2), 53.2 (d, J_{CP} = 6.0 Hz, C^tBu), 63.7 (d, J_{CP} = 11.7 Hz, C^tBu), 103.5 (d, J_{CP} = 37.7 Hz, PCCH), 123.9 (s, C_{meta}), 124.5 (s, C_{meta}), 125.2 (s, C_{para}), 144.1 (s, NC_{Ar}), 146.5 (s, CCH_{iPr}), 147.0 (s, CCH_{iPr}), 165.0 (d, J_{CP} = 5.0 Hz, NCCH). ^{31}P{^{1}H} NMR (C_6D_6, 162 MHz, 300 K): δ 99.9 (s, $\Delta\nu_{1/2}$ = 5.3 Hz).

κ^2-*N,P*-**3c**. ^{1}H NMR (C_6D_6, 500 MHz, 300 K): δ −0.27 (d, $^3J_{HP}$ = 3.1 Hz, 3H, AlMe), −0.14 (d, $^3J_{HP}$ = 3.1 Hz, 3H, AlMe), 1.06 (dm, $^2J_{HH}$ = 8.1 Hz, 1H, $^1/_2CH_{2Norb}$), 1.25 (d, $^3J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.26 (d, $^3J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.30 (s, 9H, CH_{3tBu}), 1.32 (s, 9H, CH_{3tBu}), 1.33 (m, 1H, $^1/_2CH_{2CbridgeheadCP}$), 1.38 (m, 1H, $^1/_2CH_{2CbridgeheadCP}$), 1.40 (d, $^3J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.42 (d, $^3J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.56 (m, $^2J_{HH}$ = 8.1 Hz, 1H, $^1/_2CH_{2Norb}$), 1.63 (m, 2H, $CH_{2CbridgeheadCN}$), 2.48 (br s, 1H, $CH_{bridgeheadCP}$), 2.59 (m, 1H, $^1/_2NCH_2$), 2.66 (m, 1H, $^1/_2NCH_2$), 2.82 (m, 1H, $^1/_2NCH_2$), 2.89 (m, 1H, NCH_2), 3.05 (br s, 1H, $CH_{bridgeheadCN}$), 3.52 (sept, $^3J_{HH}$ = 6.8 Hz, 1H, CH_{iPr}), 3.74 (sept, $^3J_{HH}$ = 6.8 Hz, 1H, CH_{iPr}), 7.15−7.20 (m, 3H, $H_{aromatic}$). ^{13}C NMR (C_6D_6, 126 MHz, 300 K): δ −4.2 (s, AlMe), −3.5 (s, AlMe), 25.2 (s, CH_{3iPr}), 25.4 (s, CH_{3iPr}), 25.68 (s, CH_{3iPr}), 25.84 (s, $CH_{2CbridgeheadCP}$), 27.4 (s, CH_{iPr}), 27.6 (s, CH_{iPr}), 29.2 (s, CH_{3tBu}), 29.4 (d, J_{CP} = 2.2 Hz, $CH_{2CbridgeheadCN}$), 29.7 (d, J_{CP} = 7.6 Hz, CH_{3tBu}), 42.0 (d, J_{CP} = 4.2 Hz, $CH_{bridgeheadCN}$), 43.6 (s, NCH_2), 44.2 (d, J_{CP} = 9.9 Hz, $CH_{bridgeheadCP}$), 44.3 (s, NCH_2), 46.6 (d, J_{CP} = 5.3 Hz, CH_{2Norb}), 52.5 (d, J_{CP} = 11.7 Hz, C^tBu), 52.8 (d, J_{CP} = 8.8 Hz, C^tBu), 95.5 (d, J_{CP} = 33.5 Hz, PCCH), 124.29 (s, C_{meta}), 124.32 (C_{meta}), 126.2 (s, C_{para}), 142.0 (d, J_{CP} = 3.9 Hz, NC_{Ar}), 146.7 (s, CCH_{iPr}), 148.0 (s, CCH_{iPr}), 185.3 (d, J_{CP} = 34.1 Hz, NCCH). ^{31}P{^{1}H} NMR (C_6D_6, 162 MHz, 300 K): δ 49.7 (s, $\Delta\nu_{1/2}$ = 47.5 Hz). HRMS (EI): m/z 525.37703 ($[C_{31}H_{53}AlN_3P]^+$; theoretical m/z 525.37871). Elem anal. Found: C, 70.71; H, 10.18; N, 8.03. Calcd for $C_{31}H_{53}AlN_3P$: 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 was added dropwise nBuLi (2.5 M in hexanes, 0.08 mL, 0.2 mmol, 1 equiv). The cold bath was removed, and the resultant yellow solution was stirred at room temperature for 1 h. The reaction mixture was cooled to −78 °C, and $H_3Al{\cdot}NMe_2Et$ (0.5 M in toluene, 0.4 mL, 1 equiv) was added dropwise. The cold bath was removed, the resultant yellow solution was stirred at room temperature for 20 min, and the solvent was removed in vacuo to afford the product as a yellow oil. No further purification was attempted.

^{1}H NMR (C_4D_8O, 500 MHz, 300 K): δ 0.29 (s, 3H, $SiCH_3$), 0.33 (s, 3H, $SiCH_3$), 0.84 (m, 1H, $^1/_2CH_{2Norb}$), 1.07 (d, $^3J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.08 (d, $^3J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.12 (d, $^3J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.14 (d, $^3J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.18 (m, 2H, $CH_{2CbridgeheadCP}$), 1.19 (s, 9H, CH_{3tBu}), 1.21 (s, 9H, CH_{3tBu}), 1.25 (m, 1H, $^1/_2CH_{2Norb}$), 1.54 (m, 1H, $^1/_2CH_{2CbridgeheadCN}$), 1.62 (m, 1H, $^1/_2CH_{2CbridgeheadCN}$), 2.19 (br s, 1H, $CH_{bridgeheadCP}$), 3.35 (br s, 1H, $CH_{bridgeheadCN}$), 3.54 (sept, $^3J_{HH}$ = 6.8 Hz, 1H, CH_{iPr}), 3.63 (sept, $^3J_{HH}$ = 6.8 Hz, 1H, CH_{iPr}), 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 because of extremely high line width. ^{13}C NMR (C_4D_8O, 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_{3iPr}), 26.0 (d, J_{CP} = 15.2 Hz, CH_{3iPr}), 27.2 (s, $CH_{2CbridgeheadCP}$), 28.11 (s, CH_{iPr}), 28.13 (s, CH_{iPr}), 30.1 (s, $CH_{2CbridgeheadCN}$), 32.9 (d, J_{CP} = 5.4 Hz, CH_{3tBu}), 33.4 (d, J_{CP} = 4.8 Hz, CH_{3tBu}), 42.1 (d, J_{CP} = 1.5 Hz, $CH_{bridgeheadCN}$), 46.5 (s, CH_{2Norb}), 47.2 (d, J_{CP} = 5.5 Hz, $CH_{bridgeheadCP}$), 51.4 (d, J_{CP} = 11.5 Hz, C^tBu), 51.6 (d, J_{CP} = 14.6 Hz, C^tBu), 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, NC_{Ar}), 174.2 (d, J_{CP} = 33.2 Hz, NCCH). ^{31}P NMR (C_4D_8O, 162 MHz, 300 K): δ 110.8 (q, $^2J_{PH}$ = 34 Hz). ^{7}Li NMR (C_4D_8O, 194.4 MHz, 300 K): δ −0.43 (s). HRMS (EI): m/z 528.34912 ($[C_{29}H_{52}N_3AlPSi]^+$; theoretical m/z 528.34891).

General Synthesis of 5. To a solution of ligand **1a**−**1c** in THF cooled to −78 °C was added dropwise nBuLi (2.5 M in hexanes). The cold bath was removed, and the resultant yellow solution was stirred at room temperature for 1 h. The reaction mixture was cooled to −78 °C, and a solution of $H_3Al{\cdot}NMe_3$ in THF was added dropwise. The cold bath was removed, and the resultant colorless solution was stirred at room temperature for 1 h. The solvent was removed in vacuo, and the product was extracted in hexane and dried to afford a white solid. $H_3Al{\cdot}NMe_2Et$ (0.5 M in toluene) can be used in place of $H_3Al{\cdot}NMe_3$. In this work, $H_3Al{\cdot}NMe_2Et$ was used for initial test reactions to synthesize up to 0.2 g of **5** using a procedure identical with that described above.

5a. **1a** (1.63 g, 0.0039 mol), THF (50 mL), nBuLi (1.6 mL, 0.0039 mol, 1.0 equiv), and $H_3Al{\cdot}NMe_3$ (0.84 g, 0.0037 mol, 2.4 equiv) in THF (20 mL) yielded **5a** (1.57 g, 91%).

^{1}H NMR (C_6D_6, 500 MHz, 300 K): δ 1.11 (dm, $^2J_{HH}$ = 8.1 Hz, 1H, $^1/_2CH_{2Norb}$), 1.19 (d, $^3J_{HP}$ = 14.2 Hz, 9H, CH_{3tBu}), 1.22 (d, $^3J_{HP}$ = 14.2 Hz, 9H, CH_{3tBu}), 1.28 (d, $^3J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.29 (d, $^3J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.31 (m, 2H, $CH_{2CbridgeheadCP}$), 1.42 (d,

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$^3J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.44 (d, $^3J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.51 (m, 1H, $^1/_2CH_{2CbridgeheadCN}$), 1.62 (dm, $^2J_{HH}$ = 8.1 Hz, 1H, $^1/_2CH_{2Norb}$), 1.67 (m, 1H, $^1/_2CH_{2CbirdgeheadCN}$), 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 NMR (C_6D_6, 126 MHz, 300 K): δ 24.0 (s, CH_{3iPr}), 24.7 (s, CH_{3iPr}), 25.2 (d, J_{CP} = 1.8 Hz, $CH_{2CbridgeheadCP}$), 25.8 (s, CH_{3iPr}), 25.9 (s, CH_{3iPr}), 28.0 (s, CH_{iPr}), 28.1 (s, CH_{iPr}), 29.6 (d, J_{CP} = 4.5 Hz, CH_{3tBu}), 30.1 (s, $CH_{2CbridgeheadCN}$), 30.1 (d, J_{CP} = 4.0 Hz, CH_{3tBu}), 34.1 (d, J_{CP} = 18.2 Hz, C^tBu), 34.3 (d, J_{CP} = 18.9 Hz, C^tBu), 43.6 (d, J_{CP} = 9.1 Hz, $CH_{bridgeheadCP}$), 44.1 (d, J_{CP} = 2.1 Hz, $CH_{bridgeheadCN}$), 48.6 (d, J_{CP} = 3.9 Hz, CH_{2Norb}), 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_{iPr}), 147.1 (s, CCH_{iPr}), 185.1 (d, J_{CP} = 20.1 Hz, NCCH). $^{31}P\{^1H\}$ NMR (C_6D_6, 162 MHz, 300 K): δ 8.0 (s, $\Delta\nu_{1/2}$ = 34.7 Hz). HRMS (EI): m/z 441.30855 ($[C_{27}H_{45}AlNP]^+$; theoretical m/z 441.30996). Elem anal. Found: C, 73.11; H, 10.39; N, 3.13. Calcd for $C_{27}H_{45}AlNP$: C, 73.43; H, 10.27; N, 3.17. IR (solid, cm^{-1}): 1810, 1786. IR (solution, cm^{-1}): 1811.

5b. **1b** (3.00 g, 0.0060 mol), THF (80 mL), nBuLi (2.4 mL, 0.0060 mol, 1.0 equiv), and $H_3Al{\cdot}NMe_3$ (1.28 g, 0.014 mol, 2.4 equiv) in THF (15 mL) yielded **5b** (2.95 g, 93%). Colorless crystals suitable for X-ray crystallography were grown from a saturated hexane solution at −20 °C.

^1H NMR (C_6D_6, 500 MHz, 300 K): δ 0.24 (s, 3H, $SiCH_3$), 0.29 (s, 3H, $SiCH_3$), 1.13 (d, $^2J_{HH}$ = 8.1 Hz, 1H, $^1/_2CH_{2Norb}$), 1.28 (d, $^4J_{HP}$ = 0.8 Hz, 9H, CH_{3tBu}), 1.29 (d, $^4J_{HP}$ = 0.8 Hz, 9H, CH_{3tBu}), 1.30 (d, $^3J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.31 (d, $^3J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.38 (m, 2H, $CH_{2CbridgeheadCP}$), 1.44 (d, $^3J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.45 (d, $^3J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.62 (d, $^2J_{HH}$ = 8.1 Hz, $^1/_2CH_{2Norb}$), 1.67 (m, 2H, $CH_{2CbridgeheadCN}$), 2.57 (br s, 1H, $CH_{bridgeheadCP}$), 3.12 (br s, 1H, $CH_{bridgeheadCN}$), 3.53 (sept, $^3J_{HH}$ = 6.8 Hz, 1H, CH_{iPr}), 3.74 (sept, $^3J_{HH}$ = 6.8 Hz, 1H, CH_{iPr}), 4.6 (br s, 2H, Al−H), 7.17−7.23 (m, 3H, $H_{aromatic}$). ^{13}C NMR (C_6D_6, 126 MHz, 300 K): δ 4.4 (d, J_{CP} = 1.6 Hz, $SiCH_3$), 6.3 (d, J_{CP} = 3.2 Hz, $SiCH_3$), 24.1 (s, CH_{3iPr}), 24.6 (s, CH_{3iPr}), 25.6 (d, J_{CP} = 1.0 Hz, $CH_{2CbridgeheadCP}$), 25.8 (s, CH_{3iPr}), 25.9 (s, CH_{3iPr}), 28.0 (s, CH_{iPr}), 28.3 (s, CH_{iPr}), 29.3 (s, $CH_{2CHbridgeheadCN}$), 32.3 (d, J_{CP} = 5.4 Hz, CH_{3tBu}), 32.7 (d, J_{CP} = 5.2 Hz, CH_{3tBu}), 40.7 (d, J_{CP} = 3.9 Hz, $CH_{bridgeheadCN}$), 43.9 (d, J_{CP} = 9.7 Hz, $CH_{bridgheadCP}$), 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, PCCH), 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, $C_{Ar}CH_{iPr}$), 146.5 (s, $C_{Ar}CH_{iPr}$), 187.6 (d, J_{CP} = 33.9 Hz, NCCH). $^{31}P\{^1H\}$ NMR (C_6D_6, 162 MHz, 300 K): δ 61.3 (s, $\Delta\nu_{1/2}$ = 65.4 Hz). HRMS (EI): m/z 527.33886 ($[C_{29}H_{51}AlN_3PSi]^+$; theoretical m/z 527.33998). Elem anal. Found: C, 65.95; H, 9.66; N, 7.83. Calcd for $C_{29}H_{51}AlN_3PSi$: C, 66.00; H, 9.74; N, 7.96. IR (solid, cm^{-1}): 1831, 1816. IR (solution, cm^{-1}): 1820.

5c. **1c** (2.00 g, 0.0043 mol), THF (100 mL), nBuLi (1.7 mL, 0.0043 mol, 1.0 equiv), and $H_3Al{\cdot}NMe_3$ (0.91 g, 0.010 mol, 2.4 equiv) in THF (15 mL) were mixed. The final product was further purified by recrystallization from hexanes at −20 °C to yield **5c** as colorless crystals (1.68 g, 79%). Two isomers were identifiable in the solution-phase NMR spectra in a ratio of 4:7 for κ^2-*N*,*N*-**5c** to κ^2-*N*,*P*-**5c** at 300 K (determined from the ^1H NMR spectrum).

κ^2-*N*,*N*-**5c**. ^1H NMR (C_6D_6, 500 MHz, 300 K): δ 0.91 (m, 1H, $^1/_2CH_{2Norb}$), 1.18 (d, $^4J_{HP}$ = 1.3 Hz, 9H, CH_{3tBu}), 1.23 (d, $^3J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.25 (m, 1H, $^1/_2CH_{2Norb}$), 1.31 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH_{3iPr}), 1.32 (s, 9H, CH_{3tBu}), 1.43 (m, 2H, $CH_{2CbridgeheadCP}$), 1.60 (d, $^3J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.65 (m, 1H, $^1/_2CH_{2CbridgeheadCN}$), 1.71 (m, 1H, $^1/_2CH_{2CbridgeheadCN}$), 2.56 (m, 1H, $CH_{bridgeheadCP}$), 2.70 (m, 1H, $^1/_2NCH_2$), 2.78 (m, 1H, $^1/_2NCH_2$), 2.97 (m, 1H, $CH_{bridgeheadCN}$), 3.33 (m, 1H, $^1/_2NCH_2$), 3.56 (m, 1H, $^1/_2NCH_2$), 3.85 (sept, $^3J_{HH}$ = 6.8 Hz, 1H, CH_{iPr}), 3.98 (sept, $^3J_{HH}$ = 6.8 Hz, 1H, CH_{iPr}), 4.3 (br s, 2H, AlH_2) 7.18−7.21 (m, 3H, $H_{aromatic}$). ^{13}C NMR (C_6D_6, 126 MHz, 300 K): δ 25.4 (s, $CH_{2CbridgeheadCP}$), 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_{3tBu}), 29.6 (d, J_{CP} = 10.7 Hz, CH_{3tBu}), 29.8 (d, J_{CP} = 1.8 Hz, $CH_{2CbridgeaheadCN}$), 44.2 (s, CH_{2Norb}), 45.1 (s, $CH_{bridgeheadCN}$), 45.7 (s, NCH_2), 45.8 (d, J_{CP} = 39.1 Hz, $CH_{bridgeheadCP}$), 48.8 (d, J_{CP} = 3.3 Hz, NCH_2), 53.5 (d, J_{CP} = 5.0 Hz, C^tBu), 53.8 (d, J_{CP} = 3.9 Hz, C^tBu), 104.8 (d, J_{CP} = 36.9 Hz, PCCH), 123.9 (s, C_{meta}), 124.6 (s, C_{meta}), 125.2 (s, C_{para}), 143.22 (s, NC_{Ar}), 145.8 (CCH_{iPr}), 146.53 (s, CCH_{iPr}), 167.4 (d, J_{CP} = 2.7 Hz, NCCH). $^{31}P\{^1H\}$ NMR (C_6D_6, 162 MHz, 300 K): δ 96.9 (s, $\Delta\nu_{1/2}$ = 137.9 Hz).

κ^2-*N*,*P*-**5c**. ^1H NMR (C_6D_6, 500 MHz, 300 K): δ 1.07 (dm, $^2J_{HH}$ = 8.4 Hz, 1H, $^1/_2CH_{2Norb}$), 1.29 (d, $^3J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.30 (d, $^3J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.32 (s, 9H, CH_{3tBu}), 1.35 (s, 9H, CH_{3tBu}), 1.39 (m, 2H, $CH_{2CbridgeheadCP}$), 1.42 (d, $^3J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.45 (d, $^3J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.56 (m, 1H, $^1/_2CH_{2Norb}$), 1.63 (m, 2H, $CH_{2CbridgeheadCN}$), 2.52 (m, 1H, $CH_{bridgeheadCP}$), 2.60 (m, 1H, $^1/_2NCH_2$), 2.72 (m, 1H, $^1/_2NCH_2$), 2.79 (m, 1H, $^1/_2NCH_2$), 2.88 (m, 1H, NCH_2), 3.02 (m, 1H, $CH_{bridgeheadCN}$), 3.54 (sept, $^3J_{HH}$ = 6.8 Hz, 1H, CH_{iPr}), 3.76 (sept, $^3J_{HH}$ = 6.8 Hz, 1H, CH_{iPr}), 4.6 (br s, 2H, AlH_2), 7.18−7.21 (m, 3H, $H_{aromatic}$). ^{13}C NMR (C_6D_6, 126 MHz, 300 K): δ 24.0 (s, CH_{3iPr}), 24.7 (s, CH_{3iPr}), 25.3 (s, $CH_{2CbridgeheadCP}$), 25.8 (s, CH_{3iPr}), 25.86 (s, CH_{3iPr}), 27.9 (s, CH_{iPr}), 28.1 (s, CH_{iPr}), 29.0 (d, J_{CP} = 4.6 Hz, CH_{3tBu}), 29.3 (s, $CH_{2CbridgeheadCN}$), 29.9 (d, J_{CP} = 4.6 Hz, CH_{3tBu}), 42.7 (d, J_{CP} = 4.4 Hz, $CH_{bridgeheadCN}$), 43.6 (d, J_{CP} = 9.9 Hz, $CH_{bridgeheadCP}$), 43.9 (s, NCH_2), 44.2 (s, NCH_2), 46.6 (d, J_{CP} = 4.9 Hz, CH_{2Norb}), 53.4 (d, J_{CP} = 9.8 Hz, C^tBu), 53.6 (d, J_{CP} = 5.4 Hz, C^tBu), 97.0 (d, J_{CP} = 35.3 Hz, PCCH), 124.1 (s, C_{meta}), 124.3 (s, C_{meta}), 126.4 (s, C_{para}), 141.0 (d, J_{CP} = 4.0 Hz, NC_{Ar}), 146.51 (s, CCH_{iPr}), 146.8 (s, CCH_{iPr}), 185.4 (d, J_{CP} = 34.0 Hz, NCCH). $^{31}P\{^1H\}$ NMR (C_6D_6, 162 MHz, 300 K): δ 47.8 (s, $\Delta\nu_{1/2}$ = 96.6 Hz). HRMS (EI): m/z 497.35079 ($[C_{29}H_{49}AlN_3P]^+$; theoretical m/z 497.34741). Elem anal. Found: C, 69.80; H, 9.80; N, 8.33. Calcd for $C_{29}H_{51}AlN_3PSi$: C, 69.99; H, 9.92; N, 8.44. IR (solid, cm^{-1}): 1825, 1801. IR (solution, cm^{-1}): 1823.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.9b01061.

Experimental procedures, full characterization of compounds, crystallographic details, solid-state NMR details, and solution-phase NMR spectra (PDF)

Crystallographic data (ZIP)

Accession Codes

CCDC 1905997 and 1906037−1906039 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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R.L.F. conceived and performed experiments and cowrote the manuscript, G.S.N. contributed to crystallographic studies, and M.J.C. designed and coordinated the study and cowrote the manuscript.

Notes

The authors declare no competing financial interest.

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