Neutral and Cationic Organoaluminum Complexes Utilizing a Novel Anilido−Phosphinimine Ancillary Ligand

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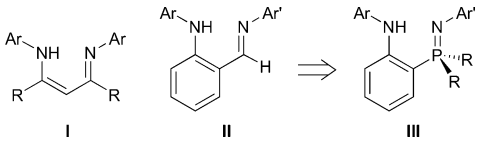
A new chelating N,N ligand family incorporating an anilido−phosphinimine donor set has been designed and an example prepared in multigram quantities in three steps using a convenient, modular synthetic approach. The ligand 1-(NHAr)-2-(PPh_2=NAr′)C_6H_4 (**1·H**; Ar = 2,6-^{i}Pr$_2$-C_6H_3; Ar′ = 2,4,5-$Me_3C_6H_2$) was prepared in three steps in a 30−35% overall yield and was fully characterized in its protio form as well as in the form of its lithium salt, **1·Li**. In both compounds, the donor array assumes a conformation in which the P=N moiety dips out of the plane formed by the four atoms in the rigid ortho-disubstituted aryl ring of the ligand backbone. The coordinating properties of the new ligand were demonstrated by the synthesis of some organoaluminum derivatives. The monomeric compounds $LAlMe_2$ (**2**) and $LAlH_2$ (**3**) were prepared by the reaction of **1·H** with $AlMe_3$ and AlH_3·NMe_3, respectively, and were fully characterized by NMR spectroscopy and X-ray crystallography. Cationic derivatives were formed by activation of **2** and **3** with either $B(C_6F_5)_3$ or $[Ph_3C]^+[B(C_6F_5)_4]^-$. All of the neutral and cationic compounds qualitatively exhibited high levels of stability in comparison to related organoaluminum compounds, illustrating the exemplary steric and electronic properties of the new ligand system.

Introduction

The need for noncyclopentadienyl ligand frameworks to support reactive electrophilic organotransition-metal complexes has resulted in a wide range of new ancillary ligands.[1] Our focus has been on development of ligands able to provide a foundation for new organogroup 3 metal chemistry.[2] To this end, we have established the emerging β-diketiminato ligand[3] ("nacnac") framework **I** as a suitable platform for the development of the



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chemistry of organoscandium cations.[4] This ligand system has many strengths as an ancillary ligand for electrophilic metals; however, in recent work directed toward the synthesis of hydrido complexes, some drawbacks to the nacnac ligand family have come to light. Rearrangements involving cleavage of the nacnac ligand structure similar to what Mindiola et al. have observed in (nacnac)$Ti^{III}R_2$ compounds[5] appear to be initiated by hydride transfer from the metal to the ligand backbone, indicating a susceptibility to nucleophilic attack.

To mitigate against the tendency toward this type of process, we developed the anilido imine donor **II**,[6] presuming that the aromatic ring in the ligand backbone would discourage nucleophilic transfer to the ligand. While this ligand has allowed for access of highly reactive yttrium cations, the isolated imine function is still subject to attack by nucleophiles (aldimines) or to deprotonation (ketimines) in ligands of this type. Similar problems were encountered in organo−group 3 compounds of the related salicylaldiminato ligands.[7]

The recent surge of activity in the use of the phosphinimine donor in organotransition-metal chemistry[8] pointed the way to the next step in the evolution of our ligand system. Incorporation of a phosphinimine instead of the imine function as in **III** should make the ligand

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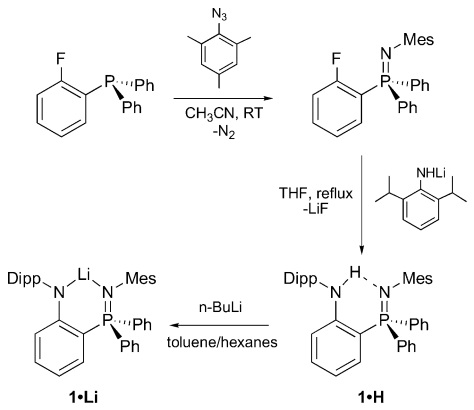
resistant to nucleophilic attack while improving its abilities as donor in comparison to the imine-based ligands **II**. In this paper, we describe the synthesis of a ligand of type **III**, where N_{Ar} is the 2,6-diisopropyl group and the PN_{Ar} aryl substituent is the mesityl group. Stephan et al. have recently reported a ligand with an amido/phosphinimine donor array based on the nacnac structure **I**;[9] the ligand family **III** offers a more rigid backbone without any tautomerization pathways to complicate the chemistry involved. Here we demonstrate the efficacy of the new ligand for stabilizing electrophilic metal centers by the synthesis and characterization of some neutral and cationic organoaluminum compounds. Although ultimately designed for implementation in group 3, organoaluminum chemistry has served as a proving ground for new monoanionic ligands and several recent studies on $LAlR_2$ derivatives are available for comparison.[10−17]

Results and Discussion

Ligand Synthesis. The synthesis of the ligand **1** is outlined in Scheme 1. Low-temperature, selective lithiation of bromo-2-fluorobenzene followed by quenching with chlorodiphenylphosphine leads to the fluorinated triphenylphosphine derivative shown.[18] The presence of the fluorine is clearly indicated in both the ^{19}F and ^{31}P NMR spectra ($^3J_{FP}$ = 53.4 Hz). Attempts at this stage to institute the anilido portion of the ligand via nucleophilic aromatic substitution (NAS)[19] failed, due to the electron-donating nature of the $-PPh_2$ group. Therefore, the phosphinimine function was introduced by a Staudinger reaction[20] with mesityl azide[21] as shown; the NAS reaction then proceeded smoothly in refluxing THF with the 2,6-^{i}Pr-C_6H_3NHLi reagent to give the protio ligand **1** in three steps with an overall yield of 30−35%.

Scheme 1



The procedure can be conveniently performed on a multigram scale using commercially available or easily prepared reagents. Furthermore, the synthesis is highly amenable to variation, potentially allowing for extensive steric and electronic tuning of this ligand system. For example, substitution on the aromatic backbone should be possible with tolerant functional groups. Use of different phosphine chloride reagents ClPRR′ will allow for variation at phosphorus, and both of the N-aryl groups can be readily changed. Examples of ligands with several different combinations of N-aryl groups have been prepared using various azide or anilidolithium reagents;[22] this contribution will focus on ligand **1** specifically.

The protio ligand **1·H** has been fully characterized by multinuclear NMR spectroscopy and X-ray crystallography (Figure 1). Characteristic NMR resonances include a signal at 9.1 ppm in the ^1H NMR spectrum for the chelated N*H*···N proton and a peak at −0.8 ppm in the $^{31}P\{^1H\}$ NMR spectrum. In the solid state, the ligand structure is confirmed and an anilido/phosphinimine ligand array is apparent. However, the five atoms in the chelating network are not coplanar, with the phophinimine nitrogen N(2) dipping below the plane defined by N(1)−C(14)−C(13)−P(1) by 0.922(3) Å; the C(14)−C(13)−P(1)−N(2) dihedral angle is 44.1(2)°. As a result, the N-aryl groups are arranged in a fundamentally different, and less symmetrical, spatial array

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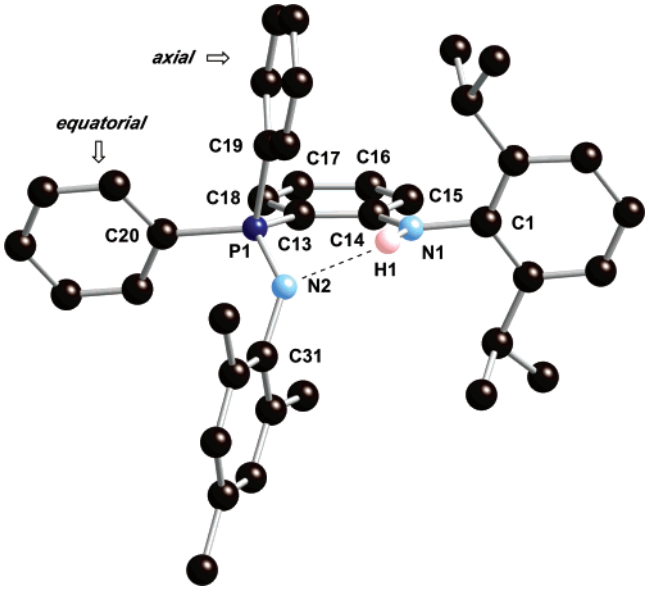


Figure 1. Crystalmaker diagram of the molecular structure of **1·H**. Selected bond distances (Å): P(1)−N(2), 1.563(2); P(1)−C(13), 1.817(2); N(1)−C(14), 1.382(3); N(1)−C(1), 1.436(3); N(2)−C(31), 1.413(3). Selected bond angles (deg): C(13)−P(1)−N(2), 116.45(10); N(1)−C(14)−C(13), 120.1(2). Selected torsion angles (deg): N(1)−C(14)−C(13)−P(1), −3.7(3); N(2)−P(1)−C(13)−C(14), 44.06(19).

in comparison to that found for the nacnac ligands, with the phosphinimine N-aryl group angling below the coordination plane of the ligand. The P-aryl groups occupy axial and equatorial orientations, with the axial phenyl group in particular showing potential for providing steric protection to a coordinated metal. The P(1)−N(2) length of 1.563(2) Å is typical of P═N double bonds.

The ligand is readily lithiated by treatment with *n*-BuLi in toluene/hexanes at −78 °C. Lithiation is indicated by a loss of the N−H proton resonance in the ^{1}H NMR spectrum, with the rest of the spectrum remaining topologically similar to that of **1·H**. In the ^{31}P{^{1}H} NMR spectrum, the signal appears downfield of that in **1·H** at 13.3 ppm, indicating strong electron donation to the Li cation relative to the proton. The material is soluble in C_6D_6, and crystals grown from this medium were examined by X-ray crystallography; the structure is shown in Figure 2. The Li cation is unsolvated, and the compound forms a dimer in which the Li is satiated by π donation from the *N*-mesityl ring of the opposing molecule; the Li(1)−C(34) and Li(1)−C(35) distances are 2.643(3) and 2.410(3) Å, respectively. Such interactions are not uncommon in unsolvated lithium salts.[23] Within the monomer, the Li(1)−N(1) and Li(1)−N(2) separations are 1.941(3) and 1.946(3) Å, surprisingly close for a ligand expected to coordinate in a more localized mode; the dimeric structure of this particular complex may play a role in equalizing these M−N lengths, since these distances are generally more disparate in other complexes.[22] The P(1)−N(2) length has increased slightly over that in the protio ligand to 1.5932(14) Å, and the ligand maintains its nonplanar coordinating style.

Organoaluminum Chemistry: Neutral Complexes. To demonstrate the new anilido phosphinimido

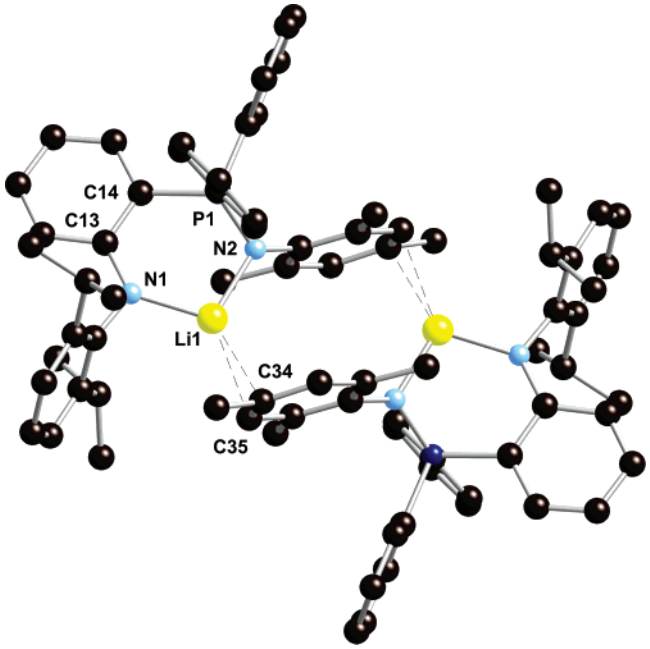
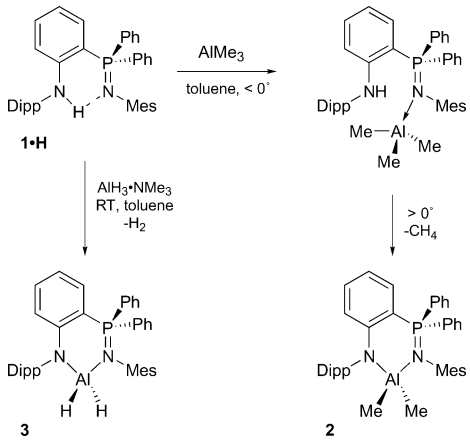


Figure 2. Crystalmaker diagram of the molecular structure of **1·Li**. Selected bond distances (Å): P(1)−N(2), 1.5932(14); P(1)−C(14), 1.7881(18); N(1)−C(13), 1.360(2); N(1)−C(1), 1.429(2); N(2)−C(31), 1.417(2); N(1)−Li(1), 1.941(3); N(2)−Li(1), 1.946(3); Li(1)−C(34), 2.643(3); Li(1)−C(35), 2.410(3). Selected bond angles (deg): C(14)−P(1)−N(2), 117.38(8); N(1)−C(13)−C(14), 120.57(15); N(1)−Li(1)−N(2), 106.31(14); Selected torsion angles (deg): N(1)−C(13)−C(14)−P(1), 11.5(2); N(2)−P(1)−C(14)−C(13), −53.57(16).

Scheme 2



ligand's coordinating ability, some organoaluminum complexes have been prepared and compared with related compounds supported by other ligand systems. While the salt **1·Li** is an effective reagent for introducing the ligand to early-transition-metal complexes,[22] **1·H** itself is all that is required to generate organoaluminum complexes (Scheme 2). Reaction between **1·H** and $AlMe_3$ below 0 °C in toluene results in rapid adduct formation, as indicated by a downfield shift in the ^{31}P{^{1}H} resonance to 22.9 ppm and an upfield shift to 5.32 ppm for the anilido proton in the ^{1}H NMR spectrum, which is no longer chelated by the two nitrogen donors. A singlet at −0.45 ppm integrated to nine protons is assigned to the $AlMe_3$ protons. As the reaction mixture is warmed to room temperature, slow evolution of CH_4 is observed with the concomitant

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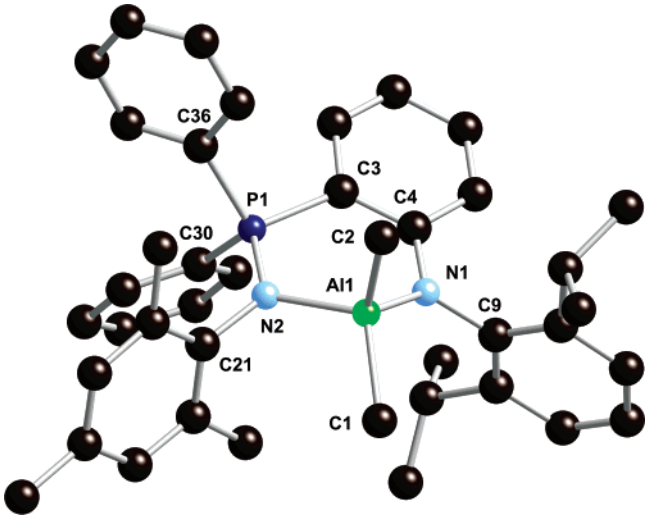

Figure 3. Crystalmaker diagram of the molecular structure of **2**. Selected bond distances (Å): P(1)−N(2), 1.6139(3); N(1)−Al(1), 1.891(3); N(2)−Al(1), 1.926(3); Al(1)−C(1), 1.972(4); Al(1)−C(2), 1.974(4); P(1)−C(4), 1.782(2). Selected bond angles (deg): N(1)−Al(1)−N(2), 99.07(12); N(1)−Al(1)−C(2), 112.99(18); N(2)−Al(1)−C(2), 107.65(15); C(1)−Al(1)−C(2), 113.7(2); C(4)−P(1)−N(2), 110.40(15).

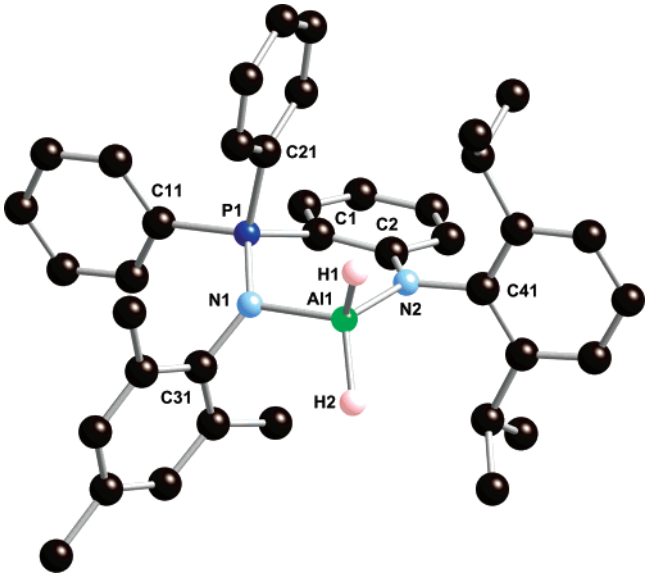

Figure 4. Crystalmaker diagram of the molecular structure of **3**. Selected bond distances (Å): P(1)−N(1), 1.6181(17); N(1)−Al(1), 1.904(2); N(2)−Al(1), 1.8921(19); Al(1)−H(1), 1.53(2); Al(1)−H(2), 1.53(2); P(1)−C(1), 1.779(2). Selected bond angle (deg): N(1)−Al(1)−N(2), 100.02(8).

appearance of a new signal in the $^{31}P\{^1H\}$ NMR spectrum at 30.0 ppm, as the dimethyl aluminum complex **2** is formed. It can be isolated as a white solid from pentane in >70% yield. Solid or solution samples of **2** that were exposed to atmosphere for time periods of 1 day or more showed no signs of decomposition, as judged by ^{31}P and ^1H NMR spectroscopy, attesting to this ligand's ability to stabilize electrophilic metal centers both sterically and electronically. While other $LAlMe_2$ compounds have been reported to exhibit moderate stability upon brief exposure to the atmosphere,[12c] **2** shows remarkable tolerance to the dry air of the western foothills.

Reaction of **1·H** with freshly prepared $AlH_3{\cdot}NMe_3$[24] rapidly generates a dihydride species **3** (Scheme 2) with loss of H_2. The NMR spectra for **3** are similar to those obtained for **2**, except that the AlMe resonances are replaced by a broad singlet integrated to two hydrogens at 4.67 ppm for the AlH_2 moieties. The IR spectrum for **3** exhibits absorptions at 1828 and 1780 cm^{-1}, typical values for asymmetric and symmetric Al−H stretches.[11d,13c]

Both the dimethyl compound **2** and the dihydride **3** were characterized by X-ray crystallography, and the molecular structures are shown as Crystalmaker diagrams in Figures 3 and 4, respectively. Although the aluminum center is of distorted-tetrahedral geometry in each case, the two structures illustrate the flexibility with which the ligand coordinates the Al center. In the dimethyl derivative, of the six atoms in the chelate array, it is the Al atom that protrudes from an idealized plane; in dihydride **3**, the P atom deviates from this putative plane. As a result, the *P*-phenyl rings are "axial" and "equatorial" in a much more pronounced way in **3** than in the dimethyl derivative **2**, with the axial phenyl group leaning toward the Al coordination environment. Perhaps this arrangement is discouraged when larger groups (Me vs H) are on Al. In any case, it is likely that the energy surface connecting various coordination geometries is quite soft. In variable-temperature NMR studies, the methyl groups on the Al remain equivalent down to −90 °C, indicating a highly fluxional system in comparison to, for example, (nacnac)ScR_2 compounds.[25]

In both **2** and **3**, the Al−N lengths are again quite similar, differing by only 0.03 and 0.01 Å, respectively. In a localized bonding picture, the amido N bond to aluminum might be expected to be shorter than the dative interaction between the phosphinimine N donor and aluminum. The similarity in these distances again illustrates the ability of the phosphinimine function to act as a strong donor, a notion supported by concomitant lengthening in the P−N bond and contraction in the P−C bonds observed in the Li and Al complexes of **1** relative to the corresponding parameters in **1·H**. The chelate bite angle of this ligand is quite wide relative to other N,N donors that have been applied to organoaluminum chemistry. In **2**, the N(1)−Al(1)−N(2) angle is 99.07(12)°, while in **3** this value is 100.02(8)°. For comparison, the N−Al−N bite angle in other complexes $LAlMe_2$ are 96.17(7)° for L = β-diketiminato,[11a,b] 83.3(1)° for L = aminotroponiminate,[13a] and ∼69° for amidinate complexes.[12] The angle for **1** is smaller than that for a bis(iminophosphorane)$AlMe_2$ (108.96(8)°) compound.[10c]

Organoaluminum Chemistry: Cationic Complexes. Low-coordination-number cationic organoaluminum compounds are an extraordinarily electrophilic class of molecules that have been implicated as catalysts for ethylene polymerization[11a,14a,b] and initiators for polyisobutylene synthesis[26] and ring-opening

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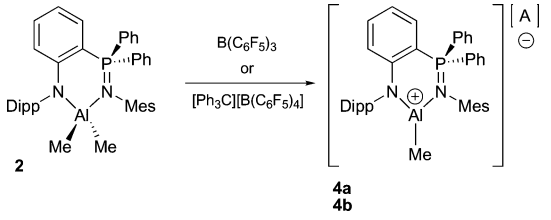
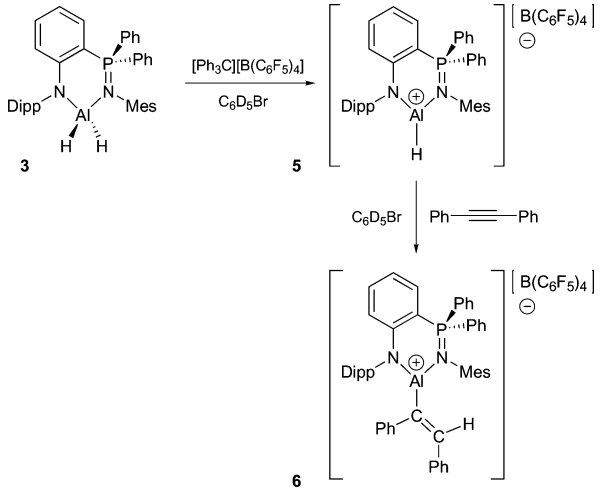
Scheme 3



Scheme 4



polymerization of propylene oxide.[13a,27] While the active species in the former process has not been firmly established,[14a,28] the role of the cationic organoaluminum species is less ambiguous in the last two reactions, where a cationic polymerization mechanism is unquestioned.

Compound **2** serves as a precursor to cationic methylaluminum derivatives **4** upon treatment with Lewis acid activators such as $B(C_6F_5)_3$ (**4a**) and $[Ph_3C]^+[B(C_6F_5)_4]^-$ (**4b**) in toluene or bromobenzene solution (Scheme 3). Cation formation is signaled by a downfield shift in the $^{31}P\{^1H\}$ NMR spectrum of about 10 ppm relative to the neutral precursor **2**. The ion pair **4a** formed from $B(C_6F_5)_3$ can be isolated as an analytically pure solid, while that obtained from $[Ph_3C]^+[B(C_6F_5)_4]^-$ was generated cleanly in situ and characterized in solution. As for other $[LAlMe]^+[MeB(C_6F_5)_3]^-$ ion pairs, the two methyl groups in **4a** were distinct in the ^1H NMR spectrum at room temperature, but EXSY spectroscopy showed that they are exchanging on the time scale of this experiment, indicating that the methide abstraction by $B(C_6F_5)_3$ is reversible. Both of these ion pairs exhibit high stability in solution, with no measurable change in the NMR spectrum after several days at room temperature. Thus, there is a low tendency toward $-C_6F_5$ back-transfer in ion pairs **4**,[13a,29] underscoring the ligand's ability to quench the positive charge at aluminum. Use of $^1/_2$ equiv of activator led to μ-methyl dimers;[12] to suppress formation of these species in the preparations of ion pairs **4**, inverse addition of the aluminum reagent to the activator was employed.

This is further illustrated by the stability of the cationic hydride compound **5** formed from **3** and $[Ph_3C]^+[B(C_6F_5)_4]^-$ (Scheme 4). Cationic aluminum hydrides tend to be even more reactive than the alkyl derivatives, often succumbing to $-C_6F_5$ back-transfer.[13] Rapid hydride abstraction yields a compound with an intact $[B(C_6F_5)_4]^-$ anion, a new set of ligand resonances, and a slightly upfield shifted signal at 4.18 ppm for the Al−H moiety, now integrating to one proton. Compound **5** is stable for long periods at room temperature and reacts slowly with diphenylacetylene to yield the hydroalumination product **6**, which was characterized in situ; methyl cations **4** exhibit no reaction with PhC≡CPh even under heating for prolonged periods.

Conclusions

We have developed a new ligand system that we believe addresses some of the shortcomings of the nacnac and anilido−imine ligands we have studied previously in our group. The new anilido−phosphinimine donor array is more resistant to nucleophilic attack or tautomerization processes and additionally offers a different steric and electronic presence about the metal center. The phosphinimine moiety is more electron donating than the imine donor, and substitution of the four-coordinate, tetrahedral phosphorus nucleus for the three-coordinate, planar imine carbon orients the N-aryl groups in a fundamentally different spatial arrangement compared to nacnac and nacnac-like ligands. Combined, these features make this an exciting ligand family to exploit as supports for electrophilic metal centers in a variety of applications. We have demonstrated the attributes of this ligand family by deploying a bulky example in cationic organoaluminum chemistry and found it to stabilize these highly reactive compounds, including a three-coordinate aluminum hydride complex.

Experimental Section

General Procedures. All operations were performed under a purified argon atmosphere using glovebox or vacuum line techniques. Toluene, hexanes, and THF solvents were dried and purified by passing through activated alumina and Q5 columns. Acetonitrile was dried over CaH_2 and distilled under reduced pressure. Diethyl ether was dried over Na and distilled under reduced pressure. Chlorobenzene was dried over CaH_2 and distilled under reduced pressure. NMR spectra were recorded at room temperature in dry, oxygen-free C_6D_6, unless otherwise noted. ^1H, $^1H\{^{31}P\}$, ^{11}B, ^{13}C, ^{19}F, ^{31}P, COSY, EXSY, and HMQC NMR experiments were performed on Bruker AC-200, AMX-300, and DRV-400 and Varian 200 MHz spectrometers. Data are given in units of ppm relative to residual solvent signals for ^1H and ^{13}C spectra. ^{11}B, ^{19}F, and ^{31}P spectra were referenced to external $BF_3{\cdot}Et_2O$, $CFCl_3$, and 85% H_3PO_4 respectively. Elemental analyses were performed by Ms. Roxanna Simank (University of Calgary). IR spectra were recorded on a Nicolet NEXUS 470 FT-IR spectrometer using KBr plates, and data are given in units of reciprocal centimeters (cm^{-1}). X-ray crystallographic analyses were performed on suitable crystals coated in Paratone oil and mounted on either a Bruker P4/RA/SMART 1000 CCD diffractometer (University of Alberta) or a Rigaku AFC6S diffractometer (University of Calgary). Details of the crystallographic data and data analysis are given in Table 1; full details can be found in the Supporting Information. *o*-$C_6H_4FP(C_6H_5)_2$[18] (^{19}F NMR,

(27) (a) Atwood, D. A.; Jegier, J. A.; Rutherford, D. *J. Am. Chem. Soc.* **1995**, *117*, 6779. (b) Jegier, J. A.; Munoz-Hernandez, M.-A.; Atwood, D. A. *J. Chem. Soc., Dalton Trans.* **1999**, 2583.

(28) Talarico, G.; Budzelaar, P. H. M.; Gal, A. W. *J. Comput. Chem.* **2000**, *21*, 398.

(29) Bochmann, M.; Sarsfield, M. J. *Organometallics* **1998**, *17*, 5908.

Table 1. Summary of Data Collection and Structure Refinement Details

	1·H	1·Li	2	3
formula	$C_{39}H_{43}N_2P$	$C_{45}H_{42}D_6LiN_2P$	$C_{41}H_{48}AlN_2P\cdot1.5C_7D_8$	$C_{39}H_{44}AlN_2P$
fw	570.72	665.80	764.96	598.71
cryst syst	orthorhombic	triclinic	monoclinic	monoclinic
a, Å	15.362(2)	11.924(2)	10.388(2)	12.0811(7)
b, Å	21.174(3)	12.300(2)	18.790(4)	14.7741(9)
c, Å	10.048(5)	13.216(3)	24.636(7)	19.7917(12)
α, deg		75.700(8)		
β, deg		79.250(8)	91.982(8)	101.6354(11)
γ, deg		81.178(13)		
V, Å^3	3268.4(17)	1833.6(6)	4805.8(19)	3460.0(4)
space group	$Pna2_1$	$P\bar{1}$	$P2_1/n$	$P2_1/c$
Z	4	2	4	4
d_{calcd}, Mg m^{-3}	1.160	1.197	1.057	1.149
μ, mm^{-1}	0.113	0.109	0.109	0.133
R1	0.038	0.049	0.075	0.0584
wR2	0.080	0.109	0.218	0.1658
wR2 (all data)	0.088	0.127	0.252	
GOF	1.035	1.01	1.14	1.030

−103.25 (d, $^3J_{F-P}$ = 53.36 Hz); ^{31}P NMR, −19.46 (d, $^3J_{P-F}$ = 53.34 Hz)), mesityl azide,[21] and $AlH_3\cdot NMe_3$[24] were prepared using literature procedures. $B(C_6F_5)_3$ was purchased from Boulder Scientific Co. and dried and sublimed prior to use. $[Ph_3C]^+[B(C_6F_5)_4]^-$ was supplied as a generous gift by Nova Chemicals Corp. All other materials were obtained from Sigma-Aldrich and purified according to standard procedures.

***o*-C$_6$H$_4$F{(C$_6$H$_5$)$_2$P═N(2,4,6-Me$_3$C$_6$H$_2$)}.** The following is based on a published procedure.[20b] A solution of mesityl azide (4.25 g, 26.40 mmol) in MeCN (25 mL) was transferred by cannula onto a mixture of *o*-$C_6H_4F\{P(C_6H_5)_2\}$ (7.40 g, 26.43 mmol) in MeCN (50 mL) at 23 °C. Dinitrogen was given off exothermically, and after 30 min of vigorous stirring a white precipitate crashed out of solution. After it was stirred for an additional 6 h, the reaction mixture was filtered and the isolated white precipitate dried in vacuo. Yield: 9.33 g (85%). IR (KBr plate): 3103 (w, aromatic C−H), 2945, 2932, 2901 (m, C−H), 1600, 1560, 1469 (s, C═C), 1340 (s, C−P), 1280, 1258, 1207, 1157 (s, P═N), 1105, 994, 859, 819 (C−C). ^{1}H NMR: 7.99 (m, $^3J_{H-H}$ = 6.32 Hz, $^4J_{H-P}$ = 1.78 Hz, $^3J_{H-F}$ = 6.28 Hz, 1H, C_6H_4PN), 7.79 (dt, $^3J_{H-H}$ = 7.64 Hz, $^4J_{H-P}$ = 1.70 Hz, 4H, *m*-$P(C_6H_5)_2$), 7.00 (m, 6H, *o,p*-$P(C_6H_5)_2$), 6.92 (s, 2H, NC_6H_2), 6.83 (m, $^3J_{H-H}$ = 7.23 Hz, 1H, C_6H_4PN), 6.73 (m, $^3J_{H-H}$ = 7.47 Hz, 1H, C_6H_4PN), 6.53 (ddd, $^3J_{H-H}$ = 7.23 Hz, $^4J_{H-P}$ = 1.78 Hz, 1H, C_6H_4PN), 2.24 (s, 9H, NC_6H_2*Me-2,4,6*). ^{13}C{^{1}H} NMR (C_7D_8): 162.3 (quaternary aromatic, *C*F) 144.8, 135.0 (2 quaternary aromatic), 134.6, 133.9, 133.5, 132.2, 132.1, 131.1, 128.4 (7 Ph), 127.3, 124.4, 116.3, (3 quaternary aromatic), 116.0 (Ph) 21.5 (NC_6H_2*Me-2,6*), 20.9 (NC_6H_2*Me-4*). ^{19}F NMR: −99.4 (d, $^3J_{F-H}$ = 6 Hz). ^{31}P NMR: −16.5. Anal. Calcd for $C_{27}H_{25}FNP$: C, 78.43; H, 6.09; N, 3.39. Found: C, 78.64; H, 6.07; N, 3.42.

Synthesis of 1·H. A 1.6 M *n*-hexane solution of ^{n}BuLi (11.25 mL, 18.00 mmol) was added to a solution of 2,6-diisopropylaniline (3.25 mL, 17.25 mmol) in THF (40 mL) at −78 °C, and the mixture was warmed to room temperature over 60 min. The resulting solution of LiNHAr was transferred by cannula onto a solution of *o*-$C_6H_4\{(C_6H_5)_2P{=}N(2,4,6\text{-}Me_3C_6H_2)\}$ (5.70 g, 13.8 mmol) in THF (50 mL) at 23 °C. The reaction mixture was stirred for 72 h at 70 °C. The mixture was then quenched with distilled H_2O (50 mL), extracted with diethyl ether (2 × 50 mL), dried over $MgSO_4$, and evaporated to dryness in vacuo. The resulting orange oil was dissolved in hot methanol (200 mL) and slowly cooled to −10 °C to give cream-colored crystals, which were dried in vacuo. Yield: 4.20 g (53%). IR (KBr plate): 3246 (m, N−H), 2962, 2902, 2852 (m, C−H), 1592, 1567, 1507, 1477, 1431 (s, C═C), 1361 (s, C−P), 1294, 1266, 1149 (s, P═N), 1109, 1134, 1023, 954 (m, C−C). ^{1}H NMR: 9.68 (s, 1H, N*H*), 7.79 (dt, $^3J_{H-H}$ = 7.68 Hz, $^4J_{H-P}$ = 1.33 Hz, 4H, *m*-$P(C_6H_5)_2$), 7.21−7.13 (m, 3H, NC_6H_3), 7.09 (dd, $^3J_{H-H}$ = 7.69 Hz, $^4J_{H-P}$ = 1.54 Hz, 1H, C_6H_4PN), 7.00−6.97 (m, 6H, *o,p*-$P(C_6H_5)_2$, C_6H_4PN), 6.88 (s, 2H, NC_6H_2), 6.39 (m, 2H, C_6H_4PN), 3.20 (sp, $^3J_{H-H}$ = 6.8 Hz, 2H, C*H*Me$_2$), 2.35 (d, $^4J_{H-H}$ = 1.3 Hz, 6H, NC_6H_2*Me-2,6*), 2.23 (d, $^4J_{H-H}$ = 2.3 Hz, 3H, NC_6H_2*Me-4*), 1.10 (d, $^3J_{H-H}$ = 6.87 Hz, 6H, CH(CH_3)$_2$), 0.93 (d, $^3J_{H-H}$ = 6.87 Hz, 6H, CH(CH_3)$_2$). ^{13}C{^{1}H} NMR: 153.8, 147.7, 144.8, 135.4, 134.4 (5 quaternary aromatic), 133.4, 133.3, 132.9, 132.6, 132.4 (5 Ph), 131.2 (quaternary aromatic), 129.5, 128.5, 127.6 (3 Ph), 124.2 (quaternary aromatic), 115.7, 113.9 (2 Ph), 112.4 (quaternary aromatic), 28.6 (*C*HMe$_2$), 24.8 (CH*Me$_2$*), 23.5 (CH*Me$_2$*), 21.7 (NC_6H_2*Me-2,6*), 20.8 (NC_6H_2*Me-4*). ^{31}P NMR: −0.8. Anal. Calcd for $C_{39}H_{43}N_2P$: C, 82.07; H, 7.59; N, 4.91. Found: C, 82.01; H, 7.45; N, 4.91.

Synthesis of 1·Li. A 1.6 M *n*-hexane solution of ^{n}BuLi (2.2 mL, 3.52 mmol) was added dropwise via syringe to a toluene (30 mL) solution of **1·H** (1.35 g, 2.37 mmol) at −78 °C. The reaction mixture was slowly warmed to 23 °C and stirred for a further 24 h. The reaction mixture was then evaporated to dryness in vacuo, and *n*-hexane (10 mL) was added. The mixture was cooled to −78 °C and filtered to give a yellow powder, which was dried in vacuo. Yield: 1.1 g (80%). IR (KBr plate): 3124, 3050 (s, aromatic C−H), 2962, 2863 (s, C−H), 1579, 1476, 1454 (s, C═C), 1339 (s, C−P), 1246, 1160, 1145 (s, P═N), 1110, 1078, 1045, 998 (C−C). ^{1}H NMR: 7.53 (dt, $^3J_{H-H}$ = 7.11 Hz, $^4J_{H-P}$ = 1.19 Hz, 4H, *m*-$P(C_6H_5)_2$), 7.28−6.94 (m, 10H, *o,p*-$P(C_6H_5)_2$, NC_6H_3, C_6H_4PN), 6.84 (dd, $^3J_{H-H}$ = 7.69 Hz, $^4J_{H-P}$ = 1.55 Hz, 1H, C_6H_4PN), 6.79 (s, 2H, NC_6H_2) 6.18 (dd, $^3J_{H-H}$ = 6.45 Hz, $^5J_{H-P}$ = 2.36 Hz, 1H, C_6H_4PN), 6.04 (dd, $^3J_{H-H}$ = 7.16 Hz, $^3J_{H-P}$ = 3.29 Hz, 1H, C_6H_4PN), 2.73 (sp, J_{H-H} = 6.92 Hz, 2H, C*H*Me$_2$), 2.21 (m, 9H, NC_6H_2*Me-2,4,6*), 1.09 (d, J_{H-H} = 6.92 Hz, 6H, CH(CH_3)$_2$), 1.04 (d, J_{H-H} = 6.92 Hz, 6H, CH(CH_3)$_2$). ^{13}C{^{1}H} NMR: 163.4, 149.9, 144.9, 134.6, 134.3 (4 quaternary aromatic), 133.5 (d, $^3J_{C-P}$ = 8.70 Hz), 132.7, 131.5 (Ph), 130.1 (quaternary aromatic), 129.6 (d, $^5J_{C-P}$ = 3.30 Hz), 128.6, 126.1, 124.1, 123.2 (Ph), 116.3 (d, $^3J_{C-P}$ = 10.02 Hz), 110.1, 109.8 (2 quaternary aromatic), 107.8 (d, $^2J_{C-P}$ = 13.88 Hz), 28.0 (*C*HMe$_2$), 26.5 (CH*Me$_2$*), 24.8 (CH*Me$_2$*), 21.3 (NC_6H_2*Me-4*), 20.8 (NC_6H_2*Me-2,6*). ^{31}P NMR: 13.3. Anal. Calcd for $C_{39}H_{42}N_2PLi$: C, 81.23; H, 7.34; N, 4.86. Found: C, 80.12; H, 7.18; N, 4.36.

Generation of the Adduct Between 1·H and AlMe$_3$. To an NMR tube charged with **1·H** (0.030 g, 0.053 mmol) and toluene-d_8 (200 μL) at −78 °C was added neat $AlMe_3$ (5.0 μL, 0.052 mmol) in toluene-d_8 (300 μL), and the resulting solution was warmed to 0 °C. The adduct was characterized in situ (methane elimination begins above 0 °C). ^{1}H NMR (C_7D_8, 270 K): 8.59 (br s, 1H, C_6H_4PN), 7.65 (br m, 4H, *m*-$P(C_6H_5)_2$), 7.80 (dd, $^3J_{H-H}$ = 7.55 Hz, 1H, C_6H_4PN), 6.99−6.94 (m, 9H, *o,p*-$P(C_6H_5)_2$, NC_6H_3), 6.72 (dd, $^3J_{H-H}$ = 7.51 Hz, 1H, C_6H_4PN), 6.61 (s, 2H, NC_6H_2), 6.12 (dd, $^3J_{H-H}$ = 7.55 Hz, 1H, C_6H_4PN), 5.36 (br s, 1H, N*H*), 2.65 (br sp, $^3J_{H-H}$ = 6.54 Hz, 2H, C*H*Me$_2$), 2.22 (m, 6H, NC_6H_4*Me-2,6*), 2.08 (d, $^4J_{H-H}$ = 2.38 Hz, 3H,

NC_6H_4*Me-4*), 0.99 (d, $^3J_{H-H}$ = 6.88 Hz, 6H, CH*Me*$_2$), 0.74 (d, $^3J_{H-H}$ = 6.80 Hz, 6H, CH*Me*$_2$), −0.45 (s, 9H, Al(C*H*$_3$)$_3$). ^{13}C{^{1}H} NMR (C_7D_8, 270 K): 152.2, 147.3, 140.0, 138.2 (4 quaternary aromatic), 135.0 (Ph), 134.2 (1 quaternary aromatic), 134.0 (Ph), 133.6 (quaternary aromatic), 133.1 (Ph), 130.2, 129.1, 128.8, 128.4, 124.4, 117.7, 113.7 (7 Ph), 108.5, 107.5 (2 quaternary aromatic), 28.0 (*C*HMe$_2$), 24.4 (CH*Me*$_2$), 23.6 (CH*Me*$_2$), 21.8 (NC_6H_2*Me-2,6*), 20.7 (NC_6H_2*Me-4*), −3.2 (Al*Me*$_3$). ^{31}P NMR (C_7D_8, 270 K): δ 22.9.

Synthesis of LAlMe$_2$ (2). A 2 M toluene solution of $AlMe_3$ (377 μL, 0.754 mmol) was added via syringe to a solution of **1·H** (430 mg, 0.753 mmol) in toluene (30 mL) at 23 °C. After it was stirred for 4 h at 50 °C, the yellow solution was evaporated to dryness in vacuo. The residue was then slurried in isopentane (15 mL) and filtered at 23 °C to collect a white solid, which was dried in vacuo. Yield: 0.35 g (75%). IR (KBr plate): 3131, 3082, 3022 (m, C−H), 2962, 2918, 2858 (s, aromatic C−H), 1594, 1540, 1466, 1430 (s, C═C), 1325, 1271 (s, C−P), 1206, 1183, 1161, 1123 (s, P═N), 1107, 1033, 995 (s, C−C). ^{1}H NMR (C_7D_8): 7.47 (dt, $^3J_{H-H}$ = 7.11 Hz, $^4J_{H-P}$ = 1.36 Hz, 4H, *m*-(C_6H_5)$_2$), 7.28−6.92 (m, 9H, *o,p*-P(C_6H_5)$_2$, N(C_6H_3)), 6.86 (m, 1H, C_6H_4PN), 6.63 (dd, $^3J_{H-H}$ = 8.05 Hz, $^4J_{H-P}$ = 1.62 Hz, 1H, C_6H_4PN), 6.59 (s, 2H, NC_6H_2), 6.53 (d, $^3J_{H-H}$ = 7.53 Hz 1H, C_6H_4PN), 6.15 (m, 1H, C_6H_4PN) 3.79 (sp, $^3J_{H-H}$ = 6.84 Hz, 2H, C*H*Me$_2$), 2.07 (d, $^4J_{H-H}$ = 2.22 Hz, 3H, NC_6H_4*Me-4*), 1.82 (d, $^4J_{H-H}$ = 1.27 Hz, 6H, NC_6H_4*Me-2,6*), 1.30 (d, $^3J_{H-H}$ = 6.84 Hz, 6H, CH*Me*$_2$), 1.23 (d, $^3J_{H-H}$ = 6.84 Hz, 6H, CH*Me*$_2$), −0.47 (s, 6H, Al(*Me*)$_2$). ^{13}C{^{1}H} NMR (C_7D_8): 163.2, 146.9, 143.4, 137.7, 137.6, 137.2 (6 quaternary aromatic), 136.1 (d, $^4J_{C-P}$ = 14.63 Hz, C_6H_4PN), 134.3 (d, $^3J_{C-P}$ = 10.12 Hz, *m*-P-(C_6H_5)$_2$), 132.2 (Ph), 130.2 (NC_6H_2), 129.2 (Ph), 128.4 (d, $^3J_{C-P}$ = 12.32 Hz, C_6H_4PN), 126.2, 124.9 (2 Ph), 120.8 (d, $^3J_{C-P}$ = 9.24 Hz, C_6H_4PN), 113.6 (d, $^2J_{C-P}$ = 15.31 Hz, C_6H_4PN), 101.1, 99.9 (2 quaternary aromatic), 28.1 (*C*HMe$_2$), 26.1 (CH*Me*$_2$), 24.8 (CH*Me*$_2$), 20.7 (NC_6H_2*Me-4*), 20.5 (NC_6H_2*Me-2,6*), −7.1 (Al*Me*$_2$). ^{31}P NMR (C_7D_8): 30.0. Anal. Calcd for $C_{41}H_{48}AlN_2P$: C, 78.57; H, 7.72; N, 4.47. Found: C, 78.17; H, 7.63; N, 4.49.

Synthesis of LAlH$_2$ (3). To a dried round-bottom flask was added freshly prepared AlH_3·NMe_3 (0.420 g, 4.71 mmol) and solid **1·H** (2.7 g, 4.74 mmol). The flask was attached to a swivelfrit apparatus and cooled to −78 °C. Toluene (50 mL) was condensed into the vessel, and the mixture was warmed to room temperature. After it was stirred for 7 h at 23 °C, the yellow-green solution was evaporated to dryness in vacuo. The residue was then slurried in isopentane (20 mL) and filtered at 23 °C to collect a white solid, which was dried in vacuo. Yield: 2.51 g (88%). IR (KBr plate): 1828, 1780 cm^{-1} (asymmetric, symmetric absorptions). ^{1}H NMR: 7.67 (dt, $^3J_{H-H}$ = 7.11 Hz, $^4J_{H-P}$ = 1.36 Hz, 4H, *m*-(C_6H_5)$_2$), 7.30 (s, 3H, NC_6H_3) 6.95 (m, 2H, C_6H_4PN), 6.88 (m, 6H, *o,p*-P(C_6H_5)$_2$), 6.55 (s, 2H, NC_6H_2), 6.45 (t, $^3J_{H-H}$ = 7.10 Hz, 1H, C_6H_4PN), 6.23 (m, 1H, C_6H_4PN), 4.67 (bs, 2H, AlH_2), 3.50 (sp, $^3J_{H-H}$ = 6.84 Hz, 2H, C*H*Me$_2$), 2.31 (s, 6H, NC_6H_4*Me-2,6*), 1.99 (s, 3H, NC_6H_4*Me-4*), 1.41 (d, $^3J_{H-H}$ = 6.84 Hz, 6H, CH*Me*$_2$), 1.10 (d, $^3J_{H-H}$ = 6.84 Hz, 6H, CH*Me*$_2$). ^{13}C{^{1}H} NMR: 160.4 (quaternary aromatic), 148.1 (C−H), 140.5, 139.0, 136.9 (3 quaternary aromatic), 134.3, 134.1, 134.0, 132.9, 131.3, 128.4 (C−H), 126.9 (quaternary aromatic), 125.1 (C−H), 118.5, 113.3, 105.4 (3 quaternary aromatic), 28.2 (*C*HMe$_2$), 25.7 (CH*Me*$_2$), 25.0 (CH*Me*$_2$), 21.0 (NC_6H_2*Me-4*), 20.6 (NC_6H_2*Me-2,6*). ^{31}P NMR: 31.9. Anal. Calcd for $C_{39}H_{44}AlN_2P$: C, 78.23; H, 7.41; N, 4.68. Found: C, 77.64; H, 7.41; N, 4.64.

Synthesis of [LAlMe]$^+$[MeB(C$_6$F$_5$)$_3$]$^-$ (4a). A 25 mL vial was charged with **2** (0.022 g, 0.035 mmol) and hexanes (10 mL). In a separate vial, $B(C_6F_5)_3$ (0.018 g, 0.035 mmol) was dissolved in hexanes (10 mL). The aluminum species was added dropwise to the clear borane solution, causing immediate formation of a white precipitate. The mixture was cooled to −35 °C for 48 h, upon which the supernatant was removed and the remaining white solid was dried in vacuo. Yield: 0.027 g (67%). ^{1}H NMR (C_7H_8): 7.29 (dt, $^3J_{H-H}$ = 6.91 Hz, $^4J_{H-P}$ = 1.40 Hz, 4H, *m*-(C_6H_5)$_2$), 7.16−7.04 (m, 9H, *o,p*-P(C_6H_5)$_2$, N(C_6H_3)), 6.88 (m, 1H, C_6H_4PN), 6.79 (dd, $^3J_{H-H}$ = 7.44 Hz, $^4J_{H-P}$ = 1.48 Hz, 1H, C_6H_4PN), 6.48 (m, 3H, NC_6H_2, C_6H_4PN), 6.27 (dd, $^3J_{H-H}$ = 7.44 Hz, $^4J_{H-P}$ = 1.48 Hz, 1H, C_6H_4PN), 2.62 (sp, $^3J_{H-H}$ = 6.84 Hz, 2H, C*H*Me$_2$), 2.09 (m, 3H, NC_6H_4*Me-4*), 1.83 (m, 6H, NC_6H_4*Me-2,6*), 1.28 (br s, 3H, B*Me*), 0.91 (d, $^3J_{H-H}$ = 6.92 Hz, 6H, CH*Me*$_2$), 0.85 (d, $^3J_{H-H}$ = 6.92 Hz, 6H, CH*Me*$_2$), 0.77 (br s, 3H, AlCH_3). ^{11}B NMR (C_7D_8): −15.2. ^{13}C{^{1}H} NMR (C_6D_5Br): 155.8 (quaternary aromatic, C−N, C_6H_4NP), 148.3 (d, $^1J_{C-F}$ = 246 Hz, MeB(C_6F_5)$_3^-$), 137.6 (quaternary aromatic, N−C, C_6H_3), 137.5 (d, $^1J_{C-F}$ = 240 Hz, MeB(C_6F_5)$_3^-$), 136.3 (d, $^1J_{C-F}$ = 240 Hz, MeB(C_6F_5)$_3^-$), 135.7 (C_6H_4), 134.9 (*p*-(C_6H_5)$_2$), 134.6 (quaternary aromatic, N−C, C_6H_2), 133.5 (C_6H_4), 133.3 (d, $^3J_{C-P}$ = 10 Hz, *m*-(C_6H_5)$_2$), 132.9 (quaternary aromatic, d, $^4J_{C-P}$ = 8 Hz, C_6H_3), 130.7 (C_6H_2), 129.5 (d, $^2J_{C-P}$ = 13 Hz, *o*-(C_6H_5)$_2$), 128.7 (*p*-C_6H_3), 125.3 (*m*-C_6H_3), 122.5, 122.0 (2 quaternary aromatic, C_6H_2), 121.4 (quaternary aromatic, d, $^1J_{C-P}$ = 85 Hz, (C_6H_5)$_2$), 119.4 (d, $^4J_{C-P}$ = 8 Hz, C_6H_4), 119.3 (d, $^2J_{C-P}$ = 13 Hz, C_6H_4), 106.9 (quaternary aromatic, d, $^1J_{C-P}$ = 100 Hz, C−P, C_6H_4PN), 28.3 (*C*HMe$_2$), 24.8 (CH*Me*$_2$), 24.1 (CH*Me*$_2$), 20.4 (NC_6H_2*Me-4*), 20.0 (NC_6H_2*Me-2,6*), −13.9 (Al*Me*), *Me*B not identified. ^{19}F NMR (C_7D_8): −131.3 (*o*-F), −163.7 (*p*-F), −166.3 (*m*-F). ^{31}P NMR (C_7D_8): 38.1. Anal. Calcd for $C_{59}H_{48}AlBF_{15}N_2P$: C, 62.23; H, 4.25; N, 2.46. Found: C, 62.89; H, 4.15; N, 2.38.

Synthesis of [LAlMe]$^+$[B(C$_6$F$_5$)$_4$]$^-$ (4b). An NMR tube charged with $[CPh_3]^+[B(C_6F_5)_4]^-$ (0.028 g, 0.030 mmol) and C_6D_5Br (0.1 mL) was cooled to −35 °C. A solution of $LAlMe_2$ (0.019 g, 0.030 mmol) in C_6D_5Br (0.4 mL) was then added dropwise to the NMR tube. The orange mixture was warmed to −30 °C before being monitored via NMR experiments. ^{1}H NMR (C_6D_5Br): 7.69 (m, 1H, C_6H_4PN), 7.41−6.90 (m, 28H, P(C_6H_5)$_2$, NC_6H_3, C(C_6H_5)$_3$), 6.59 (m, 4H, NC_6H_2, C_6H_4PN), 6.35 (m, 1H, C_6H_4PN), 2.60 (sp, $^3J_{H-H}$ = 5.58 Hz, 2H, C*H*(Me)$_2$), 2.10 (s, 3H, NC_6H_3*Me-4*), 2.04 (s, 3H, *Me*C(Ph)$_3$), 1.98 (s, 6H, NC_6H_3*Me-2,6*), 0.91 (d, $^3J_{H-H}$ = 6.60 Hz, 6H, CH*Me*$_2$), 0.86 (d, $^3J_{H-H}$ = 6.54 Hz, 6H, CH*Me*$_2$), 0.77 (s, 3H, Al*Me*). ^{11}B NMR (C_6D_5Br): −16.10. ^{19}F NMR (C_6D_5Br): −132.9 (*o*-F), −163.3 (*p*-F), − 167.1 (*m*-F). ^{31}P NMR (C_6D_5Br): 36.8.

Synthesis of [LAlH]$^+$[B(C$_6$F$_5$)$_4$]$^-$ (5). A round-bottomed flask (25 mL) was charged with $[Ph_3C]^+[B(C_6F_5)_4]^-$ (0.308 g, 0.33 mmol) and C_6H_5Cl (10 mL). A solution of $LAlH_2$ (0.200 g, 0.33 mmol) in C_6H_5Cl (5 mL) was then added dropwise to the vessel, causing a color change from orange to yellow. The vessel was attached to a swivelfrit apparatus, and the yellow solution was stirred under argon at 23 °C for 15 min. The reaction mixture was dried in vacuo and left under full vacuum for 6 h. Hexanes (15 mL) was added and the solid isolated by filtration to obtain a orange powder, which was dried in vacuo. Yield: 300 mg (70%). The ion pair is stable in solution for at least 12 h. ^{1}H NMR (C_6D_5Br): 7.46−6.94 (m, 15H), 6.65 (m, 1H, C_6H_4PN), 6.55 (s, 2H, NC_6H_2), 6.34 (m, 1H, C_6H_4PN), 4.18 (bs, 1H, Al*H*), 2.38 (sp, $^3J_{H-H}$ = 6.58 Hz, 2H, C*H*Me$_2$), 2.20 (s, 6H, NC_6H_4*Me-2,6*), 1.93 (s, 3H, NC_6H_4*Me-4*), 0.78 (d, $^3J_{H-H}$ = 6.34 Hz, 12H, CH*Me*$_2$). ^{11}B NMR (C_6D_5Br): δ −19.4. ^{13}C{^{1}H} NMR (C_6D_6): 155.8 (d, 5.4 Hz), 148.4 (d, 242.5 Hz, C_6F_5), 147.2, 143.8, 138.3 (d, 245 Hz, C_6F_5), 136.3 (d, 242.5 Hz, C_6F_5), 137.2 (d, 3.8 Hz), 135.6, 135.0 (d, 3.1 Hz), 135.0 (d, 4.6 Hz), 134.3 (d, 8.4 Hz), 133.4 (d, 10.7 Hz), 132.2 (10.7 Hz), 130.5 (d, 2.3 Hz), 129.6, 128.5, 128.2, 125.6, 121.0 (d, 102 Hz), 119.7 (d, 8.4 Hz), 118.8 (d, 14.6 Hz), 109.2 (d, 99.7 Hz), 56.8, 27.9, 25.7, 23.2, 20.5, 20.3. ^{19}F NMR (C_6D_5Br): δ-132.9 (*o*-F), −163.2 (*p*-F), −167.0 (*m*-F). ^{31}P NMR (C_6D_5Br): δ 38.7. Repeated attempts at elemental analysis of **5** failed to give satisfactory numbers; the results were consistently low in carbon by 3−5%.

Synthesis of [LAl(PhCCHPh)]$^+$[B(C$_6$F$_5$)$_4$]$^-$ (6). A solution of $LAlH_2$ (0.015 g, 0.025 mmol) in C_6D_5Br (0.4 mL) was added dropwise to an NMR tube charged with $[CPh_3]^+$-$[B(C_6F_5)_4]^-$ (0.023 g, 0.025 mmol) and C_6D_5Br (0.1 mL) at 23 °C. The NMR tube was cooled to −78 °C, and PhCCPh (0.005 g, 0.025 mmol) in C_6D_5Br (0.1 mL) was added via syringe. The

mixture was warmed to 23 °C, shaken, and allowed to react for 90 min. ^{1}H NMR (C_6D_5Br): 7.38−6.89 (m, 20H), 6.78−6.41 (m, 9H) 5.69 (s, 1H, AlPhCC*H*Ph), 5.44 (s, 1H, Ph_3C*H*), 2.51 (sp, $^{3}J_{H-H}$ = 6.82 Hz, 2H, C*H*Me_2), 2.01 (s, 3H, NC_6H_4*Me-4*), 1.92 (s, 6H, NC_6H_4*Me-2,6*), 1.01 (d, $^{3}J_{H-H}$ = 6.85 Hz, 12H, CH*Me*$_2$), 0.81 (d, $^{3}J_{H-H}$ = 6.85 Hz, 12H, CH*Me*$_2$). ^{11}B NMR (C_6D_5Br): −19.3. ^{13}C{^{1}H} NMR: 154.1 (d, 6 Hz), 150.7, 148.4 (d, 325 Hz, C_6F_5), 146.7, 143.8, 142.8, 141.9, 140.8, 138.2 (d, 325 Hz, C_6F_5), 136.2 (d, 325 Hz, C_6F_5), 137.3 (d, 3 Hz), 135.4, 135.1, 133.7 (d, 6 Hz), 133.2 (d, 14 Hz), 132.6 (14 Hz), 130.0, 129.5, 129.2, 128.1, 126.3, 125.6 (d, 20 Hz), 122.1 (d, 84 Hz), 120.0 (d, 133 Hz), 119.9 (d, 18 Hz), 118.3 (d, 10 Hz), 109.7 (d, 131 Hz), 56.8, 28.2, 24.6, 24.4, 20.2, 19.9. ^{19}F NMR (C_6D_5Br): −132.9 (*o*-F), −163.4 (*p*-F), 167.1 (*m*-F). ^{31}P NMR (C_6D_5Br): 38.4.

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Supporting Information Available: ORTEP diagrams and tables of atomic coordinates, anisotropic displacement parameters, and all bond distances, bond angles, and torsion angles for the structurally characterized molecules presented here; crystallographic data are also available as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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