Inorg. Chem. **2004**, *43*, 2166–2174

Inorganic Chemistry
Article

Aluminum Complexes Incorporating Bidentate Amido Phosphine Ligands

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Received November 27, 2003

A series of aluminum complexes supported by *o*-phenylene-derived amido phosphine ligands, *N*-(2-diphenylphosphinophenyl)-2,6-dimethylanilide ([Me-NP]$^-$) and *N*-(2-diphenylphosphinophenyl)-2,6-diisopropylanilide ([^{i}Pr-NP]$^-$), have been prepared. The reactions of trialkylaluminum with H[Me-NP] and H[^{i}Pr-NP], respectively, in refluxing toluene produced the corresponding dialkyl complexes [Me-NP]AlR$_2$ and [^{i}Pr-NP]AlR$_2$ (R = Me, Et). Deprotonation of H[Me-NP] with *n*-BuLi in THF at –35 °C followed by addition of AlCl$_3$ in toluene at –35 °C afforded [Me-NP]AlCl$_2$, which was subsequently reacted with 2 equiv of trimethylsilylmethyllithium in toluene to give [Me-NP]Al(CH$_2$SiMe$_3$)$_2$. The aluminum complexes were all characterized by ^{1}H, ^{13}C, ^{31}P, and ^{27}Al NMR spectroscopy. The solid-state structures of monomeric, four-coordinate [Me-NP]AlEt$_2$ and [^{i}Pr-NP]AlMe$_2$ and five-coordinate [Me-NP]AlCl$_2$(THF) were determined by X-ray crystallography. The ^{1}H NMR studies of [Me-NP]AlEt$_2$, [Me-NP]Al(CH$_2$SiMe$_3$)$_2$, and [^{i}Pr-NP]AlEt$_2$ indicate diastereotopic α-hydrogen atoms in these molecules. Heteronuclear COSY and NOE experiments suggest that the phosphorus donor in [Me-NP]Al(CH$_2$SiMe$_3$)$_2$ and [^{i}Pr-NP]AlEt$_2$ is coupled to only one of the diastereotopic α-hydrogen atoms that is virtually antiperiplanar with respect to the phosphorus atom.

Introduction

Organoaluminum complexes supported by monoanionic, bidentate, four-electron $[L-X]^-$ ligands are currently receiving considerable attention due to their increasing role in polymerization chemistry.[1] Several classes of ligands investigated thus far include $[N-N]^-$,[1−18] $[N-O]^-$,[19,20] and $[N-S]^-$.[21] Representative examples are depicted in Chart 1. Aluminum complexes of bidentate $[N-P]^-$ ligands are notably unexplored.[22] In an effort to expand the territory of aluminum chemistry and evaluate the possibility of catalytic polymerization thereafter, we chose to examine complexes

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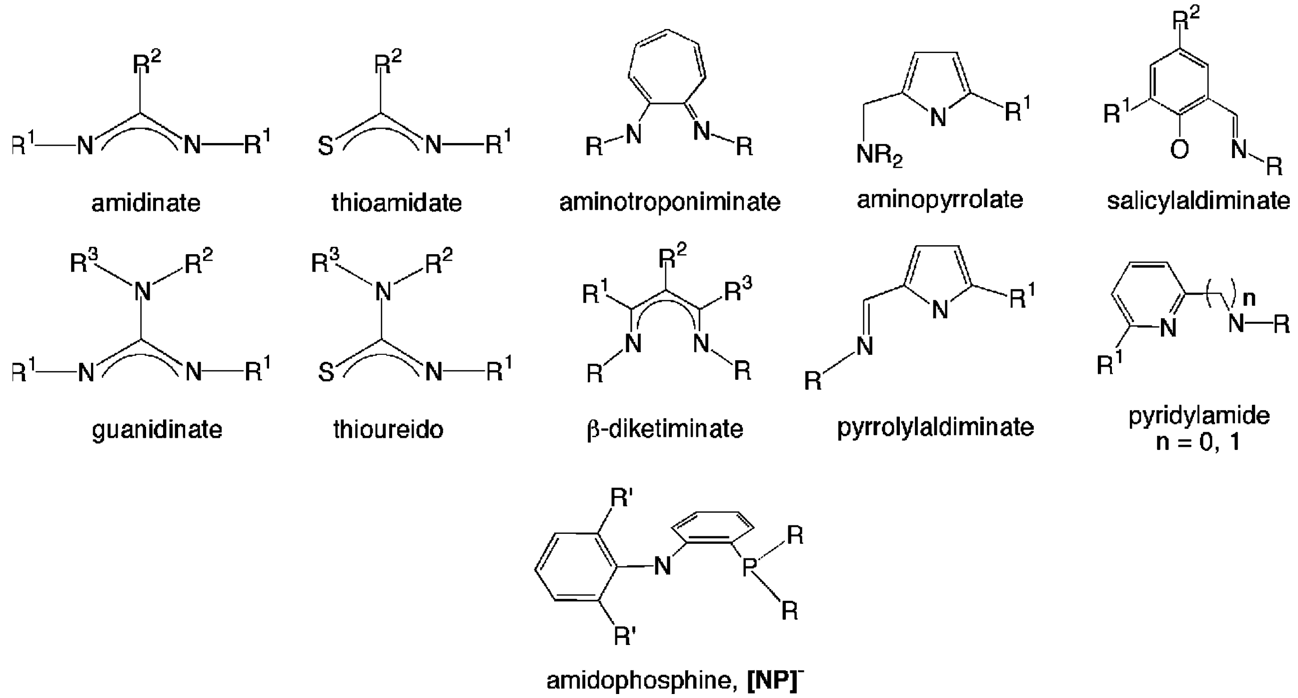
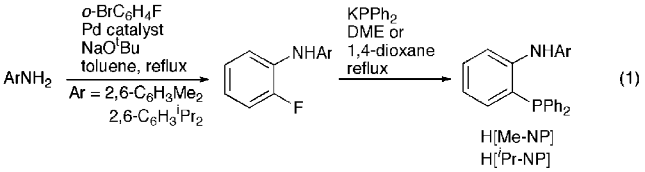
10.1021/ic035373q CCC: $27.50

Chart 1. Representative Examples of Monoanionic, Bidentate, Four-Electron $[L-X]^-$ Ligands



Scheme 1



of N-arylated amido phosphine ligands that contain the potentially rigid and robust *o*-phenylene backbone ($[NP]^-$, Chart 1). Ligands of this type can be regarded as phosphine-functionalized biaryl amides. We have recently shown that coordinatively unsaturated zinc complexes are readily accessible by the utilization of sterically demanding $[NP]^-$ ligands.[23] Recent reports by Jordan and co-workers reveal that the use of bulky $[L-X]^-$ ligands is essential for generating reactive aluminum cations for polymerization purposes.[4] In this paper, we aim to demonstrate the synthetic possibility of aluminum complexes incorporating the $[NP]^-$ ligands. Spectroscopic data concerning the steric properties of the amido phosphine ligands are discussed.

Results and Discussion

Preparation of H[Me-NP] and H[^{i}Pr-NP]. The synthesis of *N*-(2-diphenylphosphinophenyl)-2,6-diisopropylaniline (H-[^{i}Pr-NP]) has been communicated lately.[23] Following the same synthetic protocol (Scheme 1), *N*-(2-diphenylphosphinophenyl)-2,6-dimethylaniline (H[Me-NP]) is readily accessible. The phosphine compounds and their fluorine precursors were all characterized by multinuclear NMR spectroscopy and elemental analysis. Consistent with the steric size of the ortho substituents, the isopropyl derivatives require relatively harsh conditions for both palladium-catalyzed cross-coupling reaction and nucleophilic phosphanylation for high yield isolation of the desired products as compared to their methyl analogues. Solution NMR spectroscopic data indicate that the *o*-alkyl groups in these fluorine and phosphine compounds are chemically equivalent. The isopropylmethyl groups in H[^{i}Pr-NP] are diastereotopic as two doublet resonances are observed at room temperature in ^1H NMR spectroscopy. A variable temperature ^1H NMR study (50 mM in toluene-d_8) revealed that the two doublet resonances tend to broaden at temperatures higher than 110 °C, consistent with restricted rotation about the *N*-aryl bond.[24] The NH proton appears as one doublet resonance (J_{HP} = ca. 8 Hz for both H[Me-NP] and H[^{i}Pr-NP]) in ^1H NMR spectroscopy. The solid-state structure of H[Me-NP] (Table 1, Figure 1) was determined to investigate the relative orientation of the substituents at both donor atoms. The 2,6-dimethylphenyl ring is nearly perpendicular to the *o*-phenylene backbone. The N−C bond distance is slightly longer for the 2,6-dimethylphenyl group than for the *o*-phenylene backbone. The two phenyl rings at the phosphorus donor are oriented such that they are virtually orthogonal to each other. All bond distances and angles obtained are well within their expected values and comparable to those of the closely related bis(2-diphenylphosphinophenyl)amine.[25]

Syntheses and NMR Studies of Aluminum Derivatives. Alkane elimination reactions of H[Me-NP] with trialkylaluminum in toluene at 110 °C produced $[Me-NP]AlR_2$ (R = Me, Et) quantitatively (Scheme 2, eq 2). High yields of

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Table 1. Crystallographic Data for H[Me-NP]

formula	$C_{52}H_{48}N_2P_2$
fw	762.86
crystal system	monoclinic
space group	$P2_1/c$
a (Å)	14.7253(9)
b (Å)	16.8991(11)
c (Å)	16.5500(11)
β (deg)	95.384(2)
V (Å^3)	4100.2(5)
Z	4
D_{calcd} (g cm^{-3})	1.236
$2\theta_{max}$ (deg)	55.08
T (K)	293(2)
diffractometer	SMART CCD
radiation, λ (Å)	Mo Kα, 0.710 73
total reflections	25 775
independent reflections	9367
absorption coefficient (mm^{-1})	0.145
data/restraints/parameters	9367/0/517
R_{int}	0.0655
goodness of fit	0.724
final R indices [$I > 2\sigma(I)$]	R1 = 0.0433, wR2 = 0.0848
R indices (all data)	R1 = 0.1206, wR2 = 0.1200

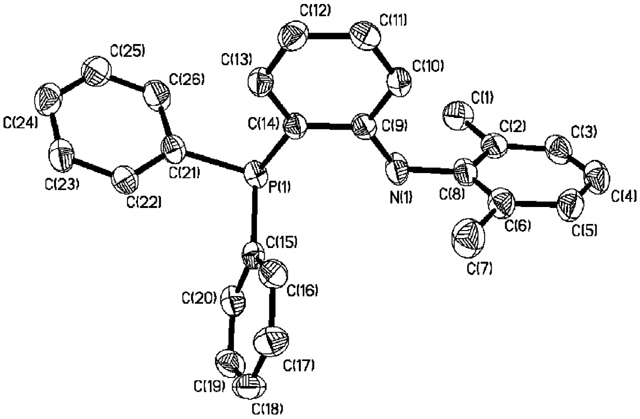

Figure 1. Molecular structure of H[Me-NP] with thermal ellipsoids drawn at the 35% probability level. The asymmetric unit cell contains two independent molecules; only one is shown. Selected bond distances (Å) and angles (deg): C(8)−N(1) 1.438(3), C(9)−N(1) 1.384(3), C(14)−P(1) 1.836(3), C(15)−P(1) 1.832(3), C(21)−P(1) 1.830(3), C(9)−N(1)−C(8) 122.9(2), C(21)−P(1)−C(15) 102.05(12), C(21)−P(1)−C(14) 101.33(11), C(15)−P(1)−C(14) 103.50(12).

[^{i}Pr-NP]AlMe$_2$ and [^{i}Pr-NP]AlEt$_2$ were obtained in a similar manner. Typically, evaporation of the reaction mixture affords the desired products that can be readily recrystallized from a concentrated THF/Et$_2$O solution. Alternatively, the aluminum derivatives are accessible by a metathetical method (Scheme 2, eq 3). The reactions of AlCl$_3$ with 1 equiv of lithium amides (either generated in situ or isolated) in toluene at −35 °C cleanly produced the dichloride compounds. Subsequent alkylation of [Me-NP]AlCl$_2$ with 2 equiv of trimethylsilylmethyllithium in toluene at room temperature generated [Me-NP]Al(CH$_2$SiMe$_3$)$_2$ in 90% isolated yield, whereas that of [^{i}Pr-NP]AlCl$_2$ with trimethylsilylmethyllithium (either 1 or 2 equiv) did not proceed at all under similar conditions,[26] suggesting significant steric repulsion between [^{i}Pr-NP]$^-$ and trimethylsilylmethyl ligands. These aluminum complexes are extremely sensitive to air and moisture but are stable, even at elevated temperatures, under an inert atmosphere for a prolonged period of time. The solution structures of these compounds were all determined by multinuclear NMR spectroscopy. Selected data are summarized in Table 2.

Scheme 2

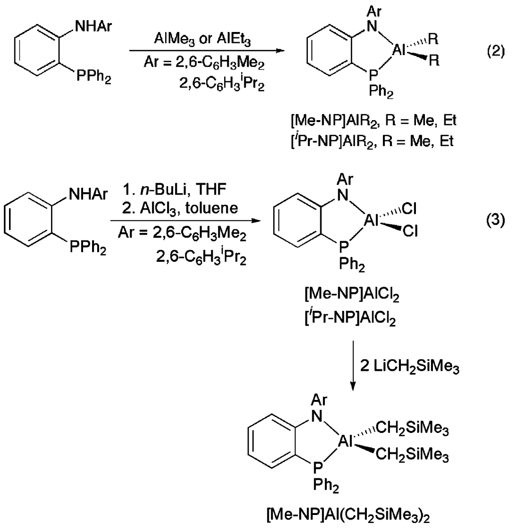

Table 2. Selected NMR Spectroscopic Data for Four-Coordinate Aluminum Complexes[a]

compound	$\delta_{H\alpha}$ ($^3J_{PH}$)	$\delta_{C\alpha}$ ($^2J_{PC}$)	δ_P ($\Delta\upsilon_{1/2}$)	δ_{Al} ($\Delta\upsilon_{1/2}$)
[Me-NP]AlCl$_2$			−36.1 (137)	94 (293)
[Me-NP]AlMe$_2$	−0.24 (4)	−8.7 (22)	−24.1 (6)	158 (10 289)
[Me-NP]AlEt$_2$	0.43 (NA)[b]	0.9 (18)	−24.0 (4)	158 (12 763)
[Me-NP]Al-(CH$_2$SiMe$_3$)$_2$	−0.30 (0), −0.39 (7)	−2.2 (16)	−24.2 (5)	159 (13 712)
[^{i}Pr-NP]AlCl$_2$			−34.4 (180)	99 (295)
[^{i}Pr-NP]AlMe$_2$	−0.23 (4)	−9.1 (20)	−21.6 (7)	151 (10 023)
[^{i}Pr-NP]AlEt$_2$	0.48 (0), 0.37 (7)	0.2 (20)	−21.4 (4)	152 (12 565)

[a] All spectra were recorded in C$_6$D$_6$ at room temperature, chemical shifts are in ppm, coupling constants are in Hz, peak widths at half-height are in Hz. [b] Not available.

The ^{1}H and ^{13}C NMR spectra of the aluminum derivatives are all consistent with a tetrahedral structure having a mirror-plane symmetry passing through the aluminum center and two donor atoms of the amido phosphine ligand. The aluminum-bound alkyl groups are chemically equivalent in all cases, as are the *o*-alkyl groups. The isopropylmethyl groups in the [^{i}Pr-NP]$^-$ derivatives are diastereotopic, again implying restricted N−Ar bond rotation in these molecules due to significant steric demand.[24] The C$_\alpha$ atoms in all dialkyl complexes appear as a doublet resonance in ^{13}C{^{1}H} NMR spectroscopy, indicating coordination of the phosphorus donor. The ^{1}H NMR spectra of [Me-NP]AlMe$_2$ and [^{i}Pr-NP]AlMe$_2$ reveal a doublet resonance for the Al−*Me* groups (Figure 2), whereas those of the others are indicative of diastereotopic α-hydrogen atoms for the Al−C*H*$_2$R fragments. Chart 2 depicts possible Newman projections for the dialkyl complexes in which the backbone and substituents of the amido phosphine ligand are omitted for clarity. The chemical nonequivalence of the H$_\alpha$ atoms in Al−C*H*$_2$R

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(26) No reaction was found at room temperature for more than a week; however, after 2 weeks at 110 °C, the reaction partially proceeded to produce a mixture of products, presumably [^{i}Pr-NP]Al(CH$_2$SiMe$_3$)$_2$ and [^{i}Pr-NP]Al(CH$_2$SiMe$_3$)Cl on the basis of ^{1}H and ^{31}P{^{1}H} NMR spectroscopy, regardless of the stoichiometry employed. The signals similar to those found for the α-hydrogen atoms in [Me-NP]Al(CH$_2$SiMe$_3$)$_2$ are observed at ca. −0.3 ppm in the ^{1}H NMR spectroscopy.

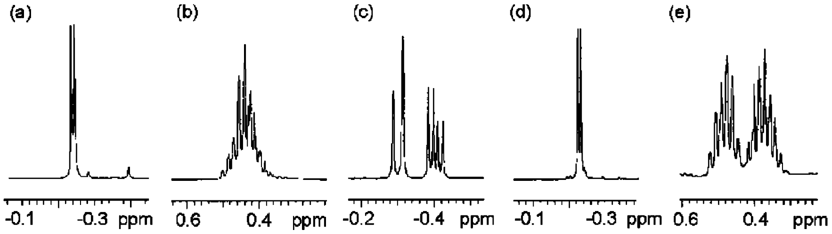
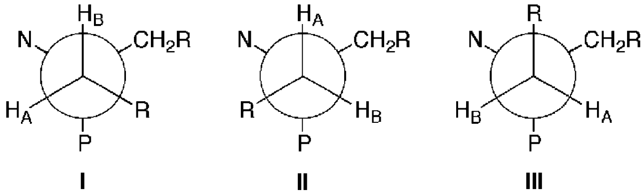


Figure 2. Multiplet resonance(s) observed for the H_α atoms in (a) [Me-NP]AlMe$_2$, (b) [Me-NP]AlEt$_2$, (c) [Me-NP]Al(CH$_2$SiMe$_3$)$_2$, (d) [^{i}Pr-NP]AlMe$_2$, and (e) [^{i}Pr-NP]AlEt$_2$ recorded in C_6D_6 at room temperature.

Chart 2. Possible Newman Projections of a Dialkyl Complex (R = H, Me, SiMe$_3$) along One of the Al$-$C$_\alpha$ Bonds



fragments is ascribable to the lack of symmetry of these molecules with respect to internal rotation involving the α-methylene groups.[27] In the case of dimethyl complexes (R = H in Chart 2), the H_α atoms are in principle chemically nonequivalent as well, as no symmetry operation exchanges these hydrogen atoms. Rapid rotation of the methyl groups about the Al$-$C bonds should be responsible for the observation of the doublet resonance. Notably, two well-resolved resonances are observed for the diastereotopic H_α atoms in both [Me-NP]Al(CH$_2$SiMe$_3$)$_2$ and [^{i}Pr-NP]AlEt$_2$ with the more upfield one having more fine-coupling. The steric demand of the amido phosphine ligands diminishes or precludes the population of rotamer II. The ^{1}H$-^{31}$P correlation spectra of [Me-NP]Al(CH$_2$SiMe$_3$)$_2$ and [^{i}Pr-NP]AlEt$_2$ reveal that the phosphorus donor in these molecules is coupled to only one of the diastereotopic α-hydrogen atoms that is shifted more upfield (see Supporting Information), thus eliminating the possibility of a structure similar to rotamer III. A ^{1}H NMR NOE experiment of [^{i}Pr-NP]AlEt$_2$ revealed NOE contacts of the isopropylmethine groups with both diastereotopic α-hydrogen atoms (+1.09% and +1.22%, respectively), consistent with a structure similar to rotamer I instead of II or III. An enhancement (+1.84%) was also observed for [^{i}Pr-NP]AlEt$_2$ between the *o*-hydrogen atoms of the PPh$_2$ moiety (7.39 ppm) and the α-hydrogen atom that is *not* coupled to the phosphorus donor (0.48 ppm), indicating this α-hydrogen's proximity to the phosphorus donor. Therefore, we conclude that the observed $^3J_{PH}$ in both [Me-NP]Al(CH$_2$SiMe$_3$)$_2$ and [^{i}Pr-NP]AlEt$_2$ is the consequence of pseudo-antiperiplanar orientation of the phosphorus donor and H_B rather than H_A in rotamer I. A similar phenomenon is also reported for the methylene hydrogen atoms in methyl 2,3-dibromo-2-methylpropionate.[28] In contrast, signals observed for the diastereotopic α-hydrogen atoms in [Me-NP]AlEt$_2$ are not resolved. The solid-state structure of [Me-NP]AlEt$_2$ was thus pursued to elucidate this phenomenon (vide infra). Though sterically demanding, the phosphorus donor of [Me-NP]AlEt$_2$, [Me-NP]Al(CH$_2$SiMe$_3$)$_2$, and [^{i}Pr-NP]AlEt$_2$ does not dissociate readily even at high temperatures, as internuclear $H_\alpha$$-$P coupling is observed for these molecules at temperatures as high as 100 °C (in toluene-d_8).

It has been well documented that the coordination number of neutral aluminum complexes correlates well with the chemical shifts of ^{27}Al NMR spectroscopy.[29] The ^{27}Al chemical shifts of 151$-$159 ppm observed for the dialkyl complexes and 94$-$99 ppm for the dichloride derivatives are within the expected region for a four-coordinate aluminum species, indicating the coordination of both donor atoms of the amido phosphine ligands. Similar chemical shifts are found for four-coordinate Al$_2$Me$_6$ (156 ppm),[30] AlEt$_3$-(thiophene) (154 ppm),[31] (^{i}Pr$_2$-ATI)AlMe$_2$ (154 ppm, ^{i}Pr$_2$-ATI = *N*,*N*′-diisopropylaminotroponiminate),[7] Al$_2$Cl$_6$ (98 ppm),[32] AlCl$_3$(PMe$_3$) (108 ppm),[33] and (^{i}Pr$_2$-ATI)AlCl$_2$ (109 ppm).[7] The ^{27}Al resonances are all much broader for dialkyl than for dichoride (Table 2), a phenomenon that has been noted previously and ascribed to the differences in the ionic character of Al$-$N versus Al$-$Cl or Al$-$C bonds.[7] It is interesting to note that all dialkyl complexes are not associated with coordinating solvents such as THF and diethyl ether, while the dichloride derivatives adopt THF readily, providing five-coordinate THF adducts as suggested by ^{27}Al NMR spectroscopy[29] (74 and 69 ppm for [Me-NP]-*Al*Cl$_2$(THF) and [^{i}Pr-NP]*Al*Cl$_2$(THF), respectively) and X-ray crystallography (vide infra). This result is in good agreement with a more electrophilic aluminum center of the four-coordinate dichloride complexes than that of their dialkyl counterparts (electronegativity: Cl 3.16, C 2.55).[34]

An upfield change in the ^{31}P chemical shift is observed for both dichloride and dialkyl complexes as compared to the corresponding ligand precursors. The phosphorus donor of the dichloride complexes appears as a broad singlet resonance ($\Delta\upsilon_{1/2}$ = 137$-$180 Hz), consistent with the fast relaxation of quadrupolar aluminum atom (^{27}Al, I = 5/2, 100% natural abundance).[29,35] Interestingly, the dialkyl complexes exhibit a relatively sharp singlet resonance ($\Delta\upsilon_{1/2}$

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Table 3. Crystallographic Data for [Me-NP]AlCl$_2$(THF), [Me-NP]AlEt$_2$, and [^{i}Pr-NP]AlMe$_2$

	{[Me-NP]AlCl$_2$-(THF)}(THF)	[Me-NP]AlEt$_2$	[^{i}Pr-NP]AlMe$_2$
formula	$C_{34}H_{39}AlCl_2NO_2P$	$C_{30}H_{33}AlNP$	$C_{32}H_{37}AlNP$
fw	622.51	465.557	493.611
crystal system	monoclinic	monoclinic	triclinic
space group	$P2_1/n$	$P2_1/c$	$P\bar{1}$
a (Å)	9.355(2)	9.7187(5)	8.6900(4)
b (Å)	9.997(2)	14.9887(10)	17.6389(9)
c (Å)	34.033(7)	18.5256(11)	19.2049(11)
α (deg)			90.020(2)
β (deg)	90.000(5)	96.725(4)	90.014(3)
γ (deg)			93.799(2)
V (Å^3)	3182.9(12)	2680.1(3)	2937.3(3)
Z	4	4	4
D_{calcd} (g cm^{-3})	1.299	1.154	1.116
$2\theta_{max}$ (deg)	55.02	49.70	50.18
T (K)	150(2)	298	298
diffractometer	SMART CCD	Kappa CCD	Kappa CCD
radiation, λ (Å)	Mo Kα, 0.710 73	Mo Kα, 0.710 73	Mo Kα, 0.710 73
total reflections	10 934	17 196	20 479
independent reflections	6147	4505	9250
absorption coefficient (mm^{-1})	0.314	0.153	0.143
data/restraints/parameters	6147/0/372	4505/0/298	9250/0/631
R_{int}	0.0701	0.189	0.138
goodness of fit	0.998	1.131	0.966
final R indices [$I > 2\sigma(I)$]	R1 = 0.0651	R1 = 0.1294	R1 = 0.0873
	wR2 = 0.1368	wR2 = 0.2825	wR2 = 0.1895
R indices (all data)	R1 = 0.1304	R1 = 0.3227	R1 = 0.2484
	wR2 = 0.1682	wR2 = 0.3950	wR2 = 0.2729

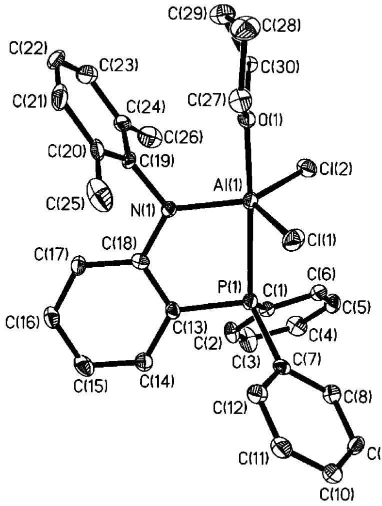

Figure 3. Molecular structure of [Me-NP]AlCl$_2$(THF) with thermal ellipsoids drawn at the 35% probability level. The asymmetric unit cell contains one unbound THF molecule, which is omitted for clarity. Selected bond distances (Å) and angles (deg): Al(1)−N(1) 1.870(4), Al(1)−O(1) 1.981(3), Al(1)−Cl(2) 2.163(2), Al(1)−Cl(1) 2.172(2), Al(1)−P(1) 2.5882(19), N(1)−Al(1)−O(1) 96.09(17), N(1)−Al(1)−Cl(2) 122.54(15), O(1)−Al(1)−Cl(2) 90.11(12), N(1)−Al(1)−Cl(1) 118.92(15), O(1)−Al(1)−Cl(1) 91.95(12), Cl(2)−Al(1)−Cl(1) 117.85(9), N(1)−Al(1)−P(1) 81.37(13), O(1)−Al(1)−P(1) 177.42(13), Cl(2)−Al(1)−P(1) 91.67(7), Cl(1)−Al(1)−P(1) 88.87(7).

= 4−7 Hz) for the phosphorus donor. Similar observations on the chemical shift change and the distinct peak widths at half-height for the dichloride and dialkyl derivatives have also been reported for other phosphine coordinated aluminum complexes.[36−38]

Solid-State Structure of [Me-NP]AlCl$_2$(THF). Colorless crystals suitable for X-ray crystallography were grown from a concentrated THF solution at −35 °C. Crystallographic details are summarized in Table 3. As illustrated in Figure 3, this compound is a five-coordinate species, consistent with ^{27}Al NMR spectroscopy. The coordination geometry is best described as trigonal bipyramidal with the phosphorus donor and the THF molecule occupying axial positions (O(1)−Al(1)−P(1) = 177.42(13)°). The aluminum center lies on the equatorial plane as indicated by the sum of the three equatorial angles of 359.31°. The Al(1)−N(1) distance of 1.870(4) Å is comparable to those of aluminum diarylamide complexes such as (t-Bu)$_2$Al[N(2,4,6-$C_6H_3Me_3$)$_2$] (1.823(4) Å)[39] and [Li(THF)$_4$][HAl(NPh$_2$)$_3$] (1.870 Å average).[40] The Al(1)−P(1) distance of 2.5882(19) Å is within the expected values for five-coordinate aluminum phosphine complexes such as *trans*-AlI$_3$(PEt$_3$)$_2$ (2.524 Å average),[41] AlCl$_2$[N(SiMe$_2$CH$_2$P^{i}Pr$_2$)$_2$] (2.5255 Å average),[36] and tris[*o*-((diphenylphosphino)methyl)phenyl]aluminum (2.729 Å average).[38] The Al−O and Al−Cl distances in [Me-NP]AlCl$_2$(THF) are almost identical to those found in *trans*-AlCl$_3$(THF)$_2$,[42] while the Cl−Al−Cl angle is slightly smaller for the former by 3.15° than the latter. The N(1)−Al(1)−P(1) binding angle of 81.37(13)° is smaller than those found in the closely related, five-coordinate AlCl$_2$[N(SiMe$_2$CH$_2$P^{i}Pr$_2$)$_2$] (86.0° average).[36] The aluminum atom is deviated from the N−phenylene−P plane by 0.3934 Å. As expected, the dimethylphenyl ring is roughly perpendicular to the N−Al−P plane (dihedral angle 91.4°).

Solid-State Structures of [Me-NP]AlEt$_2$ and [^{i}Pr-NP]AlMe$_2$. Single crystals of [Me-NP]AlEt$_2$ and [^{i}Pr-NP]AlMe$_2$ suitable for X-ray diffraction studies were grown from concentrated diethyl ether solutions at −35 °C. Figures 4 and 5 depict the ORTEP diagrams of [Me-NP]AlEt$_2$ and [^{i}Pr-NP]AlMe$_2$, respectively. Crystallographic details are summarized in Table 3. Consistent with the NMR spectroscopic data, both [Me-NP]AlEt$_2$ and [^{i}Pr-NP]AlMe$_2$ exist as monomeric, four-coordinate species with the aluminum atom being surrounded by two alkyl groups and the nitrogen and phosphorus donors of the amido phosphine ligand. The Al−N, Al−P, and Al−C distances are all typical for a tetrahedral complex of aluminum.[3,36,43] The aluminum atom in [Me-NP]AlEt$_2$ lies virtually on the N−phenylene−P plane, whereas that of [^{i}Pr-NP]AlMe$_2$ is markedly deviated from the plane by 0.6969 Å (average for the two independent molecules found in the asymmetric unit cell). This observation highlights the significant steric crowding imposed by the [^{i}Pr-NP]$^-$ ligand. A similar result is also observed for the four-

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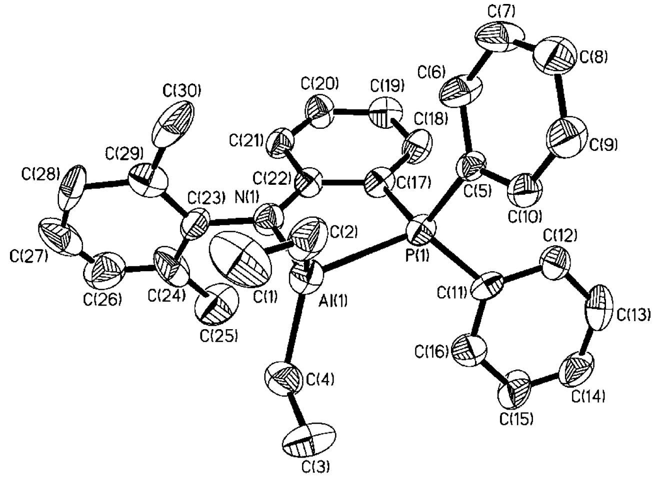

Figure 4. Molecular structure of [Me-NP]$AlEt_2$ with thermal ellipsoids drawn at the 35% probability level. Selected bond distances (Å) and angles (deg): P(1)−Al(1) 2.456(4), Al(1)−N(1) 1.894(8), Al(1)−C(4) 1.973(12), Al(1)−C(2) 1.993(13), N(1)−Al(1)−C(4) 111.7(5), N(1)−Al(1)−C(2) 119.2(5), C(4)−Al(1)−C(2) 118.1(5), N(1)−Al(1)−P(1) 84.2(3), C(4)−Al(1)−P(1) 118.4(4), C(2)−Al(1)−P(1) 100.0(4).

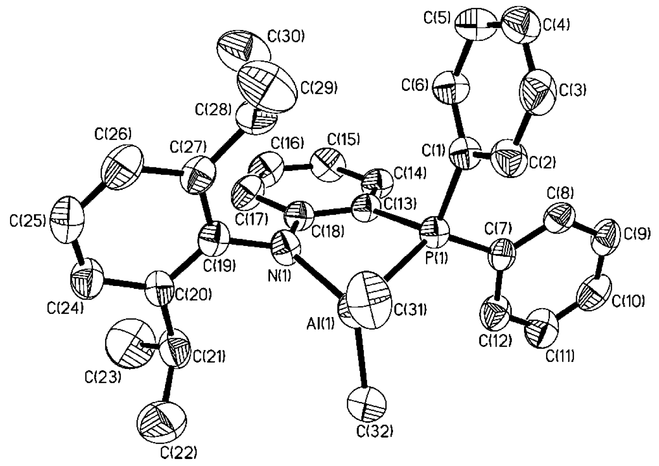

Figure 5. Molecular structure of [^{i}Pr-NP]$AlMe_2$ with thermal ellipsoids drawn at the 35% probability level. The asymmetric unit cell contains two independent molecules; only one is shown. Selected bond distances (Å) and angles (deg): P(1)−Al(1) 2.477(3), Al(1)−N(1) 1.894(6), Al(1)−C(31) 1.944(8), Al(1)−C(32) 1.965(9), N(1)−Al(1)−C(31) 114.5(4), N(1)−Al(1)−C(32) 119.0(3), C(31)−Al(1)−C(32) 116.6(4), N(1)−Al(1)−P(1) 82.1(2), C(31)−Al(1)−P(1) 113.2(3), C(32)−Al(1)−P(1) 105.6(3).

coordinate [^{i}Pr-NP]$_2$Zn, where the zinc atom is displaced by 0.6851 Å (average).[23] The binding angles of the amido phosphine ligands are 84.2(3)° and 82.1(2)° for [Me-NP]$AlEt_2$ and [^{i}Pr-NP]$AlMe_2$, respectively. These angles are comparable to those of the four-coordinate complexes that feature five-membered metallacycles such as [^{i}Pr-NP]$_2$Zn (83.695° average)[23] and (^{i}Pr$_2$-ATI)$AlMe_2$ (83.3(1)°),[43] but are significantly more acute than the ideal tetrahedral angle of 109.47°. As a result, the C−Al−C angles of 118.1(5)° and 116.6(4)° in [Me-NP]$AlEt_2$ and [^{i}Pr-NP]$AlMe_2$, respectively, are notably wider. In both molecules, the dialkylphenyl ring is approximately perpendicular to the *o*-phenylene backbone. In contrast to that found in H[Me-NP], the phosphorus atom in both [Me-NP]$AlEt_2$ and [^{i}Pr-NP]$AlMe_2$ adopts a distorted tetrahedral geometry where the two phenyl substituents are roughly displaced evenly with respect to the phenylene backbone.

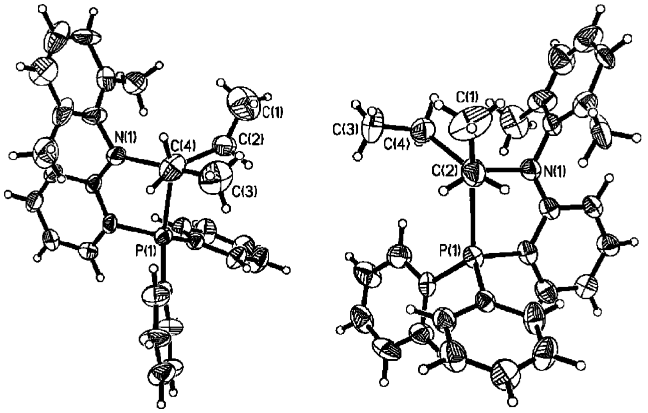

Figure 6. Two views of the molecular structure of [Me-NP]$AlEt_2$ along the Al−C(4) (left view) and Al−C(2) (right view) bonds.

Figure 6 depicts two views of molecular structure of [Me-NP]$AlEt_2$ along the Al−C bonds. The left view is a reminiscent of the rotamer I in Chart 2, featuring one of the two diastereotopic α-hydrogen atoms on C(4) being nearly antiperiplanar with respect to the phosphorus donor. The right view, however, corresponds to a mirror image of the rotamer III, in which internuclear coupling between the phosphorus donor and the two diastereotopic hydrogen atoms at C(2) becomes possible. This result is consistent with the relatively small sizes of the ligands in [Me-NP]$AlEt_2$ as compared to those in [Me-NP]Al$(CH_2SiMe_3)_2$ and [^{i}Pr-NP]$AlEt_2$, thus exhibiting the unresolved multiplet resonances for the diastereotopic α-hydrogen atoms of the former in ^{1}H NMR spectroscopy.

Conclusions

We have prepared and characterized a series of aluminum dichloride and dialkyl complexes supported by *o*-phenylene-derived amido phosphine ligands. Solution NMR and X-ray crystallographic studies reveal monomeric, four-coordinate species for these molecules. Five-coordinate dichloride complexes as a THF adduct may also be obtained. Heteronuclear COSY and NOE experiments elucidate the conformation of the α-methylene moieties in [Me-NP]Al$(CH_2SiMe_3)_2$ and [^{i}Pr-NP]$AlEt_2$. Conformations other than that found in [Me-NP]Al$(CH_2SiMe_3)_2$ and [^{i}Pr-NP]$AlEt_2$ are accessible with sterically less demanding amido phosphine and/or alkyl ligands. Studies involving the reactivity chemistry of these new molecules will be the subjects of further reports.

Experimental Section

General Procedures. Unless otherwise specified, all experiments were performed under nitrogen using standard Schlenk or glovebox techniques. All solvents were reagent grade or better and purified by standard methods. The NMR spectra were recorded on Varian instruments. Chemical shifts (δ) are listed as parts per million downfield from tetramethylsilane, and coupling constants (J) and peak widths at half-height ($\Delta\upsilon_{1/2}$) are in hertz. ^{1}H NMR spectra are referenced using the residual solvent peak at δ 7.16 for C_6D_6, δ 7.27 for $CDCl_3$, and δ 2.09 for toluene-d_8 (the most upfield resonance). ^{13}C NMR spectra are referenced using the residual solvent peak at δ 128.39 for C_6D_6 and δ 77.23 for $CDCl_3$. The assignment of the carbon atoms for all new compounds is based on DEPT ^{13}C NMR spectroscopy. ^{19}F, ^{31}P, and ^{27}Al NMR spectra are referenced externally using $CFCl_3$ in $CHCl_3$ at δ 0, 85% H_3PO_4 at δ 0, and $AlCl_3$ in D_2O at δ 0, respectively. Routine coupling constants are not listed. All NMR spectra were recorded at room temperature in specified solvents unless otherwise noted. The ^{1}H−^{31}P correlation experiments were carried out on a Varian Inova 500 MHz instrument using HMBC sequence. The NOE data were obtained with a ^{1}H NMR NOEDIF experimental apparatus. Elemental analysis was performed on a Heraeus CHN-O Rapid analyzer. For some aluminum complexes, we were not able to obtain satisfactory analysis due to extreme air and moisture sensitivity of these compounds.

Materials. Compounds *N*-(2-fluorophenyl)-2,6-diisopropylaniline, *N*-(2-diphenylphosphinophenyl)-2,6-diisopropylaniline (H[^{i}Pr-NP]), and [^{i}Pr-NP]Li(THF)$_2$ were prepared according to the procedures reported previously.[23] All other chemicals were obtained from commercial vendors and used as received.

X-ray Crystallography. Tables 1 and 3 summarize the crystallographic data for all structurally characterized compounds. Data for compounds H[Me-NP] and [Me-NP]AlCl$_2$(THF) were collected on a Bruker SMART 1000 CCD diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.7107$ Å). Structures were solved by direct methods and refined by full-matrix least-squares procedures against F^2 using SHELXTL. All full-weight non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions. Data for compounds [Me-NP]AlEt$_2$ and [^{i}Pr-NP]AlMe$_2$ were collected on a Bruker-Nonius Kappa CCD diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.7107$ Å). Structures were solved by direct methods and refined by full-matrix least-squares procedures against F^2 using maXus. All full-weight non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions. The crystals of [Me-NP]AlEt$_2$ were of poor quality but sufficient to establish the identity of this molecule. The data set contains too many weak reflections, resulting in relatively high *R*-values.

Synthesis of *N*-(2-Fluorophenyl)-2,6-dimethylaniline. A 100-mL Schlenk flask was charged with 1-bromo-2-fluorobenzene (15.584 g, 89.05 mmol), 2,6-dimethylaniline (13.034 g, 107.56 mmol, 1.2 equiv), Pd(OAc)$_2$ (0.100 g, 0.445 mmol, 0.5% equiv), bis[2-(diphenylphosphino)phenyl] ether (DPEphos, 0.36 g, 0.668 mmol, 0.75% equiv), NaO^{t}Bu (12.0 g, 125 mmol, 1.4 equiv), and toluene (30 mL) under nitrogen. The reaction mixture was heated to reflux for 1 day. Toluene was removed in vacuo, and the reaction was quenched with deionized water (150 mL). The product was extracted with CH_2Cl_2 (200 mL), and the organic portion was separated from the aqueous layer, which was further extracted with CH_2Cl_2 (15 mL × 2). The combined organic solution was dried over $MgSO_4$ and filtered. All volatiles were removed in vacuo to yield orange viscous oil, which was subjected to flash column chromatography on silica gel (9:1 hexanes/Et$_2$O). The first band (pale yellow) was collected. Solvents were removed in vacuo to give a yellowish orange solid; yield 12.23 g (64%). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.07−7.13 (m, 4, Ar), 6.87 (t, 1, Ar), 6.65 (m, 1, Ar), 6.22 (t, 1, Ar), 5.35 (br s, 1, NH), 2.22 (s, 6, CH_3). ^{19}F NMR ($CDCl_3$, 470.5 MHz) δ −138.42. ^{13}C NMR ($CDCl_3$, 125.5 MHz) δ 151.5 ($J_{CF} = 237.4$, *C*F), 137.2, 136.3, 134.7 ($J_{CF} = 10.9$, FC*C*N), 128.6 (*C*H), 126.3 (*C*H), 124.4 ($J_{CF} = 2.8$, *C*H), 117.4 ($J_{CF} = 7.3$, *C*H), 114.7 ($J_{CF} = 18.1$, *C*H), 113.1 ($J_{CF} = 3.6$, *C*H), 18.2 (CH_3). Anal. Calcd for $C_{14}H_{14}FN$: C, 78.11; H, 6.56; N, 6.51. Found: C, 77.88; H, 6.61; N, 6.48.

Synthesis of *N*-(2-Diphenylphosphinophenyl)-2,6-dimethylaniline, H[Me-NP]. A 100-mL Schlenk flask equipped with a condenser was flashed with nitrogen thoroughly. To this flask was added KPPh$_2$ (110 mL, 0.5 M in THF solution, Aldrich, 55.0 mmol). THF was removed in vacuo, and a solution of *N*-(2-fluorophenyl)-2,6-dimethylaniline (10.6 g, 49.26 mmol) in DME (50 mL) was added with a syringe. The transparent, ruby reaction solution was heated to reflux for 2 days, during which time the reaction condition was monitored by ^{31}P{^{1}H} NMR spectroscopy. All volatiles were removed from the resulting orange solution under reduced pressure, and degassed deionized water (140 mL) was added. The product was extracted with deoxygenated dichloromethane (100 mL). The dichloromethane solution was separated from the aqueous layer, from which the product was further extracted with dichloromethane (20 mL × 2). The combined organic solution was dried over $MgSO_4$ and filtered. All volatiles were removed in vacuo to yield a yellow solid. The yellow solid was purified by washing it with boiling MeOH (40 mL × 3) until it became a white powder; yield 15.98 g (85%). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.41−7.60 (m, 10, PC_6H_5), 7.07−7.14 (m, 4, Ar), 6.89 (t, 1, Ar), 6.71 (t, 1, Ar), 6.20 (m, 1, Ar), 5.90 (d, 1, NH), 2.03 (s, 6, CH_3). ^{1}H NMR (C_6D_6, 500 MHz) δ 7.47 (m, 4, Ar), 7.11 (td, 1, Ar), 7.06 (m, 6, Ar), 6.94 (m, 4, Ar), 6.61 (t, 1, Ar), 6.31 (m, 1, Ar), 6.04 (d, 1, $J_{HP} = 7$, NH), 1.98 (s, 6, CH_3). ^{31}P{^{1}H} NMR (C_6D_6, 202 MHz) δ −19.3. ^{31}P{^{1}H} NMR (Et_2O, 121.5 MHz) δ −18.9. ^{31}P{^{1}H} NMR ($CDCl_3$, 121.5 MHz) δ −19.1. ^{13}C{^{1}H} NMR ($CDCl_3$, 75.3 MHz) δ 148.6 ($J_{CP} = 17.0$), 138.2, 135.8, 135.2, 135.1, 134.1, 133.8, 130.3, 128.8 ($J_{CP} = 18.8$), 128.5 ($J_{CP} = 13.5$), 125.6, 119.9 ($J_{CP} = 9.1$), 118.2, 111.8, 18.2 (CH_3). Anal. Calcd for $C_{26}H_{24}NP$: C, 81.87; H, 6.34; N, 3.67. Found: C, 81.45; H, 6.42; N, 3.61.

General Procedures for the Synthesis of [Me-NP]AlR$_2$ and [^{i}Pr-NP]AlR$_2$ (R = Me, Et). A Teflon-sealed reaction vessel was charged with a toluene solution containing an appropriate ligand precursor and 1 equiv of $AlMe_3$ (Aldrich, 2.0 M in toluene) or $AlEt_3$ (TCI, 15% in toluene). The colorless solution was heated to 110 °C for 2 days. Evaporation of the resulting yellow solution to dryness under reduced pressure afforded the product as pale-yellow microcrystals, which were recrystallized from 1:1 THF/Et$_2$O to give pale-yellow crystals.

Synthesis of [Me-NP]AlMe$_2$. Yield 93%. ^{1}H NMR (C_6D_6, 500 MHz) δ 7.40 (m, 4, Ar), 6.97−7.20 (m, 11, Ar), 6.42 (t, 1, Ar), 6.23 (t, 1, Ar), 2.22 (s, 6, C_6H_3*Me*$_2$), −0.24 (d, 6, AlC*H*$_3$, $^3J_{HP} = 4$). ^{13}C{^{1}H} NMR (C_6D_6, 125.70 MHz) δ 160.8 (d, $J_{CP} = 20.1$, C), 144.5 (d, $J_{CP} = 4.5$, C), 137.5 (C), 135.2 (CH), 134.9 (CH), 134.0 (d, $J_{CP} = 12.8$, CH), 131.1 (d, $J_{CP} = 1.8$, CH), 129.7 (CH), 129.6 (d, $J_{CP} = 9.9$, CH), 125.7 (CH), 116.1 (d, $J_{CP} = 5.5$, CH), 114.7 (d, $J_{CP} = 6.4$, CH), 110.9 (C), 110.6 (C), 19.3 (ArCH_3), −8.7 (d, $^2J_{CP} = 22$, AlCH_3). ^{31}P{^{1}H} NMR (C_6D_6, 202.31 MHz) δ −24.1 ($\Delta\upsilon_{1/2} = 6$ Hz). ^{27}Al NMR (C_6D_6, 130.22 MHz) δ 158 ($\Delta\upsilon_{1/2} =$ 10 289 Hz). LRMS (EI) Calcd for $C_{28}H_{29}AlNP$ *m/z* 437, found *m/z* 437. Anal. Calcd for $C_{28}H_{29}AlNP$: C, 76.87; H, 6.68; N, 3.20. Found: C, 73.95; H, 6.53; N, 3.22.

Synthesis of [^{i}Pr-NP]AlMe$_2$. Yield 96%. ^{1}H NMR (C_6D_6, 500 MHz) δ 7.38 (m, 4, Ar), 7.22 (m, 3, Ar), 7.01 (m, 7, Ar), 6.90 (t, 1, Ar), 6.40 (t, 1, Ar), 6.23 (t, 1, Ar), 3.35 (septet, 2, C*H*Me$_2$), 1.12 (d, 6, CH*Me*$_2$), 1.04 (d, 6,CH*Me*$_2$), −0.23 (d, 6, AlCH_3, $^3J_{HP}$ = 4). ^{13}C{^{1}H} NMR (C_6D_6, 125.70 MHz) δ 162.2 (d, $J_{CP} = 19.1$, C), 148.0 (C), 141.9 (d, $J_{CP} = 4.5$, C), 134.8 (CH), 134.7 (CH), 134.1 (CH), 131.1 (d, $J_{CP} = 1.8$, CH), 129.5 (d, $J_{CP} = 10.0$, CH), 12.7 (CH), 125.0 (CH), 117.1 (d, $J_{CP} = 6.4$, CH), 116.6 (d, $J_{CP} =$ 6.4, CH), 112.0 (C), 111.6 (C), 28.4 (*C*HMe$_2$), 25.6 (CH*Me*$_2$), 25.2 (CH*Me*$_2$), −9.1 (d, $^2J_{CP} = 20$, Al*C*H$_3$). ^{31}P{^{1}H} NMR (C_6D_6, 202.31 MHz) δ −21.6 ($\Delta\upsilon_{1/2} = 7$ Hz). ^{27}Al NMR (C_6D_6, 130.22 MHz) δ 151 ($\Delta\upsilon_{1/2} = 10\,023$ Hz). Anal. Calcd for $C_{32}H_{37}AlNP$: C, 77.87; H, 7.56; N, 2.84. Found: C, 77.19; H, 7.53; N, 2.88.

Synthesis of [Me-NP]AlEt$_2$. Yield 98%. ^{1}H NMR (C_6D_6, 500 MHz) δ 7.46 (m, 4, Ar), 7.10 (m, 2, Ar), 7.06 (m, 1, Ar), 6.97−7.04 (m, 7, Ar), 6.94 (m, 1, Ar), 6.42 (t, 1, Ar), 6.23 (t, 1, Ar), 2.23 (s, 6, C_6H_3*Me*$_2$), 1.20 (t, 6, AlCH$_2$C*H*$_3$), 0.43 (m, 4, AlC*H*$_2$). ^{1}H NMR (C_7D_8, 500 MHz) δ 7.35 (m, 4, Ar), 6.91 (m, 10, Ar), 6.80 (t, 1, Ar), 6.30 (t, 1, Ar), 6.07 (t, 1, Ar), 2.09 (s, 6, C_6H_3*Me*$_2$), 1.05 (t, 6, AlCH$_2$C*H*$_3$), 0.28 (m, 4, AlC*H*$_2$). ^{13}C{^{1}H} NMR (C_6D_6, 125.70 MHz) δ 161.1 (d, J_{CP} = 20.8, C), 144.8 (d, J_{CP} = 4.5, C), 137.3 (C), 135.1 (CH), 134.8 (CH), 133.9 (d, J_{CP} = 12.7, CH), 131.1 (d, J_{CP} = 2.8, CH), 129.6 (CH), 129.5 (CH), 126.7 (CH), 116.2 (d, J_{CP} = 6.4, CH), 114.8 (d, J_{CP} = 6.4, CH), 110.7 (C), 110.4 (C), 19.2 (ArC*H*$_3$), 9.8 (d, $^3J_{CP}$ = 1.9, AlCH$_2$*C*H$_3$), 0.9 (d, $^2J_{CP}$ = 18, Al*C*H$_2$). ^{31}P{^{1}H} NMR (C_6D_6, 202.31 MHz) δ −24.0 ($\Delta\nu_{1/2}$ = 4 Hz). ^{27}Al NMR (C_6D_6, 130.22 MHz) δ 158 ($\Delta\nu_{1/2}$ = 12 763 Hz).

Synthesis of [^{i}Pr-NP]AlEt$_2$. Yield 92%. ^{1}H NMR (C_6D_6, 500 MHz) δ 7.39 (m, 4, Ar), 7.16 (m, 3, Ar), 6.95−7.00 (m, 7, Ar), 6.84 (m, 1, Ar), 6.36 (t, 1, Ar), 6.18 (t, 1, Ar), 3.28 (septet, 2, C*H*Me$_2$), 1.18 (t, 6, AlCH$_2$C*H*$_3$), 1.10 (d, 6, CH*Me*$_2$), 0.98 (d, 6, CH*Me*$_2$), 0.48 (m, 2, AlC*H*$_A$H$_B$, $^2J_{HH}$ = 15), 0.37 (m, 2, AlCH$_A$*H*$_B$, $^3J_{HP}$ = 7, $^2J_{HH}$ = 15). ^{1}H NMR (C_7D_8, 500 MHz) δ 7.44 (m, 4, Ar), 7.21 (m, 3, Ar), 7.02 (m, 7, Ar), 6.89 (t, 1, Ar), 6.41 (t, 1, Ar), 6.24 (t, 1, Ar), 3.32 (septet, 2, C*H*Me$_2$), 1.22(t, 6, AlCH$_2$C*H*$_3$), 1.15 (d, 6, CH*Me*$_2$), 1.03 (d, 6, CH*Me*$_2$), 0.53 (m, 2, AlC*H*$_A$H$_B$), 0.42 (m, 2, AlCH$_A$*H*$_B$). ^{13}C{^{1}H} NMR (C_6D_6, 125.70 MHz) δ 162.5 (d, J_{CP} = 20.0, C), 147.7 (C), 142.4 (d, J_{CP} = 4.5, C), 134.7 (CH), 134.7 (CH), 134.0 (CH), 131.1 (d, J_{CP} = 1.8, CH), 129.5 (d, J_{CP} = 10.0, CH), 129.5 (CH), 126.6 (CH), 125.0 (CH), 117.3 (d, J_{CP} = 5.4, CH), 116.6 (d, J_{CP} = 5.4, CH), 111.8 (C), 111.5 (C), 28.4 (*C*HMe$_2$), 25.8 (CH*Me*$_2$), 24.9 (CH*Me*$_2$), 9.8 (d, $^3J_{CP}$ = 1.8, AlCH$_2$*C*H$_3$), 0.2 (d, $^2J_{CP}$ = 20, AlCH$_2$). ^{31}P{^{1}H} NMR (C_6D_6, 202.31 MHz) δ −21.4 ($\Delta\nu_{1/2}$ = 4 Hz). ^{27}Al NMR (C_6D_6, 130.22 MHz) δ 151.8 ($\Delta\nu_{1/2}$ = 12 565 Hz). The coupling constants $^2J_{HH}$ and $^3J_{HP}$ were determined by ^{1}H NMR spectroscopy with selective decoupling of β-hydrogen atoms. LRMS (EI) Calcd for $C_{34}H_{41}$-AlNP *m*/*z* 521, found *m*/*z* 521.

Synthesis of [Me-NP]AlCl$_2$. To a solution of H[Me-NP] (2.0 g, 5.24 mmol) in THF (15 mL) at −35 °C was added *n*-BuLi (3.3 mL, 5.24 mmol, 1 equiv). The reaction mixture was naturally warmed to room temperature and stirred for 3 h. All volatiles were removed in vacuo. The red viscous residue was triturated with pentane (15 mL) to yield a yellow solid. The yellow solid was isolated from the orange solution, washed with pentane (5 mL × 3), and dried in vacuo to give [Me-NP]Li(THF)$_2$ as indicated by ^{1}H NMR spectroscopy; yield 2.67 g (99%). ^{1}H NMR (C_6D_6, 500 MHz) δ 7.58 (m, 4, Ar), 7.23 (d, 2, Ar), 7.07−7.16 (m, 8, Ar), 6.97 (m, 1, Ar), 6.38 (m, 1, Ar), 6.33 (m, 1, Ar), 3.23 (m, 8, OC*H*$_2$-CH$_2$), 2.26 (s, 6, CH$_3$), 1.19 (m, 8, OCH$_2$C*H*$_2$). Solid AlCl$_3$ (2.600 g, 1.950 mmol) was added in portions to a solution of [Me-NP]-Li(THF)$_2$ (1.00 g, 1.881 mmol) in toluene (15 mL) at −35 °C. The reaction mixture was stirred at room temperature for 4 days and filtered through a pad of Celite. Solvent was stripped from the filtrate to afford an off-white solid; yield 905 mg (100%). ^{1}H NMR (C_6D_6, 500 MHz) δ 7.53 (m, 4, Ar), 6.94−7.04 (m, 10, Ar), 6.89 (t, 1, Ar), 6.44 (t, 1, Ar), 6.22 (t, 1, Ar), 2.32 (s, 6, CH$_3$). ^{13}C{^{1}H} NMR (C_6D_6, 125.5 MHz) δ 159.2 (d, J_{CP} = 16.4, C), 143.0 (d, J_{CP} = 5.4, C), 138.0 (C), 135.2 (CH), 134.4 (CH), 134.4 (CH), 131.7 (d, J_{CP} = 2.8, CH), 129.8 (CH), 129.7 (d, J_{CP} = 3.6, CH), 126.6 (CH), 126.2 (C), 118.2 (d, J_{CP} = 6.3, CH), 115.2 (d, J_{CP} = 5.4, CH), 110.4 (d, J_{CP} = 46.3, C), 19.4 (Me). ^{31}P{^{1}H} NMR (C_6D_6, 121.5 MHz) δ −36.1 ($\Delta\nu_{1/2}$ = 137 Hz). ^{27}Al NMR (C_6D_6, 130.22 MHz) δ 94 ($\Delta\nu_{1/2}$ = 293 Hz). Recrystallization of [Me-NP]AlCl$_2$ from THF at −35 °C produced the solvated compound [Me-NP]-AlCl$_2$(THF) as colorless crystals suitable for X-ray crystallography. The recrystallization yield is typically 70%. ^{1}H NMR (C_6D_6, 500 MHz) δ 7.76 (m, 4, Ar), 7.14 (m, 1, Ar), 7.04 (m, 6, Ar), 6.97 (m, 2, Ar), 6.92 (m, 2, Ar), 6.50 (t, 1, Ar), 6.18 (t, 1, Ar), 3.58 (m, 4, OC*H*$_2$CH$_2$), 2.30 (s, 6, CH$_3$), 1.12 (m, 4, OCH$_2$C*H*$_2$). ^{13}C{^{1}H} NMR (C_6D_6, 125.5 MHz) δ 159.2 (d, J_{CP} = 20.3, C), 146.2 (d, J_{CP} = 6.4, C), 138.5 (C), 135.9 (CH), 134.6 (d, J_{CP} = 11.3, CH), 134.1 (CH), 130.8 (C), 130.5 (CH), 129.5 (CH), 129.1 (d, J_{CP} = 9.5, CH), 126.0 (CH), 118.0 (d, J_{CP} = 5.0, CH), 115.1 (d, J_{CP} = 5.9, CH), 113.3 (d, J_{CP} = 35.3, C), 71.1 (O*C*H$_2$CH$_2$), 25.3 (OCH$_2$*C*H$_2$), 19.3 (Me). ^{31}P{^{1}H} NMR (C_6D_6, 121.5 MHz) δ −34.8 ($\Delta\nu_{1/2}$ = 54 Hz). ^{27}Al NMR (C_6D_6, 130.22 MHz) δ 74 ($\Delta\nu_{1/2}$ = 351 Hz).

Synthesis of [^{i}Pr-NP]AlCl$_2$. Solid AlCl$_3$ (250 mg, 1.8749 mmol) was added in portions to a solution of [^{i}Pr-NP]Li(THF)$_2$ (1.0658 g, 1.8157 mmol) in toluene (15 mL) at −35 °C. The reaction mixture was stirred at room temperature for 4 days and filtered through a pad of Celite. Concentration of the filtrate under reduced pressure afforded [^{i}Pr-NP]AlCl$_2$ as colorless crystals which were isolated by filtration and dried in vacuo; yield 951 mg (98.1%). ^{1}H NMR (C_6D_6, 500 MHz) δ 7.38 (m, 4, Ar), 7.13 (m, 3, Ar), 6.95 (m, 2, Ar), 6.89 (m, 4, Ar), 6.79 (m, 2, Ar), 6.34 (t, 1, Ar), 6.22 (t, 1, Ar), 3.38 (septet, 2, C*H*Me$_2$), 1.18 (d, 6, CH*Me*$_2$), 0.95 (d, 6, CH*Me*$_2$). ^{13}C{^{1}H} NMR (C_6D_6, 125.70 MHz) δ 160.5 (d, J_{CP} = 14.6, C), 148.2 (C), 139.0 (d, J_{CP} = 3.6, C), 135.1 (CH), 134.5 (CH), 134.5 (CH), 132.2 (d, J_{CP} = 2.8, CH), 129.8 (d, J_{CP} = 10.8, CH), 127.7 (CH), 125.3 (CH), 124.4 (d, J_{CP} = 51.8, C), 118.7 (d, J_{CP} = 6.3, CH), 117.6 (d, J_{CP} = 5.4, CH), 109.9 (d, J_{CP} = 51.0, C), 28.7 (*C*HMe$_2$), 25.5 (CH*Me*$_2$), 25.3 (CH*Me*$_2$). ^{31}P{^{1}H} NMR (C_6D_6, 202.31 MHz) δ −34.4 ($\Delta\nu_{1/2}$ = 180 Hz). ^{27}Al NMR (C_6D_6, 130.22 MHz) δ 99 ($\Delta\nu_{1/2}$ = 295 Hz). Recrystallization of [^{i}Pr-NP]-AlCl$_2$ from THF at −35 °C afforded [^{i}Pr-NP]AlCl$_2$(THF) as colorless crystals. ^{1}H NMR (C_6D_6, 500 MHz) δ 7.55 (m, 4, Ar), 7.16 (m, 5, Ar), 7.02 (m, 5, Ar), 6.93 (t, 1, Ar), 6.42 (t, 1, Ar), 6.19 (t, 1, Ar), 3.88 (m, 4, OC*H*$_2$CH$_2$) 3.44 (septet, 2, C*H*Me$_2$), 1.19 (m, 4, OCH$_2$C*H*$_2$), 1.14 (d, 6, CH*Me*$_2$), 0.97 (d, 6, CH*Me*$_2$). ^{13}C{^{1}H} NMR (C_6D_6, 125.70 MHz) δ 159.8 (d, J_{CP} = 17.2, C), 147.8 (C), 140.2 (d, J_{CP} = 4.5, C), 134.2 (CH), 134.0 (CH), 133.9 (CH), 130.8 (d, J_{CP} = 2.6, CH), 128.8 (d, J_{CP} = 10.0, CH), 126.8 (CH), 124.6 (CH), 117.8 (d, J_{CP} = 6.4, CH), 117.0 (d, J_{CP} = 5.5, CH), 110.9 (C), 110.5 (C), 71.1 (O*C*H$_2$CH$_2$), 27.9 (*C*HMe$_2$), 25.1 (CH*Me*$_2$), 24.8 (OCH$_2$*C*H$_2$), 24.2 (CH*Me*$_2$). ^{31}P{^{1}H} NMR (C_6D_6, 202.31 MHz) δ −33.7 ($\Delta\nu_{1/2}$ = 85 Hz). ^{27}Al NMR (C_6D_6, 130.22 MHz) δ 69 ($\Delta\nu_{1/2}$ = 387 Hz). Anal. Calcd for $C_{30}H_{31}AlCl_2NP$: C, 67.42; H, 5.85; N, 2.62. Found: C, 66.99; H, 7.07; N, 2.47.

Synthesis of [Me-NP]Al(CH$_2$SiMe$_3$)$_2$. A pentane solution of LiCH$_2$SiMe$_3$ (1.1 mL, 1 M in pentane, Aldrich, 1.10 mmol, 2 equiv) was added dropwise to a solution of [Me-NP]AlCl$_2$ (300 mg, 0.55 mmol) in toluene (10 mL) at −35 °C. The reaction mixture was stirred at room temperature for 2 days. The insoluble materials thus produced were removed by filtration with a short column of Celite. Solvent was stripped and the product was obtained as a pale yellow solid; yield 286 mg (90%). Recrystallization from diethyl ether afforded colorless crystals. ^{1}H NMR (C_6D_6, 500 MHz) δ 7.46 (m, 4, Ar), 7.09 (m, 2, Ar), 7.02 (m, 8, Ar), 6.94 (m, 1, Ar), 6.43 (t, 1, Ar), 6.18 (t, 1, Ar), 2.21 (s, 6, C_6H_3*Me*$_2$), 0.028 (s, 18, SiMe$_3$), −0.30 (d, 2, AlC*H*$_A$H$_B$, $^2J_{HH}$ = 13), −0.39 (dd, 2, AlCH$_A$*H*$_B$, $^3J_{HP}$ = 7, $^2J_{HH}$ = 13). ^{13}C{^{1}H} NMR (C_6D_6, 125.70 MHz) δ 161.5 (d, J_{CP} = 20.0, C), 145.0 (d, J_{CP} = 5.5, C), 137.8 (C), 135.5 (CH), 134.9 (CH), 133.9 (d, J_{CP} = 11.8, CH), 131.2 (d, J_{CP} = 1.9, CH), 129.9 (CH), 129.6 (d, J_{CP} = 10.0, CH), 126.0 (CH), 116.3 (d, J_{CP} = 5.4, CH), 115.0 (d, J_{CP} = 6.4, CH), 111.1 (C), 110.7 (C), 19.7 (ArC*H*$_3$), 3.4 (SiMe), −2.2 (d, $^2J_{CP}$ = 16, AlCH$_2$). ^{31}P{^{1}H} NMR (C_6D_6, 202.31 MHz) δ −24.2 ($\Delta\nu_{1/2}$ = 5 Hz). ^{27}Al NMR (C_6D_6, 130.22 MHz) δ 159 ($\Delta\upsilon_{1/2}$ = 13 712 Hz). Anal. Calcd for $C_{34}H_{45}$-$AlNPSi_2$: C, 70.18; H, 7.80; N, 2.41. Found: C, 67.64; H, 6.99; N, 2.59.

Acknowledgment. We thank the National Science Council (NSC 92-2113-M-110-015) of Taiwan for financial support of this work, Mr. Wei-Ying Lee for preparation of H[^{i}Pr-NP], Ms. Chao-Lien Ho for technical assistance with NMR experiments, and Mr. Ting-Shen Kuo at the Instrumentation Center of National Taiwan Normal University for crystallographic assistance on [Me-NP]$AlEt_2$ and [^{i}Pr-NP]-$AlMe_2$.

Supporting Information Available: $^1H-^{31}P$ correlation spectra of [^{i}Pr-NP]$AlEt_2$ and [Me-NP]$Al(CH_2SiMe_3)_2$, and X-ray crystallographic data in CIF format for H[Me-NP], [Me-NP]$AlCl_2$(THF), [Me-NP]$AlEt_2$, and [^{i}Pr-NP]$AlMe_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

IC035373Q