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Synthesis and Structural Characterization of Five-Coordinate Aluminum Complexes Containing Diarylamido Diphosphine Ligands

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A series of five-coordinate aluminum complexes supported by *o*-phenylene-derived amido diphosphine ligands, $[N(o\text{-}C_6H_4PR_2)_2]^-$ ([R-PNP]$^-$; R = Ph, ^{i}Pr) and $[N(o\text{-}C_6H_4PPh_2)(o\text{-}C_6H_4P^iPr_2)]^-$ ([Ph-PNP-^{i}Pr]$^-$), have been prepared and structurally characterized. Alkane elimination reactions of trialkylaluminum with H[Ph-PNP] (**1a**), H[^{i}Pr-PNP] (**1b**), and H[Ph-PNP-^{i}Pr] (**1c**) in toluene at −35 °C respectively produced the corresponding dialkyl complexes [Ph-PNP]AlR$_2$, [^{i}Pr-PNP]AlR$_2$, and [Ph-PNP-^{i}Pr]AlR$_2$ (R = Me (**2a**−**c**), Et (**3a**−**c**), ^{i}Bu (**4a**−**c**)) in high isolated yield. The dihydride complexes [Ph-PNP]AlH$_2$ (**6a**), [^{i}Pr- PNP]AlH$_2$ (**6b**), and [Ph-PNP-^{i}Pr]AlH$_2$ (**6c**) were prepared in one-pot reactions of in situ prepared dichloride precursors (**5a**−**c**) with LiAlH$_4$ in THF at room temperature. X-ray diffraction studies of **2a**−**c**, **3b**−**c**, **5b**, and **6b** revealed a distorted trigonal-bipyramidal structure for these molecules in which the two phosphorus donors are mutually trans. The solution structures of these organoaluminum complexes were all characterized by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy. The NMR data are indicative of solution C_2 symmetry for [Ph-PNP]$^-$ and [^{i}Pr-PNP]$^-$ complexes, whereas they are indicative of C_1 for [Ph-PNP-^{i}Pr]$^-$ derivatives. The ^{1}H NMR spectra of **3a**−**c** and **4a**−**c** revealed diastereotopy for the α-hydrogen atoms in these molecules.

Introduction

Recent studies on aluminum chemistry have been focused, at least in part, on the search for appropriate ancillary ligands for reactive organoaluminum species due to their increasing role in catalytic polymerization reactions.[1] Much attention has been paid to chelating systems that contain exclusively hard donor atoms.[2−12] Studies involving hybrid chelating ligands incorporating both hard and soft donors, however, remain relatively unexplored.[13−15] In this regard, we have recently prepared a series of mononuclear aluminum complexes of bidentate [NP]$^-$ and tridentate [PNN]$^-$ ligands (Figure 1) that are amido phosphine derivatives.[16,17] Though available, examples of aluminum complexes containing tridentate amido phosphine ligands are extremely rare.[13,17] Pioneering work by Fryzuk and co-workers revealed that phosphine dissociation from certain silyl-derived $AlX_2[N(SiMe_2CH2P^iPr_2)_2]$ complexes may become facile, thereby leading to the formation of four- instead of five-coordinate species.[13]

We have recently shown that incorporation of a relatively rigid *o*-phenylene backbone in the amido diphosphine ligands may inhibit phosphine dissociation, at least to some degree, and thus effectively increase the thermal stability of the derived metal complexes.[18−23] It has also been demonstrated

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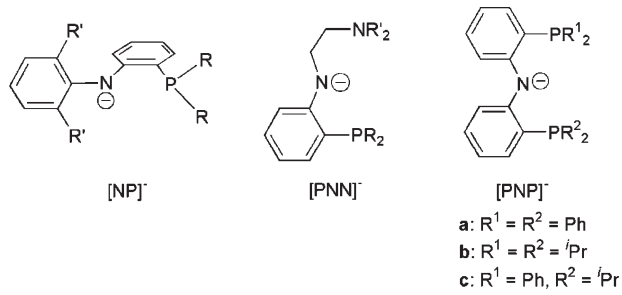


Figure 1. Representative chelating amido phosphine ligands.

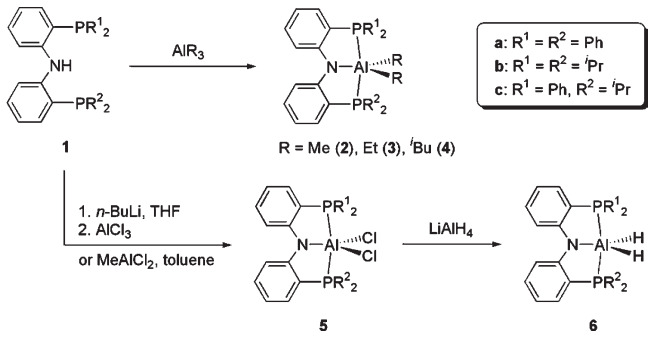
that the reactivity of these diarylamido diphosphine complexes is a function of electronic and steric characteristics of substituents at the phosphorus donors.[24−26] For instance, the reactivity of unsymmetrically substituted nickel hydride complex [Ph-PNP^{i}Pr]NiH ([Ph-PNP-^{i}Pr]$^-$ = [N(*o*-$C_6H_4PPh_2$)(*o*-$C_6H_4P^iPr_2$)]$^-$) with respect to olefin insertion is inferior to that of symmetrically substituted [Ph-PNP]NiH ([Ph-PNP]$^-$ = [N(*o*-$C_6H_4PPh_2)_2$]$^-$) but superior to that of [^{i}Pr-PNP]NiH.[25] In an effort to expand the territory of aluminum chemistry and evaluate the possibility of catalytic polymerization thereafter, we have set out to prepare a series of diarylamido diphosphine complexes of aluminum. In this contribution, we aim to illustrate the coordination chemistry of these aluminum species, taking advantage of the rigidity imposed by the *o*-phenylene backbone. In accord with a computational study on related species that contain a tolyl-derived ligand,[27] the solution NMR spectroscopic and X-ray crystallographic data reported herein are all indicative of a five-coordinate structure for these aluminum complexes.

Results and Discussion

Syntheses. Alkane elimination reactions of H[Ph-PNP][19,23] (**1a**) with AlR_3 in toluene at −35 °C produced the corresponding dialkyl complexes [Ph-PNP]-AlR_2 (R = Me (**2a**), Et (**3a**), ^{t}Bu (**4a**)) in high isolated yields (Scheme 1). Analogous reactions employing H[^{i}Pr- PNP][19] (**1b**) or H[Ph-PNP-^{i}Pr][25] (**1c**) gave [^{i}Pr-PNP]AlR_2 (**2b**−**4b**) and [Ph-PNP-^{i}Pr]AlR_2 (**2c**−**4c**), respectively. These organoaluminum complexes were all isolated as colorless or pale-yellow crystals following standard workup procedures. Interestingly, no THF or Et_2O adduct was formed in spite of the employment of these ethereal solvents in crystallization, consistent with the prediction that phosphine dissociation is not significant.[18−23,27]

Preparation of dihydride complexes was also achieved. The presumed dichloride precursors **5a**−**c** may be prepared in situ either from the metathetical reactions of $AlCl_3$ with the corresponding lithium complexes of the amido diphosphine ligands in THF at −35 °C or by the treatment of $MeAlCl_2$ with the corresponding protio ligands in toluene at −35 °C. Though not isolated, complexes **5a**−**c** are likely produced quantitatively, as evidenced by

Scheme 1



$^{31}P\{^1H\}$ NMR spectra. In an independent experiment, **5b** was isolated in 76% yield as colorless crystals suitable for X-ray diffraction analysis. Subsequent reactions of **5a**−**c** with $LiAlH_4$ in THF at room temperature afforded [Ph-PNP]AlH_2 (**6a**), [^{i}Pr-PNP]AlH_2 (**6b**), and [Ph-PNP-^{i}Pr]AlH_2 (**6c**), respectively, in high overall isolated yields. In general, complexes **2**−**6** are thermally stable but extremely sensitive to moisture. Compounds similar to **2b**, **4b**, and **5b** but derived from a tolyl backbone were prepared similarly.[27]

Solution NMR Studies of Symmetrically Substituted 2a−**6a and 2b**−**6b.** The solution NMR data are all consistent with a C_2-symmetric, five-coordinate structure for these aluminum complexes, in which the tridentate amido diphosphine ligand adopts a meridional coordination mode. Selected data are summarized in Table S1 (Supporting Information). The $^{31}P\{^1H\}$ NMR spectra exhibit a singlet resonance with chemical shifts relatively upfield[28] as compared to those of the corresponding protio ligands (**1a**, −18.6 ppm; **1b**, −13.3 ppm).[19,23] An upfield change in the ^{31}P chemical shift is also observed for [NP]$^-$- and [PNN]$^-$-derived[16,17] or other phosphine coordinated aluminum complexes.[13,14,29−31] The two aluminum-bound alkyl (**2a**−**4a** and **2b**−**4b**) or hydride (**6a**−**b**) ligands are chemically equivalent. Both phosphorus donors in these organoaluminum species are bound to the aluminum center, as evidenced by the triplet resonances observed for the α-carbon atoms in the $^{13}C\{^1H\}$ NMR spectra. In general, the ^{13}C chemical shifts of α-carbons in [^{i}Pr-PNP]$^-$ derivatives are relatively downfield as compared to those of [Ph-PNP]$^-$ analogues due to bulkier and more electron-releasing properties of the phosphorus substituents in the former.[29,32−34] A similar

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(28) The factors responsible for the upfield shift of ^{31}P resonances of these species are not clear at this stage. It has been argued (for instance, see ref 29) that a decrease in C−P−C angles upon phosphine coordination to aluminum would give a more negative ^{31}P shift, but this study shows clearly a reverse trend (see Tables S3 and S4 in the Supporting Information). The difference in electronegativity in the M−P bond and the change in the π-electron overlap seem not to correlate well either, in comparison of the data reported herein with those of group 10 metal and lithium derivatives (refs 19−20, 22−23).
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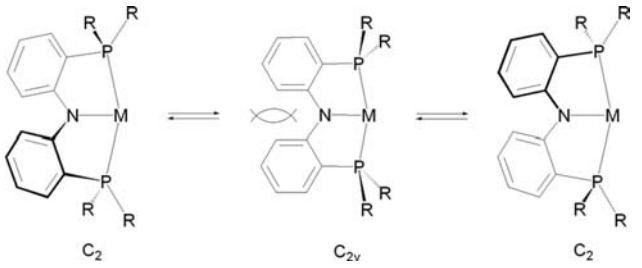
dependence on the steric nature of aluminum-bound alkyls is also observed; that is, the larger isobutyl in **4** gives more downfield shifts for α-carbon resonances than ethyl in **3** or methyl in **2**.

The solution C_2 symmetry observed for **2a**−**6a** and **2b**−**6b** is notably different from the C_{2v} symmetry found for the group 10 complexes[19,20,22−26] of these amido diphosphine ligands due to the presence of time-averaged symmetry planes in the latter, as evidenced by solution NMR data. Such a discrepancy is presumably ascribable to a slower exchange rate for aluminum species in a "flipping"[35−37] process involving two *o*-phenylene rings, as illustrated in Scheme 2. The steric repulsion between two CH moieties ortho to the amido nitrogen donor in the C_{2v} form is likely too much for M = Al to overcome the exchange barrier. A variable-temperature ^{1}H NMR study of **2b** in toluene-d_8 (60 mM) revealed that the two isopropylmethine resonances do not tend to coalesce even at 90 °C, suggesting a significant exchange barrier for the proposed flipping process in this molecule.

Interestingly, among the compounds investigated, complexes **3b** and **4b** exhibit two well-resolved multiplet resonances for the α-hydrogen atoms (Figure S1e,f, Supporting Information), consistent with the anticipated diastereotopic characteristic. The chemical nonequivalence of the α-hydrogen atoms in $AlCH_2R$ (R = H (**2a**,**b**), Me (**3a**,**b**), *i*-Pr (**4a**,**b**)) fragments is ascribable to the lack of symmetry in these molecules with respect to internal rotation involving the Al−C_α bonds.[38] With less sterically demanding hydrocarbyl groups incorporated (e.g., phosphorusbound phenyl in **2a**−**4a** or aluminum-bound methyl in **2a** and **2b**), rapid rotation about the Al−C_α bonds becomes facile, and thus the diastereotopic α-hydrogen atoms are indistinguishable on the NMR time scale.

Solution NMR Studies of Unsymmetrically Substituted 2c−**6c**. With the incorporation of the unsymmetrically substituted [Ph-PNP-^{i}Pr]$^-$ ligand, complexes **2c**−**6c** are C_1-symmetric on the NMR time scale. The ^{31}P{^{1}H} NMR spectra of these species exhibit two doublet resonances, consistent with concomitant coordination of the two distinct phosphorus donors to the aluminum center. Reminiscent of what has been found for the symmetrically substituted counterparts, the ^{31}P chemical shifts of **2c**−**6c** are relatively upfield[28] as compared to those of **1c** (−14.8 for P^{i}Pr$_2$ and −16.7 ppm for PPh_2).[25] The $^2J_{PP}$ coupling constants of 9 Hz for **2c**−**4c** and ca. 49 Hz for **5c**−**6c** are notably smaller than those found for the four-coordinate divalent nickel species such as [Ph-PNP-^{i}Pr]NiH (244 Hz),[25] [Ph-PNP-^{i}Pr]NiEt (271 Hz),[25] and [Ph-PNP-^{i}Pr]Ni(*n*-hexyl) (273 Hz).[25] Such discrepancy is perhaps a consequence of smaller P−M−P angles for the five-coordinate aluminum species than for the four-coordinate nickel derivatives. The decreased P−M−P angles for the former appear to reflect somewhat greater steric repulsion between the phosphorus substituents and two aluminum-bound anionic ligands than that arising from one nickel-bound ligand due to distinct coordination geometries. The ^{1}H and ^{13}C{^{1}H} NMR spectra of **2c**−**6c** exhibit two sets of resonances for the P^{i}Pr$_2$ moiety, indicating the absence of a symmetry plane in these molecules. Consistently, the aluminum-bound alkyls in **2c**−**4c** are chemically inequivalent. The hydride ligands in **6c** display a broad singlet resonance at 5.25 ppm ($\Delta\nu_{1/2}$ = 80 Hz) due likely to the fast relaxation of quadrupolar aluminum atoms (^{27}Al, I = 5/2, 100% natural abundance).[39,40] As anticipated, the α-hydrogen atoms in **3c** and **4c** are diastereotopic, as evidenced by the ^{1}H NMR spectra (Figure S1h,i, Supporting Information).

Scheme 2



X-Ray Studies. X-ray diffraction studies of **2a**, **2b**, **2c**, **3b**, **3c**, **5b**, and **6b** established the solid-state structures of these dialkyl, dichloride, and dihydride complexes. Crystallographic data are given in Table 1. Selected bond distances and angles are summarized in Tables 2 and 3, respectively. As depicted in Figures S2−S4 (Supporting Information), the coordination geometry of these molecules is best described as a distorted trigonal bipyramid with the two phosphorus donors being at the axial positions, consistent with that established by solution NMR spectroscopy. The aluminum center lies perfectly on the equatorial plane defined by the amido nitrogen and the two anionic, monodentate ligands as evidenced by the sum (ca. 360°) of the bond angles involving these equatorial donors. The C−Al−C angles in the dialkyl **2a**, **2b**, **2c**, **3b**, and **3c** are generally close to the ideal value of 120° for a trigonal-bipyramidal structure, but the Cl−Al−Cl angle in **5b** is relatively sharp, as anticipated from the standpoint of the higher electronegativity of Cl (3.16) than that of C (2.55).[41] Consistently, the Al−P distances of dichloride **5b** are significantly shorter than those of dialkyls.[27] In unsymmetrically substituted **2c** and **3c**, the Al−P distance corresponding to the isopropyl substituted arm (**2c**, 2.5499(18) Å; **3c**, 2.5700(13) Å) is notably shorter than that involving phenyl (**2c**, 2.7902(17) Å; **3c**, 2.8038 (13) Å), in agreement with the anticipated electron-releasing properties of these phosphorus substituents. The P−Al−P angles of dialkyls **2a**, **2b**, **2c**, **3b**, and **3c** are slightly sharper than those of dichloride **5b** and dihydride **6b**. The discrepancy in P−Al−P angles of dialkyls versus dichloride or dihydride is somewhat in accord with the observed $^2J_{PP}$ coupling constants found

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Table 1. Crystallographic Data for **2a**, **2b**, **2c**, **3b**, **3c**, **5b**, and **6b**

	[Ph-PNP]AlMe$_2$ (**2a**)	[^{i}Pr-PNP]AlMe$_2$ (**2b**)	[Ph-PNP-Pr]AlMe$_2$ (**2c**)
formula	$C_{38}H_{34}AlNP_2$	$C_{33}H_{50}AlNP_2$	$C_{32}H_{38}AlNP_2$
fw	593.58	549.66	525.55
cryst syst	monoclinic	monoclinic	triclinic
space group	$C2/c$	$P2_1/a$	$P\bar{1}$
a (Å)	19.5904(10)	15.0610(3)	9.4805(3)
b (Å)	9.7111(5)	14.6720(3)	11.5257(3)
c (Å)	18.8411(11)	15.6740(3)	16.6500(6)
α (deg)	90	90	108.584(2)
β (deg)	112.537(2)	108.1360(10)	96.379(2)
γ (deg)	90	90	107.357(2)
V (Å3)	3310.7(3)	3291.49(11)	1602.63(9)
Z	4	4	2
D_{calcd} (Mg/m^3)	1.191	1.109	1.089
$2\theta_{max}$(deg)	50.68	50.06	55.28
total reflns	10273	22662	22264
independent reflns	3008	5796	5780
abs coeff (mm $^{-1}$)	0.184	0.180	0.182
data/restraints/ params	3008/ 0/192	5796/ 0/343	5780/0/325
no. observed data	1795	4145	3398
R_{int}	0.0983	0.0753	0.1074
goodness of fit	0.977	1.051	0.847
final R indices	R1 = 0.0957	R1 = 0.0582	R1 = 0.0767
[$I > 2\sigma(I)$]	wR2 = 0.2214	wR2 = 0.1148	wR2 = 0.2232
R indices (all data)	R1 = 0.1591	R1 = 0.0883	R1 = 0.1316
	wR2 = 0.2943	wR2 = 0.1629	wR2 = 0.2612

	[Pr-PNP]AlEt$_2$ (**3b**)	[Ph-PNP-Pr]AlEt$_2$ (**3c**)	[Pr-PNP]AlCl$_2$ (**5b**)	[^{i}Pr-PNP]AlH$_2$ (**6b**)
formula	$C_{28}H_{46}AlNP_2$	$C_{34}H_{42}AlNP_2$	$C_{24}H_{36}AlCl_2NP_2$	$C_{24}H_{38}AlNP_2$
fw	485.58	553.61	498.36	429.47
cryst syst	triclinic	monoclinic	monoclinic	orthorhombic
space group	$P\bar{1}$	$P2_1/n$	$P2/a$	$Pcab$
a (Å)	9.19800(10)	9.7634(2)	17.2082(4)	11.6641(3)
b (Å)	18.7320(2)	14.2656(4)	9.2626(3)	29.3264(7)
c (Å)	19.0670(3)	22.6357(6)	18.4636(6)	29.9414(9) 90
α (deg)	62.1130(10)	90	90	90
β (deg)	86.9810(10)	91.8880(10)	116.8740(10)	90
γ (deg)	87.6650(10)	90	90	90
V (Å3)	2899.17(6)	3151.01(14)	2625.13(14)	10241.9(5)
Z	4	4	4	16
D_{calcd} (Mg/m^3)	1.112	1.167	1.261	1.114
$2\theta_{max}$ (deg)	50.14	50.70	50.64	50.70
total reflns	40129	18635	16573	31956
independent reflns	10229	5659	4770	9158
abs coeff (mm $^{-1}$)	0.196	0.189	0.415	0.214
data/restraints/ params	10229/ 0/577	5659/0/344	4770/ 0/274	9158/0/505
no. observed data	8070	4212	3684	4596
R_{int}	0.0694	0.0765	0.0816	0.1447
goodness of fit	1.061	1.107	1.224	1.099
final R indices	R1 = 0.0469	R1 = 0.0621	R1 = 0.1111	R1 = 0.0957
[$I > 2\sigma(I)$]	wR2 = 0.1116	wR2 = 0.1495	wR2 = 0.3116	wR2 = 0.2138
R indices (all data)	R1 = 0.0655	R1 = 0.0933	R1 = 0.1398	R1 = 0.2040
	wR2 = 0.1217	wR2 = 0.1764	wR2 = 0.3355	wR2 = 0.2761

for the [Ph-PNP-^{i}Pr]$^-$-derived dialkyls **2c**−**4c** versus dichloride **5c** or dihydride **6c** (vide supra). In comparison, the P−M−P angles for four-coordinate group 10 complexes of these amido diphosphine ligands are much wider, for example, [^{i}Pr-PNP]NiH (175.05(4)°),[25] [Ph- PNP]NiMe (169.05(9)°),[19] [^{i}Pr-PNP]NiMe (166.68 (5)°),[19] [Ph-PNP-^{i}Pr]Ni(*n*-hexyl) (165.65(9)°),[25] [Ph-PNP] PdCl (165.27(11)°),[22] and [Ph-PNP]PtCl (167.30(8)°).[20] The sharper P−M−P angles for M = Al versus those of M = group 10 metals are ascribed to longer M−P bonds for the former, given that the M−N and M−X (X = C, Cl) distances are very similar. This leads to a closer contact for the two CH moieties ortho to the amido nitrogen in the C_{2v} form of the aluminum species and thus a larger dihedral angle between two N-phenylene-P mean planes in the solid state. As a result, the flipping exchange barrier is much higher. Table S2 (Supporting Information) summarizes the dihedral angles of representative examples for comparison. To illustrate, two views of the X-ray structures of **2b** (left) and [^{i}Pr-PNP]NiMe (right) are depicted in Figure S5 (Supporting Information), highlighting the spatial orientation of the two aromatic CH groups ortho to the amido nitrogen donor (top) and the "wedge" formed by the two *o*-phenylene rings in the ligand backbone (bottom). Notably, the "wedge" in [^{i}Pr-PNP]NiMe is much sharper. In **2b**, both CH11 and CH14 moieties are oriented such that the transient C_{2v} structure proposed in Scheme 2 is rather inaccessible. The corresponding space available for the nickel species to undergo such exchange, however, is much larger. Consistent with the relatively short Al−P distances and acute dihedral angles found for **5b**, the

Table 2. Selected Bond Distances (Å) for **2a**, **2b**, **2c**, **3b**, **3c**, **5b**, and **6b**[a]

compound	Al−N	Al−X[a]	Al−P
[Ph-PNP]AlMe$_2$ (**2a**)	1.940(7)	1.968(6), 1.968(6)	2.6202(13), 2.6202(13)
[^{i}Pr-PNP]AlMe$_2$ (**2b**)	1.935(2)	1.969(3), 1.977(3)	2.6343(10), 2.6246(10)
[Ph-PNP-^{i}Pr]AlMe$_2$ (**2c**)	2.019(4)	1.823(6), 2.045(5)	2.5499(18), 2.7902(17)
[^{i}Pr-PNP]AlEt$_2$ (**3b**)[b]	1.9287(19)	1.977(3), 1.986(3)	2.6514(9), 2.6578(9)
[^{i}Pr-PNP]AlEt$_2$ (**3b**)[c]	1.9400(19)	1.983(2), 1.985(2)	2.6300(9), 2.6234(9)
[Ph-PNP-^{i}Pr]AlEt$_2$ (**3c**)	1.915(3)	1.978(3), 1.984(3)	2.5700(13), 2.8038(13)
[^{i}Pr-PNP]AlCl$_2$ (**5b**)[b]	1.932(10)	2.198(3), 2.198(3)	2.481(2), 2.481(2)
[^{i}Pr-PNP]AlCl$_2$ (**5b**)[c]	1.916(10)	2.201(3), 2.201(3)	2.497(2), 2.497(2)
[^{i}Pr-PNP]AlH$_2$ (**6b**)[b]	1.899(6)	1.3279, 1.3602	2.570(2), 2.590(2)
[^{i}Pr-PNP]AlH$_2$ (**6b**)[c]	1.913(6)	1.3747, 1.3677	2.543(2), 2.545(3)

[a] X represents an α-carbon, a chloride, or a hydrogen atom. [b] The data summarized represent one of the two independent molecules found in the asymmetric unit cell. [c] The data summarized represent one of the two independent molecules found in the asymmetric unit cell.

Table 3. Selected Bond Angles (deg) for **2a**, **2b**, **2c**, **3b**, **3c**, **5b**, and **6b**[a]

compound	N−Al−P	P−Al−P	P−Al−X[a]	N−Al−X[a]	X−Al−X[a]
[Ph-PNP]AlMe$_2$ (**2a**)	77.64(6), 77.64(6)	155.28(12)	96.12(18), 96.12(18), 96.36(18), 96.36(18)	120.5(2), 120.5(2)	119.0(5)
[^{i}Pr-PNP]AlMe$_2$ (**2b**)	77.65(7), 77.31(7)	154.95(4)	96.73(10), 95.72(10), 96.35(10), 96.20(10)	120.16(14), 120.14(13)	119.70(16)
[Ph-PNP-^{i}Pr]AlMe$_2$ (**2c**)	79.20(11), 73.36(11)	152.52(7)	101.89(17), 100.13(15), 87.53(17), 96.71(14)	112.7(2), 124.8(2),	121.1(3)
[^{i}Pr-PNP]AlEt$_2$ (**3b**)[b]	77.84(6), 77.79(6)	155.62(3)	93.68(8), 99.08(8), 99.59(8), 93.58(8)	122.10(10), 122.50(10)	115.40(12)
[^{i}Pr-PNP]AlEt$_2$ (**3b**)[c]	77.97(6), 78.27(6)	156.23(3)	93.74(8), 99.27(7), 99.60(7), 92.77(7)	122.24(10), 122.58(10)	115.18(11)
[Ph-PNP-^{i}Pr]AlEt$_2$ (**3c**)	80.21(8), 74.21(8)	154.40(5)	104.72(11), 98.28(11), 88.12(11), 92.46(11)	117.70(14), 116.50(14)	123.66(16)
[^{i}Pr-PNP]AlCl$_2$ (**5b**)[b]	80.18(9), 80.18(9)	160.36(18)	97.12(8), 93.93(8), 93.93(8), 97.12(8)	124.34(10), 124.34(10)	111.32(19)
[^{i}Pr-PNP]AlCl$_2$ (**5b**)[c]	79.86(9), 79.86(9)	159.72(18)	96.95(8), 94.05(8), 94.05(8), 96.95(8)	123.00(11), 123.00(11)	114.0(2)
[^{i}Pr-PNP]AlH$_2$ (**6b**)[b]	79.72(16), 79.31(16)	159.11(11)	93.2,95.7, 87.6, 104.5	112.7, 127.4	118.8
[^{i}Pr-PNP]AlH$_2$ (**6b**)[c]	79.41(16), 80.32(16)	159.60(11)	97.3, 86.8, 98.1, 91.4	104.5, 115.1,	139.4

[a] X represents an α-carbon, a chloride, or a hydrogen atom. [b] The data summarized represent one of the two independent molecules found in the asymmetric unit cell. [c] The data summarized represent one of the two independent molecules found in the asymmetric unit cell.

flipping exchange barrier of this molecule is the lowest among the aluminum species investigated. A variable-temperature ^{1}H NMR study revealed that the isopropylmethine resonances of **5b** (60 mM in toluene-d_8) coalesce at 80 °C.

Catalytic Polymerization. Preliminary studies revealed that organoaluminum complexes of these amido diphosphine ligands are highly[42] active initiators for catalytic α-olefin polymerization. In the presence of $B(C_6F_5)_3$, **2a**−**c** reacts with ethylene or 1-hexene at room temperature catalytically to produce the corresponding polymers with activities of ca. 4×10^5 g mol$_{cat}^{-1}$ h^{-1} atm^{-1} or 3×10^4 g mol$_{cat}^{-1}$ h^{-1}, respectively.

Conclusions

We have prepared and characterized a series of organoaluminum complexes of diarylamido diphosphine ligands. Solution NMR and X-ray crystallographic studies reveal a five-coordinate nature for these species in which the tridentate amido diphosphine ligands adopt a meridional coordination mode. With the incorporation of the relatively rigid *o*-phenylene in the ligand backbone, phosphine dissociation from the aluminum center of these molecules was not observed, even in the presence of coordinating solvents such

(42) Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem., Int. Ed.* **1999**, *38*, 429–447.

as THF or Et_2O. The solution symmetry of these aluminum complexes is notably lower than that of the corresponding four-coordinate group 10 derivatives. NMR studies indicate that the symmetrically substituted [Ph-PNP]$^-$ and [^{i}Pr-PNP]$^-$ complexes are C_2-symmetric, while [Ph-PNP-^{i}Pr]$^-$ derivatives are C_1. The α-hydrogen atoms in these dialkyl complexes are diastereotopic. Depending on steric demand of the substituents at phosphorus and α-carbon atoms, well-resolved multiplet resonances may be observed by ^{1}H NMR spectroscopy. Interestingly, the $^2J_{PP}$ coupling constants observed in [Ph-PNP-^{i}Pr]$^-$ complexes appear to correlate well with the P−M−P angles (M = Al or group 10 metals) established by X-ray crystallography. In the presence of B$(C_6F_5)_3$, these aluminum complexes are active initiators for catalytic α-olefin polymerization.

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. All other chemicals were obtained from commercial vendors and used as received. 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 ($\Delta\nu_{1/2}$) are in hertz. ^{1}H and ^{13}C NMR spectra are referenced to an internal solvent peak at δ 7.16 and δ 128.39, respectively, for C_6D_6. The assignment of the carbon atoms for all new compounds is based on the DEPT ^{13}C NMR spectroscopy. ^{31}P NMR spectra are referenced externally using 85% H_3PO_4 at δ 0. Routine coupling constants are not listed. Elemental analysis was performed on a Heraeus CHN-O Rapid analyzer. With multiple attempts, we were not able to obtain satisfactory analysis for some complexes reported herein due to extreme moisture-sensitivity of these derivatives.

X-Ray Crystallography. Table 1 summarizes the crystallographic data for all structurally characterized compounds. Data were collected at 200 K on a Bruker-Nonius Kappa CCD diffractometer with graphite monochromated Mo Kα radiation (λ = 0.7107 Å). Structures were solved by direct methods and refined by full-matrix least-squares procedures against F^2 using maXus or WinGX crystallographic software package. All full-weight nonhydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions. The crystals of [^{i}Pr-PNP]$AlCl_2$ (**5b**) were of poor quality but sufficient to establish the identity of this molecule.

General Procedures for Synthesis of 2a−c, 3a−c, and 4a−c. To a toluene solution of **1a**, **1b**, or **1c** at −35 °C was added AlR_3 (1 equiv, R = Me, Et, ^{i}Bu). The reaction solution was naturally warmed to room temperature with stirring. After being stirred at room temperature overnight, the reaction solution was filtered through a pad of Celite, concentrated under reduced pressure, and cooled to −35 °C to afford the product as a pale yellow or colorless solid.

Synthesis of [Ph-PNP]$AlMe_2$ (2a). Colorless crystals suitable for X-ray diffraction analysis were grown by layering THF on a concentrated toluene solution at −35 °C. Yield: 83%. ^{1}H NMR (C_6D_6, 500 MHz): δ 7.56 (t, 4, J = 7.5, Ar), 7.48 (t, 4, J = 7.5, Ar), 7.01 (m, 16, Ar), 6.92 (t, 2, J = 7.75, Ar), 6.59 (t, 2, J = 7.5, Ar), 0.14 (t, 6, $^3J_{HP}$ = 6, AlMe_2). ^{31}P{^{1}H} NMR (C_6D_6, 202.31 MHz): δ −19.66. ^{13}C{^{1}H} NMR (C_6D_6, 125.5 MHz): δ 159.89 (m, C), 134.32 (m, CH), 134.16 (m, CH), 134.05 (s, CH), 133.32 (m, C), 132.80 (m, C), 132.48 (s, CH), 130.30 (s, CH), 129.75 (s, CH), 129.28 (m, CH), 129.21 (m, CH), 124.32 (m, C), 121.72 (s, CH), 121.02 (s, CH), −5.94 (t, $^2J_{CP}$ = 32.13, AlMe_2). Anal. calcd for $(C_{38}H_{34}AlNP_2)(THF)_2$: C, 74.87; H, 6.84; N, 1.90. Found: C, 74.78; H, 6.87; N, 2.37.

Synthesis of [^{i}Pr-PNP]$AlMe_2$ (2b). Colorless crystals suitable for X-ray diffraction analysis were grown by layering pentane on a concentrated diethyl ether solution at −35 °C. Yield: 81%. ^{1}H NMR (C_6D_6, 500 MHz): δ 7.28 (m, 2, Ar), 7.02 (m, 4, Ar), 6.72 (t, 2, J = 7, Ar), 2.07 (m, 2, CHMe$_2$), 1.79 (m, 2, CHMe2), 1.12 (dd, 6, CHMe_2), 1.07 (dd, 6, CHMe_2), 1.04 (dd, 6, CHMe_2), 0.85 (dd, 6, CHMe_2), −0.10 (t, 6, $^3J_{HP}$ = 5.5, AlMe_2). ^{31}P{^{1}H} NMR (C_6D_6, 202.31 MHz): δ −17.66. ^{13}C{^{1}H} NMR (C_6D_6, 125.5 MHz): δ 160.89 (t, J_{CP} = 11.04, C), 133.19 (s, CH), 131.41 (s, CH), 121.43 (t, J_{CP} = 1.76, CH), 119.34 (s, CH), 119.22 (d, J_{CP} = 6.40, C), 23.31 (br s, CHMe$_2$), 19.80 (t, J_{CP} = 4.14, CHMe_2), 19.70 (t, J_{CP} = 3.14, CHMe_2), 19.63 (m, CHMe$_2$), 19.26 (t, J_{CP} = 7.41, CHMe_2), 16.91 (br s, CHMe_2), −1.83 (t, $^2J_{CP}$ = 34.45, AlMe_2). Anal. calcd for $C_{26}H_{42}AlNP_2$: C, 68.23; H, 9.26; N, 3.06. Found: C, 67.86; H, 9.25; N, 3.04.

Synthesis of [Ph-PNP-^{i}Pr]$AlMe_2$ (2c). Colorless crystals suitable for X-ray diffraction analysis were grown by layering diethyl ether on a concentrated toluene solution at −35 °C. Yield: 78%. ^{1}H NMR (C_6D_6, 500 MHz): δ 7.55 (m, 4, Ar), 7.44 (dt, 1, J = 1.5 and 7.5, Ar), 7.22 (dd, 1, J = 5.5 and 7.5, Ar), 7.13 (m, 1, Ar), 7.05 (m, 6, Ar), 6.99 (m, 1, Ar), 6.90 (m, 2, Ar), 6.69 (t, 1, J = 7.5, Ar), 6.61 (t, 1, J = 7, Ar), 2.01 (m, 1, CHMe$_2$), 1.77 (m, 1, CHMe$_2$), 1.01 (dd, 3, CHMe_2), 1.03 (dd, 3, CHMe_2), 1.00 (dd, 3, CHMe_2), 0.84 (dd, 3, CHMe_2), 0.09 (dd, 3, $^3J_{HP}$ = 5 and 5.5, AlMe), −0.06 (dd, 3, $^3J_{HP}$ = 5 and 5.5, AlMe). ^{31}P{^{1}H} NMR (C_6D_6, 202.31 MHz): δ −15.63 (d, 1, $^2J_{PP}$ = 8.70, P^{i}Pr2), −20.89 (d, 1, $^2J_{PP}$ = 8.70, PPh$_2$). ^{13}C{^{1}H} NMR (C_6D_6, 125.5 MHz): δ 161.71 (dd, J_{CP} = 1.38 and 18.83, C), 158.86 (dd, J_{CP} = 1.88 and 22.46, C), 135.50 (d, J_{CP} = 3.26, C), 134.79 (s, CH), 134.62 (d, J_{CP} = 3.64, C), 134.43 (d, J_{CP} = 15.19, CH), 134.22 (d, J_{CP} = 15.56, CH), 132.89 (s, CH), 132.21 (s, CH), 131.73 (s, CH), 129.71 (s, CH), 129.37 (s, CH), 129.19 (d, J_{CP} = 7.28, CH), 129.06 (d, J_{CP} = 7.28, CH), 126.71 (d, J_{CP} = 16.44, C), 121.90 (s, CH), 121.87 (s, CH), 121.14 (d, J_{CP} = 2.26, CH), 119.31 (d, J_{CP} = 3.77, CH), 117.39 (d, J_{CP} = 25.60, C), 23.05 (d, J_{CP} = 6.90, CHMe$_2$), 19.97 (d, J_{CP} = 12.30, CHMe$_2$), 19.56 (d, J_{CP} = 5.90, CHMe_2), 19.43 (d, J_{CP} = 5.02, CHMe_2), 19.16 (d, J_{CP} = 11.92, CHMe_2), 17.16 (d, J_{CP} = 3.64, CHMe_2), −3.28 (dd, $^2J_{CP}$ = 32.88 and 33.01, AlMe), −5.17 (dd, $^2J_{CP}$ = 28.74 and 29.74, AlMe). Anal. calcd for $C_{32}H_{38}AlNP_2$: C, 73.13; H, 7.29; N, 2.67. Found: C, 73.58; H, 7.34; N, 2.42.

Synthesis of [Ph-PNP]$AlEt_2$ (3a). Yield: 81%. ^{1}H NMR (C_6D_6, 500 MHz): δ 7.56 (m, 8, Ar), 7.03 (m, 16, Ar), 6.94 (td, 2, Ar), 6.59 (t, 2, J = 7.5, Ar), 1.31 (t, 6, J = 8.5, $AlCH_2Me$), 0.80 (m, 4, $AlCH_2$Me). ^{31}P{^{1}H} NMR (C_6D_6, 202.31 MHz): δ −20.53. ^{13}C{^{1}H} NMR (C_6D_6, 125.5 MHz): δ 160.38 (m, C), 134.39 (m, CH), 133.95 (m, CH), 133.86 (m, CH), 133.55 (m, C), 133.44 (m, C), 132.48 (s, CH), 130.19 (s, CH), 129.87 (s, CH), 129.31 (m, CH), 129.26 (m, CH), 124.04 (dd, J_{CP} = 28.80 and 1.76, C), 121.74 (s, CH), 121.09 (s, CH), 10.82 (t, $^3J_{CP}$ = 2.76, $AlCH_2Me$), 3.49 (t, $^2J_{CP}$ = 28.87, $AlCH_2$Me). Anal. calcd for $C_{40}H_{38}AlNP_2$: C, 77.27; H, 6.17; N, 2.25. Found: C, 77.43; H, 6.55; N, 2.55.

Synthesis of [^{i}Pr-PNP]$AlEt_2$ (3b). Colorless crystals suitable for X-ray diffraction analysis were grown by layering pentane on a concentrated diethyl ether solution at −35 °C. Yield: 87%. ^{1}H NMR (C_6D_6, 500 MHz): δ 7.23 (dd, 2, J = 4 and 8, Ar), 7.02 (m, 4, Ar), 6.72 (t, 2, J = 7.5, Ar), 2.13 (m, 2, CHMe$_2$), 1.84 (m, 2, CHMe$_2$), 1.47 (t, 6, J = 8, $AlCH_2CH_3$), 1.14 (dd, 6, CHMe_2), 1.10 (dd, 6, CHMe_2), 1.04 (dd, 6, CHMe_2), 0.84 (dd, 6, CHMe_2), 0.43 (m, 2, $AlCH_AH_B$), 0.36 (m, 2, $AlCH_AH_B$). ^{31}P{^{1}H} NMR (C_6D_6, 202.31 MHz): δ −16.76. ^{13}C{^{1}H} NMR (C_6D_6, 125.5 MHz): δ 161.00 (m, J_{CP} = 10.542, C), 133.16 (s, CH), 131.31 (s, CH), 121.56 (t, J_{CP} = 2.26, CH), 119.38 (s, CH), 118.89 (m, C), 23.71 (s, CHMe2), 19.79 (m, CHMe2), 19.52 (t, J_{CP} = 4.14, CHMe_2), 19.26 (t, $^3J_{CP}$ = 6.90, CHMe_2), 16.58 (t, $^3J_{CP}$ = 2.76, CHMe_2), 12.12 (t, $^3J_{CP}$ = 5.40, $AlCH_2CH_3$), 5.39 (t, $^2J_{CP}$ = 32.00, $AlCH_2CH_3$). Anal. calcd for

$C_{28}H_{46}AlNP_2$: C, 69.24; H, 9.55; N, 2.89. Found: C, 69.60; H, 9.21; N, 2.59.

Synthesis of [Ph-PNP-^{i}Pr]AlEt$_2$ (3c). Colorless crystals suitable for X-ray diffraction analysis were grown by layering diethyl ether on a concentrated toluene solution at −35 °C. Yield: 88%. ^{1}H NMR (C_6D_6, 500 MHz): δ 7.59 (dt, 2, Ar), 7.54 (dt, 2, Ar), 7.21 (m, 1, Ar), 7.13 (m, 1, Ar), 7.05 (m, 7, Ar), 6.99 (m, 1, Ar), 6.91 (m, 2, Ar), 6.68 (t, 1, J = 7, Ar), 6.62 (t, 1, J = 7, Ar), 2.07 (m, 1, C*H*Me$_2$), 1.85 (m, 1, C*H*Me$_2$), 1.47 (t, 3, J = 8, AlCH$_2$C*H*$_3$), 1.26 (t, 3, J = 8, AlCH$_2$C*H*$_3$), 1.09 (dd, 3, CH*Me*$_2$), 1.06 (dd, 3, CH*Me*$_2$), 1.04 (dd, 3, CH*Me*$_2$), 0.84 (dd, 3, CH*Me*$_2$), 0.79 (m, 1, AlC*H*$_A$H$_B$), 0.57 (m, 2, AlC*H*$_2$), 0.50 (m, 1, AlCH$_A$*H*$_B$). ^{31}P{^{1}H} NMR (C_6D_6, 202.31 MHz): δ −14.92 (d, $^2J_{PP}$ = 9.10, P^{i}Pr$_2$), −20.38 (d, $^2J_{PP}$ = 9.10, PPh$_2$). ^{13}C{^{1}H} NMR (C_6D_6, 125.5 MHz): δ 161.89 (d, J_{CP} = 18.20, C), 159.25 (dd, J_{CP} = 1.76 and 22.84, C), 135.65 (d, J_{CP} = 3.26, C), 135.26 (d, J_{CP} = 3.26, C), 134.78 (s, CH), 134.48 (d, J_{CP} = 15.19, CH), 133.89 (d, J_{CP} = 15.56, CH), 132.74 (s, CH), 132.15 (s, CH), 131.73 (s, CH),129.66 (s, CH), 129.39 (s, CH), 129.17 (d, J_{CP} = 6.78, CH), 129.09 (d, J_{CP} = 7.28, CH), 126.10 (d, C), 121.89 (s, CH), 121.85 (s, CH), 121.12 (d, J_{CP} = 2.64, CH), 119.37 (d, J_{CP} = 3.64, CH), 117.24 (d, J_{CP} = 24.72, C), 23.24 (d, J_{CP} = 5.52, *C*HMe$_2$), 20.08 (d, J_{CP} = 11.42, CH*Me*$_2$), 19.68 (d, J_{CP} = 6.40, CH*Me*$_2$), 19.18 (d, J_{CP} = 8.66, CH*Me*$_2$), 19.12 (d, J_{CP} = 2.39, CH*Me*$_2$), 16.85 (d, J_{CP} = 4.52, CH*Me*$_2$), 11.54 (dd, $^3J_{CP}$ = 3.64 and 5.52, AlCH$_2$*C*H$_3$), 10.96 (t, $^3J_{CP}$ = 2.26, AlCH$_2$*C*H$_3$), 4.75 (dd, $^2J_{CP}$ = 24.72 and 30.25, AlCH$_2$*C*H$_3$), 3.64 (dd, $^2J_{CP}$ = 26.98 and 27.36, AlCH$_2$*C*H$_3$). Anal. calcd for $C_{34}H_{42}AlNP_2$: C, 73.74; H, 7.65; N, 2 0.53. Found: C, 73.70; H, 7.12; N, 2.48.

Synthesis of [Ph-PNP]Al^{i}Bu$_2$ (4a). Yield: 78%. ^{1}H NMR (C_6D_6, 500 MHz): δ 7.65 (dt, 4, Ar), 7.51 (dt, 4, Ar), 7.13 (m, 4, Ar), 7.06 (m, Ar), 6.99 (m, Ar), 6.61 (t, 2, J = 7.5, Ar), 2.13 (m, 2, AlCH$_2$C*H*Me$_2$), 1.12 (d, 6, AlCH$_2$CH*Me*$_2$), 0.99 (d, 6, AlCH$_2$CH*Me*$_2$), 0.74 (m, 4, AlC*H*$_2$CHMe$_2$). ^{31}P{^{1}H} NMR (C_6D_6, 202.31 MHz): δ −20.12. ^{13}C{^{1}H} NMR (C_6D_6, 125.5 MHz): δ 160.38 (m, C), 135.23 (m, CH), 134.63 (d, J_{CP} = 11.42, C), 134.38 (s, CH), 133.95 (m, CH), 133.54 (d, J_{CP} = 12.80, C), 132.58 (s, CH), 130.30 (s, CH), 130.11 (s, CH), 129.47 (t, J_{CP} = 3.64, CH), 129.30 (t, J_{CP} = 3.36, CH), 124.16 (dd, J_{CP} = 1.76 and 5.48, C), 122.38 (t, J_{CP} = 1.88, CH), 121.41 (s, CH), 29.73 (s, AlCH$_2$CH*Me*$_2$), 28.47 (s, AlCH$_2$CH*Me*$_2$), 28.05 (t, $^3J_{CP}$ = 2.76, AlCH$_2$*C*HMe$_2$), 25.32 (t, $^2J_{CP}$ = 26.10, AlC*H*$_2$CHMe$_2$). Anal. calcd for $C_{44}H_{46}AlNP_2$: C, 77.96; H, 6.85; N, 2.07. Found: C, 77.92; H, 6.36 ; N, 2.54.

Synthesis of [^{i}Pr-PNP]Al^{i}Bu$_2$ (4b). Yield: 89%. ^{1}H NMR (C_6D_6, 500 MHz): δ 7.23 (dd, 2, J = 3.5 and 8, Ar), 7.02 (m, 4, Ar), 6.72 (t, 2, J = 4.75, Ar), 2.16 (m, 2, C *H*Me$_2$), 2.04 (m, 2, AlCH$_2$C*H*Me$_2$), 1.85 (m, 2, C*H*Me$_2$), 1.33 (d, 6, J = 6.5, AlCH$_2$CH*Me*$_2$), 1.24 (d, 6, AlCH$_2$CH*Me*$_2$), 1.18 (dd, 6, CH*Me*$_2$), 1.14 (dd, 6, CH*Me*$_2$), 1.04 (dd, 6, CH*Me*$_2$), 0.84 (dd, 6, CH*Me*$_2$), 0.44 (dd, 2, J = 4 and 13.5, AlC*H*$_A$H$_B$), 0.29 (m, 2, AlCH$_A$*H*$_B$). ^{31}P{^{1}H} NMR (C_6D_6, 202.31 MHz): δ −17.56. ^{13}C{^{1}H} NMR (C_6D_6, 125.5 MHz): δ 160.56 (m, C), 133.08 (s, CH), 131.23 (s, CH), 121.87 (t, J_{CP} = 2.26, CH), 119.42 (s, CH), 118.93 (m, C), 30.29 (s, CH*Me*$_2$), 28.73 (t, J_{CP} = 6.90, *C*HMe$_2$), 28.47 (m, AlCH$_2$CHMe$_2$), 28.36 (s, CH*Me*$_2$), 24.00 (s, *C*HMe$_2$), 20.04 (m, *C*HMe$_2$), 19.88 (t, J_{CP} = 4.14, CH*Me*$_2$), 19.85 (t, J_{CP} = 3.14, CH*Me*$_2$), 18.96 (t, J_{CP} = 6.90, CH*Me*$_2$), 16.31 (t, J_{CP} = 2.76, CH*Me*$_2$). Anal. calcd for $C_{32}H_{54}AlNP_2$: C, 70.95; H, 10.05; N, 2.59. Found: C, 71.56; H, 10.45; N, 2.65.

Synthesis of [Ph-PNP-^{i}Pr]Al^{i}Bu$_2$ (4c). Yield: 88%. ^{11}H NMR (C_6D_6, 500 MHz): δ 7.65 (t, 2, J = 7.5, Ar), 7.50 (t, 2, J = 8, Ar), 7.22 (m, 2, Ar), 7.12 (m, 2, Ar), 7.04 (m, 6, Ar), 6.92 (m, 2, Ar), 6.70 (t, 1, J = 7.5, Ar), 6.62 (t, 1, J = 7.5, Ar), 2.15 (m, 3, C*H*Me$_2$), 1.90 (m, 1, C*H*Me$_2$), 1.24 (m, 6, CH*Me*$_2$), 1.10 (m, 15, CH*Me*$_2$), 0.85 (m, 3, CH*Me*$_2$), 0.69 (m, 1, AlC*H*$_A$H$_B$), 0.64 (m, 1, AlCH$_A$*H*$_B$), 0.50 (m, 1, AlC*H*$_{A'}$H$_{B'}$), 0.42 (m, 1, AlCH$_{A'}$*H*$_{B'}$). ^{31}P{^{1}H} NMR (C_6D_6, 202.31 MHz): δ −14.86 (d, 1, $^2J_{PP}$ = 9.10, P^{i}Pr$_2$), −18.90 (d, 1, $^2J_{PP}$ = 9.10, PPh$_2$). ^{13}C{^{1}H} NMR (C_6D_6, 125.5 MHz): δ 161.68 (d, J_{CP} = 18.32, C), 158.60 (dd, J_{CP} = 1.88 and 23.85, C), 136.57 (s, C), 135.94 (s, C), 135.18 (s, CH), 134.57 (d, J_{CP} = 15.56, CH), 133.94 (d, J_{CP} = 15.56, CH), 132.73 (s, CH), 132.15 (s, CH), 131.66(s, CH), 129.43 (s, CH), 129.31 (s, CH), 129.08 (d, J_{CP} = 6.40, CH), 129.48 (d, J_{CP} = 7.41, CH), 127.61 (d, J_{CP} = 11.92, C), 123.13 (d, J_{CP} = 3.64, CH), 121.65 (s, CH), 121.60 (d, J_{CP} = 4.64, CH), 119.01 (d, J_{CP} = 3.64, CH), 116.52 (d, J_{CP} = 24.72, C), 29.82 (s, CH*Me*$_2$), 29.33 (s, CH*Me*$_2$), 28.71 (s, CH*Me*$_2$), 28.64 (s, CH*Me*$_2$), 28.21 (m, *C*HMe$_2$), 28.11 (m, *C*HMe$_2$), 26.13 (m, AlC*H*$_2$CHMe$_2$), 25.94 (m, AlC*H*$_2$CHMe$_2$), 23.13 (d, J_{CP} = 7.28, *C*HMe$_2$), 20.78 (d, J_{CP} = 10.92, *C*HMe$_2$), 19.75 (d, J_{CP} = 6.40, CH*Me*$_2$), 19.57 (d, J_{CP} = 4.52, CH*Me*$_2$), 19.04 (d, J_{CP} = 10.04, CH*Me*$_2$), 17.08 (d, J_{CP} = 3.64, CH*Me*$_2$). Anal. calcd for $C_{38}H_{50}AlNP_2$: C, 74.84; H, 8.27; N, 2.30. Found: C, 74.78; H, 7.92; N, 2.35.

Synthesis of [^{i}Pr-PNP]AlCl$_2$ (5b). Method 1. To a prechilled toluene (3 mL) solution of [^{i}Pr-PNP]Li(OEt$_2$) (230 mg, 0.48 mmol) at −35 °C was added solid trichloroaluminum (64 mg, 0.48 mmol). The reaction solution was naturally warmed to room temperature with stirring. After being stirred at room temperature for 26 h, the reaction solution was filtered through a pad of Celite, which was further washed with toluene (ca. 2 mL). The combined filtrate was concentrated under reduced pressure and cooled to −35 °C to afford the product as a pale-yellow solid. Yield: 180 mg (76%). Colorless crystals suitable for X-ray diffraction analysis were grown from a concentrated toluene solution at −35 °C.

Method 2. To a prechilled toluene solution (0.6 mL) of **1b** (8 mg, 0.02 mmol) at −35 °C was added MeAlCl$_2$ (0.02 mL, 1 M in hexane, 0.02 mmol). The solution was transferred to a Teflon-sealed NMR tube and examined by ^{31}P{^{1}H} NMR spectroscopy, which showed quantitative formation of **5b** in 15 min.

^{1}H NMR (C_6D_6, 500 MHz): δ 7.29 (dd, 2, J = 4.5 and 8, Ar), 7.02 (t, 2, J = 7.75, Ar), 6.92 (t, 2, J = 6.25, Ar), 6.68 (t, 2, J = 7, Ar), 2.14 (m, 2, C*H*Me$_2$), 2.11 (m, 2, C*H*Me$_2$), 1.31 (dd, 6, J = 7 and 15, CH*Me*$_2$), 1.26 (dd, 6, J = 7 and 17, CH*Me*$_2$), 1.12 (dd, 6, J = 7 and 15.5, CH*Me*$_2$), 0.79 (dd, 6, J = 7 and 10.5, CH*Me*$_2$). ^{31}P{^{1}H} NMR (C_6D_6, 202.31 MHz): δ 20.10. ^{13}C{^{1}H} NMR (C_6D_6, 125.5 MHz): δ 157.94 (dd, J_{CP} = 4.14 and 15.12, C), 133.45 (s, CH), 132.24 (s, CH), 120.14 (t, J_{CP} = 2.39, CH), 119.41 (t, J_{CP} = 2.76, CH), 115.87 (d, J_{CP} = 31.50, C), 22.71 (d, J_{CP} = 13.68, *C*HMe$_2$), 19.42 (d, J_{CP} = 18.20, *C*HMe$_2$), 19.06 (br s, CH*Me*$_2$), 18.21 (d, J_{CP} = 10.17, CH*Me*$_2$), 16.48 (d, J_{CP} = 6.90, CH*Me*$_2$). Anal. calcd for $C_{24}H_{36}AlCl_2NP_2$: C, 57.82; H, 7.28; N, 2.81. Found: C, 57.24; H, 7.40; N, 2.73.

General Procedures for Synthesis of 6a−c. To a THF solution of **1a**, **1b**, or **1c** at −35 °C was added *n*-BuLi (1 equiv). The reaction solution was stirred at room temperature for 1 h and cooled to −35 °C again. Solid AlCl$_3$ (1 equiv) was added. The reaction mixture was stirred at room temperature for 1 h. The ^{31}P{^{1}H} NMR spectra (THF, 80.95 MHz) of a reaction aliquot at this moment revealed the presence of the presumed **5a** at −29.43 ppm, **5b** at −21.01 ppm, or **5c** at −18.11 (d, 1, $^2J_{PP}$ = 47.64, P^{i}Pr$_2$) and −30.84 (d, 1, $^2J_{PP}$ = 47.64, PPh$_2$) ppm. Solid LiAlH$_4$ (1 equiv) was then added at room temperature. The reaction mixture was stirred at room temperature for 1 h. All volatiles were removed in vacuo. The product was extracted with toluene followed by filtration with Celite. Evaporation of toluene under reduced pressure gave an off-white solid.

Synthesis of [Ph-PNP]AlH$_2$ (6a). Yield: 76%. The dichloride **5a** could be alternatively prepared in situ by the addition of 1 equiv of MeAlCl$_2$ to **1a** in toluene at −35 °C. ^{11}H NMR (C_6D_6, 500 MHz): δ 7.70 (m, 4, Ar), 7.57 (m, 4, Ar), 7.17 (m, 4, Ar), 7.04 (m, 4, Ar), 6.99 (m, 8, Ar), 6.88 (td, 2, Ar), 6.57 (t, 4, Ar), 5.51 (br s, 2, $\Delta\nu_{1/2}$ = 132, AlH). ^{31}P{^{1}H} NMR (C_6D_6, 202.31 MHz): δ −27.35 ($\Delta\nu_{1/2}$ = 4.7). ^{13}C{^{1}H} NMR (C_6D_6, 125.5 MHz): δ 159.27 (t, J_{CP} = 10.92, C), 134.63 (s, CH), 134.53 (d, J_{CP} = 7.28, CH), 134.15 (t, J_{CP} = 6.40, CH), 132.48 (s, CH), 132.25 (dd, J_{CP} = 10.54 and 12.30, C), 130.95 (dd,

J_{CP} = 10.54 and 9.16, C), 130.67 (s, CH), 130.03 (s, CH), 129.42 (t, J_{CP} = 4.52, CH), 129.19 (t, J_{CP} = 4.52, CH), 122.25 (dd, J_{CP} = 17.44 and 15.56, C), 120.97 (t, J_{CP} = 1.88, CH), 120.34 (t, J_{CP} = 1.88, CH). Anal. calcd for $C_{36}H_{30}AlNP_2$: C, 76.44; H, 5.35; N, 2.48. Found: C, 76.03; H, 5.09; N, 2.37.

Synthesis of [^{i}Pr-PNP]AlH$_2$ (6b). Colorless crystals suitable for X-ray diffraction analysis were grown by layering pentane on a concentrated diethyl ether solution at −35 °C. Yield: 83%. ^{1}H NMR (C_6D_6, 500 MHz): δ 7.40 (dd, 2, J = 3 and 8, Ar), 7.07 (t, 2, Ar), 7.04 (m, 2, Ar), 6.75 (t, 2, J = 7.5, Ar), 4.93 (br s, 2, $\Delta\nu_{1/2}$ = 35, AlH), 2.07 (m, 2, C*H*Me$_2$), 1.84 (m, 2, C*H*Me$_2$), 1.21 (dd, 6, CH*Me*$_2$), 1.12 (dd, 6, CH*Me*$_2$), 1.08 (dd, 6, CH*Me*$_2$), 0.85 (dd, 6, CH*Me*$_2$). ^{31}P {^{1}H} NMR (C_6D_6, 202.31 MHz): δ −20.64. ^{13}C {^{1}H} NMR (C_6D_6, 125.5 MHz): δ 160.47 (t, J_{CP} = 9.54, C), 133.60 (s, CH), 131.59 (s, CH), 120.15 (s, CH), 119.53 (s, CH), 117.69 (t, J_{CP} = 11.92, C), 23.09 (s, *C*HMe$_2$), 20.12 (t, J_{CP} = 5.02, *C*HMe$_2$), 19.70 (t, J_{CP} = 2.76, CH*Me*$_2$), 19.33 (t, J_{CP} = 5.90, CH*Me*$_2$), 19.03 (t, J_{CP} = 3.26, CH*Me*$_2$), 16.78 (t, J_{CP} = 1.88, CH*Me*$_2$). Anal. calcd for $C_{24}H_{38}AlNP_2$: C, 67.10; H, 8.92; N, 3.26. Found: C, 66.60; H, 8.13; N, 3.78.

Synthesis of [Ph-PNP-^{i}Pr]AlH$_2$ (6c). Yield: 87%. The dichloride **5c** could be alternatively prepared in situ by the addition of 1 equiv of $MeAlCl_2$ to **1c** in toluene at −35 °C. ^{1}H NMR (C_6D_6, 500 MHz): δ 7.68 (m, 2, Ar), 7.65 (m, 2, Ar), 7.35 (dd, 1, Ar), 7.23 (dd, 1, Ar), 7.15 (m, 1, Ar), 7.05 (td, 1, Ar), 7.00 (m, 4, Ar), 6.94 (m, 4, Ar), 6.66 (dt, 2, Ar), 5.25 (br s, 2, $\Delta\nu_{1/2}$ = 80, AlH), 2.03 (m, 1, C*H*Me$_2$), 1.85 (m, 1, C*H*Me$_2$), 1.15 (dd, 3, CH*Me*$_2$), 1.11 (dd, 3, CH*Me*$_2$), 1.07 (dd, 3, CH*Me*$_2$), 0.84 (dd, 3, CH*Me*$_2$). ^{31}P{^{1}H} NMR (C_6D_6, 202.31 MHz): δ −17.19 (d, 1, $^2J_{PP}$ = 49.97, P^{i}Pr$_2$), −28.54 (d, 1, $^2J_{PP}$ = 49.97, PPh$_2$). ^{13}C {^{1}H} NMR (C_6D_6, 125.5 MHz): δ 160.68 (d, J_{CP} = 17.32, C), 159.08 (d, J_{CP} = 22.84, C), 135.06 (s, CH), 134.46 (d, J_{CP} = 14.68, CH), 134.26 (d, J_{CP} = 12.80, CH), 133.41 (d, J_{CP} = 16.44, C), 133.28 (s, CH), 132.04 (s, CH), 131.98 (s, CH), 131.85 (s, C), 130.30 (s, CH), 129.77 (s, CH), 129.19 (d, J_{CP} = 32.12, CH), 129.15 (d, J_{CP} = 14.68, CH), 128.68 (s, CH), 123.08 (d, J_{CP} = 27.48, C), 121.24 (d, J_{CP} = 4.52, CH), 120.67 (d, J_{CP} = 3.64, CH), 119.85 (d, J_{CP} = 3.64, CH), 119.43 (d, J_{CP} = 4.52, CH), 116.84 (d, J_{CP} = 25.60, C), 22.91 (d, J_{CP} = 7.28, *C*HMe$_2$), 19.97 (d, J_{CP} = 13.81, *C*HMe$_2$), 19.51 (d, J_{CP} = 4.52, CH*Me*$_2$), 19.19 (d, J_{CP} = 11.04, CH*Me*$_2$), 19.00 (d, J_{CP} = 5.52, CH*Me*$_2$), 16.67 (d, J_{CP} = 5.40, CH*Me*$_2$). Anal. calcd for $C_{30}H_{34}AlNP_2$: C, 72.41; H, 6.89; N, 2.82. Found: C, 72.90; H, 6.33; N, 2.99.

Catalytic Ethylene Polymerization. A chlorobenzene solution (0.25 mL) of B(C_6F_5)$_3$ (2.5 μmol) was added to a toluene solution (5 mL) of **2** (2.625 μmol) at room temperature. To this solution was introduced ethylene (1 atm) at room temperature for 2 min with stirring. The reaction was quenched with MeOH (ca. 1 mL). All volatiles were removed under reduced pressure (ca. 100 mTorr at 70 °C) until the product weight remained constant.

Catalytic 1-Hexene Polymerization. A chlorobenzene solution (0.25 mL) of B(C_6F_5)$_3$ (2.5 μmol) was added to a 1-hexene solution (2 g) of **2** (2.625 μmol) at room temperature. The reaction was stirred at room temperature for 30 min and quenched with MeOH (ca. 1 mL). All volatiles were removed under reduced pressure (ca. 100 mTorr at 70 °C) until the product weight remained constant.

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Supporting Information Available: X-ray crystallographic data in CIF format for **2a**−**c**, **3b**−**c**, **5b**, and **6b**. This material is available free of charge via the Internet at http://pubs.acs.org.