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Organoaluminium complexes incorporating an amido phosphine chelate with a pendant amine arm[†]

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The palladium-catalyzed aryl amination of 1-bromo-2-fluorobenzene with N,N-dimethylethylenediamine quantitatively produces N-(dimethylaminoethyl)-2-fluoroaniline, which subsequently reacts with KPPh₂ in 1,4-dioxane to afford N-(dimethylaminoethyl)-2-diphenylphosphinoaniline (H[PNN]). The reactions of trialkylaluminium with H[PNN] in toluene generate the corresponding aluminium dialkyl complexes [PNN]AlR₂ (R = Me, Et, *i*-Bu). The solution NMR spectroscopic and X-ray crystallographic studies are indicative of a trigonal bipyramidal geometry for these aluminium complexes in which the amino nitrogen atom is *trans* to the phosphorus donor of the [PNN]⁻ ligand. This study presents rare examples of structurally characterized, five-coordinate aluminium hydrocarbyl complexes supported by phosphine-derived ligands.

Introduction

There has been considerable interest in recent years in the search for appropriate ancillary ligands for the preparation of organoaluminium complexes, due to their increasing role in polymerization chemistry.1 While the vast majority of the preceding studies involved chelating ligands with exclusively hard donor atoms,¹⁻²⁰ we chose to examine the aluminium complexes of hybrid ligands that contain both hard and soft donors. In this regard, we have recently prepared a series of mononuclear aluminium dialkyl complexes supported by bidentate diarylamido phosphine ligands $(1, Fig. 1)^{21}$ and explored the subsequent catalytic polymerization. In a parallel pursuit, chemistry involving the tridentate variations of amido phosphine ligands such as 2 and 3 is also investigated. Ligands of these types represent amido phosphine derivatives bearing symmetric and unsymmetric donor arms, respectively, for binding to a metal. Though available, examples of aluminium complexes containing tridentate amido phosphine ligands are extremely rare.22 We present herein the preparation and characterization of organoaluminium derivatives incorporating 3, a ligand that may also be regarded as an o-phenylene derived amido phosphine chelate that contains an aliphatic pendant arm.



Fig. 1 o-Phenylene derived chelating amido phosphine ligands.

Experimental

General procedures

Unless otherwise specified, all experiments were performed under nitrogen using standard Schlenk or glovebox techniques.

† Electronic supplementary information (ESI) available: Molecular structures of [PNN]AlEt₂ and [PNN]Al(*i*-Bu)₂. See http://www.rsc.org/suppdata/dt/b5/b502873f/

All solvents were reagent grade or better and purified by standard methods. The trialkylaluminium complexes were obtained in solutions from Tokyo Chemical Industry (TCI) company. All other chemicals were obtained from commercial vendors (Aldrich, Strem) 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 ($\Delta v_{1/2}$) are in hertz. ¹H NMR spectra are referenced using the residual solvent peak at δ 7.16 for C₆D₆ and δ 7.27 for CDCl₃. ¹³C NMR spectra are referenced using the residual solvent peak at δ 128.39 for C₆D₆ and δ 77.23 for CDCl₃. The assignment of the carbon atoms for all new compounds is based on DEPT ¹³C NMR spectroscopy. ¹⁹F, ³¹P, and ²⁷Al NMR spectra are referenced externally using CFCl₃ in CHCl₃ at δ 0, 85% H₃PO₄ at δ 0, and AlCl₃ in D₂O at δ 0, respectively. Routine coupling constants are not listed. All NMR spectra were recorded at room temperature in specified solvents. The ${}^{1}H{-}^{31}P$ correlation spectrum of [PNN]Al(*i*-Bu)₂ was acquired on a Varian Inova 500 MHz instrument using the HMBC sequence. Elemental analysis was performed on a Heraeus CHN-O Rapid analyzer. With multiple attempts, we were not able to obtain satisfactory analysis for aluminium complexes due to extreme air- and moisture-sensitivity of these compounds.

X-Ray crystallography

Table 1 summarizes the crystallographic data for all structurally characterized compounds. Data were collected on a Bruker-Nonius Kappa CCD diffractometer with graphite monochromated Mo-K α radiation ($\lambda = 0.7107$ 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 non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions. The crystals of [PNN]AlEt₂ were of poor quality but sufficient to establish the identity of this molecule.

CCDC reference numbers 264438–264441.

See http://www.rsc.org/suppdata/dt/b5/b502873f/ for crystallographic data in CIF or other electronic format.

Synthesis of N-(dimethylaminoethyl)-2-fluoroaniline

A Schlenk flask was sequentially charged with tris(dibenzylideneacetone)dipalladium (Pd₂(dba)₃, 26 mg, 0.028 mmol,

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Table 1	Crystallographic	data for	H[PNN],	[PNN]AlMe ₂ ,	[PNN]AlEt ₂ , an	nd [PNN]Al(i-Bu) ₂
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Compound	H[PNN]	[PNN]AlMe ₂	[PNN]AlEt ₂	[PNN]Al(<i>i</i> -Bu) ₂
Formula	$C_{22}H_{25}N_2P$	$C_{24}H_{30}AlN_2P$	C ₂₆ H ₃₄ AlN ₂ P	$C_{30}H_{42}AlN_2P$
M	348.41	404.45	432.50	488.61
$D_{\rm calc}/{\rm g}~{\rm cm}^{-3}$	1.165	1.181	1.162	1.146
Crystal system	Orthorhombic	Triclinic	Monoclinic	Triclinic
Space group	$P2_{1}2_{1}2_{1}$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
a/Å	7.2152(2)	9.9523(2)	9.2620(3)	11.1571(1)
b/Å	11.5571(3)	11.1101(3)	29.066(1)	13.1017(2)
c/Å	23.8166(8)	11.7142(3)	9.8432(5)	20.6768(3)
$a/^{\circ}$	90	80.2789(9)	90	73.4062(5)
$\beta/^{\circ}$	90	74.9271(9)	111.149(3)	89.8788(6)
y/°	90	65.7727(9)	90	78.4122(6)
$V/Å^3$	1986.0(1)	1137.63(5)	2471.4(2)	2832.70(6)
Z	4	2	4	4
T/K	200(2)	293(2)	200(2)	100(2)
Diffractometer	Kappa CCD	Kappa CCD	Kappa CCD	Kappa CCD
Radiation, λ/Å	Μο Κα, 0.71073	Μο Κα, 0.71073	Μο Κα, 0.71073	Μο Κα, 0.71073
$2\theta_{\rm max}/^{\circ}$	50.04	50.04	50.00	50.22
Total reflections	9678	11107	11346	33913
Independent reflections	3473	3992	3909	9981
$R_{\rm int}$	0.0745	0.0497	0.0867	0.0771
μ/mm^{-1}	0.145	0.171	0.162	0.148
Data/restraints/parameters	3473/0/226	3992/0/254	3909/0/272	9981/0/642
Goodness of fit	1.100	1.054	1.036	1.054
Final R indices $[I > 2\sigma(I)]$: R1, wR2	0.0537, 0.1314	0.0501, 0.1309	0.0695, 0.1691	0.0558, 0.1443
R indices (all data): R1, wR2	0.0844, 0.1669	0.0848, 0.1589	0.1146, 0.1921	0.0834, 0.1776

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0.49% racemic-2,2'-bis(diphenylphosphino)-1,1'equiv), binaphthyl (rac-BINAP, 27 mg, 0.043 mmol, 0.75% equiv), sodium tert-butoxide (0.770 g, 8.00 mmol, 1.4 equiv), N,N-dimethylendiamine (0.503 g, 5.71 mmol), 1-bromo-2-fluorobenzene (1.000 g, 5.71 mmol), and toluene (25 mL) under nitrogen. The reaction mixture was heated to reflux with stirring for 2 d. Toluene was removed in vacuo and the reaction was quenched with deionized water (25 mL). The product was extracted with CH₂Cl₂ (25 mL) and the organic portion was separated from the aqueous layer, which was further extracted with CH_2Cl_2 (10 mL \times 3). The combined organic solution was dried over MgSO₄ and filtered. All volatiles were removed in vacuo to yield a viscous, tan oil that was directly used for the subsequent nucleophilic phosphanylation without further purification, yield 0.948 g (91.1%). ¹H NMR (CDCl₃, 500 MHz) δ 7.03 (t, 1, Ar), 6.99 (d, 1, Ar), 6.72 (t, 1, Ar), 6.65 (dq, 1, Ar), 4.57 (br s, 1, NH), 3.19 (t, 2, NCH₂CH₂), 2.59 (t, 2, NCH₂CH₂), 2.29 (s, 6, NMe₂). ¹⁹F NMR (CDCl₃, 470.5 MHz) δ -137.64. ¹³C{¹H} NMR (CDCl₃, 125.5 MHz) δ 151.4 (d, CF, ¹J_{CF} = 238.3 Hz), 136.8 (d, FCCN, ${}^{2}J_{CF} = 11.8$ Hz), 124.3 (d, CH, $J_{\rm CF} = 3.1$ Hz), 116.1 (d, CH, $J_{\rm CF} = 6.8$ Hz), 114.0 (d, CH, $J_{\rm CF} =$ 18.2 Hz), 111.8 (d, CH, $J_{CF} = 3.6$ Hz), 57.6 (s, NCH₂), 44.9 (s, NMe₂), 40.6 (s, NCH₂).

Synthesis of *N*-(dimethylaminoethyl)-2-diphenylphosphinoaniline, H[PNN]

A 250-mL Schlenk flask equipped with a condenser was flushed with nitrogen thoroughly. To this flask was added KPPh₂ (89 mL, 0.5 M in THF solution, Aldrich, 44.5 mmol). THF was removed *in vacuo* and a solution of *N*-(dimethylaminoethyl)-2fluoroaniline (8.119 g, 44.5 mmol) in 1,4-dioxane (60 mL) was added with a syringe. The transparent, ruby reaction solution was heated to reflux for 7 d, during which time the reaction condition was monitored by ³¹P{¹H} NMR spectroscopy. All volatiles were removed from the resulting orange solution under reduced pressure and degassed deionized water (30 mL) was added. The product was extracted with deoxygenated dichloromethane (30 mL). The dichloromethane solution was separated from the aqueous layer, from which the product was further extracted with dichloromethane (15 mL × 2). The combined organic solution was dried over MgSO₄ and filtered. All volatiles were removed in vacuo to yield a reddish brown oil. Diethyl ether (20 mL) was added resulting in a pale vellow solution containing a black precipitate. The diethyl ether solution was passed through a pad of Celite to remove the insoluble solid, which was further washed with diethyl ether $(20 \text{ mL} \times 2)$ until the washings were colorless. Pentane (10 mL) was added to the combined diethyl ether solutions (total volume 60 mL) and the solution was cooled to -35 °C for 1 d to afford the product as colorless crystals, which were isolated and dried in vacuo; yield 1.237 g (79.8%). ¹H NMR (C₆D₆, 500 MHz) δ 7.47 (m, 4, Ar), 7.27 (td, 1, Ar), 7.14 (td, 1, Ar), 7.06 (m, 6, Ar), 6.68 $(t, 1, Ar), 6.62 (dd, 1, Ar), 5.58 (d, 1, J_{HP} = 6 Hz, NH), 2.86 (td, 1, J_{HP} = 6 Hz, NH), 2.86 (td, 1, Ar), 5.58 (d, 1, J_{HP} = 6 Hz, NH), 2.86 (td, 1, Ar), 5.58 (d, 1, J_{HP} = 6 Hz, NH), 2.86 (td, 1, Ar), 5.58 (d, 1, J_{HP} = 6 Hz, NH), 2.86 (td, 1, Ar), 5.58 (d, 1, J_{HP} = 6 Hz, NH), 2.86 (td, 1, Ar), 5.58 (d, 1, J_{HP} = 6 Hz, NH), 2.86 (td, 1, Ar), 5.58 (d, 1, J_{HP} = 6 Hz, NH), 2.86 (td, 1, Ar), 5.58 (d, 1, J_{HP} = 6 Hz, NH), 2.86 (td, 1, J_{HP} = 6 Hz, NH), 5.58 (td, 1, J_$ 2, NCH₂), 2.14 (t, 2, NCH₂), 1.86 (s, 6, NMe₂). ${}^{31}P{}^{1}H{}$ NMR $(C_6D_6, 202.3 \text{ MHz})\delta - 19.3.^{31}P{^1H} \text{ NMR} (THF, 80.953 \text{ MHz})$ $\delta - 19.0.^{31}P{^{1}H} NMR$ (pentane, 80.953 MHz) $\delta - 17.4.^{31}P{^{1}H}$ NMR (Et₂O, 80.953 MHz) δ -18.3. ¹³C{¹H} NMR (C₆D₆, 125.5 MHz) δ 152.1 (d, J_{CP} = 17.2 Hz, C), 137.0 (d, J_{CP} = 9.9 Hz, C), 135.3 (d, J_{CP} = 3.6 Hz, CH), 134.7 (s, CH), 134.5 (s, CH), 131.4 (s, CH), 129.1 (d, $J_{CP} = 3.5$ Hz, CH), 120.1 (d, $J_{\rm CP} = 9.2$ Hz, C), 117.7 (d, $J_{\rm CP} = 1.8$ Hz, CH), 110.9 (d, $J_{\rm CP} =$ 2.6 Hz, CH), 57.9 (s, NCH2), 45.1 (s, NMe2), 41.7 (s, NCH2). Anal. Calcd. for C₂₂H₂₅N₂P: C, 75.82; H, 7.24; N, 8.04. Found: C, 75.47; H, 7.24; N, 7.93%.

Synthesis of [PNN]AlMe₂

Solid H[PNN] (100 mg, 0.28 mmol) was dissolved in toluene (6 mL) and cooled to -35 °C. To this cold solution was added AlMe₃ (0.14 mL, 2.0 M in toluene, TCI, 0.28 mmol) dropwise. After being stirred at room temperature for 2 d, the reaction solution was filtered through a pad of Celite and concentrated under reduced pressure to ca. 1 mL. Pentane (5 drops) was layered on top and the solution was cooled to -35 °C to afford the product as colorless crystals suitable for X-ray diffraction analysis; yield 113.4 mg (97.7%). ¹H NMR (C_6D_6 , 500 MHz) δ 7.54 (t, 4, Ar), 7.37 (t, 1, Ar), 7.20 (t, 1, Ar), 7.03 (m, 6, Ar), 6.66 (t, 1, Ar), 6.61 (t, 1, Ar), 2.84 (t, 2, NCH₂), 2.16 (t, 2, NCH₂), 1.75 (s, 6, NMe₂), -0.31 (d, 6, ${}^{3}J_{HP} = 6.5$, AlMe₂). ${}^{31}P{}^{1}H{}$ NMR (C₆D₆, 202.3 MHz) δ –28.4 ($\Delta v_{1/2}$ = 3.6). ³¹P{¹H} NMR (toluene, 80.95 MHz) δ -27.7. ¹³C NMR (C₆D₆, 125.5 MHz) δ 161.5 ($J_{CP} = 24.6$), 136.6 (CH), 135.4 ($J_{CP} = 9.2$), 134.0 ($J_{CP} = 9.2$) 14.6, CH), 133.0 (CH), 129.1 (CH), 128.9 (*J*_{CP} = 7.3, CH), 116.7 $(J_{CP} = 18.2)$, 115.6 $(J_{CP} = 3.6$, CH), 112.0 $(J_{CP} = 6.4$, CH), 57.3 (NCH₂), 45.2 (NCH₂), 44.8 (NMe₂), -6.1 (² $J_{CP} = 34.6$, AlMe₂). ²⁷Al NMR (C₆D₆, 130.22 MHz) δ 123.6 ($\Delta v_{1/2} = 9113$). Anal. Calcd. for C₂₄H₃₀AlN₂P: C, 71.27; H, 7.48; N, 6.93. Found: C, 69.29; H, 8.47; N, 6.52%.

Synthesis of [PNN]AlEt₂

A Teflon-sealed reaction vessel containing a toluene solution (6 mL) of H[PNN] (100 mg, 0.28 mmol) and AlEt₃ (218.4 mg, 15% in hexane, TCI, 0.28 mmol) was heated in an oil bath to 100 °C for 24 h. After being filtered through a pad of Celite, the reaction solution was concentrated under reduced pressure to ca. 1 mL. The concentrated solution was layered with pentane (5 drops) and cooled to -35 °C to afford the product as colorless crystals; yield 86.1 mg (69.4%). ¹H NMR (C_6D_6 , 500 MHz) δ 7.59 (td, 4, Ar), 7.37 (td, 1, Ar), 7.22 (td, 1, Ar), 7.03 (m, 6, Ar), 6.67 (t, 1, Ar), 6.62 (t, 1, Ar), 2.83 (t, 2, NCH₂), 2.15 (t, 2, NCH₂), 1.79 (s, 6, NMe₂), 1.28 (t, 6, AlCH₂CH₃), 0.28 (dq, 4, ${}^{3}J_{\rm HP} = 7$, AlCH₂CH₃). Selective irradiation on the β -hydrogen atoms at 1.28 ppm led to a doublet resonance for the α -hydrogen atoms with ${}^{3}J_{HP}$ of 7 Hz. ${}^{31}P{}^{1}H{}$ NMR (C₆D₆, 202.3 MHz) δ – 26.9 ($\Delta v_{1/2} = 3.5$). ³¹P{¹H} NMR (toluene, 80.95 MHz) δ -26.4. ¹³C NMR (C_6D_6 , 125.5 MHz) δ 161.7 ($J_{CP} = 24.5$), 136.5 (CH), 135.5 ($J_{CP} = 8.2$), 133.8 ($J_{CP} = 14.5$, CH), 132.9 (CH), 129.1 (CH), 129.0 ($J_{CP} = 7.3$, CH), 116.8 ($J_{CP} = 17.2$), 115.8 ($J_{CP} =$ 2.8, CH), 112.1 ($J_{CP} = 5.4$, CH), 57.7 (NCH₂), 45.2 (NCH₂), 44.8 (NMe₂), 11.5 (AlCH₂CH₃), 2.4 (${}^{2}J_{CP} = 28.2$, AlCH₂). ${}^{27}Al$ NMR (C₆D₆, 130.22 MHz) δ 117.0 ($\Delta v_{1/2}$ = 14599). Anal. Calcd. for C₂₆H₃₄AlN₂P: C, 72.20; H, 7.92; N, 6.48. Found: C, 69.12; H, 7.68; N, 6.11%.

Synthesis of [PNN]Al(*i*-Bu)₂

A Teflon-sealed reaction vessel containing a toluene solution (6 mL) of H[PNN] (100 mg, 0.28 mmol) and Al(*i*-Bu)₃ (379 mg, 15% in hexane, TCI, 0.28 mmol) was heated in an oil bath to 100 °C for 24 h. After being filtered through a pad of Celite, the reaction solution was concentrated under reduced pressure to ca. 1 mL. The concentrated solution was layered with pentane (5 drops) and cooled to -35 °C to afford the product as colorless crystals suitable for X-ray diffraction analysis; yield 93.0 mg (66.3%). ¹H NMR (C₆D₆, 500 MHz) δ 7.59 (t, 4, Ar), 7.38 (t, 1, Ar), 7.28 (t, 1, Ar), 7.07 (m, 2, Ar), 7.03 (m, 4, Ar), 6.70 (t, 1, Ar), 6.63 (t, 1, Ar), 2.88 (t, 2, NCH₂), 2.22 (t, 2, NCH₂), 1.97 (m, 2, AlCH₂CHMe₂), 1.84 (s, 6, NMe₂), 1.00 (d, 6, AlCH₂CHMe_AMe_B), 0.97 (d, 6, AlCH₂CHMe_AMe_B), 0.33 (m, 2, ${}^{2}J_{\rm HH} = 15$, ${}^{3}J_{\rm HP} = 7$, AlC H_{A} H_B), 0.16 (m, 2, ${}^{2}J_{\rm HH} = 14$, ${}^{3}J_{\rm HP} = 9$, AlCH_A*H*_B). Selective decoupling of β -hydrogen atoms at 1.97 ppm revealed two well-resolved doublet of doublets resonances for the diastereotopic α -hydrogen atoms. ³¹P{¹H} NMR (C₆D₆, 202.3 MHz) δ -25.1 ($\Delta v_{1/2} = 4$). ³¹P{¹H} NMR (toluene, 80.95 MHz) δ -25.0. ¹³C NMR (C₆D₆, 125.5 MHz) δ 161.7 ($J_{\rm CP}$ = 24.5), 137.0 (CH), 136.3 ($J_{\rm CP}$ = 6.4), 135.3 (CH), 134.1 ($J_{CP} = 14.6$, CH), 133.4 ($J_{CP} = 10.9$, CH), 132.9 (CH), 116.5 ($J_{CP} = 17.2$), 115.8 (CH), 112.5 ($J_{CP} = 5.4$, CH), 57.7 (NCH₂), 45.4 (NMe₂), 45.1 (NCH₂), 29.9 (AlCH₂CHMe₂), 27.9 (AlCH₂CHMe₂), 27.8 (AlCH₂CHMe₂), 24.1 (${}^{2}J_{CP} = 30.8$, A1CH₂CHMe₂). ²⁷Al NMR (C₆D₆, 130.22 MHz) δ 115 (Δv_{1/2} too broad to be determined). Anal. Calcd. for C₃₀H₄₂AlN₂P: C, 73.74; H, 8.66; N, 5.73. Found: C, 72.85; H, 8.51; N, 5.76%.

Results and discussion

To assess the synthetic accessibility to ligands of type **3**, we first attempted the preparation of *N*-(dimethylaminoethyl)-2-diphenylphosphinoaniline (H[PNN]) as it is readily available following the previously established protocol.^{23–25} As shown in eqn. (1),



the fluorine compound can be isolated as a viscous oil in quantitative yield from the cross-coupling reaction^{26,27} of 1-bromo-2-fluorobenzene with N,N-dimethylethylenediamine catalyzed by $Pd_2(dba)_3$ in the presence of *rac*-BINAP as the cocatalyst and sodium tert-butoxide as the base in refluxing toluene. Subsequent nucleophilic phosphanylation^{28,29} with KPPh₂ in refluxing 1,4-dioxane produces H[PNN] as colorless crystals in 80% yield. Both H[PNN] and its fluorine precursor were fully characterized by multinuclear NMR spectroscopy. Analogous to those found for the bidentate analogues of the type 1,^{21,25} the NH proton in H[PNN] is observed as a doublet resonance due to its internuclear coupling with the phosphorus atom $(J_{\rm HP} = 6 \text{ Hz})$. Colorless crystals of H[PNN] suitable for X-ray diffraction analysis were grown from a concentrated pentane solution at -35 °C. Crystallographic details are summarized in Table 1. As depicted in Fig. 2, compound H[PNN] represents itself as an excellent precursor for a tridentate meridional ligand, at least from a geometric point of view. As anticipated, the two phenyl rings at the phosphorus donors are orientated such that they are nearly orthogonal to each other (dihedral angle 85.4°). The N(1)–C bond distance is slightly longer for the aliphatic substituent than for the aromatic counterpart.



Fig. 2 Molecular structure of H[PNN] with thermal ellipsoids drawn at the 35% probability level. Selected bond distances (Å) and angles (°): P(1)–C(7) 1.829(4), P(1)–C(13) 1.836(4), P(1)–C(1) 1.841(4), N(1)–C(18) 1.372(5), N(1)–C(19) 1.441(5), N(2)–C(21) 1.437(7), N(2)–C(22) 1.448(6), N(2)–C(20) 1.459(5); C(7)–P(1)–C(13) 102.90(18), C(7)–P(1)–C(1) 102.81(17), C(13)–P(1)–C(1) 101.46(16), C(18)–N(1)–C(19) 122.0(3), C(21)–N(2)–C(22) 110.8(4), C(21)–N(2)–C(20) 111.6(4), C(22)–N(2)–C(20) 112.4(4).

Alkane elimination reactions of H[PNN] with trialkylaluminium in toluene produced the corresponding [PNN]AlR₂ (R = Me, Et, i-Bu) in high yield (eqn. (2)).



These organoaluminium complexes are all colorless crystalline solids that are readily available by layering pentane on top of the concentrated reaction solutions at -35 °C. The solution NMR data for these molecules are all consistent with five-coordinate aluminium complexes having a mirror-plane symmetry passing

Table 2 Selected NMR spectroscopic data^a

Compound	$\delta_{ m Hlpha}({}^{3}J_{ m PH})$	$\delta_{\rm Ca}(^2J_{\rm PC})$	$\delta_{\mathrm{P}}\left(\Delta v_{1/2} ight)$	$\delta_{\rm Al} \left(\Delta v_{1/2} \right)$
H[PNN] [PNN]AIMe ₂ [PNN]AIEt ₂ [PNN]Al(<i>i</i> -Bu) ₂	-0.31(7) $0.28(7)^{b}$ $0.33(7)^{b}$ $0.16(0)^{b}c$	-6.1 (35) 2.4 (28) 24.1 (31)	-19.3 -28.4 (4) -26.9 (4) -25.1 (4)	124 (9113) 117 (14599) 115 (NA) ^d

^{*a*} All spectra were recorded in C₆D₆ at room temperature, chemical shifts in ppm, coupling constants in Hz, peak widths at half-height in Hz. ^{*b*} The coupling constants were determined by ¹H NMR spectroscopy with selective decoupling of β-hydrogen atoms. ^{*c*} The larger ³J_{PH} found for the signal at 0.16 ppm than that at 0.33 ppm was further confirmed by ¹H–³¹P correlation spectroscopy. ^{*d*} Not available; too broad to be determined.

through the aluminium center and the three donor atoms of the meridional [PNN]- ligand. Table 2 summarizes the selected NMR data. In all cases, the two aluminium-bound alkyl ligands are chemically equivalent, as are the methyl groups in the pendant amine arm, as indicated by the ¹H and ¹³C NMR spectra. The phosphorus donor appears as a singlet resonance at ca. -27 ppm for these molecules, a value that is shifted relatively upfield from that of H[PNN] at -19 ppm. A similar upfield change in the ³¹P chemical shift is also observed for other phosphine coordinated aluminium complexes^{21,22,30,31} as compared to the corresponding free phosphine ligands. The coordination of the soft phosphorus donor in [PNN]- to the hard aluminium center is further supported by the ¹H and ¹³C NMR spectra. For instance, the methyl ligands in [PNN]AlMe₂ are observed as a doublet resonance at -0.31 ppm with ${}^{3}J_{\rm HP}$ of 6.5 Hz in the ¹H NMR spectrum and a doublet at -6.1 ppm with ${}^{2}J_{CP}$ of 34.6 Hz in the ${}^{13}C{}^{1}H$ NMR spectrum. Selective decoupling of β-hydrogen atoms in [PNN]AlEt₂ and [PNN]Al(*i*-Bu)₂ unambiguously elucidates the internuclear coupling of the a-hydrogen atoms with the phosphorus donor. These results are in sharp contrast to that of the aluminium dimethyl complex supported by a salicylaldiminate ligand bearing a pendant triarylphosphine donor, in which the phosphorus atom is not associated with the aluminium center.³² Interestingly, among the compounds investigated, [PNN]Al(i-Bu)₂ exhibits two well-resolved multiplet resonances for the α-hydrogen atoms, consistent with the anticipated diastereotopic characteristic. The chemical non-equivalence of the α -hydrogen atoms in the Al- CH_2R (R = H, Me, *i*-Pr) fragments is ascribable to the lack of symmetry of these molecules with respect to internal rotation involving the Al-C bonds.33 With smaller aluminium-bound alkyls, rapid rotation about the Al-C bonds happens readily and the diastereotopic α-hydrogen atoms are indistinguishable on the NMR timescale, as has been described in aluminium chemistry involving the bidentate diarylamido phosphine ligands of the

type 1.²¹ Consistently, two doublet resonances are observed for the isobutylmethyl groups in [PNN]Al(*i*-Bu)₂ in the ¹H NMR spectrum. The aluminium atom in these dialkyl complexes appears as a broad signal at *ca.* 120 ppm in the ²⁷Al NMR spectrum, a result that is notably different from that found for the four-coordinate aluminium dialkyl complexes supported by 1,²¹ but consistent with what one anticipates for five-coordinate aluminium dialkyl complexes.³⁴⁻³⁶ Similar ²⁷Al chemical shift and peak width at half-height have also been reported for the five-coordinate organoaluminium phosphine complexes such as tris[*o*-((diphenylphosphino)methyl)phenyl]aluminium.³¹

The solid-state structures of [PNN]AlMe₂, [PNN]AlEt₂, and [PNN]Al(*i*-Bu)₂ have been determined by X-ray crystallography. As depicted in Figs. 3, S1, and S2 (see ESI[†]), respectively, the X-ray structures of [PNN]AlMe2, [PNN]AlEt2, and [PNN]Al(i-Bu)₂ are rather similar. Table 3 summarizes the selected bond distances and angles. The coordination geometry for these molecules is best described as trigonal bipyramidal with the amido nitrogen and the two α -carbon atoms occupying the equatorial positions. The aluminium center lies virtually on the equatorial plane, as indicated by the sum of the three equatorial bond angles of 358.8° for [PNN]AlMe₂, 358.6° for [PNN]AlEt₂, and 358.3° for [PNN]Al(*i*-Bu)₂. The small dihedral angle found between the N(amine)-Al-N(amide) and P-Al-N(amide) planes in [PNN]AlMe2 (1.4°), [PNN]AlEt2 (5.0°), and $[PNN]Al(i-Bu)_2$ (4.5°) is indicative of a meridional coordination mode for the tridentate [PNN]- ligand. The Al-amide, Alamine, Al-C, and Al-P distances are all within the expected values.^{8,31,37-42} For instance, the Al-P bond lengths of 2.756(1) Å, 2.748(2) Å, and 2.783(1) Å for [PNN]AlMe₂, [PNN]AlEt₂, and [PNN]Al(i-Bu)2, respectively, are comparable to those of the



Fig. 3 Molecular structure of $[PNN]AlMe_2$ with thermal ellipsoids drawn at the 35% probability level.

Table 3	Selected bond distances (A	Å) and angles	(°) for [PNN]AlMe ₂	, [PNN]AlEt2, and	[PNN]Al(i-Bu)2
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Compound	[PNN]AlMe ₂	[PNN]AlEt ₂	[PNN]Al(i-Bu)2 "	
Al–P	2.756(1)	2.748(2)	2.783(1)	
Al–N(amide)	1.901(2)	1.928(3)	1.914(2)	
Al-N(amine)	2.134(2)	2.115(4)	2.098(2)	
Al–C	1.967(3), 1.978(3)	1.974(4), 1.993(4)	1.990(3), 1.998(3)	
C-Al-C	120.1(2)	113.7(2)	117.6(1)	
C-Al-N(amide)	120.8(1), 117.9(1)	119.2(2), 125.7(2)	121.2(1), 119.5(1)	
C-Al-N(amine)	98.3(1), 99.5(1)	102.0(2), 98.3(2)	98.8(1), 101.6(1)	
N-Al-N	83.11(9)	82.7(1)	82.84(9)	
N(amide)–Al–P	75.77(7)	75.7(1)	75.67(7)	
N(amine)–Al–P	158.84(8)	157.9(1)	158.05(7)	
C–Al–P	91.4(1), 91.7(1)	93.0(1), 90.4(1)	88.69(8), 92.95(9)	

^a The asymmetric unit cell contains two independent molecules whose structural parameters are similar to one to the other. The data summarized correspond to one of the molecules.

five-coordinate phosphine complexes of aluminium hydrocarbyl such as tris[o-((diphenylphosphino)methyl)phenyl]aluminium (2.7295 Å average).³¹ It should be noted that examples of structurally characterized, five-coordinate phosphine complexes containing Al-C bond(s) are extremely rare.43 In sharp contrast to the results described herein, the X-ray structure of the closely related Al[N(SiMe₂CH₂PⁱPr₂)₂](CH₂Ph)₂ reveals that only two rather than three donor atoms of the potentially tridentate amido phosphine ligand are bound to the aluminium center, thereby resulting in a four-coordinate species.²² Interestingly, the Al-P distance is slightly longer for [PNN]AlR₂ than for the fourcoordinate [1]AlR₂, e.g., $[o-(2,6-Me_2C_6H_3N)C_6H_4PPh_2]AlEt_2$ (2.456(4) Å)²¹ due perhaps to the accommodation of the two five-membered rings in the meridional tridentate ligand for the former. It is also anticipated from a purely steric viewpoint that the Al-P distance in a five-coordinate species is longer than that in a four-coordinate compound. Nevertheless, the dissociation of the phosphorus atom from aluminium seems not to occur readily on the NMR timescale. As a result, the P-Al-N(amide) angles for [PNN]AlR₂ (ca. 75.7°) are notably smaller than those found for the aluminium complexes supported by 1, e.g., [o-(2,6- $^{i}Pr_{2}C_{6}H_{3}N)C_{6}H_{4}PPh_{2}]AlMe_{2}$ (82.1(2)°),²¹ although both ligand systems incorporate an o-phenylene for the connection of the amido nitrogen and the phosphorus donors.

In summary, a new monoanionic, tridentate amido phosphine ligand possessing a pendant amino functionality has been prepared and employed for the coordination chemistry of aluminium. Both rigid o-phenylene and flexible ethylene moieties are incorporated in the ligand backbone of [PNN] for the connection of the three donor atoms. The chelating feature of [PNN]- allows for the facile isolation of a series of fivecoordinate aluminium dialkyl complexes, which represent rare examples of structurally characterized, five-coordinate phosphine complexes containing the Al-C bond(s). The phosphorus donor is *trans* to the dimethylamino nitrogen atom in these trigonal bipyramidal molecules. Diastereotopic α-hydrogen atoms are recognized for higher aluminium-bound alkyls in which the rotation about the Al-C bonds is comparatively hindered on the NMR timescale. The coordination of the soft phosphorus donor to the hard aluminium center is confirmed by both solution NMR spectroscopy and X-ray crystallography. Studies involving the reactivity chemistry of these new molecules will be the subjects of further reports.

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