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Imido analogs of aluminophosphates: syntheses and X-ray structures of $\{LiAl[OP(N^tBu)_2(NH^tBu)]_2\}_2$ and the mono- and di-methylaluminum complexes of the anions $[OP(N^tBu)_x(NH^tBu)_{3-x}]^{x-}$ ($x = 1, 2$)

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Abstract

The reaction of $OP(NH^tBu)_3$ with trimethylaluminum in 1:1 or 2:1 molar ratios in hydrocarbon solvents yields the complexes $\{Me_2Al(\mu\text{-}N^tBu)_2P(\mu\text{-}O)(NH^tBu)AlMe_2[OP(NH^tBu)_3]\}$ (**1**) and $MeAl[(\mu\text{-}N^tBu)(\mu\text{-}O)P(NH^tBu)_2]_2$ (**2**). The dimeric complex $\{LiAl[OP(N^tBu)_2(NH^tBu)]_2\}_2$ (**3**) is obtained by treatment of $OP(NH^tBu)_3$ with $LiAlH_4$ in toluene. Complexes **1**–**3** were characterized by multinuclear NMR spectroscopy and by X-ray crystallography, which revealed different bonding modes for the anions $[OP(N^tBu)(NH^tBu)_2]^{2-}$ and $[OP(N^tBu)_2(NH^tBu)]^{2-}$. © 2002 Published by Elsevier Science B.V.

Keywords: Aluminum; Phosphate; Imido derivatives; Structures; X-ray diffraction

1. Introduction

Aluminophosphates (AlPOs) are the subject of much interest because they form microporous materials with possible applications as molecular sieves or in catalysis [1]. Several methods have been explored for generating AlPOs with different molecular architectures, viz. templation by fluoride ions [2] or organic ammonium cations [3,4]. Attention has also been directed recently to Group 13 phosphonates as soluble models for phosphate materials [5–13]. A possible alternative approach to the generation of AlPOs with unique properties is the substitution of one (or more) of the oxo (O^{2-}) ligands with isoelectronic imido (NR^{2-}) groups. The ability to change the size of the R groups allows the possibility of controlling the structure of the clusters formed by alkali-metal derivatives of heteroleptic imido/oxo anions with p-block element centers. In recent studies, we have demonstrated that subtle changes in the R group can significantly alter the size of the fundamental building block in polycyclic lithium imidosulfites [14] and bis(imido)sulfates [15].

In a preliminary investigation of the synthesis and structures of imido derivatives of aluminophosphates, e.g. $Al[OP(N^tBu)_3]$, we have carried out the reactions of $OP[NH^tBu)]_3$ with (a) trimethylaluminum and (b) lithium aluminum hydride. We report here the synthesis, spectroscopic characterization and X-ray structures of $\{Me_2Al(\mu\text{-}N^tBu)_2P(\mu\text{-}O)(NH^tBu)AlMe_2[OP(NH^tBu)_3]\}$ (**1**), $MeAl[(\mu\text{-}N^tBu)(\mu\text{-}O)P(NH^tBu)_2]_2$ (**2**), and $\{LiAl[OP(N^tBu)_2(NH^tBu)]_2\}_2$ (**3**).

2. Experimental

Solvents (n-hexane, toluene (Na/benzophenone)) were dried and distilled before use. The reagents NH_2^tBu and Me_3Al (2.0 M in hexanes) were commercial samples (Aldrich) used as received. $LiAlH_4$ was purified by extraction with diethyl ether followed by filtration and removal of the solvent from the filtrate under vacuum. The compound $OP(NH^tBu)_3$ was prepared from $OPCl_3$ and the primary amine NH_2^tBu by a modified literature procedure [16]. The handling of air- and moisture-sensitive materials was performed under

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an atmosphere of argon gas using standard Schlenk techniques or a glove box.

^{1}H-NMR spectra were collected with a Bruker AM-200 spectrometer. ^{31}P-NMR spectra were obtained with a Varian XL-200 spectrometer and chemical shifts are reported relative to 85% H_3PO_4. Solid-state ^{13}C-, ^{27}Al-, and ^{31}P-NMR studies were performed using a Bruker AMX-300 spectrometer operating at 75.48, 78.20 and 121.50 MHz, respectively, with a BL4 probe and a spin range of 8–14 kHz; chemical shifts are reported relative to Me_4Si, $Al(NO_3)_3$ and Na_2HPO_4, respectively. The Analytical Services Laboratory of the Department of Chemistry, University of Calgary, provided elemental analyses.

*2.1. Synthesis of $\{Me_2Al(\mu\text{-}N^tBu)_2P(\mu\text{-}O)(NH^tBu)\text{-}AlMe_2[OP(NH^tBu)_3]\}$ (**1**)*

A clear solution of Me_3Al (2 M, 1.14 ml, 2.28 mmol) was added dropwise to a stirred slurry of $OP(NH^tBu)_3$ (0.600 g, 2.28 mmol) in *n*-hexane or toluene (20 ml) at 23 °C and the mixture was stirred for 18 h. The volume of the solution was reduced by approximately one-half under vacuum. After 12 h at 23 °C, colorless crystals were formed and the mother liquor was decanted by a cannula. The crystalline solid was dried under dynamic vacuum and identified as $\{Me_2Al(\mu\text{-}N^tBu)_2P(\mu\text{-}O)(NH^tBu)AlMe_2[OP(NH^tBu)_3]\}$ (0.378 g, 0.59 mmol, 52%). ^{1}H-NMR (C_6D_6): δ 2.39 (d, $^2J_{PNH} = 10$ Hz, NH), 2.27 (d, $^2J_{PNH} = 10$ Hz, NH), 1.60 (s, 18H, ^{t}Bu), 1.47 (s, 9H, ^{t}Bu), 1.45 (s, 27H, ^{t}Bu), −0.09 (s, 3H, Me), −0.11 (s, 3H, Me), −0.28 (s, 6H, Me). ^{31}P-NMR (C_6D_6): δ 3.27 (s), −0.49 (s). Anal. Found: C, 52.34; H, 11.48; N, 12.77. Calc. for $C_{28}H_{70}N_6Al_2O_2P_2$: C, 52.65; H, 11.04; N, 13.16%.

*2.2. Synthesis of $MeAl[(\mu\text{-}N^tBu)(\mu\text{-}O)P(NH^tBu)_2]_2$ (**2**)*

A clear solution of Me_3Al (2 M, 1.14 ml, 2.28 mmol) was added dropwise to a stirred slurry of $OP(NH^tBu)_3$ (1.200 g, 4.56 mmol) in *n*-hexane (30 ml) at 23 °C. The mixture was heated to reflux and stirred for 18 h. The volume of the solution was reduced to approximately one-quarter of the original volume under vacuum and the solution was then heated to 70 °C and allowed to deposit crystals for 3 h at 23 °C. The crystallization procedure was repeated twice to give $MeAl[(\mu\text{-}N^tBu)(\mu\text{-}O)P(NH^tBu)_2]_2$ (1.100 g, 1.94 mmol, 85%). ^{1}H-NMR (C_6D_6): δ 2.25 (broad, s, NH), 1.55 (s, 18H, ^{t}Bu), 1.30 (s, 36H, ^{t}Bu), −0.09 (s, 3H, Me). ^{31}P-NMR (C_6D_6): δ 11.50 (s). Anal. Found: C, 51.89; H, 10.51; N, 14.43. Calc. for $C_{25}H_{61}N_6AlO_2P_2$: C, 52.98; H, 10.85; N, 14.83%.

*2.3. Synthesis of $\{LiAl[OP(N^tBu)_2(NH^tBu)]_2\}_2$ (**3**)*

A slurry of $LiAlH_4$ (0.190 g, 4.75 mmol) in toluene (15 ml) was added dropwise to a slurry of $OP(NH^tBu)_3$ (2.50 g, 9.50 mmol) in toluene (20 ml). Bubbles of H_2 gas were evolved slowly and the mixture was stirred for 18 h at 23 °C. The solvent was removed from the cloudy solution under vacuum to give a fine pale-yellow powder, which was washed with toluene (3 × 10 ml). The remaining solvent was removed under vacuum and $\{LiAl[OP(N^tBu)_2(NH^tBu)]_2\}_2$ (**3**) was obtained as a fine white powder (2.330 g, 1.93 mmol, 81%). Clear plates of **3**·C_7H_8 were obtained from a concentrated solution of **3** in toluene kept at room temperature for 8 days. ^{1}H-NMR (C_6D_6): δ 1.67 (d, 9H, $^4J_{PNCCH} = 0.68$ Hz, ^{t}Bu), 1.58 (d, 9H, $^4J_{PNCCH} = 0.70$ Hz, ^{t}Bu), 1.52 (d, 9H, $^4J_{PNCCH} = 0.69$ Hz, ^{t}Bu), 1.47 (d, 9H, $^4J_{PNCCH} = 0.69$ Hz, ^{t}Bu), 1.45 (d, 9H, $^4J_{PNCCH} = 0.68$ Hz, ^{t}Bu), 1.36 (s, 9H, ^{t}Bu). ^{27}Al-NMR (solid state): δ −183.14 ($W_{1/2} =$ 278 Hz). ^{13}C-NMR (solid state): δ 52.65 (C(CH$_3$)$_3$), 51.35 (2 × C(CH$_3$)$_3$), 50.70 (2 × C(CH$_3$)$_3$), 50.18 (C(CH$_3$)$_3$), 36.19 (C(CH$_3$)$_3$), 34.39 (C(CH$_3$)$_3$), 34.02 (2 × C(CH$_3$)$_3$), 32.91 (2 × C(CH$_3$)$_3$). ^{31}P-NMR (solid state): δ 12.17, −4.88. Anal. Found: C, 51.59; H, 10.04; N, 14.93. Calc. for $C_{55}H_{120}N_{12}Al_2Li_2O_4P_4$: C, 51.79; H, 10.14; N, 15.10%.

*2.4. Crystal structures of **1**, **2** and **3**·C_7H_8*

Crystal data for **1**, **2** and **3**·C_7H_8 are summarized in Table 1. All data collections were carried out with a Bruker AXS P4/RA/SMART 1000 CCD instrument using monochromated Mo–K$_\alpha$ radiation ($\lambda = 0.71073$ Å).

1: Cell parameters were determined using SMART [17] software and refined with SAINT [18]. The structure was solved using the heavy atom method (Patterson) in the centrosymmetric space group *Pnma* (No. 62) (SHELXS-97, [19]) and refined by full-matrix least-squares method on F^2 with SHELXL-97-2 [20].

The nitrogen atom and one carbon atom of one N^{t}Bu group (N(4A), N(4B), C(43A), C(43B)) were disordered over two sites with partial occupancy factors of 0.5 each in both cases. The other non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included at geometrically idealized positions and were not refined.

***2* and *3*·C_7H_8**: The procedures used for data collection and the refinement of the structures of **2** and **3**·C_7H_8 were the same as those described above for **1**. Both structures were solved by direct methods. Three carbon atoms of the disordered toluene molecule in **3**·C_7H_8 were positioned over two sites with partial occupancy factors of 0.50 each.

Table 1
Crystal data and structure refinement parameters for **1**, **2** and **3**

	1	**2**	**3**·C_7H_8
Empirical formula	$C_{28}H_{70}N_6Al_2O_2P_2$	$C_{25}H_{61}N_6AlO_2P_2$	$C_{55}H_{120}N_{12}Al_2Li_2O_4P_4$
Formula weight	638.80	566.72	1205.35
Temperature (°C)	−80(2)	−80(2)	−80(2)
Crystal system	Orthorhombic	Orthorhombic	Monoclinic
Space group	*Pnma* (#62)	*Iba*2 (#45)	$P2_1/n$ (#14)
Unit cell dimensions			
a (Å)	25.1500(17)	19.561(3)	15.1850(8)
b (Å)	14.7597(10)	11.028(2)	10.6573(6)
c (Å)	11.0507(7)	16.023(3)	23.4217(11)
β (°)			103.9232(9)
V (Å^3)	4102.1(5)	3456.2(11)	3679.0(3)
Z	4	4	2
D_{calc} (g cm^{-3})	1.034	1.089	1.088
Absorption coefficient (mm^{-1})	0.178	0.180	0.173
Unique data	4371	2688	6968
Observed data	3390	2295	5662
Parameters refined	220	165	370
R	0.0653	0.0426	0.0545
R_w	0.1827	0.1002	0.1597

$R_1 = [\Sigma||F_o|-|F_c||]/[\Sigma|F_o|]$ for $[F_o^2>2\sigma(F_o^2)]^e$. $wR_2 = \{[\Sigma w(F_o^2-F_c^2)^2]/[\Sigma w(F_o^2)^2]\}^{1/2}$ (all data).

3. Results and discussion

The reaction of OP(NH^{t}Bu)$_3$ with trimethylaluminum in a 1:1 molar ratio in hexane or toluene at 23 °C produces a mixture of products. The major component, which was isolated in 52% yield, was identified by X-ray crystallography as {Me$_2$Al(μ-N^{t}Bu)$_2$P(μ-O)(NH^{t}Bu)AlMe$_2$[OP(NH^{t}Bu)$_3$]} (**1**). The structure of **1** is depicted in Fig. 1 and selected bond distances and bond angles are summarized in Table 2. The reagent OP(NH^{t}Bu)$_3$ is doubly deprotonated by two equivalents of Me$_3$Al to give the [OP(N^{t}Bu)$_2$(NH^{t}Bu)]$^{2-}$ dianion, which is *N*,*N*′-chelated to one Me$_2$Al$^+$ cation and connected in an *O*-monodentate fashion to the second Me$_2$Al$^+$ cation. The coordination sphere of the latter Al center is completed by the neutral O-donor ligand OP(NH^{t}Bu)$_3$. The *N*,*N*′ bonding mode of [OP(N^{t}Bu)$_2$(NH^{t}Bu)]$^{2-}$ is reminiscent of the ligand behavior of [O$_2$S(N^{t}Bu)$_2$]$^{2-}$ in covalent P(III) derivatives [21,22].

As a result of a crystallographic mirror plane, an interesting feature of the structure of **1** is the coplanarity of the ten-atom sequence C(1)/C(2), Al(1), P(1), O(1), Al(2), O(2), P(2), N(3) and C(30). The four-membered AlN$_2$P ring is essentially planar with distorted tetrahedral geometries at Al(1) and P(1). The endocyclic bond angles ∠NAlN and ∠NPN are 77.62(16) and 95.2(2)°, respectively. The geometry at the bridging nitrogens is almost planar (Σ∠N(2) = 357.1°) with ∠P(1)N(2)Al(1) = 93.54(15)°. The Al–N distance of 1.900(3) Å is typical for four-coordinate Al complexes [23]. The endocyclic bond length [P(1)–N(2)] of 1.612(3) Å is significantly shorter than the exocyclic P(1)–N(1) bond (1.657(3) Å). Surprisingly, there is no significant difference in the Al–O distances involving the neutral OP(NH^{t}Bu)$_3$ ligand and the anionic {Me$_2$Al(μ-N^{t}Bu)$_2$P(O)(NH^{t}Bu)]$^-$ fragment whereas the P–O distance in the former (1.466(3) Å) is, as expected, significantly shorter than that in the latter (1.539(3) Å). The bond angles at Al(2) range from 101.04(15) (∠OAlO) to 114.1(5)° (∠CAlC).

NMR data indicate that the solid-state structure of **1** is maintained in solution. The ^{1}H-NMR spectrum of **1** in C$_6$D$_6$ exhibits three resonances for N^{t}Bu groups in the integrated area ratio 2:1:3 corresponding to the two

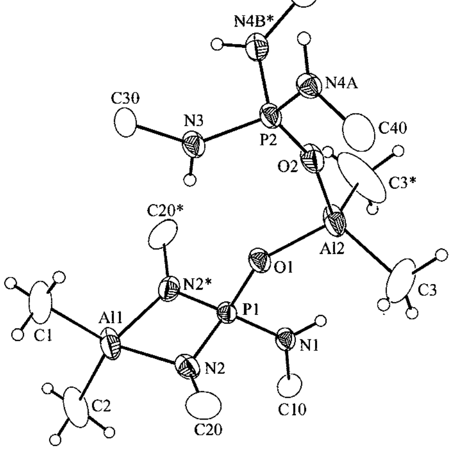


Fig. 1. ORTEP diagram of {Me$_2$Al(μ-N^{t}Bu)$_2$P(μ-O)(NH^{t}Bu)AlMe$_2$-[OP(NH^{t}Bu)$_3$]} (**1**). Ellipsoids are drawn at the 30% level. For clarity, only the α-carbon atoms of ^{t}Bu groups are shown.

Table 2
Selected bond lengths (Å) and bond angles (°) for **1** [a]

Bond lengths			
P(1)–O(1)	1.539(3)	P(1)–N(1)	1.657(3)
P(2)–O(2)	1.466(3)	Al(1)–C(2)	1.988(6)
P(1)–N(2)	1.612(3)	Al(1)–C(1)	1.990(6)
P(2)–N(3)	1.606(3)	Al(2)–C(3)	1.945(3)
P(2)–N(4A)	1.592(3)		
Al(1)–N(2)	1.900(3)		
Al(2)–O(2)	1.774(3)		
Al(2)–O(1)	1.773(3)		
Bond angles			
O(1)P(1)N(1)	100.94(17)	O(1)P(1)N(2)	115.34(14)
N(1)P(1)N(2)	115.49(12)	N(2)P(1)N(2) [b]	95.2(2)
N(2)Al(1)C(1)	116.33(17)	N(2)Al(1)N(2) [b]	77.62(16)
C(2)Al(1)C(1)	110.93(3)	N(2)Al(1)C(2)	116.10(17)
P(1)O(1)Al(2)	145.4(2)	P(1)N(2)Al(1)	93.54(15)
O(2)Al(2)C(3)	108.7(2)	P(2)O(2)Al(2)	161.0(2)
O(1)Al(2)O(2)	101.04(15)	O(1)Al(2)C(3)	111.7(2)
		C(3)Al(2)C(3) [b]	114.1(5)

[a] Symmetry transformation used to generate equivalent atoms.
[b] *x*, −*y*+1/2, *z*.

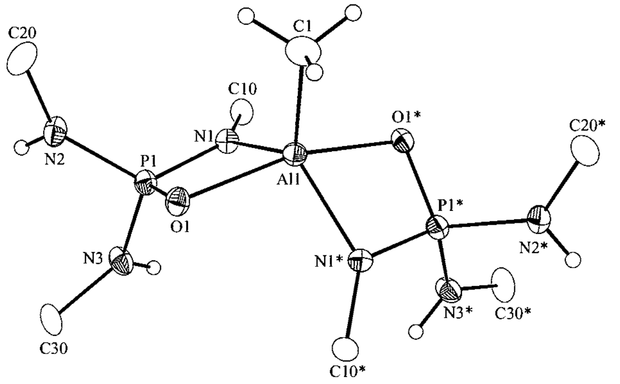


Fig. 2. ORTEP diagram of MeAl[(μ-N^{t}Bu)(μ-O)P(NH^{t}Bu)$_2$]$_2$ (**2**). Ellipsoids are drawn at the 30% level. For clarity, only the α-carbon atoms of ^{t}Bu groups are shown.

Table 3
Selected bond lengths (Å) and bond angles (°) for **2** [a]

Bond lengths			
P(1)–O(1)	1.519(2)	P(1)–N(1)	1.606(4)
P(1)–N(2)	1.645(3)	P(1)–N(3)	1.646(3)
Al–N(1)	1.928(2)	Al–C(1)	1.978(5)
Al–O(1)	1.9847(18)		
Bond angles			
O(1)P(1)N(1)	97.88(11)	O(1)P(1)N(2)	109.91(14)
N(1)P(1)N(2)	121.86(13)	O(1)P(1)N(3)	117.56(13)
N(1)P(1)N(3)	110.13(13)	N(2)P(1)N(3)	100.65(14)
N(1)AlN(1) [b]	123.10(16)	N(1)AlC(1)	118.45(8)
N(1)AlO(1)	74.07(9)	N(1) [b]AlO(1)	96.84(9)
C(1)AlO(1)	99.39(7)	N(1)AlO(1) [b]	96.84(9)
O(1)AlO(1) [b]	161.21(13)	P(1)O(1)Al	94.29(9)
P(1)N(1)Al	93.73(10)		

[a] Symmetry transformation used to generate equivalent atoms.
[b] −*x*, −*y*+1, *z*.

bridging N^{t}Bu groups, the terminal NH^{t}Bu group, and the three NH^{t}Bu groups of the OP(NH^{t}Bu)$_3$ ligand, respectively. The latter resonance (δ 1.05) is shifted upfield compared to that of the free ligand (δ 1.30). Three resonances at δ −0.09, −0.11 and −0.28 in the ratio 1:1:2 are observed for the two Me$_2$Al units. The first two signals are attributed to the inequivalent methyl groups of the Me$_2$Al$^+$ cation in the four-membered ring. The ^{31}P-NMR spectrum of **1** shows two equally intense resonances at δ 3.27 and −0.09, cf. δ 5.53 for OP(NH^{t}Bu)$_3$ in C$_6$D$_6$.

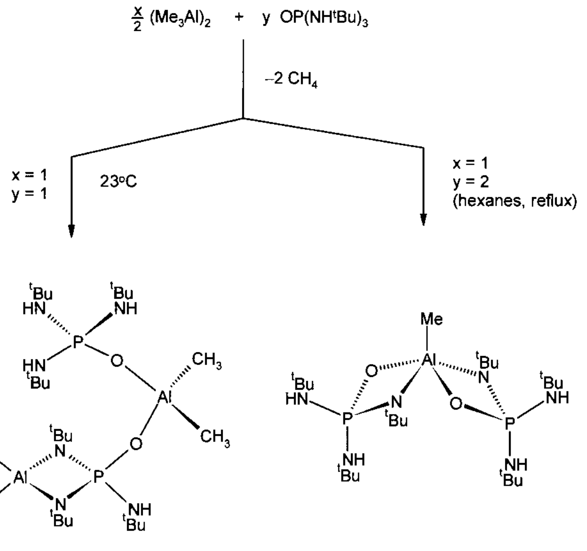
When the reaction of OP(NH^{t}Bu)$_3$ with trimethylaluminum is carried out in a 2:1 molar ratio in *n*-hexane at reflux or in toluene at 75 °C, the complex MeAl[(μ-N^{t}Bu)(μ-O)P(NH^{t}Bu)$_2$]$_2$ (**2**) is isolated in ca. 85% yield. The structure of **2** was determined by X-ray crystallography (see Fig. 2) and selected bond distances and bond angles are given in Table 3. Complex **2** consists of two monoanionic [OP(N^{t}Bu)(NH^{t}Bu)$_2$]$^-$ ligands, which are both *N*,*O*-chelated to the MeAl^{2+} dication. The aluminum atom is in a distorted trigonal bipyramidal geometry with equatorial bond angles ∠NAlN = 123.1 and ∠NAlC = 118.5° and a distinctly non-linear axial arrangement, ∠OAlO = 161.2° (cf. 156.2–158.8° for related five-coordinate aluminum complexes [24]). The CH$_3$–Al unit occupies a crystallographic twofold axis. The four-membered AlNPO rings are essentially planar. The Al–O distance of 1.9847(18) Å falls outside the range of 1.779–1.928 Å observed for 5-coordinate Al complexes whereas the Al–N distance of 1.928(2) Å is typical [24]. The P–O bond length of 1.519(2) Å is unexceptional and the endocyclic *d*(P–N) is ca. 0.04 Å shorter than the mean value of the exocyclic P–N bond length, as found for **1**. The monoanionic ligand [(^{t}BuNH)$_2$P(O)(N^{t}Bu)]$^-$ subtends an angle of 74.07(9)° at Al.

Consistent with the solid-state structure, the ^{1}H-NMR spectrum of **2** in C$_6$D$_6$ shows three resonances at δ −0.09, 1.30 and 1.55 in the ratio 1:12:6 attributable to the MeAl unit, the four terminal NH^{t}Bu groups, and the two bridging N^{t}Bu groups, respectively. The resonance for the NH protons appears as a broad singlet at δ 2.25. The ^{31}P-NMR spectrum of **2** exhibits a singlet at δ 11.50.

In summary, as indicated in Scheme 1, the reaction of OP(NH^{t}Bu)$_3$ with Me$_3$Al in *n*-hexane or toluene in a 1:1 molar ratio generates **1** as the major product. The presence of **2** (and other unidentified products) can be detected in the reaction mixture by ^{1}H- and ^{31}P-NMR spectroscopy. The formation of **2** is favored by increasing the temperature of the reaction and the yield of **2** is optimized, at ca. 85%, by using a 2:1 molar ratio of the reagents in boiling *n*-hexane.

In a previous study, we showed that the reagent LiAlH$_4$ readily deprotonates SO$_2$(NH^{t}Bu)$_2$ in THF at room temperature to give the single-strand polymer

$\{Li(THF)_2Al[SO_2(N^tBu)_2]_2\}_\infty$ [15]. As an extension of this approach to complex imido/oxo anions of p-block elements, we attempted to triply deprotonate $OP(NH^tBu)_3$ by reaction with $LiAlH_4$. However, only the $[OP(N^tBu)_2(NH^tBu)]^{2-}$ dianion is generated even after prolonged reflux in toluene with an excess of $LiAlH_4$. When this reaction is carried out in a 1:2 molar ratio, the complex $\{LiAl[OP(N^tBu)_2(NH^tBu)]_2\}_2$ (**3**) is obtained in 80% yield. The structure of $\mathbf{3}\cdot C_7H_8$ was determined by X-ray crystallography (see Fig. 3). Selected bond distances and bond angles are given in Table 4. Interestingly, the $[OP(N^tBu)_2(NH^tBu)]^{2-}$ ligand adopts two different chelating modes, *N*,*N′* and *N*,*O*, towards the aluminum center in **3**. The two halves of the centrosymmetric dimer are linked by two three-coordinate Li^+ ions, which display *O*-monodentate coordination to the *N*,*N′*-chelated ligand and *O*,*N* chelation of the other $[OP(N^tBu)_2(NH^tBu)]^{2-}$ dianion. Access to the cavity of the resulting twelve-membered $Al_2P_2O_4N_2Li_2$ ring is partially impeded by ^{t}Bu substituents (on N(1)).



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Scheme 1.

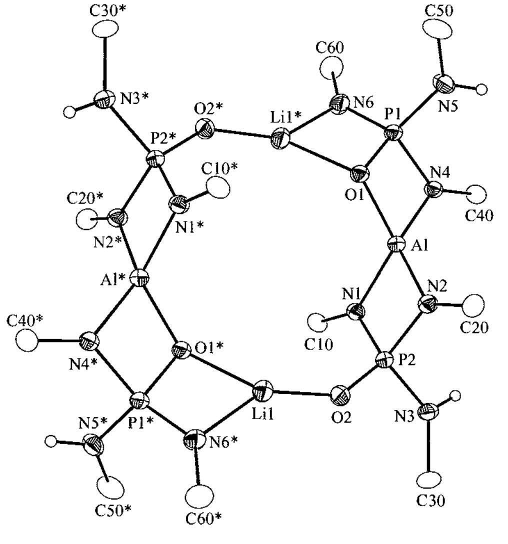

Fig. 3. ORTEP diagram of $\{LiAl[OP(N^tBu)_2(NH^tBu)]_2\}_2$ $(\mathbf{3})\cdot C_7H_8$. Ellipsoids are drawn at the 30% level. For clarity, only the α-carbon atoms of ^{t}Bu groups are shown. The toluene molecule is not included.

Table 4
Selected bond lengths (Å) and bond angles (°) for **3** [a]

Bond lengths			
P(1)–N(6)	1.558(2)	P(1)–O(1)	1.6056(14)
P(1)–N(5)	1.650(2)	P(1)–N(4)	1.6538(17)
P(2)–O(2)	1.4931(15)	P(2)–N(1)	1.6500(18)
P(2)–N(2)	1.6515(18)	P(2)–N(3)	1.6588(18)
Al–O(1)	1.8055(15)	Al–N(2)	1.8348(18)
Al–N(1)	1.8408(18)	Al–N(4)	1.8518(18)
O(1)–Li(1) [b]	1.983(4)	O(2)–Li(1)	1.796(4)
N(6)–Li(1) [b]	2.000(4)		
Bond angles			
N(6)P(1)O(1)	101.38(9)	N(6)P(1)N(5)	115.99(11)
O(1)P(1)N(5)	112.15(9)	N(6)P(1)N(4)	127.32(11)
O(1)P(1)N(4)	92.56(8)	N(5)P(1)N(4)	104.45(9)
O(2)P(2)N(1)	117.68(9)	O(2)P(2)N(2)	117.92(9)
N(1)P(2)N(2)	91.62(9)	O(2)P(2)N(3)	106.39(9)
N(1)P(2)N(3)	112.01(9)	N(2)P(2)N(3)	110.86(9)
O(1)AlN(2)	121.57(8)	O(1)AlN(1)	124.01(7)
N(2)AlN(1)	80.20(8)	O(1)AlN(4)	80.19(7)
N(2)AlN(4)	131.82(8)	N(1)AlN(4)	125.56(8)
P(1)O(1)Al	95.19(7)	P(1)O(1)Li(1) [b]	90.72(13)
AlO(1)Li(1) [b]	131.10(16)	P(2)O(2)Li(1)	143.41(16)
P(2)N(1)Al	93.99(9)	P(2)N(2)Al	94.15(9)
O(2)Li(1)N(6)	145.2(2)	O(2)Li(1)O(1) [b]	135.30(2)
O(1) [b]Li(1)N(6)	75.85(15)	O(2)Li(1)P(1) [b]	163.50(3)
P(1)N(4)Al	91.85(8)	P(1)N(6)Li(1) [b]	91.52(15)

[a] Symmetry transformation used to generate equivalent atoms.
[b] $-x, -y+1, -z$.

As indicated in Table 4, one of the P–N bond lengths (P(1)–N(6)) in **3** is ca. 0.1 Å shorter than the other five P–N bonds, which fall within the narrow range 1.650–1.659 Å. Furthermore, the P(1)–O(1) distance is substantially longer than the P(2)–O(2) bond, 1.6056(14) versus 1.4931(15) Å (cf. d(P=O) = 1.5016(12) Å in $Al(NMe_2)_3\cdot OPPh_3$ [25]). Although this difference may be partly attributable to the different coordination numbers of the two oxygen atoms, 3 versus 2, it may also indicate delocalization of the negative charge of the complex anion $[(^tBuN)(^tBuNH)P(\mu\text{-}O)(\mu\text{-}N^tBu)Al(\mu\text{-}N^tBu)_2P(O)(NH^tBu)]^-$ over the N(6)–P(1)–O(1) unit. The mean Al–N and Al–O bond distances of 1.842 and 1.805 Å, respectively, are typical for 4-coordinate Al [26,27]. There is a substantial difference of almost 0.2 Å for the Li–O distances involving the two- and three-coordinate oxygen atoms, as has been observed previously [28].

The four-membered PN_2Al, PONAl and PONLi are all almost planar with maximum deviations from planarity of 0.0125(7), 0.0284(7) and 0.0497(13) Å, respectively. The $[OP(N^tBu)_2(NH^tBu)]^{2-}$ ligands subtend identical bond angles of 80.2° at Al via either *N*,*O* or *N*,*N* chelation. The endocyclic bond angle $\angle$OLiN is 75.85(15)°.

The ^{1}H-NMR spectrum of **3** in C_6D_6 shows six equally intense resonances in the region δ 1.36–1.67 corresponding to the six inequivalent ^{t}Bu groups attached to nitrogen atoms N(1)–N(6), suggesting that the solid-state structure is maintained in C_6D_6 solution. The solid-state ^{31}P-NMR spectrum exhibits two resonances at δ 12.17 and -4.88 and the solid-state ^{27}Al-NMR spectrum revealed one signal at δ -183.1.

4. Conclusions

These preliminary studies of imido analogs of aluminophosphate show that the AlPO analog $Al[OP(N^tBu)_3]$ is not accessible from the reaction of $OP[NH^tBu]_3$ and trimethylaluminum. Partial deprotonation occurs to give the anions $[OP(N^tBu)_x(NH^tBu)_{3-x}]^{x-}$ ($x = 1, 2$) which engage in *O*,*N* or *N*,*N* chelation to the aluminum center. The prevalence of four-membered ring formation in **1**–**3**, in contrast to the eight-membered rings observed for aluminophosphonates [29], likely results from the steric influence of bulky ^{t}Bu groups. Future attempts to generate imido analogs of AlPO materials will target derivatives with a lower N/O ratio, e.g. $Al[O_3P(NR)]$, and smaller R groups.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 162602, 162603 and 162604 for compounds **1**, **2** and **3**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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