# Structural insights into mono-amido tris-alkyl potassium aluminates†‡

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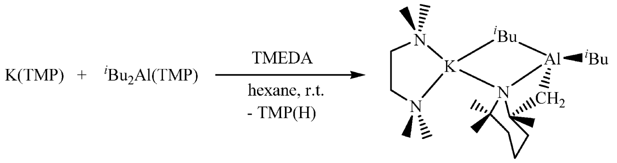
Co-complexation of a potassium amide with $^i$Bu$_3$Al in the presence of the tridentate chelating ligand PMDETA results in a series of potassium aluminates of general formula [PMDETA·K(μ-amide)(μ-$^i$Bu)Al($^i$Bu)$_2$] [where amide = TMP (**6**); DMP (**7**); HMDS (**8**)] which have been characterized by solution NMR spectroscopy and X-ray crystallography. Their solid-state structures contain a central KNAlC ring whose degree of puckering is dictated by the differing interactions between the potassium centre and the aluminium bound anionic ligands.

## Introduction

Lagging behind the well developed TMP-zincate[1] and TMP-magnesiate[2] chemistry, the emerging area of alkali-metal alkyl-TMP-aluminates has only recently been explored.[3] First reported in 2004 by Uchiyama *et al.*, lithium TMP-aluminate "$^i$Bu$_3$Al(TMP)Li" [prepared by mixing triisobutylaluminium ($^i$Bu$_3$Al) with lithium 2,2,6,6-tetramethylpiperidide (LiTMP) in THF] was found to be an excellent base in THF solutions, realizing high chemo- and regioselective deprotonative aluminations of functionalized aromatic and hetero-aromatic compounds as well as of functionalized allylic compounds.[4–6] It has been alluded to that the active base in these deprotonative reactions is the mono-amido tris-alkyl THF solvate [THF·Li(μ-TMP)(μ-$^i$Bu)Al($^i$Bu)$_2$] **1**, which was isolated from hexane solution and crystallographically characterized.[5] Our own research group have reported several Lewis base derivatives of complex **1**, of formula [L·Li(μ-TMP)(μ-$^i$Bu)Al($^i$Bu)$_2$] {where L is TMP(H) **2**, Et$_3$N **3** or PhC(=O)N$^i$Pr$_2$ **4**}.[7] In a study of the use of such compounds in proton abstraction reactions, compound **4** was found to initiate an unexpected fragmentation reaction when reacted with the cyclic ether 1,4-dioxane, yielding the novel dilithium dialuminium hexaalkyl aggregate [{[PhC(=O)N($^i$Pr)$_2$]·Li[O(CH$_2$)$_2$OC(H)=CH$_2$]Al($^i$Bu)$_3$}$_2$·(1,4-dioxane)].[7] In 2006, the first sodium alkyl-TMP-aluminate was reported by our research group.[8] Structural information of both the base [TMEDA·Na(μ-TMP)-(μ-$^i$Bu)Al($^i$Bu)$_2$] **5** (TMEDA = *N*,*N*,*N′*,*N′*-tetramethylethylenediamine) and the product of metalation with phenylacetylene, [2TMEDA·Na(μ-C≡CPh)(μ-$^i$Bu)Al($^i$Bu)$_2$], were obtained, both products having been synthesised from hexane solution. There are currently no examples of mono-TMP tris-alkyl potassium aluminates in the Cambridge Structural Database (CSD).[9] In fact there is only one structural example of a monoamido tris-alkyl potassium aluminate in the CSD. Reported by Roesky *et al.*, the transmetallation reaction of [2,6-$^i$Pr$_2$C$_6$H$_3$N(SiMe$_3$)AlCl$_2$]$_2$ with six molar equivalents of potassium phenylacetylide (KC≡CPh) produces the dimeric complex [THF·K{2,6-$^i$Pr$_2$C$_6$H$_3$N(SiMe$_3$)Al(C≡CPh)$_3$}]$_2$.[10] Furthermore, the first reported reaction of a potassium TMP-aluminate has produced a novel result which justified a structural study of such heavier alkali metal derivatives. To elaborate, remarkably the TMP anion undergoes a deprotonation of one of its methyl arms *via* a bimetallic base mixture of KTMP, $^i$Bu$_2$Al(TMP), and TMEDA in a 1 : 1 : 1 ratio, to generate a TMP* dianion [=NC(Me)$_2$(CH$_2$)$_3$C(Me)(CH$_2$)], which is trapped in the dialkyl potassium aluminate [(TMEDA)·K(TMP*)(μ-$^i$Bu)Al($^i$Bu)] (Scheme 1).[11] This exciting development followed the earlier finding that a base mixture of LiTMP, $^i$Bu$_2$Al(TMP), and TMEDA or PMDETA (PMDETA is *N*,*N*,*N′*,*N″*,*N″*-pentamethyldiethylenetriamine) self-metalates each donor molecule at the relatively non-acidic α-C*H*$_3$N position.[12]



**Scheme 1** Production and trapping of a TMP dianion.

In this present paper we report the first detailed structural study of mono-amido tris-alkyl potassium aluminates. Our focus here was on the effect of the amido ligand, so we have synthesized three new such aluminates containing different amido functions [TMP, DMP (*cis*-2,6-dimethylpiperidide) or HMDS (1,1,1,3,3,3-hexamethyldisilazide)], but keeping the remainder of the composition the same. Subtle but significant structural differences are revealed between the new aluminates.

## Results and discussion

Using tridentate PMDETA as the supporting donor ligand for potassium, the mono(amido) tris(iso-butyl) aluminates [synthesized *via* the co-complexation of the relevant potassium amide, PMDETA and $^i$Bu$_3$Al (Scheme 2)] of general formula [PMDETA·K(μ-amide)(μ-$^i$Bu)Al($^i$Bu)$_2$] [where amide = TMP (**6**), DMP (**7**), or HMDS (**8**)] can be isolated in crystalline

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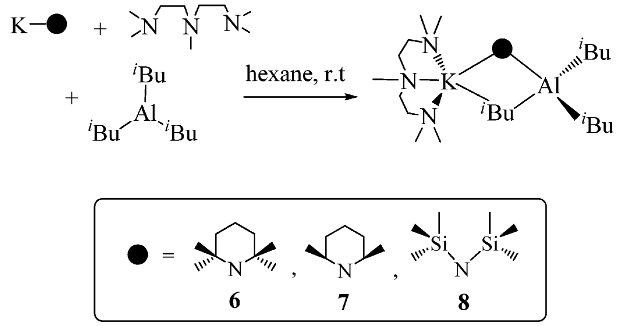

**Scheme 2** Co-complexation route to the new potassium aluminates.

**Table 1** Comparison of bond lengths (Å) and angles (°) within complexes **6**, **7** and **8**

| Parameter | **6** | **7** | **8** |
|---|---|---|---|
| Al–N$_{(amide)}$ | 1.995(8) | 1.8918(14) | 1.9626(14) |
| Al–C$_{(bridging)}$ | 2.031(11) | 2.0470(17) | 2.0489(19) |
| Al–C$_{(terminal)}$ | 2.038(11),<br>2.047(10) | 2.0236(17),<br>2.0344(18) | 2.0122(19),<br>2.0292(18) |
| K–N$_{(amide)}$ | 2.952(8) | 2.8675(15) | 3.0164(15) |
| K–N$_{(PMDETA)}$ | 2.832(8),<br>2.852(9),<br>2.869(9) | 2.8386(15),<br>2.8720(16),<br>2.9446(15) | 2.8192(16),<br>2.8341(16),<br>2.9260(16) |
| K–C$_{(bridging)}$ | 3.111(8) | 3.0483(17) | 3.0184(17) |
| K–N$_{(amide)}$–Al | 100.0(3) | 86.55(5) | 90.25(5) |
| N$_{(amide)}$–Al–C$_{(bridging)}$ | 103.1(3) | 105.56(6) | 109.01(7) |
| Al–C$_{(bridging)}$–K | 94.2(3) | 79.22(5) | 88.58(6) |
| C$_{(bridging)}$–K–N$_{(amide)}$ | 62.6(2) | 63.99(4) | 65.54(4) |

yields of 17, 33, and 52% respectively. The lower than expected yields can be explained by the high solubility of these compounds in hexane solution rather than by unclean reactions. $^1$H NMR spectroscopic analysis of the filtrates revealed further quantities of **6**, **7**, or **8**, with no resonances of possible disproportionation products observed.

## Solid state analysis

The three potassium aluminates **6**, **7**, and **8** share a common structural motif (Fig. 1). Pertinent bond parameters are presented in Table 1 while crystallographic data are listed in Table 2. At the centre of their molecular structures lies a four-element (KNAlC) ring. Only the central ring of **6** is planar (sum of internal angles, 360°), whereas those in **7** (335.31°) and **8** (353.38°) are distinctly non-planar, forming a folded geometry. This core ring of each complex contains a mixed $^i$Bu–amide bridging set, and the molecular structures are completed by two terminal $^i$Bu ligands on Al and a chelating PMDETA (*N*,*N*′,*N*″-attached) on K. In each complex, Al displays a distorted tetrahedral geometry [mean angle around

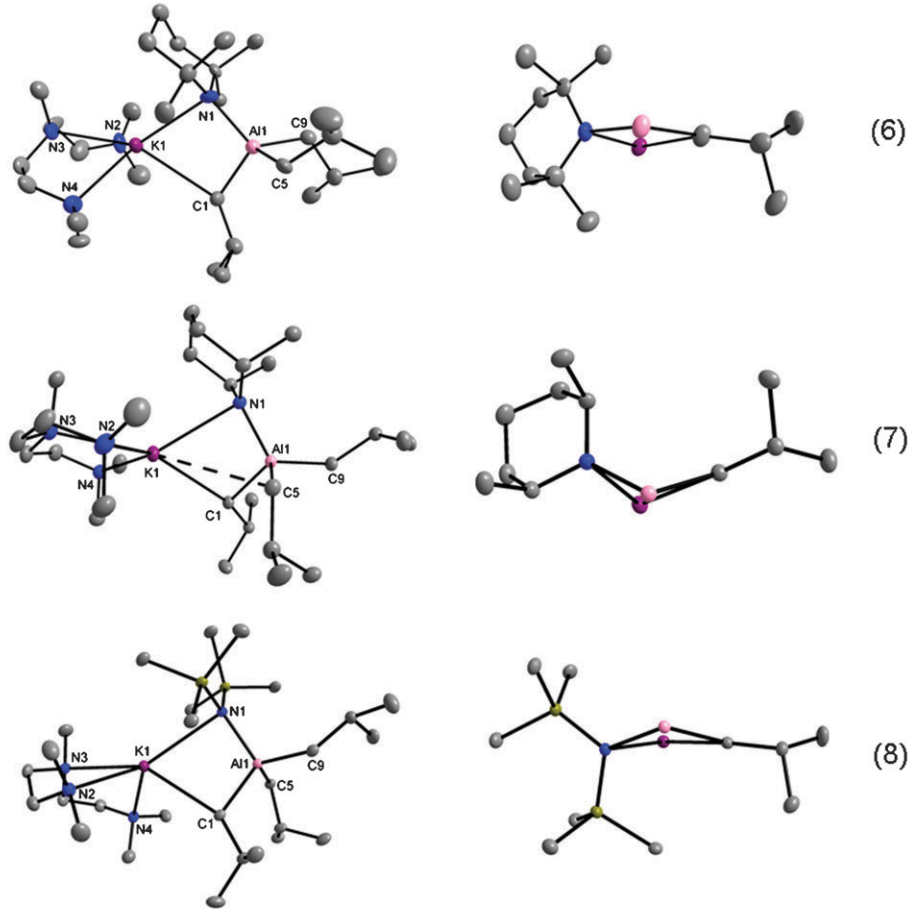

**Fig. 1** Molecular structures of potassium aluminates **6**, **7**, and **8** with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms and minor disordered components of **6** and **7** are omitted for clarity. Their respective central rings, minus terminal $^i$Bu groups and PMDETA ligand, are also shown.

**Table 2** Crystallographic data and refinement details for complexes **6**, **7**, and **8**

| | **6** | **7** | **8** |
|---|---|---|---|
| Empirical formula | $C_{30}H_{68}AlKN_4$ | $C_{28}H_{64}AlKN_4$ | $C_{27}H_{68}AlKN_4Si_2$ |
| Mol. mass | 550.96 | 522.91 | 571.11 |
| $T$/K | 123(2) | 123(2) | 123(2) |
| Crystal system | Orthorhombic | Monoclinic | Monoclinic |
| Space group | $Pna2_1$ | $P2_1/n$ | $P2_1/n$ |
| $a$/Å | 16.505(3) | 11.3887(5) | 11.5276(6) |
| $b$/Å | 11.562(3) | 18.1965(8) | 18.4028(8) |
| $c$/Å | 18.948(4) | 16.9006(8) | 17.3602(9) |
| $\alpha$/° | 90 | 90 | 90 |
| $\beta$/° | 90 | 105.222(5) | 93.669(5) |
| $\gamma$/° | 90 | 90 | 90 |
| $V$/Å$^3$ | 3616.0(14) | 3379.5(3) | 3675.2(3) |
| $Z$ | 4 | 4 | 4 |
| $\rho_{calcd}$/Mg m$^{-3}$ | 1.012 | 1.028 | 1.032 |
| Measured reflections | 8896 | 18 993 | 49 892 |
| Unique reflections [$I > 2\sigma(I)$] | 4713 [$R_{int}$ = 0.0896] | 6485 [$R_{int}$ = 0.0446] | 9769 [$R_{int}$ = 0.0786] |
| Data/restraints/parameters | 4713/33/337 | 6485/0/336 | 9769/0/334 |
| GooF on $F^2$ | 0.940 | 0.985 | 0.796 |
| $R_1$, w$R_2$ [$I > 2\sigma(I)$] | 0.0783, 0.1992 | 0.0513, 0.1234 | 0.0414, 0.0887 |
| $R_1$, w$R_2$ [all data] | 0.1589, 0.2606 | 0.0615, 0.1268 | 0.0843, 0.0984 |
| Largest diff. peak/hole/e Å$^{-3}$ | 0.647/−0.861 | 0.482/−0.328 | 0.537/−0.566 |

Al: **6**, 109.5°; **7**, 109.3°; **8**, 109.4°] with bond angles ranging from 99.0(4)–119.9(4)° in **6**, 104.83(7)–117.35(7)° in **7** and 101.12(8)–116.83(8)° in **8**. In every case, Al forms shorter bonds to the amido nitrogen [**6**, 1.995(8) Å; **7**, 1.8918(14) Å; **8**, 1.9626(14) Å] than to the α-carbon atom of either the bridging or terminal $^i$Bu groups by at least 0.036 Å, 0.132 Å, and 0.050 Å in complexes **6**, **7** and **8** respectively.

This trend follows that of the difference [0.037 Å] in bond lengths of Al–N bonds [mean bond length, 1.953 Å] and the modestly longer Al–C bonds [mean bond length, 1.990 Å] calculated from the many aluminium complexes within the CSD.[9] Within the molecular structure of complex **7**, the Al–N bond is noticeably shorter than the mean bond distance, probably due to the less steric hindrance associated with the DMP amide in comparison to the bulkier TMP and HMDS amides. Potassium forms weaker interactions with the nitrogen atom of the amide and the carbon atom of the bridging $^i$Bu group, in comparison to those of aluminium, with the K–N$_{(amide)}$ bonds being shorter in length [in complexes **6** and **7**, by 0.159 Å and 0.181 Å, respectively] compared to the K–C$_{(^i\text{Bu})}$ bond; however in complex **8** these bonds are indistinguishable in length [difference in bond lengths, 0.002 Å]. In each structure, the K–N bond lengths associated with the PMDETA ligand are the shortest interactions that the K cation forms and are also relatively similar to one another in length, as identified from the narrow range of K–N$_{(PMDETA)}$ bond lengths [2.8192(16)–2.9446(15) Å], and are on average 0.08 Å shorter than the K–N$_{(amide)}$ bond lengths. With respect to the bond angles within the three structures, the biggest difference can be seen in the K–N$_{(amide)}$–Al and K–C$_{(bridging)}$–Al junctions. The greater the folding in the central ring, the more these angles decrease to compensate. Closer inspection of the molecular structure of **7** reveals an interesting feature. The $CH_2$ of one of the terminal $^i$Bu groups [C(5)] makes a long, weak contact with K [K(1)–C(5) separation length, 3.567(2) Å {for comparison, K(1)···C(9) separation = 5.323(2) Å}], as the methyl atoms of the DMP ligand point away from K. The result of this conformation that the DMP ligand adopts is that a gap appears on the coordination sphere of K, into which the $CH_2$ of a terminal $^i$Bu group can encroach. This long interaction in turn destroys the planarity [335.31°] of the KNAlC ring as a consequence. TMP, in comparison, has two methyl groups orientated towards K and two pointing away from it. These extra methyl groups (*cf.* those in DMP) prevent either of the $CH_2$ units of the terminal $^i$Bu groups from forming any interactions with the K cation due to their more extreme steric presence, forcing them to stay a large distance away, which in turn provides a planar central ring as a result. Space filling models of these two complexes (Fig. 2) highlight these interactions.

The slight deviation from planarity in the central ring [353.38°] in **8** can be attributed in part to inequivalent long range interactions of the methyl groups of HMDS to potassium [K–C$_{(HMDS)}$ bond lengths from Si(1): K(1)–C(13), 3.719(2) Å; K(1)–C(14), 3.488(2) Å; K(1)–C(15), 5.373(2) Å. K–C$_{(HMDS)}$ bond lengths from Si(2): K(1)–C(16), 3.480(2) Å; K(1)–C(17), 5.447(2) Å; K(1)–C(18), 5.037(2) Å]. From analysis of these bond lengths, K forms very weak contacts to two methyl groups of one $SiMe_3$ unit and one to the other $SiMe_3$, and these inequivalent interactions help to distort the plane of the ring to a small, but noticeable degree.

## Solution studies

Complexes **6** and **7** both exhibit good solubility in d$_{12}$-cyclohexane [d$_{12}$-Cy] solution. However, **8** was found to be insoluble in d$_{12}$-Cy, but in contrast readily dissolved in $C_6D_6$ solution. Thus, all three complexes could be characterized by $^1$H and $^{13}$C NMR spectroscopy. As compounds **6** and **7** were dissolved using the same solvent-system, their NMR signals can be compared directly to each other to determine what effect the amide group has on the resonance patterns observed. The $^i$Bu resonances in the $^1$H NMR spectra show that under the conditions of the experiment these alkyl groups are chemically equivalent in solution as only one set of resonances are observed. The major difference between the two spectra as

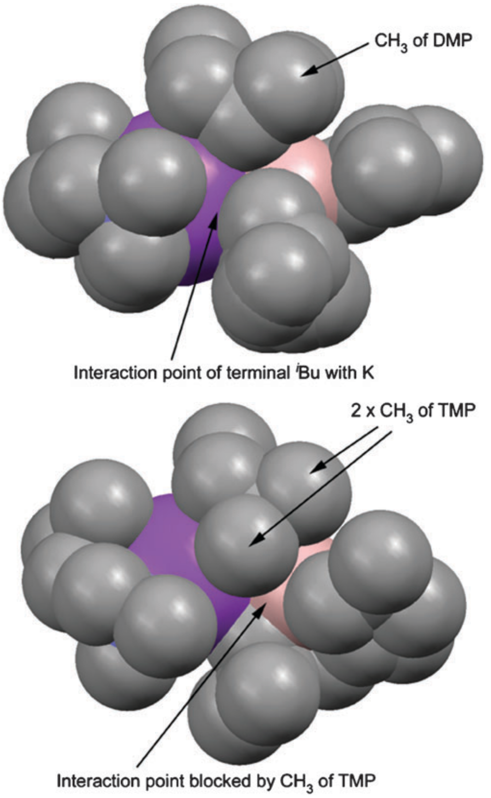

**Fig. 2** Space filling models of structures **6** (bottom) and **7** (top). K = purple, Al = pink, C = grey. Hydrogen atoms are omitted for clarity.

expected is that the resonance attributed to the $^i$Bu CH$_2$ group is found at a different chemical shift in **7** than in **6** (upfield by 0.14 ppm), indicating that the CH$_2$ hydrogen atoms in **7** are more shielded than in **6**. A complementary difference in chemical shift can be seen in the $^{13}$C NMR spectra, where the CH$_2$ carbon resonates at 32.4 ppm for **6** and at a lower frequency [27.3 ppm] for **7**, mirroring the direction of chemical shift change in the $^1$H NMR spectra. The resonances for the $^i$Bu CH and CH$_3$ groups, significantly further away from the attached metal centres, have exactly the same $^1$H NMR resonance values [1.92 and 0.94 ppm respectively], and almost identical $^{13}$C NMR chemical resonances [**6**: 28.1 and 30.0 ppm respectively. **7**: 28.2 and 29.8 ppm respectively]. The fact that the bridging and terminal $^i$Bu groups display only one set of resonances suggests a degree of fluxionality and that the long range K(1)–C(5) interaction seen in the solid state structure of **7** is probably not significant enough to be maintained in solution. The resonances attributed to the amides (TMP and DMP) and PMDETA move in the expected directions for metallated and cation-bound amines respectively [*cf.* $^1$H and $^{13}$C NMR spectra of the parent free amines].

Although not a direct comparison as the $^1$H and $^{13}$C NMR spectra of **8** were recorded in C$_6$D$_6$ solution, it is the only complex of the three where the CH$_2$ resonance of the chemically equivalent $^i$Bu groups resides at a positive chemical shift value [0.15 ppm]. In comparison to $^1$H and $^{13}$C NMR data of other known literature alkali-metal aluminates (with a similar structural motif, see Table 3), the resonance of 0.15 ppm is within the reported chemical shift range of 0.38–0.14 ppm for the CH$_2$ hydrogen atoms of the $^i$Bu groups, as are the values obtained for the CH [2.43 ppm, range = 2.45–2.28 ppm] and CH$_3$ components of the $^i$Bu ligands [1.42 ppm, range = 1.43–1.33 ppm]. Interestingly, the $^{13}$C NMR chemical shift of the CH$_2$ carbon has never been identified in the NMR data of the literature comparisons, however, in the $^{13}$C NMR spectrum of **8**, combined with evidence from $^1$H–$^{13}$C coupling NMR techniques, the CH$_2$ carbon resonance was identified under the methyl resonance of the $^i$Bu groups [at 30.0 ppm].

## Conclusion

In summary, the successful isolation and characterization of three new PMDETA-solvated mixed amido/alkyl potassium aluminates have been disclosed. Subtle differences in the way the potassium cation interacts with the anionic ligands resulting in differing degrees of puckering with regard to the central KNAlC ring have been highlighted. Studies are currently underway to quantify the use of compounds **6**, **7**, and **8** as bimetallic bases towards organic substrates given that lithium and sodium mono-amido tris-alkyl aluminates have been previously shown to be active bases.

## Experimental

### Reagents and general procedures

All reactions and manipulations were performed under a protective argon atmosphere using either standard Schlenk techniques or a glove box. Hexane was dried by heating to reflux over sodium benzophenone ketyl and then distilled under nitrogen prior to use. PMDETA and HMDS(H) were distilled over CaH$_2$ and stored over 4 Å molecular sieves prior to use. TMP(H) and DMP(H) were stored over 4 Å molecular sieves prior to use. $^i$Bu$_3$Al was purchased from Aldrich and used as received. KCH$_2$SiMe$_3$ was prepared by literature

**Table 3** Comparison of $^1$H NMR chemical shifts (ppm) of complexes **6**, **7** (both in C$_6$D$_{12}$) and **8** (in C$_6$D$_6$) with literature alkali-metal aluminates of similar structural motif (in C$_6$D$_6$)

| Compound | Alkali metal | Ligand | Amide | CH$_2$($^i$Bu) | CH($^i$Bu) | CH$_3$($^i$Bu) |
|---|---|---|---|---|---|---|
| **2** | Li | TMP(H) | TMP | 0.14 | 2.28 | 1.33 |
| **3** | Li | NEt$_3$ | TMP | 0.20 | 2.36 | 1.36 |
| **4** | Li | *N*,*N*-Diisopropyl benzamide | TMP | 0.38 | 2.35 | 1.36 |
| **5** | Na | TMEDA | TMP | 0.21 | 2.45 | 1.43 |
| **6** | K | PMDETA | TMP | −0.17 | 1.92 | 0.94 |
| **7** | K | PMDETA | DMP | −0.31 | 1.90 | 0.94 |
| **8** | K | PMDETA | HMDS | 0.15 | 2.43 | 1.42 |

methods.[1h] NMR spectra were recorded on a Bruker DPX 400 MHz spectrometer operating at 400.13 MHz for $^1H$ and 100.62 MHz for $^{13}C$. All $^{13}C$ spectra were proton decoupled.

**Synthesis of 6.** An oven-dried Schlenk tube containing 0.24 g (2 mmol) of $KCH_2SiMe_3$ was filled with hexane (10 mL). 0.42 mL (2 mmol) of PMDETA, followed by 0.34 mL (2 mmol) of TMP(H) were then injected into the reaction mixture to form a homogeneous solution. Finally, 2 mL (2 mmol) of 1 M $^i\mathrm{Bu}_3\mathrm{Al}$ solution were introduced, and the Schlenk tube was placed in the freezer at −28 °C to yield a crop of colourless crystals (0.19 g, 17% yield). $^1H$ NMR (400.13 MHz, 298 K, $d_{12}$-Cy): $\delta$ = 2.43–2.33 [8H, m, 4 × $CH_2$ of PMDETA], 2.25 [15H, s, 5 × $CH_3$ of PMDETA], 1.92 [3H, septet, $J$ = 6.5 Hz, 3 × CH of $^i$Bu], 1.66 [2H, m, 1 × $\gamma CH_2$ of TMP], 1.32–1.22 [16H, m, 4 × $CH_3$ and 2 × $\beta CH_2$ of TMP], 0.94 [18H, d, $J$ = 5.4 Hz, 6 × $CH_3$ of $^i$Bu], −0.17 ppm [6H, d, $J$ = 9.3 Hz, 3 × $CH_2$ of $^i$Bu]. $^{13}C\{^1H\}$ (100.62 MHz, 298 K, $C_6D_{12}$): $\delta$ = 58.2 [2 × $CH_2$ of PMDETA], 56.3 [2 × $CH_2$ of PMDETA], 53.1 [2 × quaternary C of TMP], 46.0 [4 × $CH_3$ of PMDETA], 44.8 [2 × $\beta CH_2$ of TMP], 42.9 [1 × $CH_3$ of PMDETA], 34.8 [4 × $CH_3$ of TMP], 32.4 [3 × $CH_2$ of $^i$Bu], 30.0 [6 × $CH_3$ of $^i$Bu], 28.1 [3 × CH of $^i$Bu], 19.3 [1 × $\gamma CH_2$ of TMP].

**Synthesis of 7.** This was prepared in the same manner as described above for **6** using the different amine DMP(H) (0.27 mL, 2 mmol) to yield a crop of colourless crystals (0.35 g, 33%). $^1H$ NMR (400.13 MHz, 298 K, $d_{12}$-Cy): $\delta$ = 3.37 [2H, m, 2 × $\alpha$CH of DMP], 2.37 [8H, m, 4 × $CH_2$ of PMDETA], 2.26 [12H, s, 4 × $CH_3$ of PMDETA], 2.24 [3H, s, 1 × $CH_3$ of PMDETA], 1.98–1.82 [4H, m, 3 × CH of $^i$Bu and 1 × $\gamma CH_2$ of DMP], 1.47–1.40 [5H, m, 2 × $\beta CH_2$ and 1 × $\gamma CH_2$ of DMP], 1.15 [6H, d, $J$ = 6.8 Hz, 2 × $CH_3$ of DMP], 0.94 [18H, d, $J$ = 6.6 Hz, 6 × $CH_3$ of $^i$Bu], −0.31 ppm [6H, d, $J$ = 6.8 Hz, 3 × $CH_2$ of $^i$Bu]. $^{13}C\{^1H\}$ (100.62 MHz, 298 K, $C_6D_{12}$): $\delta$ = 58.1 [2 × $CH_2$ of PMDETA], 56.3 [2 × $CH_2$ of PMDETA], 47.6 [2 × $\alpha$CH of DMP], 45.8 [4 × $CH_3$ of PMDETA], 42.7 [1 × $CH_3$ of PMDETA], 34.2 [2 × $\beta CH_2$ of DMP], 29.8 [6 × $CH_3$ of $^i$Bu], 28.2 [3 × CH of $^i$Bu], 27.3 [2 × $CH_3$ of DMP and 3 × $CH_2$ of $^i$Bu], 16.4 ppm [1 × $\gamma CH_2$ of DMP].

**Synthesis of 8.** This was prepared in the same manner as described above for **6** using the silylamine HMDS(H) (0.42 mL, 2 mmol) to yield a crop of colourless crystals (0.59 g, 52%). $^1H$ NMR (400.13 MHz, 298 K, $C_6D_6$): $\delta$ = 2.43 [3H, septet, $J$ = 6.3 Hz, 3 × CH of $^i$Bu], 1.88 [12H, s, 4 × $CH_3$ of PMDETA], 1.77 [11H, s, 1 × $CH_3$ and 4 × $CH_2$ of PMDETA], 1.42 [18H, d, $J$ = 6.7 Hz, 6 × $CH_3$ of $^i$Bu], 0.51 [18H, s, 6 × $CH_3$ of HMDS], 0.15 ppm [6H, d, $J$ = 7.1 Hz, 3 × $CH_2$ of $^i$Bu]. $^{13}C\{^1H\}$ (100.62 MHz, 298 K, $C_6D_6$): $\delta$ = 57.1 [2 × $CH_2$ of PMDETA], 55.1 [2 × $CH_2$ of PMDETA], 45.5 [4 × $CH_3$ of PMDETA], 42.3 [1 × $CH_3$ of PMDETA], 30.0 [6 × $CH_3$ and 3 × $CH_2$ of $^i$Bu], 27.8 [3 × CH of $^i$Bu], 7.4 ppm [6 × $CH_3$ of HMDS].

## Crystal structure determination

All measurements were made with an Oxford Diffraction Gemini S Diffractometer using either Cu ($\lambda$ = 1.54180 Å, **6**) or Mo (0.71073 Å, **7** and **8**) $K_\alpha$ radiation. All structures were solved using SHELXS-97, while refinement was to convergence against $F^2$ using SHELXL-97.[13] Disorder in the PMDETA ligand of **6** was modelled over two sites with a 2 : 1 site occupancy ratio. Disorder in a terminal $^i$Bu group of **7** was modelled over two sites with a 4 : 1 site occupancy ratio. In Fig. 1 only the major components are shown for clarity.‡

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