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### **Dalton Transactions**

# Synthesis and temperature–dependent NMR studies of monomeric and dimeric tris(dialkylamino)alanes

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## Electronic Supplementary Information

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	bond
<b>A</b>	Al1A–N3A
	Al1A–N4A
	Al1A–N1A
	Al1A–N2A
N6B N6B	Al2A–N5A
	Al2A–N6A
	Al2A–N1A
	Al2A–N2A
N2B Al2B	Al1A–Al2A
AIIB	Al1B–N4B
	Al1B–N3B
N5B V	Al1B–N1B
N3B N3B	Al1B–N2B
	Al2B–N6B
	Al2B–N5B
	Al2B–N1B
	Al2B–N2B
	AllB-Al2B
	angle
	N6A Alia-Nia-A
	Al1A–N2A–A
	N1A-Al1A-N
AllA	Al2A N1A–Al2A–N
	N3A–Al1A–N
NIA NIA	N5A–Al2A–N
	N5A Al1B–N1B–A
	Al1B–N2B–A
	N1B-Al1B-N
	N1B–Al2B–N
	N4B-Al1B-N

Al2A–N2A	1.9926(10)
Al1A–Al2A	2.8311(5)
Al1B–N4B	1.8225(12)
Al1B–N3B	1.8227(12)
Al1B–N1B	1.9854(11)
Al1B–N2B	1.9894(11)
Al2B-N6B	1.8121(12)
Al2B–N5B	1.8222(11)
Al2B–N1B	1.9781(11)
Al2B-N2B	1.9802(11)
Al1B–Al2B	2.8300(5)
angle	value, °
Al1A-N1A-Al2	2A 91.28(4)
Al1A-N2A-Al2	2A 90.91(4)
N1A-Al1A-N2	A 88.74(4)
N1A-Al2A-N2	A 88.17(4)
N3A-Al1A-N4	A 113.68(5)
N5A-Al2A-N6	A 113.82(5)
Al1B-N1B-Al2	2B 91.13(4)
Al1B-N2B-Al2	2B 90.95(4)
N1B-Al1B-N2	B 88.16(4)
N1B-Al2B-N2	B 88.62(4)
N4B-Al1B-N3	B 112.85(6)
N6B-Al2B-N5	B 113.48(5)

value, Å

1.8134(11)

1.8213(11)

1.9763(10) 1.9797(10)

1.8232(12)

1.8238(12)

1.9836(10)

Fig. ESI.1 Asymmetric unit of tris(diethylamino)alane (left); selected bond lengths and angles (right).



Fig. ESI.2 Asymmetric unit of tris(*N*-methylpiperazino)alane (left); selected bond lengths and angles (right).

#### Synthetic procedures



Fig. ESI.3 Example of a powder diffractogram of the separated lithium chloride.

#### Aluminum titration

 $AlH_3 \cdot \frac{1}{5}Et_2O_{(s)}$  is carefully deactivated by diffusion of water vapor. The substance is then transferred to a 100 mL beaker containing 20 mL of distilled water and 10 mL of hydrochloric acid  $(2 \text{ mol L}^{-1})$ . The suspension is heated to boiling and the resulting clear solution is transferred to a 100 mL volumetric flask. To 25 mL of the solution, 30 mL of an EDTA solution  $(0.025 \text{ mol L}^{-1})$  and 1 mL of hydrochloric acid  $(2 \text{ mol L}^{-1})$ . The suspension is heated to boiling and the resulting clear solution is transferred to a 100 mL volumetric flask. To 25 mL of the solution, 30 mL of an EDTA solution  $(0.025 \text{ mol L}^{-1})$  and 1 mL of hydrochloric acid  $(2 \text{ mol L}^{-1})$  are added. The solution is boiled for 10 min and then cooled to room temperature. A pH value of 7 is adjusted with CH<sub>3</sub>COONa. By adding a spatula tip of a xylenol orange/KNO<sub>3</sub> trituration (1:100), the solution takes on an intense yellow color. Using a ZnSO<sub>4</sub> solution  $(0.2 \text{ mol L}^{-1})$ , the yellow solution is titrated until an orange color is apparent.

#### Temperature-dependent NMR spectra



Fig. ESI.4 Temperature-dependent <sup>1</sup>H NMR spectra of tris(diisopropylamino)alane.



Fig. ESI.5 Temperature-dependent <sup>13</sup>C NMR spectra of tris(diisopropylamino)alane.



Fig. ESI.6 Temperature-dependent <sup>1</sup>H NMR spectra of tris(dimethylamino)alane.



Fig. ESI.7 Temperature-dependent <sup>13</sup>C NMR spectra of tris(dimethylamino)alane.



Fig. ESI.8 Temperature-dependent <sup>1</sup>H NMR spectra of tris(pyrrolidino)alane.



Fig. ESI.9 Temperature-dependent <sup>13</sup>C NMR spectra of tris(pyrrolidino)alane.



Fig. ESI.10 Temperature-dependent <sup>1</sup>H NMR spectra of tris(piperidino)alane.



Fig. ESI.11 Temperature-dependent <sup>13</sup>C NMR spectra of tris(piperidino)alane.