Dimethylaluminium Alkoxides: A Physico-chemical Investigation†

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Compounds of the type $[Me_2Al(\mu\text{-}OR)]_x$ (R = Me, Et, $\mathrm{Pr^n}$, $\mathrm{Pr^i}$, $\mathrm{Bu^n}$, $\mathrm{Bu^i}$, $\mathrm{Bu^s}$, $\mathrm{Bu^t}$, $n\text{-}C_5H_{11}$, $CH_2CH_2\mathrm{Pr^i}$, $CH_2\mathrm{Bu^t}$, $n\text{-}C_6H_{13}$, $n\text{-}C_8H_{17}$, $n\text{-}C_{10}H_{21}$ or $n\text{-}C_{12}H_{25}$) have been synthesised and studied by ^1H, ^{13}C, ^{17}O and ^{27}Al NMR, IR and mass spectrometry. With the exception of R = $CH_2CH_2\mathrm{Pr^i}$, all the compounds with branched-chain alkoxide substituents are purely dimeric ($x = 2$), while the former and the *n*-alkyl derivatives exist in solution as an equilibrium between dimeric ($x = 2$) and trimeric ($x = 3$) forms. Equilibrium constants and ΔH and ΔS for the trimer–dimer equilibria in solution were obtained for R = $\mathrm{Pr^n}$. These results, and the NMR spectroscopic data, are interpreted on the basis of steric interactions and ring strain. The kinetics of conversion of $[Me_2Al(O\mathrm{Pr^n})]_3$ into $[Me_2Al(O\mathrm{Pr^n})]_2$ has been investigated, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ determined, and the identity of the reaction intermediates probed by NMR and mass spectrometry. *Ab initio* molecular orbital calculations have been carried out on the model compounds $[H_2Al(\mu\text{-}OH)]_2$ and $[H_2Al(\mu\text{-}OH)]_3$. Their relative energies and calculated structures are considered in relation to experimental data.

The elimination-condensation reaction sequence (1) which occurs between a Group 13 metal alkyl (M = Al, Ga or In) and a Brønsted acid, is undoubtedly the cornerstone of much of the

$$MR_3 + HX \longrightarrow R_2MX + HR \qquad (1)$$

organometallic chemistry of these elements.[1,2] In the majority of cases cyclisation occurs to give di- and tri-meric species, the actual degree of association being determined by a balance between steric effects, valence-angle strain, entropy, and the nature of possible intermediates involved in the reaction. Several workers have rationalised the factors that determine the degree of aggregation purely on the basis of solid-state X-ray crystallographic structure determinations.[3] The results of these *qualitative* studies have now become part of the folklore of Group 13 chemistry. Surprisingly, however, only a few studies have attempted to obtain *quantitative* information concerning the effects of ring substitution on the aggregation number of these cyclic compounds.[4,5] It would therefore seem clear that a thorough systematic investigation of a single system would prove invaluable in the context of furthering our understanding of this phenomenon. In view of our interest in the chemistry of aluminium alkoxides and aryloxides,[6] we have chosen dimethylaluminium alkoxides, $[Me_2Al(\mu\text{-}OR)]_x$, as the subject of such a study.

The earliest report of the preparation of a dimethylaluminium alkoxide was that of the methoxide **1** *via* the exchange reaction (2).[7] However, subsequently, Mole[8] showed

$$2AlMe_3 + Al(OMe)_3 \longrightarrow \underset{\mathbf{1}}{3Me_2Al(OMe)} \qquad (2)$$

that **1** could be more conveniently prepared by the solvolysis of trimethylaluminium [equation (3)]. Based on molecular weight

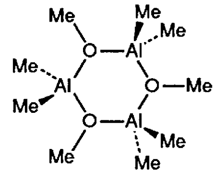
$$AlMe_3 + MeOH \longrightarrow Me_2Al(OMe) + MeH \qquad (3)$$

studies[9,10] and later confirmed by electron diffraction[11] compound **1** was demonstrated to be trimeric (**I**) adopting a non-planar six-membered Al_3O_3 ring structure. More recently, a wide variety of dimethylaluminium alkoxides have been reported,[12] however in all cases where their molecularity was determined by solution molecular weight measurements they were found to exist as dimers (**II**). It is perhaps tempting, therefore, to conclude that the presence of ligands sterically more hindered than the methyl of the methoxide group precludes the formation of trimeric compounds. This apparent clear-cut division between the di- and tri-meric forms is clouded by the report that the phenoxide exists as an equilibrium mixture of both dimer and trimer as determined by solution molecular weight and ^1H NMR spectroscopy [equation (4)].[7,8,13] Furthermore, although the methoxide is isolated as

$$3[Me_2Al(\mu\text{-}OPh)]_2 \rightleftharpoons 2[Me_2Al(\mu\text{-}OPh)]_3 \qquad (4)$$

the trimer, from the reaction of $AlMe_3$ and MeOH in benzene solution, the initial product appears to contain a dimeric species that is converted quantitatively into the trimer in a matter of minutes [equation (5)].[13]

$$AlMe_3 + MeOH \xrightarrow{C_6H_6} [Me_2Al(\mu\text{-}OMe)]_2 \xrightarrow{\text{minutes}} [Me_2Al(\mu\text{-}OMe)]_3 \qquad (5)$$



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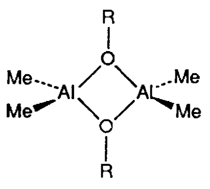

II

In view of these observations several important questions are raised. Why do only dimethylaluminium methoxide and phenoxide have trimeric forms? If other alkoxides do indeed exist in both tri- and di-meric forms how can they be isolated, and what factors control the relative stability of each form? Finally, if there is conversion between oligomers what is the reaction mechanism, and can intermediates be observed or

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† *Supplementary data available* (No. SUP 56898, 19 pp): equilibrium and kinetic data. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

Table 1 Selected ^{1}H, ^{13}C and ^{17}O NMR data for $[Me_2Al(\mu\text{-}OR)]_x$ (x = 2 or 3)[a]

	^{1}H				^{13}C				^{17}O	
	OCH_2		Al–CH_3		OCH_2		Al–CH_3			
R	D	T	D	T	D	T	D	T	D	T
1 Me	—	3.04	—	−0.59	—	50.7	—	−10.7	—	−20.6
2 Et	3.37	3.65	−0.53	−0.52	64.1	65.4	−10.4	−9.5	18.5	−19.8
3 Pr^n	3.37	3.65	−0.51	−0.47	64.8	66.3	−10.5	−9.1	15.9	−19.8
4 Pr^i	3.86[b]	—	−0.51	—	66.9[b]	—	−8.7	—	44.6	—
5 Bu^n	3.44	3.75	−0.56	−0.54	62.8	64.8	−10.7	−9.1	11.8	−17.5
6 Bu^i	3.29	—	−0.62	—	70.2	—	−10.7	—	15.0	—
7 Bu^s	3.67[b]	—	−0.59	—	72.3[b]	—	−8.5	—	40.2	—
8 Bu^t	—	—	−0.45	—	74.5[c]	—	−6.1	—	61.8	—
9 $n\text{-}C_5H_{11}$	3.46	3.78	−0.51	−0.48	63.2	65.1	−10.6	−9.1	11.6	−19.8
10 $CH_2CH_2Pr^i$	3.55	3.80	−0.60	−0.55	61.6	63.8	−10.6	−9.1	13.8	−19.0
11 CH_2Bu^t	3.31	—	−0.41	—	74.5	—	−10.3	—	9.9	—
12 $n\text{-}C_6H_{13}$	3.48	3.75	−0.59	−0.56	63.3	65.1	−10.6	−9.1	12.7	−18.8
13 $n\text{-}C_8H_{17}$	3.49	3.77	−0.55	−0.52	63.3	65.1	−10.5	−9.1	15.8	−18.9
14 $n\text{-}C_{10}H_{21}$	3.50	3.83	−0.39	−0.36	63.3	65.1	−10.4	−9.0	*d*	*d*
15 $n\text{-}C_{12}H_{25}$	3.50	3.86	−0.39	−0.34	63.3	65.1	−10.4	−9.0	*d*	*d*

[a] δ in ppm, full data given in the Experimental section; D = dimer, T = trimer. [b] $OCHR_2$. [c] OCR_3. [d] Not observed due to excessive linewidths.

isolated? It is in an effort to address these questions that the present study has been undertaken.

Results and Discussion

Synthetic and Spectroscopic Studies.—Reaction of $AlMe_3$ with 1 molar equivalent of an alcohol in hexane, either at room temperature or −78 °C, results in the evolution of a gas, presumably methane, and the formation of the appropriate dimethylaluminium alkoxide in essentially quantitative yield [equation (6): R = Me **1**,[7,8] Et **2**,[14] Pr^n **3**, Pr^i **4**,[8,12b] Bu^n **5**,

$$AlMe_3 + ROH \longrightarrow Me_2Al(OR) + MeH \qquad (6)$$

Bu^i **6**, Bu^s **7**, Bu^t **8**,[8,12c] C_5H_{11} **9**, $CH_2CH_2Pr^i$ **10**, CH_2Bu^t **11**, C_6H_{13} **12**, C_8H_{17} **13**, $C_{10}H_{21}$ **14** or $C_{12}H_{25}$ **15**]. The dimethylaluminium alkoxide compounds are all air-sensitive, volatile, colourless liquids except for **1**, **8** and **11** which are crystalline solids at room temperature.

The mass spectra (see Experimental section) of compounds **1**–**3**, **5**, **6**, **9** and **10** all show peaks due to the appropriate trimer (*i.e.* either $3M^+$ or $3M^+$ − Me). Those for **4**, **7**, **8** and **11** gave only peaks due to the dimers (*i.e.* either $2M^+$ or $2M^+$ − Me). The low volatility of compounds **12**–**15** precluded meaningful mass spectral characterisation. The fragmentation pattern for all compounds, **1**–**11**, was analogous to those observed previously for **1**, $[Et_2Al(\mu\text{-}OEt)]_x$ and $[Bu^i{}_2Al(\mu\text{-}OBu^i)]_x$.[15]

The room-temperature ^{1}H and ^{13}C NMR spectra (Table 1) obtained for compounds **2**, **3**, **5**, **9**, **10**, **12** and **13** each contain two sets of resonances for the aluminium methyl and alkoxide groups. Based on solution molecular weight measurements (see below and Experimental section), comparison with the literature precedent,[4,5] the corresponding ^{17}O NMR spectra (see below), and from our variable-temperature studies (see below) we have assigned the more upfield of the two shifts of the aluminium-methyl resonance in the ^{1}H and ^{13}C NMR spectra to the dimers $[Me_2Al(\mu\text{-}OR)]_2$ (the downfield resonance being due to the trimer).[16,17] The remaining peaks were assigned based on their relative integrations (see Experimental section). It should be noted that the relative intensity of the peaks due to the two oligomers is unchanged between solutions in C_6D_6, [$^2H_8$]toluene, $CDCl_3$ and CD_2Cl_2. By contrast, the ^{1}H and ^{13}C NMR spectra (Table 1) for compounds **1**, **4**, **6**–**8** and **11** all give a single set of resonances, indicative of the presence of a single oligomeric form, consistent with literature values for solution molecular weight measurements, *i.e.* trimer for **1**,[7,8] and dimer for **4**, **6**–**8** and **11**.[8,12b,c]

We have shown previously[18,19] that the ^{13}C NMR shifts of the aluminium-methyl resonance in Me_3AlPR_3 complexes is primarily dependent on the steric bulk of the phosphine ligand; the bulkier phosphines force the aluminium to become more distorted from planarity, and the increased p character in the Al–C bond is reflected by the downfield shift of the Al–CH_3 carbon resonance. As can be seen from Table 1 there is a similar dependence of the aluminium-methyl ^{13}C shift on the steric bulk of the alkoxide in both the dimers and the trimers; that is, the greater the steric bulk of the oxygen's substituents, the more downfield is the shift of the methyl resonance. This result can be rationalised in the following manner: the greater the steric bulk of the alkoxide, the greater is the interligand repulsion, which in turn leads to a distortion of the Al_xO_x ring, closing the Al–O–Al and opening the O–Al–O angles. The rehybridisation at aluminium caused by this distortion results in the closing of the C–Al–C angle, with a concomitant increase in the p character of the Al–C bond.

Given this correlation, the ^{13}C NMR signal for the aluminium methyl should provide a spectroscopic probe of the steric effect of the alkoxide alkyl group on the geometry of the Al_xO_x ring. Thus, for the dimers $[Me_2Al(\mu\text{-}OR)]_2$ methyl substitution at the alkoxide α-carbon results in a downfield shift in the Al–CH_3 ^{13}C NMR resonance: Et (δ −10.4) *versus* Pr^i (δ −8.7) *versus* Bu^t (δ −6.1). On the other hand, branching at the alkoxide β-carbon has little effect on the Al–Me ^{13}C NMR chemical shifts and, presumably, the structure of the dimeric Al_2O_2 core: Pr^n (δ −10.5) *versus* Bu^i (δ −10.7) *versus* CH_2Bu^t (δ −10.3).

The ^{17}O NMR spectra obtained for compounds existing in both di- and tri-meric forms (**2**, **3**, **5**, **9**, **10**, **12** and **13**) consist of two resonances in two distinct ranges, δ 11.6–18.5 and −17.5 to −20.6. Those with negative δ, *i.e.* upfield of water (δ 0.00), may be assigned to the trimer by comparison with the methoxide **1** (δ −20.6), while the downfield resonances, positive δ, are consistent with the dimeric forms.[20]

Since for each compound the identity of the substituents at oxygen are constant, *i.e.* two $AlMe_2$ moieties and the appropriate alkyl group, the ^{17}O NMR chemical shift differences between the di- and tri-meric forms must be primarily due to the change of hybridisation at oxygen, resulting from the opening of the Al–O–Al angle in going from a four-membered Al_2O_2 to a six-membered Al_3O_3 ring. These angles, obtained from *ab initio* calculation (see below) for the model compounds

$[H_2Al(\mu\text{-}OH)]_2$ and $[H_2Al(\mu\text{-}OH)]_3$, are 100.1 and 127.8° respectively. From this we can conclude that a downfield shift in the ^{17}O NMR is consummate with a closing of the Al–O–Al bond angle.[21] We propose, therefore, that in the absence of any significant electronic effects of different alkyl substituents, a downfield shift in the ^{17}O NMR signal on substitution of the alkoxide is indicative of a reduction in the Al–O–Al angle as a result of increased interligand steric interaction, *i.e.* the larger the steric bulk of the alkoxide alkyl substituents the greater is its steric repulsion with the aluminium methyl groups. In order to lessen this effect a closing in the Al–O–Al bond angle occurs with a concomitant increase in the $R(O)\cdots Me(Al)$ interligand distances. The narrow range observed for the ^{17}O NMR chemical shifts for both di- and tri-meric forms of straight-chain alkoxide compounds (see Table 1) would suggest that increasing the chain length has minimal effect on the steric bulk of the alkoxide. This observation is consistent with our measurements of the dimer/trimer equilibrium constants at 298 K for the *n*-alkyl derivatives (see below).

By contrast with the *n*-alkoxide derivatives the ^{17}O NMR spectral chemical shifts for the branched-chain dimeric compounds are highly dependent on the steric bulk of the alkoxide. Thus methyl substitutions at the alkoxide α-carbon result in a significant downfield shift in the ^{17}O NMR resonance, Et (δ 18.5) *versus* Pr^i (δ 44.6) *versus* Bu^t (61.8), while little significant variation is observed in the ^{17}O NMR chemical shifts for methyl substitutions at the alkoxide β-carbon Pr^n (δ 15.9) *versus* Bu^i (δ 15.0) *versus* CH_2Bu^t (δ 9.9). However, these trends are difficult to interpret since a similar shift distribution is observed for the parent α-substituted alcohols, *i.e.* EtOH (δ 60), Pr^iOH (δ 38), Bu^tOH (δ 70).

Unfortunately, it is difficult to corroborate these spectroscopic results with structural data. However, it should be noted that the Al–O–Al angle obtained from the gas-phase electron diffraction of $[Me_2Al(\mu\text{-}OBu^t)]_2$ **8**, 98.1°,[22] is indeed smaller than both that calculated for $[H_2Al(\mu\text{-}OH)]_2$ (100.1°) and observed in the X-ray structural determination of the sterically less demanding 2-allyl-6-methylphenoxide derivative (100.9°).[12h]

The ^{27}Al NMR resonances for the alkoxides **1**–**15** (δ 136–152) vary very little from that of $AlMe_3$ (δ 155, $W_{\frac{1}{2}}$ = 630 Hz) and dimeric dimethylaluminium siloxides (δ 152–160).[23] Given the large linewidths it is clearly impossible to resolve separate resonances for the di- or tri-meric forms. However, it is interesting that the ^{27}Al NMR resonances for the straight-chain derivatives show linewidths (see Experimental section) that are proportional to the alkoxide chain length.

The ^{13}C NMR resonances of the aluminium methyl and the ^{17}O chemical shifts of the alkoxides indicate that the structure of the dimeric Al_2O_2 moiety is not influenced by substitution at distances greater than or equal to that of the alkoxide β-carbon. No equivalent spectroscopic series is available for the trimer. However, the mere existence of a isolable trimer for $CH_2CH_2Pr^i$ (**10**) but not for Bu^i (**6**)* suggests that for the trimeric $[Me_2Al(\mu\text{-}OR)]_3$ substitution at the alkoxide γ-carbon does not disturb the Al_3O_3 core unduly.

For the *n*-alkoxide derivatives the relative quantities of species assigned as dimer and trimer present in the reaction mixture upon removal of solvent are dependent on the temperature of the $AlMe_3$ solution to which the alcohols were added. Fig. 1 shows a plot of the percentage of trimer formed in the reaction mixture as a function of chain length $O(CH_2)_nH$, n = 1–8, for the reaction carried out at 298 and 195 K. It can clearly be seen that decreasing the reaction temperature increases the relative quantity of trimer produced. From this we may conclude that the trimeric forms are the thermodynamic products while the dimers are the kinetically favoured products. This is in agreement with our variable-temperature NMR studies, and the results of previous workers.[4,5]

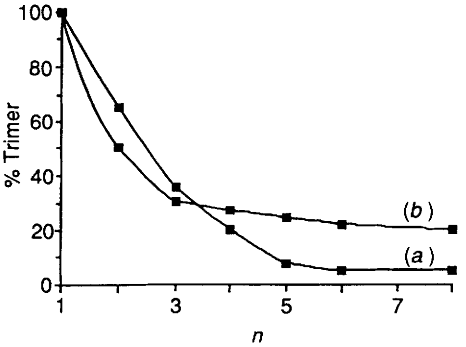

Fig. 1 Plot of the percentage of $[Me_2Al(\mu\text{-}OR)]_3$ formed from the reaction of $AlMe_3$ with ROH at 298 (*a*) and 195 K (*b*) *versus* the number of carbon atoms (*n*) in the alkoxide, $O(CH_2)_nH$

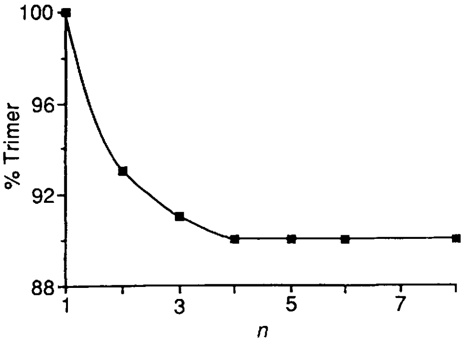

Fig. 2 Plot of the equilibrium (at 298 K) percentage of $[Me_2Al(\mu\text{-}OR)]_3$ as a function of the alkoxide $O(CH_2)_nH$ chain length (*n*)

If the dimer and trimer mixtures are allowed to equilibrate, the dimer is slowly ($t_{\frac{1}{2}}$ *ca.* weeks at 298 K) converted into the trimer [equation (7)].

$$[Me_2Al(OR)]_2 \longrightarrow \tfrac{2}{3}[Me_2Al(OR)]_3 \qquad (7)$$

Compound **2** has been previously prepared and purified by distillation.[14] The resulting product was determined to exist purely in a dimeric form, however no observation of the long-term stability (reconversion into the trimeric form) was reported.

Fig. 2 is a plot of the equilibria percentage of trimer at 298 K as a function of chain length. Heating the mixture results in conversion of the trimer into the dimer ($t_{\frac{1}{2}}$ *ca.* min to hours at 298–420 K) [equation (8)]. The conversion of trimer into dimer

$$[Me_2Al(OR)]_3 \longrightarrow \tfrac{3}{2}[Me_2Al(OR)]_2 \qquad (8)$$

and *vice versa* is totally reversible with temperature, implying the presence of an equilibrium. Since at each equilibrium temperature there appears to be only dimer and trimer present (*i.e.* greater than 99% of the total integration of all OCH_2 resonances, see below), this would imply the presence of the equilibrium (9). Analogous equilibria have been previously proposed for aluminium amides, see refs. 4 and 5.

$$2[Me_2Al(OR)]_3 \overset{K_{eq}}{\rightleftharpoons} 3[Me_2Al(OR)]_2 \qquad (9)$$

$$K_{eq} = [(Me_2AlOR)_2]^3/[(Me_2AlOR)_3]^2 \qquad (10)$$

The ^1H NMR spectra of a $[^2H_8]$toluene solution of the *n*-propoxide derivative **3** were obtained at various temperatures (25–90 °C) from which the relative concentration of dimer and trimer may be calculated and subsequently the equilibrium

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* It is worth noting that although the mass spectrum of compound **6** contains peaks due to a trimer species, the ^1H, ^{13}C and ^{17}O NMR spectra only contain resonances due to a single, dimeric, moiety.

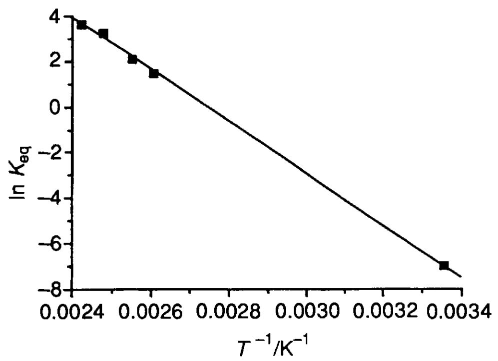


Fig. 3 Temperature dependence of the equilibrium constant, K_{eq}, for the conversion of $[Me_2Al(\mu\text{-}OPr^n)]_3$ into $[Me_2Al(\mu\text{-}OPr^n)]_2$ (R = 0.999)

Table 2 Selected equilibria data for $Me_2Al(OPr^n)$ in toluene[a]

T/K	x_{trimer}[b]	[trimer][c]/mol dm^{-3}	K_{eq}[d]/mol dm^{-3}
298	0.936	0.861	9.13×10^{-4}
384	0.396	0.396	4.35
392	0.341	0.341	7.66
404	0.218	0.218	31.1
413	0.204	0.204	37.4

[a] From ^1H NMR spectra measured in $[^2H_8]$toluene. [b] x_{trimer} = mole fraction of $Me_2Al(OPr^n)$ existing as the trimer. [c] Total concentration of $Me_2Al(OPr^n)$, 2.759 mol dm^{-3}. [d] $K_{eq} = [(Me_2AlOPr^n)_2]^3/[(Me_2AlOPr^n)_3]^2$.

Table 3 Selected kinetic data for the trimer to dimer rearrangement of $Me_2Al(OPr^n)$[a]

T/K	$[\text{trimer}]_i$[b]/mol dm^{-3}	$10^5\ k_{obs}$[c]/dm^3 mol^{-1} s^{-1}
380	0.637	2.76
387	0.627	3.85
397	0.651	4.13
401	0.690	7.16
402	0.616	7.91

[a] From ^1H NMR spectra measured in $[^2H_8]$toluene. [b] Initial concentration of $[Me_2Al(\mu\text{-}OPr^n)]_3$. [c] Second-order rate constant, see text.

constants, K_{eq} (see Table 2). The temperature dependence of the equilibrium constant (Fig. 3) allows the determination of ΔH and ΔS for the conversion of $[Me_2Al(\mu\text{-}OPr^n)]_3$ into $[Me_2Al(\mu\text{-}OPr^n)]_2$ to be 95(2) kJ mol^{-1} and 260(10) J K^{-1} mol^{-1} respectively, *i.e.* 47.5 kJ mol^{-1} for the reaction shown in equation (8). The experimentally determined value for ΔH is slightly smaller than, but consistent with, the value calculated (ΔH = 123.6 kJ mol^{-1}) for the model reaction [equation (11)].

$$2[H_2Al(OH)]_3 \rightleftharpoons 3[H_2Al(OH)]_2 \qquad (11)$$

Since steric factors should destabilise the trimer to a greater extent than the dimer, the substitution of Al–H and OH for Al–Me and OPr^n respectively would be predicted to lower the ΔH, which is indeed observed.

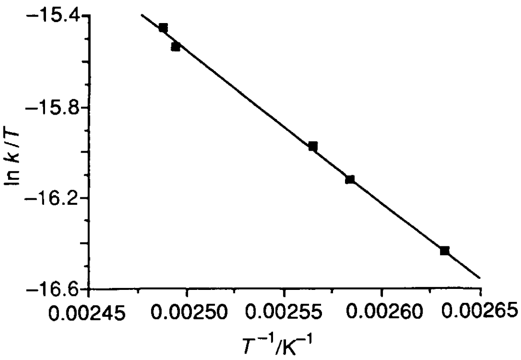
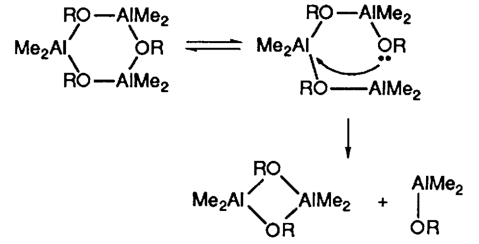


Fig. 4 Eyring plot for the determination of $\Delta H^‡$ and $\Delta S^‡$ for the conversion of $[Me_2Al(\mu\text{-}OPr^n)]_3$ into $[Me_2Al(\mu\text{-}OPr^n)]_2$ (R = 0.998)



(12)

It is conceivable that the uncatalysed trimer to dimer conversion may occur *via* one of the three pathways proposed by Sauls *et al.*[5] for the related amido-bridged species. (*a*) Ring opening, followed by attack at an internal aluminium by the terminal alkoxide, resulting in a four-membered ring and a free monomer, which may dimerise [equation (12)]. This mechanism was proposed on the basis of evidence for the presence of monomer,[24] however one may expect the monomer to react as readily with the dimer so formed as well as another monomer or the initial trimer. The former would, of course, be counter productive. (*b*) Dissociation to monomers and subsequent recombination. As noted by Sauls *et al.*[5] this would seem highly unlikely since three Al–O bonds must be broken (a high-energy process). (*c*) Ring opening of the trimer followed by attack on a further trimeric unit using the available lone pair on the oxygen atom in an intermediate involving five-co-ordinate aluminium, in an analogous method to that proposed by Storr and Thomas.[4] The proposal of a five-co-ordinate aluminium intermediate may be rationalised in terms of the known five-co-ordination chemistry of aluminium,[25] and the observation that the equivalent isomerisation for gallium is very slow, suggesting a high energy barrier consistent with the lesser stability of five-co-ordinate gallium.[26]

As reported previously,[13] the conversion of dimer into trimer for the methoxide [equation (5)] is rapid, occurring in a few minutes and making it difficult to make kinetic measurements. Unfortunately, the analogous reaction for the longer-chain alkoxides [equation (7)] occurs over a period of months, which is also inconvenient for kinetic measurements! Fortunately the reverse reaction, the trimer to dimer conversion [equation (8)], is completed in a few hours at 90–130 °C. As with the equilibrium studies, the *n*-propoxide, compound **3**, was chosen as a representative compound, since the ^1H NMR chemical shifts of the alkoxide α-CH_2 group in the trimer are distinct from those of the dimer. The conversion reaction was studied in $[^2H_8]$toluene solution over a range of concentrations to determine the molecularity of the reaction. Once obtained the rate data for a single concentration were recorded over a range of temperatures (90–130 °C).

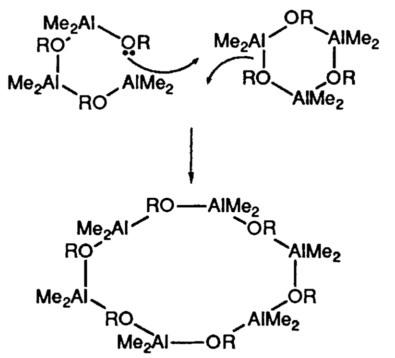
When trimeric compound **3** is heated to a temperature T the ^1H NMR signal due to the α-CH_2 protons disappears along with the concomitant appearance of the appropriate signal for the dimer. A plot of the time dependence of the trimer's concentration [trimer] indicates a concentration dependence for the half-life $t_{\frac{1}{2}}$ consistent with non-first order kinetics, over all concentrations. A plot of 1/[trimer] *versus* time, t, indicates second-order kinetics [equation (13)] and allows

$$-d[\text{trimer}]/dt = k[\text{trimer}]^2 \qquad (13)$$

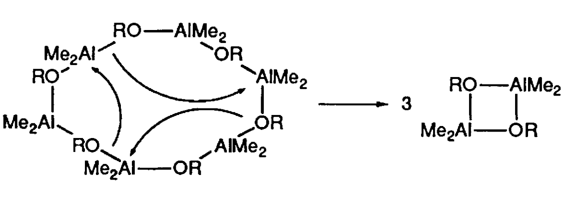
the determination of the second-order rate constant, k (see

Table 3). The enthalpy ($\Delta H^{\ddagger}$) and entropy ($\Delta S^{\ddagger}$) of activation were obtained from the appropriate Eyring plot (Fig. 4), as 55(3) kJ mol^{-1} and −120(20) J K^{-1} mol^{-1}. The enthalpy is as would be expected, larger than the enthalpy of the overall reaction (ΔH = 46.45 kJ mol^{-1}), however its value is not very informative regarding the mechanism since values in the range 40–146 kJ mol^{-1} cannot readily be interpreted.[27] Given the second-order nature of the reaction, an associative mechanism would be expected, and the negative value of $\Delta S^{\ddagger}$ confirms this.

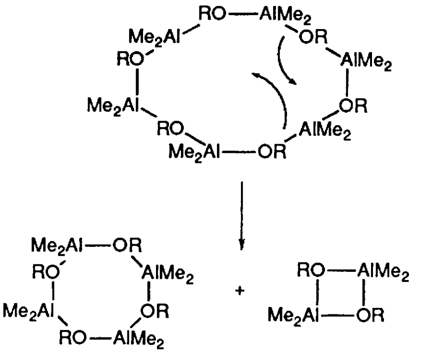
Based on our observation of a second-order reaction with respect to the trimer, we propose that the mechanism of trimer to dimer conversion is that originally proposed by Storr and Thomas[4] for cyclic imino derivatives of aluminium and discussed in (*c*) above, *i.e.* ring opening of a trimer followed by attack on a neighbouring ring in the rate-determing step to yield a hexamer [equation (14)]. While the hexamer may subsequently decompose to three dimers [equation (15)], such a concerted mechanism is unlikely due to the distortion required for the simultaneous formation of three new Al • • • O interactions * or, as is more likely, to a dimer and tetramer[28] [equation (16)] from which two further dimers are formed [equation (17)].



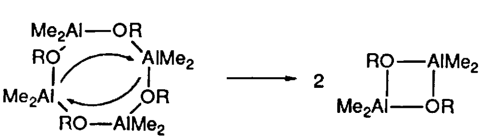
(14)



(15)



(16)



(17)

this mechanistic pathway is valid the hexamer and tetramers should be observable as intermediates. In fact, signals consistent with a new [Me$_2$Al(μ-OR)]$_x$ oligomer are discernible from the baseline in the ^{1}H NMR spectra *during* the conversion of [Me$_2$Al(μ-OPr^n)]$_3$ into [Me$_2$Al(μ-OPr^n)]$_2$. However, based on the ^{1}H NMR spectra no evidence for the value of *x* is available.

Since solution molecular weight measurements are by their very nature equilibrium experiments and the intermediates are obviously not observed in significant quantities (< 1% by ^{1}H NMR spectroscopy) at equilibrium, we cannot directly determine the value of *x* (degree of association) in solution. However, mass spectrometry data do allow us to infer the value of *x* under non-equilibrium conditions. Thus, the mass spectrum of compound **3** consists of peaks due to oligomers up to and including the trimer (see Experimental section). If the sample is heated on the sample probe to 250 °C to promote the trimer to dimer conversion additional fragments due to hexamer (m/z = 681, $6M^+$ − Me) and tetramer (m/z = 449, $4M^+$ − Me) are observed after only a few seconds. After several minutes the mass spectrum is consistent with a distribution of isomers up to the octamer (m/z = 913, $8M^+$ − Me). These observations are consistent in part with the mechanism proposed in equations (16) and (17).

Given the excruciatingly slow rate of dimer to trimer conversion we propose that this does not occur *via* the reverse of the mechanism shown in equations (16) and (17). Unfortunately, however, it is not possible to propose an alternative based on the information currently available.

Theoretical Studies.—In order to gain further understanding of the steric effects on the structure and relative stability of di- and tri-meric aluminium alkoxides we have carried out *ab initio* calculations on the model compounds [H$_2$Al(μ-OH)]$_2$ **16** and [H$_2$Al(μ-OH)]$_3$ **17**. Gropen *et al.*[29] have previously reported a study on the dimer, however the structural parameters were taken directly from the gas-phase structure of **8**. The only parameter to be varied was the angle between the O–H bond and the plane of the Al$_2$O$_2$ ring, which from energy minimisation was found to be 25°. The authors concluded that the planarity at oxygen observed for all experimentally determined structures was as a result of steric repulsion between the substituents on the O and Al atoms. Since a direct comparison with experimental data is sought, the oxygen was confined to planarity for all calculations.

The calculated structural and geometrical data for compounds **16** and **17** are given in Table 4. For both molecules the calculated Al–H and O–H distances are comparable to those determined experimentally.[30] As can be seen from Table 4, the Al–O distance and O–Al–O and Al–O–Al angles in the dimer **16** are within experimental error of the range reported from X-ray and electron diffraction studies.[12g] This would suggest that the Al$_2$O$_2$ core is relatively insensitive to steric effects of the bridging alkoxide. We have previously reached a similar conclusion for gallium alkoxide and alkyl peroxide dimers.[31] We note that the H–Al–H angle (119.6°) is also within the range of R–Al–R angles (115.4–121.7°) suggesting that little steric repulsion exists between the alkyl substituents on aluminium.

In contrast to the results for the dimer **16**, the calculated structure for the trimer **17** is significantly different from that reported for [Me$_2$Al(μ-OMe)]$_3$ **1**.[11] Both compounds have C_{3v} symmetry and a chair structure, however the trigonal distortion in **17** is more pronounced than in **1**. Since this trend is the opposite to that proposed on steric grounds[11] we are unable at present to develop a satisfactory explanation until further examples of trimeric alkoxide-bridged compounds of aluminium are isolated.

Conclusion

It has been shown that dimethylaluminium alkoxides, Me$_2$Al(OR), with straight-chain hydrocarbon substituents,

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* We note that an analogous mechanism has been proposed by Sauls *et al.*[5] for aminoalanes [R$_2$Al(NR'$_2$)].

Table 4 HF/3-21G(*) Structural parameters for $[\mathrm{H_2Al}(\mu\text{-OH})]_x$ (x = 2 or 3) in comparison to experimental values for $[\mathrm{R_2Al}(\mu\text{-OR}')]_x$ (R, R′ = alkyl)

Molecule	Parameter[a]	Calculated HF/3-21G(*)	Experimental[b]
$[\mathrm{H_2Al}(\mu\text{-OH})]_2$	Al–O	1.835	1.837–1.864
	Al–H	1.592	
	O–H	0.960	
	Al···Al	2.814	2.779–2.886
	O···O	2.356	
	O–Al–O	79.9	79.1–82.0
	O–Al–H	112.7	
	H–Al–H	119.6	115.4–121.7
	Al–O–Al	100.1	98.1–100.7
	Al–O–H	129.9	
$[\mathrm{H_2Al}(\mu\text{-OH})]_3$	Al–O	1.840	1.851
	Al–H	1.591	
	O–H	0.967	
	Al···Al	3.305	3.297
	O···O	2.797	2.90
	Al···O	3.554	
	O–Al–O	98.9	103.2
	O–Al–H	108.0	
	H–Al–H	123.1	117.3
	Al–O–Al	127.8	125.8
	Al–O–H	115.9	

[a] Distances in Å, angles in °. [b] Parameters taken from ref. 12(*g*).

R exist in solution in both di- and tri-meric forms, *i.e.* $[\mathrm{Me_2Al(OR)}]_2$ and $[\mathrm{Me_2Al(OR)}]_3$ respectively. The exchange between oligomers is sufficiently slow that they may readily be differentiated by ^{1}H, ^{13}C and ^{17}O NMR spectroscopy, and hence the relative concentrations of the oligomers can be determined. The primary factor that controls the relative stability of the two oligomers is the steric bulk of the alkyl substituents R. Thus, for straight-chain alkyls the trimer is favoured, while for branched chains, except when the branch is sufficiently distant, *e.g.* $\mathrm{CH_2CH_2Pr^i}$, the dimer is favoured. Where both species are present simultaneously in solution the trimer is the thermodynamically favoured oligomer, consistent with theoretical calculations. The mechanism for the transformation of the trimer into the dimer for $\mathrm{Me_2Al(OPr^n)}$ is second order with respect to the trimer concentration, and thus analogous to the results previously reported for the aminoalanes, $\mathrm{Me_2Al(NR_2)}$.[4,5]

Experimental

Elemental analyses were performed by Oneida Research Services, Whitesborough, NY. All the compounds are readily hydrolysed and/or oxidised, and in several cases difficulty was observed in obtaining constant analysis. In these cases the results of multiple analysis are given. It should be noted, however, these discrepancies were not manifested in the NMR studies, and more importantly do not affect our conclusions. The IR spectra (4000–400 cm^{-1}) were recorded on a Nicolet DX-5 FTIR spectrometer as neat liquids or Nujol mulls on KBr plates, ^{1}H and ^{13}C NMR spectra (see Table 1 and Experimental section) on a Bruker AM-500 spectrometer with chemical shifts reported relative to $\mathrm{SiMe_4}$ (external, ^{1}H) and $\mathrm{C_6D_6}$ (^{13}C). All NMR spectra were, unless otherwise stated, recorded in $\mathrm{C_6D_6}$. The ^{1}H NMR spectral assignments were determined by selective decoupling and ^{1}H–^{1}H correlation spectroscopy (COSY) experiments. The latter were made by use of a standard pulse sequence with a 45° mixing pulse, a 1–2 s relaxation delay, and a resolution of *ca.* 4 Hz per point. The free induction decays were not weighted before Fourier transformation, and the spectral matrix was symmetrised about the diagonal. The ^{17}O and ^{27}Al NMR spectra (see Table 1 and Experimental section) were recorded on a Bruker WM-30 spectrometer and chemical shifts are reported *versus* water and $[\mathrm{Al(H_2O)_6}]^{3+}$ respectively. Mass spectra were recorded using a JEOL AX-505H mass spectrometer and associated data system. Instrument parameters were: electron impact (EI) ionisation with 70 eV electron beam energy, 3 keV ion energy (eV $\approx$ 1.60 × 10^{-19} J) and 1500 mass resolution. Spectra were recorded over a mass range sufficient to reveal the presence, if any, of the octametric species. Molecular weight measurements were carried out in hexane using an apparatus similar to that of Clark.[32]

A 2 mol dm^{-3} solution of $\mathrm{AlMe_3}$ in hexane (Aldrich) was used as supplied. All alcohols and solvents were dried, distilled from magnesium turnings, and degassed prior to use. The compounds $[\mathrm{Me_2Al}(\mu\text{-OMe})]_3$, $[\mathrm{Me_2Al}(\mu\text{-OEt})]_2$, $[\mathrm{Me_2Al}(\mu\text{-OPr^i})]_2$ and $[\mathrm{Me_2Al}(\mu\text{-OBu^t})]_2$ were prepared by variations of literature methods.[8,12,14]

$[\mathrm{Me_2Al}(\mu\text{-OMe})]_3$ **1**.—A solution of MeOH (4.05 cm^3, 3.21 g, 100 mmol) in hexane (25 cm^3) was added dropwise to a stirred solution of 2 mol dm^{-3} $\mathrm{AlMe_3}$ in hexane (50 cm^3, 100 mmol) at room temperature. The resulting solution was stirred for 1 h and the volatiles removed *in vacuo* yielding colourless crystals. Yield 8.8 g, 33.3 mmol. NMR: ^{1}H, δ 3.04 (3 H, s, $\mathrm{OCH_3}$) and −0.59 (6 H, s, Al–$\mathrm{CH_3}$); ^{13}C, δ 50.7 ($\mathrm{OCH_3}$) and −10.7 ($\mathrm{AlCH_3}$); ^{17}O, δ −20.6 ($W_{\frac{1}{2}}$ = 130 Hz); ^{27}Al, δ 147 ($W_{\frac{1}{2}}$ = 800 Hz).

$[\mathrm{Me_2Al}(\mu\text{-OEt})]_2$–$[\mathrm{Me_2Al}(\mu\text{-OEt})]_3$ **2**.—A solution of EtOH (5.88 cm^3, 4.61 g, 100 mmol) in hexane (30 cm^3) was added dropwise to a stirred solution of 2 mol dm^{-3} $\mathrm{AlMe_3}$ in hexane (50 cm^3, 100 mmol), at either −78 or 25 °C (see text for details). The resulting solution was stirred for several hours, after which the volatiles were removed *in vacuo* affording the dimer–trimer mixture in essentially quantitative yield. Molecular weight (hexane), 276 (trimer, 306; dimer, 204). NMR: ^{1}H, dimer, δ 3.37 [2 H, q, *J*(H–H) = 7.1, $\mathrm{OCH_2}$], 0.91 [3 H, t, *J*(H–H) = 7.1, $\mathrm{OCH_2C}H_3$] and −0.53 (6 H, s, Al–$\mathrm{CH_3}$); trimer, δ 3.65 [2 H, q, *J*(H–H) = 7.0, $\mathrm{OCH_2}$], 0.97 [3 H, t, *J*(H–H) = 7.0 Hz, $\mathrm{OCH_2C}H_3$] and −0.52 (6 H, s, Al-$\mathrm{CH_3}$); ^{13}C, dimer, δ 64.1 ($\mathrm{OCH_2}$), 17.7 ($\mathrm{OCH_2}C\mathrm{H_3}$) and −10.4 (Al–$\mathrm{CH_3}$); trimer, δ 65.4 ($\mathrm{OCH_2}$), 18.0 ($\mathrm{OCH_2}C\mathrm{H_3}$) and −9.5 (Al–$\mathrm{CH_3}$); ^{17}O, dimer, δ 18.5 ($W_{\frac{1}{2}}$ = 255 Hz); trimer, δ −19.8 ($W_{\frac{1}{2}}$ = 149 Hz); ^{27}Al, δ 150 ($W_{\frac{1}{2}}$ = 790 Hz).

$[\mathrm{Me_2Al}(\mu\text{-OPr^n})]_2$–$[\mathrm{Me_2Al}(\mu\text{-OPr^n})]_3$ **3**.—This compound was prepared in a manner analagous to that for **2**; yield *ca.* 100% (Found: C, 51.9; H, 11.2. Calc. for $\mathrm{C_5H_{13}AlO}$: C, 51.7; H, 11.3%). Molecular weight (hexane), 301 (trimer, 348; dimer, 232). Mass spectrum (EI): *m*/*z* 333 (3M^+ − Me), 217 (2M^+ − Me) and 101 (M^+ − Me). NMR: ^{1}H, dimer, δ 3.37 [2 H, t, *J*(H–H) = 6.9, $\mathrm{OCH_2}$], 1.30 [2 H, m, *J*(H–H) = 6.9, *J*(H–H′) = 7.4, $\mathrm{OCH_2C}H_2$], 0.63 [3 H, t, *J*(H–H) = 7.4, $\mathrm{OCH_2CH_2C}H_3$] and −0.51 (6 H, s, Al–$\mathrm{CH_3}$); trimer, δ 3.65 [2 H, t, *J*(H–H) = 7.6, $\mathrm{OCH_2}$], 1.51 [2 H, m, *J*(H–H) = 7.6, *J*(H–H′) = 7.4, $\mathrm{OCH_2C}H_2$], 0.62 [3 H, t, *J*(H–H) = 7.4 Hz, $\mathrm{OCH_2CH_2C}H_3$] and −0.47 (6 H, s, Al–$\mathrm{CH_3}$); ^{13}C, dimer, δ 64.8 ($\mathrm{OCH_2}$), 25.8 ($\mathrm{OCH_2}C\mathrm{H_2}$), 10.0 ($\mathrm{OCH_2CH_2}C\mathrm{H_3}$) and −10.5 (Al–$\mathrm{CH_3}$); trimer, δ 66.3 ($\mathrm{OCH_2}$), 25.6 ($\mathrm{OCH_2}C\mathrm{H_2}$), 9.48 ($\mathrm{OCH_2CH_2}C\mathrm{H_3}$) and −9.1 (Al–$\mathrm{CH_3}$); ^{17}O, dimer, δ 15.9 ($W_{\frac{1}{2}}$ = 394 Hz); trimer, δ −19.8 ($W_{\frac{1}{2}}$ = 170 Hz); ^{27}Al, δ 136 ($W_{\frac{1}{2}}$ = 1955 Hz). IR (neat): 2966s, 2935s, 2886s, 1580m, 1400m, 1195s, 1064s, 1020m, 985s, 697s and 641m cm^{-1}.

$[\mathrm{Me_2Al}(\mu\text{-OPr^i})]_2$ **4**.—This compound was prepared in a manner analogous to that for **1**; isolated yield *ca.* 78% (Found: C, 51.7; H, 11.2. Calc. for $\mathrm{C_5H_{13}AlO}$: C, 51.7; H, 11.3%). Mass spectrum (EI): *m*/*z* 217 (2M^+ − Me) and 117 (M^+ + 1). NMR: ^{1}H, δ 3.86 [1 H, spt, *J*(H–H) = 6.5, OCH], 1.01 [6 H, d, *J*(H–H) = 6.5 Hz, $\mathrm{OCH(C}H_3)_2$] and −0.51 (6 H, s, Al–$\mathrm{CH_3}$); ^{13}C, δ 66.9 (OCH), 25.4 [$\mathrm{OCH(}C\mathrm{H_3)_2}$] and −8.7 (Al–$\mathrm{CH_3}$); ^{17}O, δ 44.6 ($W_{\frac{1}{2}}$ = 203 Hz); ^{27}Al, δ 148 ($W_{\frac{1}{2}}$ = 1330 Hz).

[Me$_2$Al(μ-OBu^n)]$_2$–[Me$_2$Al(μ-OBu^n)]$_3$ **5**.—This compound was prepared in a manner analogous to that of **2**; yield *ca.* 95% (Found: C, 55.0; H, 11.4. Calc. for C$_6$H$_{15}$AlO: C, 55.3; H, 11.6%). Mass spectrum (EI): *m*/*z* 375 (3M^+ − Me), 333 (3M^+ − Bu^n), 303 (3M^+ − 2Me − Bu^n), 245 (2M^+ − Me) and 173 (2M^+ − 2Me − Bu^n). NMR: ^{1}H, dimer, δ 3.44 [2 H, t, J(H–H) = 6.9, OCH$_2$], 1.36 (2 H, m, OCH$_2$CH_2), 1.17 (2 H, m, CH$_2$CH_3), 0.71 [3 H, t, J(H–H) = 7.7, CH$_2$CH_3] and −0.56 (6 H, s, Al–CH$_3$); trimer, δ 3.75 [2 H, t, J(H–H) = 7.7, OCH$_2$], 1.55 (2 H, m, OCH$_2$CH_2), 1.10 (2 H, m, CH_2CH$_3$), 0.76 [3 H, t, J(H–H) = 6.9 Hz, CH$_2$CH_3] and −0.54 (6 H, s, Al–CH$_3$); ^{13}C, dimer, δ 62.8 (OCH$_2$), 34.8 (OCH$_2$*C*H$_2$), 19.0 (*C*H$_2$CH$_3$), 13.6 (CH$_2$*C*H$_3$) and −10.7 (Al–CH$_3$); trimer, δ 64.8 (OCH$_2$), 34.6 (OCH$_2$*C*H$_2$), 18.8 (*C*H$_2$CH$_3$), 13.8 (CH$_2$*C*H$_3$) and −9.1 (Al–CH$_3$); ^{17}O, dimer, δ 11.8 ($W_{\frac{1}{2}}$ = 420 Hz); trimer, δ −17.5 ($W_{\frac{1}{2}}$ = 270 Hz); ^{27}Al, δ 149 ($W_{\frac{1}{2}}$ = 2110 Hz). IR (neat): 2962s, 2932s, 2894m, 2877m, 1464m, 1202s, 1058m, 1027m, 1016m, 1001m, 961s, 948s, 937s, 846m, 687vs and 641s cm^{-1}.

[Me$_2$Al(μ-OBu^i)]$_2$ **6**.—This compound was prepared in a manner analogous to that of **2**; yield *ca.* 75% (Found: C, 54.9; H, 11.6. Calc. for C$_6$H$_{15}$AlO: C, 55.3; H, 11.6%). Mass spectrum (EI): *m*/*z* 375 (3M^+ − Me), 245 (2M^+ − Me) and 173 (2M^+ − 2Me − Bu^n). NMR: ^{1}H, δ 3.29 [2 H, d, J(H–H) = 7.3, OCH$_2$], 1.60 (1 H, m, OCH$_2$CH), 0.75 [6 H, d, J(H–H) = 6.1 Hz, OCH$_2$CH(CH_3)$_2$] and −0.62 (6 H, s, Al–CH$_3$); ^{13}C, δ 70.2 (OCH$_2$), 31.0 (OCH$_2$*C*H), 19.0 [OCH$_2$CH(*C*H$_3$)$_2$] and −10.7 (Al–CH$_3$); ^{17}O, δ 15.0 ($W_{\frac{1}{2}}$ = 240 Hz); ^{27}Al, δ 151 ($W_{\frac{1}{2}}$ = 2270 Hz). IR (neat): 2959s, 2930s, 2879s, 1474m, 1397m, 1369m, 1195s, 1041s, 1008m, 985m, 945m, 809m, 622m, 699s and 640m cm^{-1}.

[Me$_2$Al(μ-OBu^s)]$_2$ **7**.—This compound was prepared in a manner analogous to that of **1**; isolated yield *ca.* 85% (Found: C, 55.0; H, 12.1. Calc. for C$_6$H$_{15}$AlO: C, 55.3; H, 11.6%). Mass spectrum (EI): *m*/*z* 245 (2M^+ − Me) and 173 (2M^+ − 2Me − Bu^s). NMR: ^{1}H, δ 3.67 [1 H, d, J(H–H) = 6.3, OCH], 1.49 (2 H, m, OCHCH_2), 1.29 (2 H, m, OCHCH$_2$), 1.29 (2 H, m, OCHCH$_2$), 1.05 [3 H, d, J(H–H) = 7.0, OCH(CH$_3$)], 0.71 [3 H, t, J(H–H) = 7.4 Hz, CH$_2$CH_3] and −0.59 (6 H, s, Al–CH$_3$); ^{13}C, δ 72.3 (OCH), 32.3 (OCH*C*H$_2$), 22.6 (OCH*C*H$_3$), 10.1 (CH$_2$*C*H$_3$) and −8.5 (Al–CH$_3$); ^{17}O, δ 40.2 ($W_{\frac{1}{2}}$ = 481 Hz); ^{27}Al, δ 148 ($W_{\frac{1}{2}}$ = 1720 Hz). IR (neat): 2972s, 2933s, 2888m, 1383m, 1195s, 1106m, 1031m, 994s, 922m, 695s and 654m cm^{-1}.

[Me$_2$Al(μ-OBu^t)]$_2$ **8**.—This compound was prepared in a manner analogous to that of **1**; isolated yield *ca.* 80%. Mass spectrum (EI): *m*/*z* 245 (2M^+ − Me). NMR: ^{1}H, δ 1.17 [9 H, s, OC(CH_3)$_3$] and −0.45 (6 H, s, Al–CH$_3$); ^{13}C, δ 74.5 [O*C*(CH$_3$)$_3$], 31.4 [OC(*C*H$_3$)$_3$] and −6.1 (Al–CH$_3$); ^{17}O, δ 61.8 ($W_{\frac{1}{2}}$ = 230 Hz); ^{27}Al, δ 146 ($W_{\frac{1}{2}}$ = 1330 Hz).

[Me$_2$Al(μ-OC$_5$H$_{11}$)]$_2$–[Me$_2$Al(μ-OC$_5$H$_{11}$)]$_3$ **9**.—This compound was prepared in a manner analogous to that of **2**; yield *ca.* 98% (Found: C, 58.0; H, 11.9. Calc. for C$_7$H$_{17}$AlO: C, 58.3; H, 11.9%). Mass spectrum (EI): *m*/*z* 361 (3M^+ − C$_5$H$_{11}$), 331 (3M^+ − 2Me − C$_5$H$_{11}$) and 273 (2M^+ − Me). NMR: ^{1}H, dimer, δ 3.46 [2 H, t, J(H–H) = 6.9, OCH$_2$], 1.39 [2 H, m, J(H–H) = 6.9, OCH$_2$CH_2], 1.10 (4 H, m, CH_2CH_2CH$_3$), 0.80 [3 H, t, J(H–H) = 6.2, CH$_2$CH$_2$CH_3] and −0.51 (6 H, s, Al–CH$_3$); trimer, δ 3.78 [2 H, t, J(H–H) = 7.7, OCH$_2$], 1.61 [2 H, m, J(H–H) = 7.7, OCH$_2$CH_2], 1.10 (4 H, m, CH_2CH_2CH$_3$), 0.80 [3 H, t, J(H–H) = 6.9 Hz, CH$_2$CH$_2$CH_3] and −0.48 (6 H, s, Al–CH$_3$); ^{13}C, dimer, δ 63.2 (OCH$_2$), 32.5 (OCH$_2$*C*H$_2$), 27.9 (*C*H$_2$CH$_2$CH$_3$), 22.5 (CH$_2$*C*H$_2$CH$_3$), 14.0 (CH$_2$CH$_2$*C*H$_3$) and −10.6 (Al–CH$_3$); trimer, δ 65.1 (OCH$_2$), 32.3 (OCH$_2$*C*H$_2$), 27.7 (*C*H$_2$CH$_2$CH$_3$), 22.6 (CH$_2$*C*H$_2$CH$_3$), 14.0 (CH$_2$CH$_2$*C*H$_3$) and −9.1 (Al–CH$_3$); ^{17}O, dimer, δ 11.6 ($W_{\frac{1}{2}}$ = 580 Hz); trimer, δ −19.8 ($W_{\frac{1}{2}}$ = 380 Hz); ^{27}Al, δ 151 ($W_{\frac{1}{2}}$ = 2220 Hz). IR (neat): 2958s, 2931s, 2895 (sh), 2863m, 1202s, 1043m, 964s, 668vs and 640m cm^{-1}.

[Me$_2$Al(μ-OCH$_2$CH$_2$Pr^i)]$_2$–[Me$_2$Al(μ-OCH$_2$CH$_2$Pr^i)]$_3$ **10**.—This compound was prepared in a manner analogous to that of **2**; yield *ca.* 95% (Found: C, 57.5; H, 12.0. Calc. for C$_7$H$_{17}$AlO: C, 58.3; H, 11.9%). Mass spectrum (EI): *m*/*z* 361 (3M^+ − CH$_2$CH$_2$Pr^i), 331 (3M^+ − 2Me − CH$_2$CH$_2$Pr^i) and 273 (2M^+ − Me). NMR: ^{1}H, dimer, δ 3.58 [2 H, t, J(H–H) = 8.0, OCH$_2$], 1.52 [2 H, dt, J(H–H) = 8.0, J(H–H′) = 7.9, OCH$_2$CH_2], 1.38 [1 H, m, CH(CH$_3$)$_2$], 0.75 [6 H, d, J(H–H) = 6.1, CH(CH_3)$_2$] and −0.60 (6 H, s, Al–CH$_3$); trimer, δ 3.80 [2 H, t, J(H–H) = 7.9, OCH$_2$], 1.52 [2 H, dt, J(H–H) = 8.0, J(H–H′) = 7.9], 1.35 [1 H, m, CH(CH$_3$)$_2$], 0.75 [6 H, d, J(H–H) = 6.1 Hz, CH(CH_3)$_2$] and −0.55 (6 H, s, Al–CH$_3$); ^{13}C, dimer, δ 61.6 (OCH$_2$), 41.7 (OCH$_2$CH_2), 24.6 [*C*H(CH$_3$)$_2$], 22.3 [CH(CH$_3$)$_2$] and −10.6 (Al–CH$_3$); trimer, δ 63.8 (OCH$_2$), 41.3 (OCH$_2$*C*H$_2$), 25.4 [*C*H(CH$_3$)$_2$], 22.6 [CH(*C*H$_3$)$_2$] and −9.1 (Al–CH$_3$); ^{17}O, dimer, δ 13.8 ($W_{\frac{1}{2}}$ = 170 Hz); trimer, δ −19.0 ($W_{\frac{1}{2}}$ = 150 Hz); ^{27}Al, δ 150 ($W_{\frac{1}{2}}$ = 2150 Hz). IR (neat): 2958m, 2900s, 2890m, 1195m, 1041s, 985s, 699s and 640m cm^{-1}.

[Me$_2$Al(μ-OCH$_2$Bu^t)]$_2$ **11**.—This compound was prepared in a manner analogous to that of **1**; isolated yield *ca.* 75% (Found: C, 58.0; H, 11.6. Calc. for C$_7$H$_{17}$AlO: C, 58.3; H, 11.9%). Mass spectrum (EI): *m*/*z* 273 (2M^+ − Me) and 187 (2M^+ − 2Me − CH$_2$Bu^t). NMR: ^{1}H, δ 3.31 (2 H, s, OCH$_2$), 0.77 [9 H, s, C(CH_3)$_3$] and −0.41 (6 H, s, Al–CH$_3$); ^{13}C, δ 74.5 (OCH$_2$), 34.4 [*C*(CH$_3$)$_3$], 26.2 [C(*C*H$_3$)$_3$] and −10.3 (Al–CH$_3$); ^{17}O, δ 9.9 ($W_{\frac{1}{2}}$ = 350 Hz); ^{27}Al, δ 151 ($W_{\frac{1}{2}}$ = 1950 Hz). IR (Nujol): 2959s, 2930s, 2870m, 1470w, 1190m, 1043m, 966s, 660s and 641m cm^{-1}.

[Me$_2$Al(μ-OC$_6$H$_{13}$)]$_2$–[Me$_2$Al(μ-OC$_6$H$_{13}$)]$_3$ **12**.—This compound was prepared in a manner analogous to that of **2**; yield *ca.* 100% (Found: C, 59.6, 61.0; H, 12.4, 12.5. Calc. for C$_8$H$_{19}$AlO: C, 60.7; H, 12.1%). NMR: ^{1}H, dimer δ 3.48 [2 H, t, J(H–H) = 6.9, OCH$_2$], 1.65 [2 H, m, J(H–H) = 6.9, OCH$_2$CH_2], 1.20 (2 H, m, CH_2CH$_3$), 1.12 (4 H, m, CH_2CH_2CH$_2$CH$_3$), 0.82 [3 H, t, J(H–H) = 7.2, CH$_2$CH_3] and −0.59 (6 H, s, Al–CH$_3$); trimer, δ 3.75 [2 H, t, J(H–H) = 6.9, OCH$_2$], 1.57 [2 H, m, J(H–H) = 6.9, OCH$_2$CH_2], 1.20 (2 H, m, CH_2CH$_3$), 1.12 (4 H, m, CH_2CH_2CH$_2$CH$_3$), 0.82 [3 H, t, J(H–H) = 7.2 Hz, CH$_2$CH_3] and −0.56 (6 H, s, Al–CH$_3$); ^{13}C, dimer, δ 63.3 (OCH$_2$), 32.8 (OCH$_2$*C*H$_2$), 31.6 (*C*H$_2$CH$_2$CH$_2$CH$_3$), 25.6 (*C*H$_2$CH$_2$CH$_3$), 22.9 (*C*H$_2$CH$_3$), 14.1 (CH$_2$*C*H$_3$) and −10.6 (Al–CH$_3$); trimer, δ 65.1 (OCH$_2$), 32.6 (OCH$_2$*C*H$_2$), 31.7 (*C*H$_2$CH$_2$CH$_2$CH$_3$), 25.3 (*C*H$_2$CH$_2$CH$_3$), 22.9 (*C*H$_2$CH$_3$), 14.1 (CH$_2$*C*H$_3$) and −9.1 (Al–CH$_3$); ^{17}O, dimer, δ 12.7 ($W_{\frac{1}{2}}$ = 880 Hz); trimer, δ −18.8 ($W_{\frac{1}{2}}$ = 406 Hz); ^{27}Al, δ 143 ($W_{\frac{1}{2}}$ = 2270 Hz). IR (neat): 2957s, 2930vs, 2894s, 1466m, 1460m, 1201s, 1061m, 1050m, 980m, 912w, 889s and 640m cm^{-1}.

[Me$_2$Al(μ-OC$_8$H$_{17}$)]$_2$–[Me$_2$Al(μ-OC$_8$H$_{17}$)]$_3$ **13**.—This compound was prepared in a manner analogous to that of **2**; yield *ca.* 90% (Found: C, 63.8, 63.8; H, 11.9, 11.8. Calc. for C$_{10}$H$_{23}$AlO: C, 64.4; H, 12.5%). NMR: ^{1}H, dimer, δ 3.49 [2 H, t, J(H–H) = 6.8, OCH$_2$], 1.42 [2 H, m, J(H–H) = 6.9, OCH$_2$CH_2], 1.17 [10 H, m, (CH_2)$_5$CH$_3$], 0.88 [3 H, t, J(H–H) = 6.6, CH$_2$CH_3] and −0.55 (6 H, s, Al–CH$_3$); trimer, δ 3.77 [2 H, t, J(H–H) = 7.7, OCH$_2$], 1.60 [2 H, m, J(H–H) = 6.9, OCH$_2$CH_2], 1.17 [10 H, m, (CH_2)$_5$CH$_3$], 0.88 [3 H, t, J(H–H) = 6.6 Hz, CH$_2$CH_3] and −0.52 (6 H, s, Al–CH$_3$); ^{13}C, dimer, δ 63.3 (OCH$_2$), 32.8 (OCH$_2$*C*H$_2$), 32.1 (OCH$_2$CH$_2$*C*H$_2$), 29.6 (*C*H$_2$*C*H$_2$CH$_2$CH$_2$CH$_3$), 25.9 (*C*H$_2$CH$_2$CH$_3$), 23.0 (*C*H$_2$CH$_2$), 13.9 (CH$_2$*C*H$_3$) and −10.5 (Al–CH$_3$); trimer, δ 65.1 (OCH$_2$), 32.6 (OCH$_2$*C*H$_2$), 32.1 (OCH$_2$CH$_2$*C*H$_2$), 29.6 (*C*H$_2$*C*H$_2$CH$_2$CH$_2$CH$_3$), 25.6 (*C*H$_2$CH$_2$CH$_3$), 23.0 (*C*H$_2$CH$_3$), 14.3 (CH$_2$*C*H$_3$) and −9.1 (Al–CH$_3$); ^{17}O, dimer, δ 15.8 ($W_{\frac{1}{2}}$ = 765 Hz); trimer, δ −18.9 ($W_{\frac{1}{2}}$ = 1010 Hz); ^{27}Al, δ 149 ($W_{\frac{1}{2}}$ = 2740 Hz). IR (neat): 2956s, 2928vs, 2871s, 2857vs, 1479w, 1466m, 1201vs, 1054w, 1044m, 1033m, 982s, 886m, 766m, 691s and 641m cm^{-1}.

$[Me_2Al(\mu\text{-}OC_{10}H_{21})]_2$–$[Me_2Al(\mu\text{-}OC_{10}H_{21})]_3$ **14**.—This compound was prepared in a manner analogous to that of **2**; yield *ca.* 90% (Found: C, 67.8, 68.1, 68.2; H, 12.0, 12.1, 12.4. Calc. for $C_{12}H_{27}AlO$: C, 67.2; H, 12.7%). NMR: ^1H, dimer, δ 3.50 [2 H, t, *J*(H–H) = 6.8, OCH_2], 1.44 (2 H, m, $OCH_2C\textit{H}_2$), 1.26 [10 H, m, $(C\textit{H}_2)_5CH_2CH_3$], 1.15 (4 H, m, $C\textit{H}_2C\textit{H}_2CH_3$), 0.91 [3 H, t, *J*(H–H) = 7.0, $CH_2C\textit{H}_3$] and −0.39 (6 H, s, Al–CH_3); trimer, δ 3.83 [2 H, t, *J*(H–H) = 7.8, OCH_2], 1.67 (2 H, m, $OCH_2C\textit{H}_2$), 1.27 (10 H, m, $(C\textit{H}_2)_5CH_2CH_2CH_3$], 1.15 (4 H, m, $C\textit{H}_2C\textit{H}_2CH_3$), 0.91 [3 H, t *J*(H–H) = 7.0 Hz, $CH_2C\textit{H}_3$] and −0.36 (6 H, s, Al–CH_3); ^{13}C, dimer, δ 63.3 (OCH_2), 32.8 ($OCH_2\textit{C}H_2$), 32.3 ($OCH_2CH_2\textit{C}H_2$), 29.8, 29.6, 29.5, 29.4 [$(\textit{C}H_2)_4CH_2CH_2CH_3$], 25.8 ($\textit{C}H_2CH_2CH_3$), 23.0 ($\textit{C}H_2CH_3$), 14.3 ($CH_2\textit{C}H_3$) and −10.4 (Al–$CH_3$); trimer, δ 65.1 ($OCH_2$), 32.6 ($OCH_2\textit{C}H_2$), 32.3 ($OCH_2CH_2\textit{C}H_2$), 29.7, 29.6, 29.5, 29.4, [$(\textit{C}H_2)_4CH_2CH_2CH_3$], 25.6 ($\textit{C}H_2CH_2CH_3$), 23.0 ($\textit{C}H_2CH_3$), 14.3 ($CH_2\textit{C}H_3$) and −9.0 (Al–$CH_3$); ^{27}Al, δ 152 ($W_{\frac{1}{2}}$ = 3520 Hz). IR (neat): 2955m (sh), 2925s, 2855m, 1466m, 1201s, 968m, 688s, 664m and 640m cm^{-1}.

$[Me_2Al(\mu\text{-}OC_{12}H_{25})]_2$–$[Me_2Al(\mu\text{-}OC_{12}H_{25})]_3$ **15**.—This compound was prepared in a manner analogous to that of **2**; yield *ca.* 90% (Found: C, 68.6, 69.0; H, 12.9, 13.1. Calc. for $C_{14}H_{31}AlO$: C, 69.3; H, 12.9%). NMR: ^1H, dimer, δ 3.50 [2 H, t, *J*(H–H) = 6.8, OCH_2], 1.44 (2 H, m, $OCH_2C\textit{H}_2$), 1.29 [12 H, br m, $(C\textit{H}_2)_7CH_2CH_2CH_3$], 1.16 (4 H, m, $C\textit{H}_2C\textit{H}_2CH_3$), 0.91 [3 H, t, *J*(H–H) = 6.9, $CH_2C\textit{H}_3$] and −0.39 (6 H, s, Al–CH_3); trimer, δ 3.86 [2 H, t, *J*(H–H) = 7.6 Hz, OCH_2], 1.44 (2 H, m, $OCH_2C\textit{H}_2$), 1.29 [12 H, br m, $(C\textit{H}_2)_7CH_2CH_2CH_3$], 1.16 (4 H, m, $C\textit{H}_2C\textit{H}_2CH_3$), 0.91 [3 H, t, *J*(H–H) = 6.9 Hz, $CH_2C\textit{H}_3$] and −0.34 (6 H, s, Al–CH_3); ^{13}C, dimer, δ 63.3 (OCH_2), 32.8 ($OCH_2\textit{C}H_2$), 32.3 ($OCH_2CH_2\textit{C}H_2$), 30.1, 30.0, 29.9, 29.8, 29.5 [$(\textit{C}H_2)_6CH_2CH_2CH_3$], 25.8 ($\textit{C}H_2CH_2CH_3$), 23.1 ($\textit{C}H_2CH_3$), 14.3 ($CH_2\textit{C}H_3$) and −10.4 (Al–$CH_3$); trimer, δ 65.1 ($OCH_2$), 32.6 ($OCH_2\textit{C}H_2$), 32.3 ($OCH_2CH_2\textit{C}H_2$), 30.1, 30.0, 29.9, 29.7, 29.6 [$(\textit{C}H_2)_6CH_2CH_2CH_3$], 25.6 ($\textit{C}H_2CH_2CH_3$), 23.1 ($\textit{C}H_2CH_3$), 14.3 ($CH_2\textit{C}H_3$) and −9.0 (Al–$CH_3$); ^{27}Al, δ 150 ($W_{\frac{1}{2}}$ = 4500 Hz). IR (neat): 2954s, 2925vs, 2854s, 1466m, 1201s, 963m, 690s and 640m cm^{-1}.

Equilibrium Studies.—Solution molecular weight measurements on compounds **2** and **3** confirm, in part, the presence of an equilibrium between trimeric and dimeric forms, since the experimental values are intermediate between those for the dimer and trimer. However, the data are of insufficient accuracy to enable equilibrium constants to be determined at ambient temperatures, let alone temperatures at which the conversion of trimer into dimer occurs at a reasonable rate (> 100 °C). Since, no difference in the relative intensity of the peaks due to the two oligomers is observed in different solvents, the use of hexane for the molecular weight measurements (where a low boiling point is required) and [$^2H_8$]toluene for the variable-temperature NMR equilibrium (where a high boiling solvent is required for safety) does not effect the values of K_{eq}. Thus, ^1H NMR spectroscopy was used to determine the relative concentrations of the two oligomers (see text and SUP 56898). A solution of dimethylaluminium *n*-propoxide was prepared in [$^2H_8$]toluene (for which a density of 0.94 g l^{-1} was assumed).[5] The sample was flame-sealed in a series of 5 mm NMR tubes. **CAUTION**: The use of thick walled NMR tubes is recommended, since significant pressure is produced. The tube was heated for several days in a temperature-controlled oven (384 K), and the ^1H NMR spectrum obtained until no change was observed. Constancy of the spectrum was taken as evidence for the attainment of equilibrium. This process was repeated for each of the temperatures given in Table 2. Alternate points on the ln *K vs* 1/*T* plot were obtained during upward and downward passages over the temperature range spanned. Since both sets of points fell on the same line we consider that equilibration was achieved. Since the peaks for the α-CH_2 protons of the alkoxide group are well separated for the dimer and trimer they were used to determine the relative amount of each species. Molar fractions, calculated concentrations, and equilibrium constants (K_{eq}) are summarised in Table 2.

Kinetic Studies.—A series of samples of dimethylaluminium *n*-propoxide existing as a mixture of dimer and trimer that had equilibrated at room temperature to give *ca.* 90% of the latter was accurately weighed (±0.005 g) into a series of 5 mm NMR tubes (*ca.* 0.1 g per tube). [$^2H_8$]Toluene (*ca.* 0.25 cm^3) was added to each tube and the mass of solvent determined, and thus the concentration of $Me_2Al(OPr^n)$. The tubes were then flame sealed under a dry nitrogen atmosphere. **CAUTION**: The use of thick walled NMR tubes is recommended, since significant pressure is produced. All the samples were heated to the appropriate temperature within the NMR spectrometer (see Table 3), and a series of ^1H NMR spectra was collected every 20 min for approximately 6 h, see SUP 56898. The temperature of the NMR spectrometer probe was calibrated using the chemical shifts of ethylene glycol. As with the equilibrium studies, the integration of the α-CH_2 proton resonances was used to determine the relative quantity of dimer and trimer. No significant decomposition of the compound was observed during the data collection. Selected data are given in Table 3.

Computational Methods.—*Ab initio* all-electron molecular orbital (MO) calculations were performed using the GAUSSIAN 86[33] suite of programs. Optimised structures were determined at the Hartree–Fock level with the 3-21G(*) basis set.[34] We have previously found the HF/3-21G(*) model to give good descriptions of the structures of organoaluminium compounds.[35] In this work we are seeking not the prediction of absolute structures, but rather a qualitative explanation for observed structural features. In this regard, bearing in mind limit on computer time, we do not feel the application of a larger basis set is warranted. To determine the relative energy of each species with electron correlation included, we performed second-order Møller–Plesset (MP2) calculations.[36]

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