

Synthesis of Al(III) silsesquioxane complexes and their exploitation for the ring opening polymerisation of *rac*-lactide

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Abstract:

In this paper we report the synthesis and characterisation of silsesquioxane tethered Al(III) complexes. The complexes have been characterised by multi-nuclear NMR spectroscopy and depending upon the bulk of the ligand either Al(L)Me₂ or Al(L)₂Me complexes were isolated. We also report the first solid-state structure of a tethered Al-silsesquioxane complex of the form Al(L)Me₂. All complexes and heterogeneous analogues were tested for the ring opening polymerisation of *rac*-lactide, with narrow molecular weight polylactide formed.

Keywords:

Lactide, silsesquioxane, polymerisation

1. Introduction:

In recent years there has been an explosion of interest in the ring opening polymerisation (ROP) of lactide (LA).¹ This is due to the properties of the final polymer, namely its biodegradability and biocompatibility coupled with the fact that LA can be prepared from sustainable sources.² There have been many elegant examples of the preparation of discrete homogeneous catalysts for this process based on group 1-4 metals,³ Zn(II)⁴, lanthanides,^{3f, 5} Al(III)⁶ and metal free initiated systems.⁷ The investigation of novel initiators for the controlled ROP of LA is a significant area of current research. Many ligand types have been employed with these metals systems namely salan^{6d}, salen^{6f}, salalen^{3j, 3l, 6b}, β -diketimates^{4c} and simple phenolates.^{1c} The polymers produced *via* traditional organometallic initiators contain heavy metal residues, which may have detrimental effects on polymer performance, especially for biological applications.⁸ Heterogeneous initiators offer the potential to negate this problem and can also offer advantages in polymer processing.^{4a, 9} To this end several groups have demonstrated the use of heterogeneous initiators for the production of polyesters.^{4a, 9-10} The majority of these examples have involved reacting a support with a simple metal-alkoxide. For example, Hamaide have developed silica based yttrium complexes for the polymerization of ϵ -caprolactone.¹¹ Whilst these methods have produced interesting results this approach does not allow the steric or electronic environment around the metal centre to be altered. Further examples include those by C.W. Jones who have immobilised Coates' Zn- β -diiminate initiators to SBA-15 for the ROP of lactide.¹² This area is not limited to silica and it is also possible to use polystyrene as a support, for example Bu₂SnCl₂ can be heterogenised onto polystyrene beads and is a recyclable catalyst for the ROP of ϵ -caprolactone.¹³

The use of silsesquioxane complexes as models of heterogeneous catalysts is well established.¹⁴ The vast majority of these literature examples involve the reaction of the parent trisilanol directly with a metal centre.¹⁵ These have been exploited to great effect in other polymerisation processes and epoxidation reactions.^{14c, 16} Furthermore, we and Monticelli have shown that simple Ti-POSS (POSS = polyhedral oligomeric silsesquioxanes) complexes are active for the ROP of lactide.¹⁷ Also, we have recently shown that Zn(II) silsesquioxane complexes and heterogeneous systems can act as initiators for the polymerisation.^{4a} With this in mind we now report the use of Al(III) silsesquioxane complexes for the ROP of *rac*-lactide

together with their heterogeneous counterparts. Aluminium complexes are prevalent in the literature,⁶ thus the further exploitation and heterogenisation of this metal centre will be of interest. Furthermore, there are no reported examples of the heterogenisation of Al(III) for the ROP of *rac*-lactide.

2. Results and discussion:

2.1 Synthesis of ligands, complexes and heterogeneous initiators:

The ligands utilised are shown in scheme 1 and were prepared *via* modified literature procedures.^{4a} Initially the ligands were reacted with one equivalent of AlMe₃ in toluene. From analysis of the ¹H NMR spectrum of the reaction of ligands **1H** and **3H** with AlMe₃ two species were observed, under this 1-to-1 stoichiometry. One series of resonances was due to Al(**1/3**)₂Me and other set due to Al(**1/3**)Me₂ respectively; unfortunately attempts to purify these mixtures proved fruitless. We have also tried to vary the concentration and the equivalents of AlMe₃ added in an attempt to prepare the dialkyl complexes in a pure form with ligands **1H** and **3H**, however all attempts produced a mixture of complexes. For example, the addition of 2 equivalents of AlMe₃ to 1 equivalent of ligand did not aid in the formation of the dialkyl complex, with 2 clearly distinct Al-alkyl resonances in the ¹H NMR spectrum. Fortunately, if the reaction were repeated with 2 equivalents of ligand per metal centre pure complexes of the form Al(**1/3**)₂Me were isolated. For example, in the ¹H NMR spectrum of Al(**1**)₂Me a 2H-imine resonance was observed at 7.68 ppm and a resonance was also seen at -0.42 ppm corresponding to an Al-CH₃ and consequently a resonance at 2.0 ppm was present in the ¹³C{¹H} NMR spectrum. The ²⁹Si{¹H} NMR spectrum for these complexes yielded three resonances in the appropriate range, analogous to that observed for the free ligand. However, when one equivalent of **2H** was reacted with one equivalent of AlMe₃ the complex Al(**2**)Me₂ was formed in solution and in the solid-state (Figure 1). In the ¹H NMR spectrum a 6H singlet was observed at -0.25 ppm for the Al-CH₃ and a 1H singlet at 7.66 ppm. In the ²⁹Si{¹H} NMR spectrum four resonances were observed. Upon recrystallisation in hexane suitable crystals of Al(**2**)Me₂ were isolated. The solid-state structure was in agreement with the solution-state structure. The Al(1) centre is in a pseudo tetrahedral environment with the C(1)-Al(1)-C(2) angle being 120.8(3)° and the O(1)-Al(1)-N(1) angle being 95.02(18)°. The Al(1)-C(1) length of 1.954(6) Å and the Al(1)-C(2)

distance of 1.965(6) Å are in agreement with literature precedent, as are the Al(1)-O(1) and Al(1)-N(1) distance of 1.771(4) and 1.951(5) Å respectively.^{6b, 6d} To the best of our knowledge the only other crystallographically reported structures of a silsesquioxane tethered complex are the Zn(II) complexes we reported in 2010.^{4a} This strategy will aid the understanding of ligated heterogeneous catalysts, just as silsesquioxanes have for metals supported on pure silica.¹⁴ The metric data associated with the ligand fragment of Al(2)Me₂ are in agreement with the Zn(II) examples.^{4a} Presumably in the case of 2H the sterically demanding nature of the ligand coupled with ortho *t*Bu did not facilitate the formation of the two ligand-to-one metal complex.

The ligands were tethered to silica as shown in scheme 2, following literature procedures.^{4a} The species were characterised *via* elemental analysis and solid-state NMR spectroscopy, which successfully demonstrated that the tethering process had been successful. These heterogeneous ligands were reacted with AlMe₃ to generate the tethered initiators and a heterogeneous initiator was prepared by reacting SiO₂ directly with AlMe₃ as a comparison to the ligand tethered system.

2.4 Catalytic results

Initially the homogeneous initiators were investigated. The alkoxide was generated *in-situ* by the addition of 1 equivalent of benzyl alcohol per Al-CH₃ bond, Table 1. The polymerisations were conducted at 80 °C for 24 hours. The GPC data are in agreement with only one polymer chain growing per metal centre (irrespective of the number of Al-CH₃ linkages per complex) with the experimental values being close to the calculated value for 100% conversion. The isolated PLA had relatively narrow molecular weight distributions, indicative of a controlled process. For Al(2)Me₂ it was necessary to add an equivalent of BzOH (C₆H₅CH₂OH) per Al-CH₃ moiety to minimise the potential of the metal-alkyl bond to initiate the polymerisation in an uncontrolled manner. Based on the empirical data presented herein initiators based on Al(1/3)₂Me and Al(2)Me₂ afford PLA with analogous properties (in-terms of molecular weight, conversion and tacticity). The isolated polymer had a slight isotactic bias, as evidenced from analysis of the methine region of the ¹H homonuclear decoupled NMR spectrum. Analysis of the polymer *via* MALDI-ToF mass spectrometry revealed that the repeat unit was 72 gmol⁻¹, indicative of a small degree of transesterification, and the end groups, as expected, were BzO- and H-. The

heterogeneous initiators were also trialled in solution, the target ratio of active centres-to-monomer was 100:1 based on the loading of the silica support. Again narrow molecular weight PLA was obtained, in the case of initiator **Het-1** PLA with a strong isotactic bias was isolated after 24 hrs – albeit after prolonged reaction the PLA was more atactic in character. This is potentially due to transesterification or epimerisation caused by the acidic SiOH species present in the heterogeneous catalyst. Furthermore, silica supported AlMe₃ was shown to be very poor in comparison to the tethered systems, indicating that the tethered ligand-Al species is critical for successful polymerisation for the heterogeneous system. The heterogeneous initiators were also trialled without the addition of BzOH (table 2) and these cases low conversions were observed and from the GPC the polymerisation is clearly uncontrolled, thus also highlighting the importance of the BzOH initiator in our system. Analysis of the final polymer from **Het-2** showed there to be 431 ppm of aluminium after workup, whilst the PLA produced from the analogous homogeneous initiator had 2500 ppm, indicating a significant reduction in metal content. However, the quantity of aluminium in the final polymer in the heterogeneous system is higher than expected. This may be due to leaching or removal and solubilisation of the aluminium ions during the termination and work-up steps. Work is currently on-going to improve the initiator further, but this does illustrate that heterogeneous initiators can offer advantages over homogeneous systems.

3. Conclusions:

In conclusion a series of aluminium silsesquioxane complexes have been prepared and characterised. The complexes are all active for the ROP of *rac*-lactide. The solid-state structure of a silsesquioxane tethered species is reported and discussed. Heterogeneous initiators were also prepared which were shown to be active for the polymerisation.

4. Acknowledgments:

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5. Experimental:

5.1 General:

For the preparation and characterisation of metal complexes, all reactions and manipulations were performed under an inert atmosphere of argon using standard Schlenk or glovebox techniques. *rac*-LA (Aldrich) was recrystallised from toluene and sublimed twice prior to use. All other chemicals were purchased from Aldrich. All solvents used in the preparation of metal complexes and polymerisation reactions were dry and obtained *via* SPS (solvent purification system). ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded on a Bruker 250, 300 or 400 MHz instrument and referenced to residual solvent peaks. Coupling constants are given in Hertz. Elemental analyses were performed by Mr. A. K. Carver at the Department of Chemistry, University of Bath. Aluminium analysis was conducted *via* ICP-AES by Medac Ltd. The ligands were prepared using a previously reported methodology.^{4a}

5.2 Synthesis of Aluminium Complexes:

Al(**1**)₂Me Ligand **1H** (0.978 g, 1 mmol) was dissolved in THF (10 ml) to which a 2M solution of Al(Me)₃ in heptane (0.25 ml, 0.50 mmol) was added. The solution turned from yellow to clear and a gas was observed. The reaction was stirred for 60 minutes at 20 °C, heated to reflux, and the solvent was removed *in-vacuo* to yield a pale yellow residue. The residue was dissolved in hexane and crystallised to form 320 mg of a pale yellow crystalline solid in a 32 % yield. ^1H (C₆D₆) -0.42 (s, 3H, Al-CH₃), 0.84 (m, 4H, Si-CH₂ tether, 28H, Si-CH₂), 1.06 (84H, m, CH₃), 2.07 (14H, m, CH), 2.37 (m, 4H, CH₂ tether), 3.47 (m, 2H, CH₂ tether), 3.83 (m, 2H, CH₂ tether), 6.65 (m, 2H, Ar-H), 6.89 (m, 2H, Ar-H), 7.10 (m, 2H, Ar-H), 7.31 (m, 2H, Ar-H), 7.68 (s, 2H, CH=N). $^{13}\text{C}\{^1\text{H}\}$ (C₆D₆) 2.0 (Al-CH₃) 11.2 (Si-CH₂, tether), 23.6 (CH₂, ⁱbutyl), 25.0 (CH, ⁱbutyl), 25.0 (Si-CH₂, tether), 26.5 (CH₃, ⁱbutyl), 60.8 (CH₂-N), 68.4 (CH₂-N), 117.4 (Ar), 121.1 (Ar), 122.2 (Ar), 134.0 (Ar), 135.1 (Ar), 165.2 (C, Ar-O), 167.5 (CH, C=N). $^{29}\text{Si}\{^1\text{H}\}$ (C₆D₆) -67.4, -67.2, -67.1. Calc. C 46.3 %, H 7.62 %, N 1.40 %

Found C 45.2 %, H 7.52 %, N 1.42 %

Al(2)Me₂ Ligand 2H (0.26 g, 0.24 mmol) was dissolved in THF (10 ml) to which a 2M solution of Al(Me)₃ in heptane (0.12 ml, 0.24 mmol) was added. The solution turned from yellow to clear and a gas was observed. The reaction was stirred for 60 minutes at 20 °C, heated to reflux, and the solvent was removed *in-vacuo*. The residue was dissolved in hexane and crystallised to form 130 mg of a white crystalline solid in a 47 % yield. ¹H (C₆D₆) -0.25 (s, 6H, Al-CH₃), 0.85 (m, 2H, Si-CH₂ tether, 14H, Si-CH₂), 1.06 (42H, m, CH₃), 1.30 (9H, s, CH₃), 1.57 (9H, s, CH₃), 1.87 (m, 2H, CH₂ tether), 2.07 (7H, m, CH), 3.12 (m, 2H, CH₂ tether), 6.74 (m, 1H, Ar-H), 7.32 (m, 1H, Ar-H), 7.66 (m, 1H, CH=N). ¹³C{¹H} (C₆D₆) 2.0 (Al-CH₃) 10.7 (Si-CH₂, tether), 23.6 (CH₂, ⁱbutyl), 25.0 (Si-CH₂, tether), 25.0 (CH, ⁱbutyl), 26.5 (CH₃, ⁱbutyl), 30.2 (CH₃, *tert*-butyl), 32.1 (CH₃, *tert*-butyl), 34.7 (CH₃, *tert*-butyl), 36.2 (CH₃, *tert*-butyl), 60.5 (CH₂-N), 119.5 (Ar), 129.5 (Ar), 132.2 (Ar), 139.4 (Ar), 141.4 (Ar), 162.6 (Ar), 172.4 (CH, C=N). ²⁹Si{¹H}(C₆D₆) -67.5, -67.4, -67.2, -67.1. Calc. C 50.3 %, H 8.43 %, N 1.22 % Found C 50.2 %, H 8.98 %, N 1.14 %

Al(3)₂Me Ligand 3H (1.05 g, 1 mmol) was dissolved in THF (10 ml) to which a 2M solution of Al(Me)₃ in heptane (0.25 ml, 0.50 mmol) was added. The solution turned from yellow to clear and a gas was observed. The reaction was stirred for 60 minutes at 20 °C, heated to reflux, and the solvent was removed *in-vacuo* to yield 350 mg of a pale yellow residue in a 33 % yield. ¹H (C₆D₆) -0.44 (s, 3H, Al-CH₃), 0.85 (m, 4H, Si-CH₂ tether) (28H, m, Si-CH₂), 1.06 (84H, m, CH₃), 2.07 (14H, m, CH) (m, 4H, CH₂ tether), 3.72 (m, 2H, CH₂ tether), 4.15 (m, 2H, CH₂ tether), 6.49 (m, 2H, Ar-H), 6.89 (m, 2H, Ar-H), 7.30 (m, 2H, Ar-H), 7.32 (s, 2H, CH=N). ¹³C{¹H} (C₆D₆) 1.8 (Al-CH₃) 10.9 (Si-CH₂, tether), 23.4 (CH₂, ⁱbutyl), 24.6 (Si-CH₂, tether), 24.8 (CH, ⁱbutyl), 26.3 (CH₃, ⁱbutyl), 60.1 (CH₂-N), 121.4 (Ar), 121.8 (Ar), 126.7 (Ar), 131.5 (Ar), 134.1 (Ar), 158.0 (Ar), 165.2 (CH, C=N). ²⁹Si{¹H}(C₆D₆) -67.5, -67.4, -67.1. Calc. C 43.3 %, H 6.94 %, N 1.31 % Found C 42.9%, H 6.77%, N 1.31 %

5.3 Synthesis of heterogeneous catalysts:

Het-NH₂: SiO₂ (pore diameter 60 Å, Davisil) was dried at 130 °C under vacuum for 5 h. The dried silica (5 g) was added to methanol (20 ml) to give a suspension to which

(3-aminopropyl)trimethoxysilane (0.87 ml, 0.90 g, 5 mmol) was added and stirred vigorously for 24 h. The reaction mixture was filtered and washed with copious methanol and the solid dried under vacuum at 80 °C for 5 h to yield the amine functionalised silica. Found C 4.45%, H 1.30%, N 1.56%.

Het-1-3H: The dry amine functionalised silica (1 g) was suspended in methanol (20 ml) to which salicylaldehyde was added (0.11 ml, 0.12 g, 1 mmol) or 3,5-di-tert-butyl-2-hydroxybenzaldehyde was added (0.23 g, 1 mmol), or 3,5-dichloro-2-hydroxybenzaldehyde was added (0.19 g, 1 mmol). The suspension was stirred vigorously for 24 h after which it was filtered and the solid washed with copious amounts of methanol. The resulting solid was dried under vacuum at 80 °C for 5 h. **Het-1H** C 9.97%, H 1.45%, N 1.11%. **Het-2H** C 14.4%, H 2.33%, N 1.07%. **Het-3H** C 9.48%, H 1.30%, N 1.06%

Het 1-3Al In a typical procedure the silica ligand (0.50 g) was suspended in dry THF (10 ml) to which a 2M solution of AlMe₃ in heptane (0.25 ml, 0.5 eq, 0.50 mmol) was added. The solid product was washed 3 times with dry THF (10 ml) to yield an Aluminium(III) complex. **Het-1Al** C 11.9%, H 1.85%, N 1.18%, Al 2.75 %. **Het-2Al** C 16.9%, H 2.72%, N 1.43%, Al 1.43 %. **Het-3Al** C 12.2%, H 1.63%, N 1.14%, Al 2.03 %.

5.4 X-ray Crystallography

All data were collected on a Nonius Kappa CCD area detector diffractometer using Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) at 150 K, and the structure was solved by direct methods and refined on all F^2 data using the SHELXL-97 suite of programs.¹⁸ Crystal data for Al(2)Me₂: C₄₈H₉₆AlNO₁₃Si₈, $M = 1146.96$, colourless block, $0.20 \times 0.10 \times 0.10 \text{ mm}^3$, triclinic, space group $P-1$, $a = 11.051(2)$, $b = 14.642(2)$, $c = 20.958(3) \text{ \AA}$, $\alpha = 95.969(4)$, $\beta = 97.641(5)$, $\gamma = 103.574(11)^\circ$, $V = 3234.9(7) \text{ \AA}^3$, $Z = 2$, $D_c = 1.178 \text{ g/cm}^3$, $F_{000} = 1240$, $2\theta_{\text{max}} = 48.8^\circ$, 27015 reflections collected, 10377 unique ($R_{\text{int}} = 0.0732$). Final $GoF = 1.068$, $R_1 = 0.0688$, $wR_2 = 0.1442$, R indices based on 6441 reflections with $I > 2\sigma(I)$ (refinement on F^2), 640 parameters, 0 restraints, $\mu = 0.233 \text{ mm}^{-1}$.

5.5 Polymerisation runs:

For homogeneous polymerisations a monomer:initiator ratio of 100:1 was used. In all cases toluene (10 ml) was added to a Schlenk followed by the initiator and 1 eq of BzOH for each Al-CH₃ unit in the complex, the lactide (1 g) was added and the flask heated for the 24 hrs at 80 °C. For heterogeneous polymerisations a monomer:initiator ratio of 100:1 was used. In all cases toluene (10 ml) was added to a Schlenk followed by the appropriate amount of initiator and 2 eq of BzOH, the lactide (1 g) was added and the flask heated for the specified time at 80 °C. For simplicity a catalyst loading of 1 mmol g⁻¹ Het-AlMe₂ was assumed. The reaction was quenched by the addition of methanol (2 ml). ¹H NMR spectroscopy (CDCl₃) and GPC (THF) were used to determine tacticity and molecular weights (M_n and M_w) of the polymers produced; P_r (the probability of heterotactic linkages) were determined by analysis of the methine region of the homonuclear decoupled ¹H NMR spectra. Gel Permeation Chromatography (GPC) analyses were performed on a Polymer Laboratories PL-GPC 50 integrated system using a PLgel 5 µm MIXED-D 300 × 7.5 mm column at 35 °C, THF solvent (flow rate 1.0 ml/min). The polydispersity index (PDI) was determined from M_w/M_n where M_n is the number average molecular weight and M_w the weight average molecular weight. The polymers were referenced to 11 narrow molecular weight polystyrene standards with a range of M_w 615 – 568,000 Da.

6. Supplementary material

CCDC number 875368 contains the supplementary crystallographic data for this paper and can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

7. References:

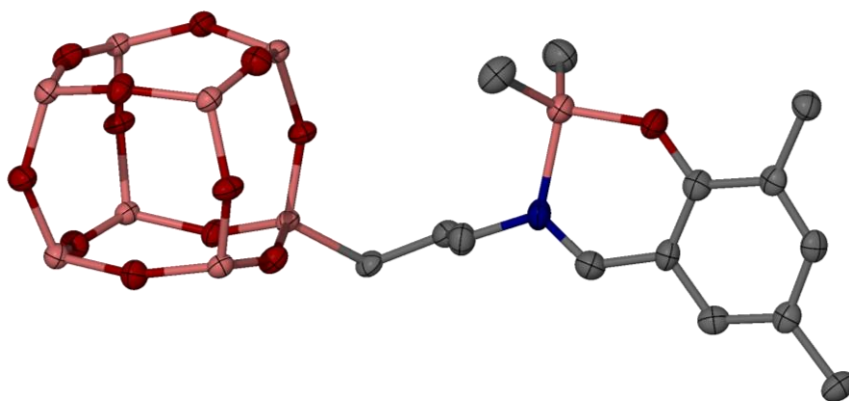
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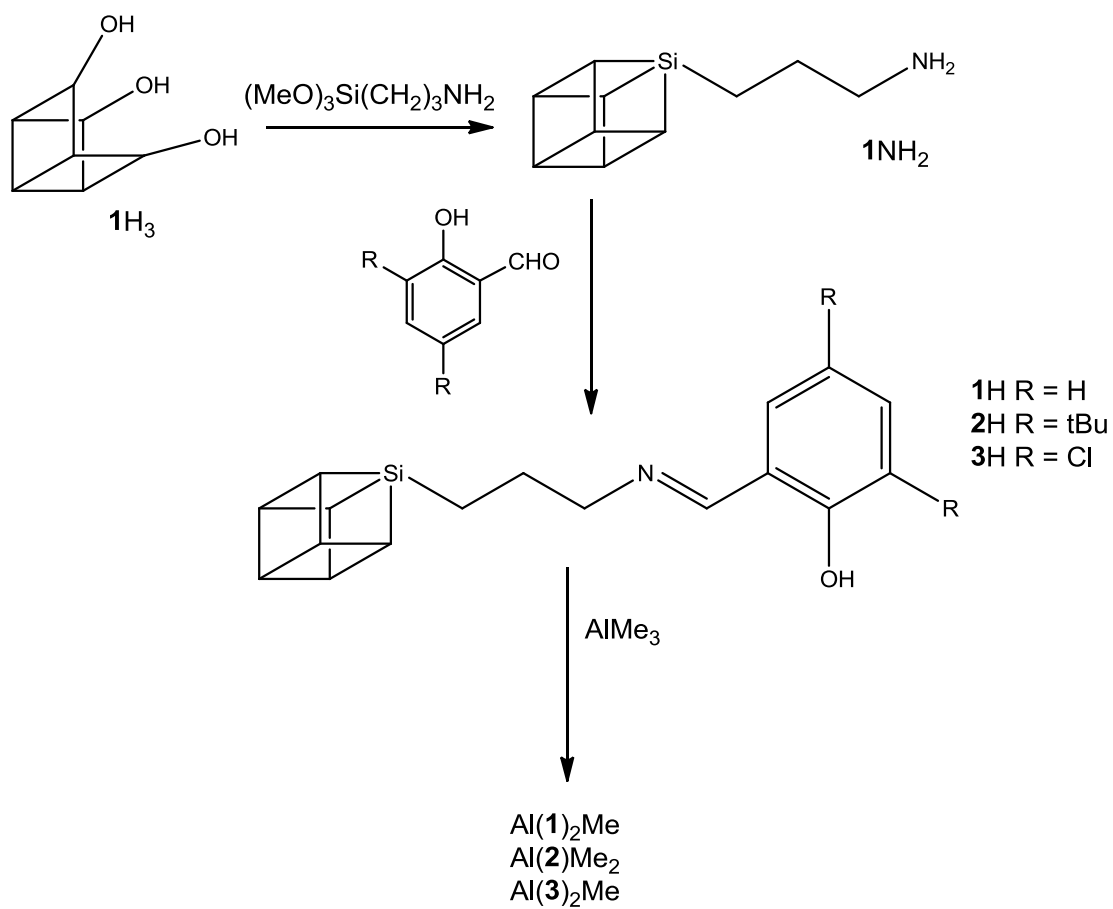
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Graphical Abstract:



The synthesis, characterisation and catalytic activity of a series of aluminium silsesquioxane complexes together with their heterogeneous counterparts are investigated.

Figures, scheme and tables:



Scheme 1: Schiff base precursors and complexes utilised in this study.

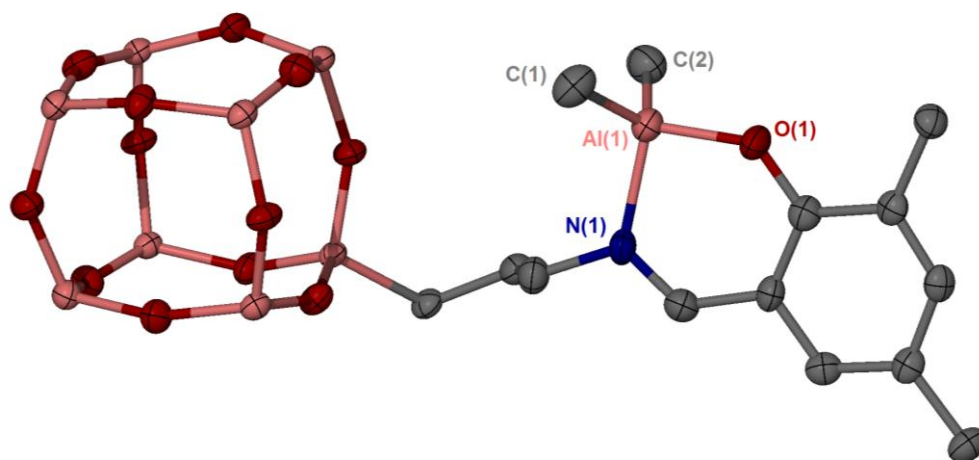
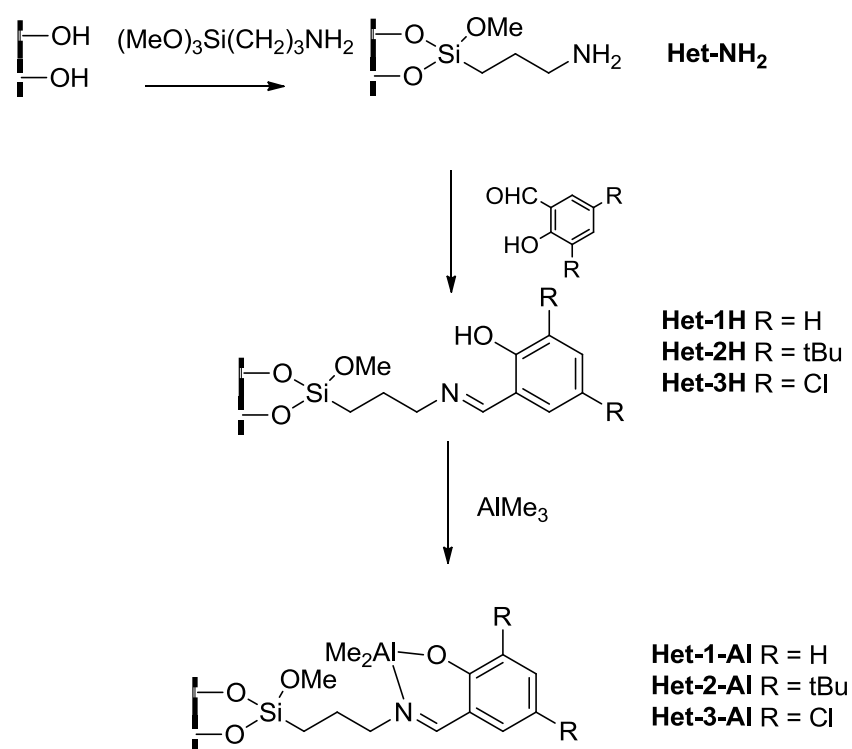


Figure 1: Single Crystal Structure for Al(2)Me_2 . The ellipsoids are shown at the 50% probability level, the H-atoms, the *i*Bu groups of the silsesquioxane and methyl groups of the *t*Bu moieties have been removed for clarity.



Scheme 2: Synthesis of the heterogeneous initiators employed in this study.

Complex	Conv.(%) ^a	M_n^b	PDI ^b	P_r^c
Al(1) ₂ Me	99	13850	1.36	0.41
Al(2)Me ₂	99	12500	1.16	0.46
Al(3) ₂ Me	99	13000	1.23	0.44

Table 1: Homogeneous initiators for the ROP of *rac*-LA. Conditions [LA]:[Initiator]:[BzOH] = 100:1:1 – there is one equivalent of BzOH per Al-Me, temperature = 80 °C, time = 24 hrs. ^a conversion as determined *via* ¹H NMR spectroscopy, ^b determined from GPC (in THF) referenced to polystyrene. ^c calculated from the ¹H homonuclear decoupled NMR (CDCl₃) analysis.

Catalyst	Time/hrs	Conv.(%) ^c	M_n^d	PDI ^d	P_r^e
SiO ₂ -AlMe ^a	24	5	-	-	-
Het-1 ^a	24	61	5400	1.11	0.32
Het-1 ^a	72	98	8100	1.19	0.53
Het-2 ^a	24	95	10450	1.11	0.55
Het-2 ^a	72	97	8450	1.52	0.53
Het-3 ^a	24	47	3250	1.12	0.41
Het-3 ^a	72	64	4250	1.09	0.43
Het-1 ^b	24	26	20110	1.12	0.5
Het-2 ^b	24	24	47250	1.11	0.38
Het-3 ^b	24	11	33400	2.27	0.44

Table 2: Heterogeneous initiators for the ROP of *rac*-LA.. ^a Conditions [LA]:[Initiator]:[BzOH] = 100:1:1 – there is one equivalent of BzOH per Al-Me (N.B. it is assumed that there are two Al-Me groups per active centre, temperature = 80 °C. ^b without the presence of BzOH, , temperature = 80 °C. ^c conversion as determined *via* ¹H NMR spectroscopy, ^d determined from GPC (in THF) referenced to polystyrene. ^e calculated from the ¹H homonuclear decoupled NMR (CDCl₃) analysis.