# SUPPORTING INFORMATION

## Modifying Methylalumoxane via Alkyl Exchange

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#### 1) Additional Experimental Details

#### ESI-MS Details

For all regular addition experiments a stock solution (3 mL) was prepared by dilution of MAO (0.5 mL of 1.5 M (10%) or 0.15 mL of 4.6 M (30%)) and 0.5 or 0.16 mL of a premade PhF solution of OMTS (0.015 M) to give a mixture with an AI:OMTS ratio of 100:1 ([AI] = 0.25M). 0.2 mL of this solution was further diluted to 3 mL to give mixture with final [AI] of 0.0167M.

<u>iBu<sub>3</sub>Al addition</u>: A stock solution of 0.00167 M *i*Bu<sub>3</sub>Al was prepared by dilution of 10  $\mu$ L of *i*Bu<sub>3</sub>Al (1M in toluene) to 6 mL with PhF. The following amounts of this solution were added to the to the 0.0167M solution of MAO/OMTS (AI:OMTS 100:1) to give the desired AI:R<sub>3</sub>Al ratios. All mixtures were allowed to equillibriate for 5 minutes before being analyzed by ESI-MS in negative ion mode (see Figure 1 for spectra).

100:1 - 0.3 mL of 0.00167M *i*Bu<sub>3</sub>Al stock solution (final MAO [AI] = 0.015M)

100:5 - 1.5 mL of 0.00167M  $iBu_3AI$  stock solution (final MAO [AI] = 0.011M)

100:10 - 3 mL of 0.00167M *i*Bu<sub>3</sub>Al stock solution (final MAO [AI] =  $8.4 \times 10^{-3}$ M)

100:15 - 4.5 mL of 0.00167M *i*Bu<sub>3</sub>Al stock solution (final MAO [AI] =  $6.7 \times 10^{-3}$ M)

100:20 - 6.0 mL of 0.00167M *i*Bu<sub>3</sub>Al stock solution (final MAO [AI] = 5.6 10<sup>-3</sup>M)

For the reverse reaction  $Me_3AI$  (2M in toluene) was added to the 100:20 AI: $R_3AI$  mixture in 0.1 mL increments (2x) and the speciation was subsequently analyzed in negative ion mode (see Figure S3 for spectra).

<u>Positive ion spectra comparison:</u> A stock solution of 0.033 M *i*Bu<sub>3</sub>Al was prepared by diluting 0.1 mL *i*Bu<sub>3</sub>Al (1M in toluene) to 3 mL using PhF. 0.1 mL of this stock solution was added to the 0.0167M MAO/OMTS (Al:OMTS 100:1) stock solution to give a solution with Al: *i*Bu<sub>3</sub>Al of 100:15 (final MAO [Al] = 0.016M). The mixture was equillibriated for 5 min. and then it's postive ion ESI-MS spectrum was taken. To observe the speciation when *i*Bu<sub>3</sub>Al was added before ionization a stock solution of 0.0167 M MAO was prepared. To 3 mL of this solution were added 0.1 mL of the 0.033 M *i*Bu<sub>3</sub>Al solution. The mixture was allowed to equillibriated for 5 min. after which it's postive ion ESI-MS spectrum was collected (see Figure 2b and Figure S4 for spectra).

<u>*nOct*<sub>3</sub>Al addition</u>: A stock solution of 0.0050 M *n*Oct<sub>3</sub>Al was prepared by dilution of 63  $\mu$ L of *n*Oct<sub>3</sub>Al (0.48M in hexane) to 6 mL with PhF. 3.0 mL of this solution was added to 3 mL of a 0.0167M stock solution of MAO/OMTS (AI:OMTS 100:1) to give and *n*Oct<sub>3</sub>Al to MAO Al ratio of 100:30. The mixture was allowed to equillibriate for 30 minutes before being analyzed by ESI-MS in negative ion mode (See Figure 4b for spectrum).

100:30 - 3.0 mL of 0.0050 M *n*Oct<sub>3</sub>Al stock solution (final MAO [Al] =  $8.4 \times 10^{-3}$ M)

<u>Et<sub>3</sub>Al addition</u>: Stock solutions 0.00167 M and 0.0050M Et<sub>3</sub>Al were prepared by dilution of 5  $\mu$ L and 15  $\mu$ L of Et<sub>3</sub>Al (1.9M in toluene) to 6 mL with PhF. The following amounts of the solutions were added to the 0.0167M solution of MAO/OMTS (AI:OMTS 100:1) to give the desired AI:R<sub>3</sub>Al ratios. All mixtures were allowed to equillibriate for 5 minutes before being analyzed by ESI-MS in negative ion mode (see Figure 4a and Figure S5 for all spectra).

100:1 - 0.3 mL of 0.00167M  $nOct_3AI$  stock solution (final MAO [AI] = 0.015M)

100:5 - 1.5 mL of 0.00167M nOct<sub>3</sub>Al stock solution (final MAO [AI] = 0.011M)

100:10 - 3.0 mL of 0.00167M *n*Oct<sub>3</sub>Al stock solution (final MAO [AI] =  $8.4 \times 10^{-3}$ M)

100:20 - 2.0 mL of 0.0050 M *n*Oct<sub>3</sub>Al stock solution (final MAO [Al] =  $1.0 \ 10^{-2}$ M)

100:30 - 3.0 mL of 0.0050 M *n*Oct<sub>3</sub>Al stock solution (final MAO [AI] =  $8.4 \times 10^{-3}$ M)

<u>PSI experiments:</u> all glassware was oven-dried overnight before use. Reagents were stored and manipulated in a glovebox under an inert atmosphere. 0.4 mL of a 0.25M AI MAO/OMTS (100:1) stock solution was diluted to 6 mL of PhF and placed in a glass vial ([AI] =0.0167M The vial was attached to a rubber septum and a 178  $\mu$ m ID PTFE tubing was immersed in the MAO/OMTS solution, and the other end of the tubing was connected to the ESI-MS source. A UHMWPE (10 $\mu$ m) frit was installed at the beginnig of the PTFE tubing to prevent blocking of the capillary which hinders consistent data recording. This way the solution was filtered before injection into the ESI-MS thus preventing blocking of the capillary. The experiment was started, and as soon as a stable ion count of **16,6** was observed the R<sub>3</sub>Al solutions described below were added at once

<u>iBu<sub>3</sub>Al aluminum addition</u>: A stock solution of *i*Bu<sub>3</sub>Al was prepared by dilution of 0.1mL of *i*Bu<sub>3</sub>Al (1M in toluene) to 4mL solution with PhF ([*i*Bu<sub>3</sub>Al] 0.025M). 0.4 mL of this solution was added to the MAO/OMTS solution as soon as a stable count of **16,6** was observed to give a Al: *i*Bu<sub>3</sub>Al ratio of 100:10 and the spectrum was recorded until no further ions were observed (see Figure 5 for spectrum).

For the Al:  $iBu_3Al$  ratio of 100:1 experiment a stock solution of  $iBu_3Al$  was prepared by dilution of 0.25mL of  $iBu_3Al$  (1M in toluene) to 4mL solution with PhF ([ $iBu_3Al$ ] 0.062M). 0.1 mL of this solution was added to the MAO/OMTS solution as soon as a stable count of **16,6** was observed to give a Al:  $iBu_3Al$  ratio of 100:1 and the spectrum was recorded until no further ions were observed (see Figure S6 for spectrum).

<u>*nOct*<sub>3</sub>Al addition</u>: A stock solution of  $nOct_3Al$  was prepared by dilution of 0.21 mL of 0.48 M  $nOct_3Al$  solution to 4 mL with of PhF ([ $nOct_3Al$ ] 0.025M). 0.4 mL of this solution was added to the MAO/OMTS solution as soon as a stable count of **16,6** was observed to give a Al: $nOct_3Al$  ratio of 100:10 and the spectrum was recorded until no further ions were observed (see Figure S7 for spectrum).

<u>Et<sub>3</sub>Al addition</u>: A stock solution of Et<sub>3</sub>Al was prepared by dilution of 0.053mL of Et<sub>3</sub>Al (1.9 M in toluene) to 4mL solution with PhF ([Et<sub>3</sub>Al] 0.025M). 0.4 mL of this solution was added to the MAO/OMTS solution as soon as a stable count of **16,6** was observed to give a Al:Et<sub>3</sub>Al ratio of 100:10 and the spectrum was recorded until no further ions were observed (see Figure S8 for spectrum).

#### 2) Additional MS Spectra



**Figure S1.** Negative ion spectrum of MMAO-12 + 5 mol% OMTS in PhF with [AI] = 0.01 M. MAO anions shown in black, and oxidized anions in red and those containing 1 Oct group in blue (assignments are tentative as MS/MS analyses were not possible due to extremely low intensities).



Figure S2. Positive ion mass spectrum of MMAO-12 + 5 mol% OMTS in PhF.



**Figure S3.** Negative ion ESI-MS spectra in PhF of 30 wt% MAO modified with 20 mol% *i*Bu<sub>3</sub>AI (a), 20 mol% *i*Bu<sub>3</sub>AI and 0.1 mL Me<sub>3</sub>AI (2M, b), 20 mol% *i*Bu<sub>3</sub>AI and 0.2 mL Me<sub>3</sub>AI (2M, c). Number of Me/*i*Bu substitutions in [(MeAIO)<sub>16</sub>(Me<sub>3</sub>AI)<sub>6</sub>Me]<sup>-</sup> shown in red.



Figure S4 Positive ion spectra in PhF of 30 wt% MAO with 15%  $iBu_3AI$  added before ionization. MAO-AI:OMTS = 100:1.



**Figure S5.** Negative ion ESI-MS spectra in PhF of 30 wt% MAO modified with 1 mol% Et<sub>3</sub>AI (a), 5 mol% Et<sub>3</sub>AI (b), 10 mol% Et<sub>3</sub>AI (c), 20 mol% Et<sub>3</sub>AI (d). All at an OMTS:AI ratio of 1:100. Number of Me/Et substitutions in [(MeAIO)<sub>16</sub>(Me<sub>3</sub>AI)<sub>6</sub>Me]<sup>-</sup> shown in red.



Figure S6. PSI of 1 mol% *i*Bu<sub>3</sub>Al modified MAO/OMTS with Al:OMTS 100:1 in PhF.



Figure S7. PSI of 10 mol% nOct<sub>3</sub>AI modified MAO/OMTS with AI:OMTS 100:1 in PhF.



Figure S8. PSI of 10 mol% Et<sub>3</sub>AI modified MAO/OMTS with AI:OMTS 100:1 in PhF.

### 3) MS/MS Spectra

Only the first few losses are assigned for clarity.



Figure S9. MS/MS spectrum of species containing one Me/*i*Bu substitution (*m*/*z* of 1417).



Figure S10. MS/MS spectrum of species containing two Me/*i*Bu substitutions (*m*/*z* of 1459).



Figure S11. MS/MS spectrum of species containing three Me/*i*Bu substitutions (*m*/*z* of 1501).



Figure S12. MS/MS spectrum of species containing four Me/*i*Bu substitutions (*m*/*z* of 1543).



Figure S13. MS/MS spectrum of species containing five Me/*i*Bu substitutions (*m*/*z* of 1585).



Figure S14. MS/MS spectrum of species containing one Me/nOct substitution (m/z of 1473).



Figure S15. MS/MS spectrum of species containing two Me/nOct substitutions (m/z of 1571).



Figure S16. MS/MS spectrum of species containing three Me/nOct substitutions (m/z of 1669).



Figure S17. MS/MS spectrum of species containing four Me/nOct substitutions (*m*/*z* of 1767).



Figure S18. MS/MS spectrum of species containing one Me/Et substitution (*m*/*z* of 1389).



Figure S19. MS/MS spectrum of species containing two Me/Et substitutions (*m/z* of 1403).



Figure S20. MS/MS spectrum of species containing three Me/Et substitutions (m/z of 1417).



Figure S21. MS/MS spectrum of species containing four Me/Et substitutions (*m/z* of 1431).

#### 4) DFT Calculations on iBu exchange

DFT calculations using the M06-2X/TZVP method,<sup>1,2</sup> as recommended for aluminum alkyl compounds containing bridging alkyl groups,<sup>3</sup> were conducted by substitution of all Me positions in **16,6** (Figure 6) by *i*Bu groups.



Figure S22. Structure of the different Me sites in a model for (MeAIO)<sub>16</sub>(Me<sub>3</sub>AI)<sub>6</sub>.

There are a total of 34 different Me sites available in the neutral model for MAO. These sites can be classified according to whether the Me is terminal or bridging and also the local environment adjacent to the AI-Me group undergoing substitution. There are a total of nine types of sites (Figure S22).

First, it should be noted that a single substitution of Me by iBu at the most favorable site is thermodynamically favoured by ca. -27.3 kJ (mol cage)<sup>-1</sup> in the gas phase according to eqn. 1)

2 16,6 + 2 
$$iBu_3AI \rightarrow 2$$
 16,6, $iBu$  +  $iBu_2AIMe_2AIiBu_2$  1)

Evidently, in the absence of significant steric interactions in the substituted cage (*vide infra*), the reaction is favoured due to the driving force for dimerization of the by-product in eqn. 1. If another alkyl aluminum was involved in the exchange, such as *i*Bu<sub>2</sub>AIMe<sub>2</sub>AIMe<sub>2</sub>AI/Bu<sub>2</sub> one can predict that the driving force will be significantly reduced (by about half) as both sides of the equation now feature dimeric trialkylaluminums.

There are six different types of terminal Me (Me<sub>t</sub>) groups in this structure, depending on the number of O atoms bonded to AI (0-3), and whether there are just terminal vs. bridging Me (Me<sub>b</sub>) groups bonded to the AI. Though there is considerable variation in the substitution energies for Me<sub>t</sub> of a given type (as much as 40 kJ mol<sup>-1</sup>), the average substitution energies, as a function of the number of attached O atoms, are roughly comparable:  $12.4 \pm 11.7$  kJ mol<sup>-1</sup> for three,  $10.9 \pm 4.8$  kJ mol<sup>-1</sup> for two,  $10.1 \pm 3.1$  kJ mol<sup>-1</sup> for one, and  $11.6 \pm 0.9$  kJ mol<sup>-1</sup> for none, respectively. This suggests minimal electronic effects on the substitution

process, as might be expected. Indeed, for those isomers featuring the highest substitution energy, spacefilling models reveal significant vDW contacts involving the iBu group and adjacent AI-Me groups that cannot be relieved through bond rotations.

Entry	$\Delta E$ (kJ mol <sup>-1</sup> )	Site # <sup>a</sup>	Site Type <sup>b</sup>	Entry	$\Delta E$ (kJ mol <sup>-1</sup> )	Site # <sup>a</sup>	Site Type <sup>b</sup>
1	0.0	1	O <sub>3</sub> AIMe <sub>t</sub>	18	18.8	3	$O_2AIMe_tMe_b$
2	4.3	1	O <sub>3</sub> AIMe <sub>t</sub>	19	7.1	4	$OAI(\mathbf{Me}_t)_2Me_b$
3	4.5	1	O <sub>3</sub> AIMe <sub>t</sub>	20	7.2	4	$OAI(\mathbf{Me}_t)_2Me_b$
4	5.2	1	O <sub>3</sub> AIMe <sub>t</sub>	21	10.5	4	$OAI(\mathbf{Me}_t)_2Me_b$
5	5.8	1	O <sub>3</sub> AIMe <sub>t</sub>	22	11.8	4	$OAI(\mathbf{Me}_t)_2Me_b$
6	12.1	1	O <sub>3</sub> AIMe <sub>t</sub>	23	8.8	5	$OAIMe_t(Me_b)_2$
7	14.6	1	O <sub>3</sub> AIMe <sub>t</sub>	24	15.1	5	$OAIMe_t(Me_b)_2$
8	17.8	1	O <sub>3</sub> AIMe <sub>t</sub>	25	10.6	6	$(\mathbf{Me}_t)_2 AI(Me_b)_2$
9	19.2	1	O <sub>3</sub> AIMe <sub>t</sub>	26	11.5	6	$(\mathbf{Me}_t)_2 AI(Me_b)_2$
10	40.1	1	O <sub>3</sub> AIMe <sub>t</sub>	27	11.6	6	$(\mathbf{Me}_t)_2 AI(Me_b)_2$
11	5.9	2	O <sub>2</sub> AI(Me <sub>t</sub> ) <sub>2</sub>	28	12.8	6	$(\mathbf{Me}_t)_2 AI(Me_b)_2$
12	8.9	2	O <sub>2</sub> AI(Me <sub>t</sub> ) <sub>2</sub>	29	9.6	7	O <sub>2</sub> AIMe <sub>t</sub> Me <sub>b</sub>
13	10.7	2	O <sub>2</sub> AI(Me <sub>t</sub> ) <sub>2</sub>	30	13.6	8	$OAI(Me_t)_2 Me_b$
14	11.6	2	O <sub>2</sub> AI(Me <sub>t</sub> ) <sub>2</sub>	31	8.7	9	$(Me_t)_2AI(\mathbf{Me_b})_2$
15	12.7	2	O <sub>2</sub> AI(Me <sub>t</sub> ) <sub>2</sub>	32	12.6	9	$(Me_t)_2AI(\mathbf{Me_b})_2$
16	14.8	2	O <sub>2</sub> AI(Me <sub>t</sub> ) <sub>2</sub>	33	25.0	9	$(Me_t)_2AI(\mathbf{Me_b})_2$
17	3.7	3	$O_2AIMe_tMe_b$	34	25.4	9	$(Me_t)_2 AI(\boldsymbol{Me_b})_2$

Table S-1. Relative Energy Changes upon Substitution of *i*Bu for Me at different sites in 16,6.

a. See Figure S22 for numbering scheme. b. See Figure S22 for structures of these groups.

Table S-2. Consecutive substitution of 16,6 by *i*Bu groups according to the reaction:

Substitution	Δ <i>E</i> (kJ/mol)ª	∆G (kJ/mol)ª	$\Delta G_{\rm c}  (\text{kJ/mol})^{\rm a}$	$\Delta G_n$ (kJ/mol) <sup>a,b</sup>
1	-120.0	-54.7	-74.4	-54.7
2	-233.3	-79.0	-125.5	-39.5
3	-345.8	-127.7	-193.4	-42.6
4	-454.7	-154.4	-244.3	-38.6
5	-565.9	-180.7	-296.2	-36.1
6	-671.8	-188.2	-332.8	-31.4
7	-771.4	-225.3	-389.0	-32.2
8	-873.5	-259.6	-443.5	-32.4
9	-969.5	-284.1	-489.7	-31.6
10	-1075.3	-304.8	-535.1	-30.5

2 **16,6** + 2n *i*Bu<sub>3</sub>Al  $\rightarrow$  2 **16,6**(*i*Bu)<sub>n</sub> + n *i*Bu<sub>2</sub>AlMe<sub>2</sub>Al/Bu<sub>2</sub> with n = 1-10.

a. Energies are reported per mole of the by-product  $iBu_2AIMe_2AIiBu_2$ ;  $\Delta G_c$  includes a correction of -  $\frac{2}{3}T\Delta S$  for the condensed phase.<sup>4</sup> b. Free energy change per *i*Bu group.

When the *i*Bu group is in bridging position, the energies again vary considerably, though as expected the average energy ( $15.8 \pm 7.5 \text{ kJ}$  mol-1) is significantly higher than for substitution at a terminal position. Examination of the lower energy structures suggest that there are both  $\alpha$ - and  $\beta$ -agostic C-H interactions with Al which cannot be accessed in the higher energy structures, mainly due to steric constraints. In any event, the results do suggest that *i*Bu can enter a bridging position which is key to the exchange process, especially in the case of the basal OAl<sub>2</sub>Me<sub>5</sub> sites.

In terms of poly-substitution, we examined this systematically by replacing Me with *i*Bu in an iterative manner, starting off with the lowest energy mono-substituted isomer, proceeding to the next lowest energy position while avoiding vicinal, germinal, or other unfavorable *i*Bu-*i*Bu interactions. The energy and free energy changes for each substitution are summarized in Table S-2. The first substitution is the most exergonic, with subsequent substitutions decreasing in free energy, reflecting increasing steric hindrance with continued substitution of open positions. Cartesian coordinates of all structures are available in file coordinates.xyz.

#### 5) References

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