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# Insertion, elimination and isomerisation of olefins at alkylaluminium hydride: an experimental and theoretical study

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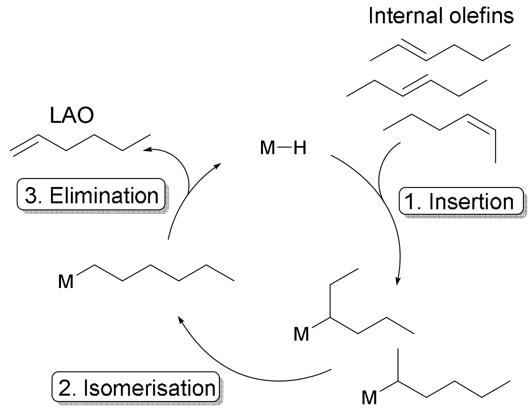
The insertion, elimination and isomerisation of octenes with di-*n*-octylaluminium hydride [$HAl(Oct)_2$], tri-*n*-octylaluminium [$Al(Oct)_3$] and *sec*-octylaluminium species have been studied as individual steps in a putative aluminium based contrathermodynamic olefin isomerisation process. While elimination of 1-octene from [$Al(Oct)_3$] is energetically unfavourable, the process is driven by high temperature vacuum distillation, leading to very high selectivity to 1-octene (>97%). At high conversions the [$HAl(Oct)_2$] so obtained exists predominately as hydride-bridged cyclic oligomers, whereas at low conversion the mixed alkyl/hydride-bridged dimer [$(Oct)_2Al(\mu\text{-}H)(\mu\text{-}Oct)Al(Oct)_2$] is the major species. Di-*n*-octylaluminium hydride recovered after olefin elimination may be recycled and is active toward re-insertion of octenes. Internal octenes (*cis*- and *trans*-2-, 3- and 4-octene) only partially insert however, and even after prolonged heating there is no significant secondary to primary alkyl isomerisation evident.

## Introduction

Straight–chained 1-alkenes, known as linear α-olefins (LAOs), are an extremely important feedstock of the petrochemical industry which are employed in the manufacture of polymers, lubricants and surfactants, amongst other uses.[1] The most common route to produce LAOs involves metal-catalysed ethylene oligomerisation,[2-4] and much recent work has focussed on the development of catalysts for selective production of co-monomer range olefins (particularly 1-hexene and 1-octene).[5-9]

An attractive alternative to oligomerisation of ethylene is the conversion of *n*-alkanes into LAOs. The dehydrogenation of alkanes to mono-olefins is already carried out on an industrial scale, however the process leads to a mixture of predominately internal olefins.[10] The conversion of internal olefins into α-olefins, which is a contrathermodynamic process, is therefore required in order to develop an overall *n*-alkane to LAO conversion route. Such an approach has some potential advantages over direct functionalisation of alkanes (alkane activation), as the resultant α-olefins could be used directly in a great number of existing industrial processes. For this reason, we have recently started investigating potential routes for this transformation.

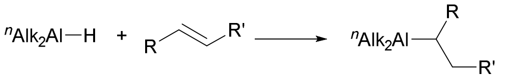


**Scheme 1.** Proposed metal-hydride based cycle for contrathermodynamic isomerisation of olefins.

One possibility for contrathermodynamic isomerisation of internal olefins is represented in the cycle shown in Scheme 1, and involves three steps. The first is insertion of an internal olefin into a M–H bond to generate a *sec*-alkylmetal compound. In the second step, which is really a series of steps, the *sec*-alkyl group undergoes isomerisation to form a primary alkyl metal species. The tendency of some transition metal[11] and group 13[12,13] secondary alkyls to isomerise to primary alkyls is well known. The third step involves β-hydride elimination of an α-olefin and, if done under kinetic control (essentially rapid removal of the liberated olefin), might lead to α-olefin selectively. While the overall cycle is stoichiometric with respect to the metal, the ability to recycle the metal hydride could lead to a catalytic process. Each of these individual steps is known to occur to at least some extent at different metal complexes; the challenge lies in putting them all together into a complete cycle.

Our first investigations in this area focussed on the use of alkylboranes as the catalyst in Scheme 1.[14] The first two steps, insertion and isomerisation, are well known aspects of the classical hydroboration work of Brown.[12,15] We found however that primary alkylboranes stumble at the final hurdle, olefin release. It did not prove possible to remove useful amounts of α-olefin from tri-*n*-alkylboranes and theoretical studies showed that the equilibrium concentration of free olefin is extremely low even at elevated temperatures.[14] These results prompted us to switch focus to alkylaluminium compounds, which is the subject of the present work.

The reactivity of olefins with alkylaluminiums and aluminium hydrides formed the basis of much of Ziegler's studies, along with others, beginning in the 1950s.[13,16,17] As such, much is already known about the individual steps shown in Scheme 1, although as discussed below, uncertainties still remain, particularly with respect to internal olefin reactivity. The cycle envisaged with aluminium involves shuttling between $R_2AlH$ and $AlR_3$, as removal of more than one alkyl group was expected to lead to decomposition (discussed below). Beginning with the first step (Reaction 1), Ziegler showed that α-olefins insert relatively rapidly into $R_2Al$–H, and that the reaction goes to practical completion, whereas internal olefins insert much more slowly.[18] Other studies found likewise,[19] with one[20] showing that internal olefins insert around 200 times more slowly than α-olefins. The rate of insertion of internal olefins is one factor, but a related yet separate factor to consider is also the equilibrium position of this reaction. It is known that β-branched alkylaluminiums, for example triisobutylaluminium, exist with an appreciable equilibrium concentration of free olefin and dialkylaluminium hydride, and also that tri-*sec*-alkylaluminiums cannot be prepared by insertion of internal olefins; insertion stops once (*sec*-alkyl)$_2$AlH has formed.[13,21] However, to the best of our knowledge, the extent to which Reaction 1 progresses (which places only one *sec*-alkyl group on Al in addition to two existing *n*-alkyl groups) is less clear, this being the reaction of most interest for the first step of Scheme 1.



(1)

In terms of the second step (isomerisation), the tendency of *sec*-alkyl groups bound to aluminium to slowly isomerise to primary alkyls at elevated temperatures has been noted, for example Al–$^i$Pr → Al–$^n$Pr.[17,21] This process occurs via reversible β-hydride elimination/insertion reactions (chain walking), so its rate will obviously depend on the rate of elimination and re-insertion. Given that internal olefins are known to insert only very slowly, the isomerisation of deep internal olefins may likewise be expected to be slow. The question then, with regards to the first two steps, is whether internal olefins can insert to a sufficient degree and then isomerise fast enough for the reaction to be of practical use.

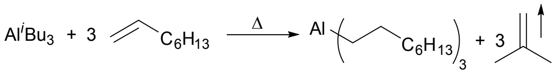
The removal of olefin from β-branched trialkylaluminiums, as per step 3 in Scheme 1, is well known. The best example is triisobutylaluminium, which yields [$HAl^iBu_2$] and isobutene when heated to around 100 °C under vacuum.[22] As mentioned above, β-branched alkylaluminiums exist with measureable equilibrium concentrations of free olefin, and as such the relative ease of this reaction can be understood. On the other hand, for tri-*n*-alkylaluminiums it has been concluded that the equilibrium lies too heavily to the side of trialkylaluminium for this reaction to be useful. Additionally, elimination is slower, insertion of the liberated olefin into remaining Al–C bonds is possible, and dialkylaluminium hydride has a tendency to decompose at elevated temperature.[13] There are however two examples in the patent literature where an α-olefin has been selectively liberated from a tri-*n*-alkyl aluminium.[23,24] There is clearly a need to further investigate the scope and practical value of the elimination reaction with respect to LAOs.

There are also a number of reports, predominately in the patent literature, where olefin insertion and isomerisation is promoted by the addition of a catalytic amount of transition metal complex (in addition to stoichiometric aluminium).[25-27] The effect such isomerisation catalysts might have on the selectivity of the elimination step is unknown, so we have in the first instance investigated the uncatalysed reactions of $R_2AlH$ and $AlR_3$. Herein we report our first results looking into the use of alkylaluminiums for the cycle shown in Scheme 1. The reactivity of $R_2AlH$ and $AlR_3$, and aluminium speciation during olefin insertion and elimination has been studied.

## Results and Discussion

The reactions shown in Scheme 1 have been studied with tri-*n*-octylaluminium [$Al(Oct)_3$] and di-*n*-octylaluminium hydride [$HAl(Oct)_2$] and the elimination from/insertion of octenes to these. The most convenient entry into this chemistry is to prepare [$Al(Oct)_3$] via olefin displacement from [$Al^iBu_3$] (Reaction 2). When this reaction is carried out with LAOs such as 1-octene, care is needed to prevent dimerisation reactions.[13] We found that using only stoichiometric (three equivalents) of 1-octene resulted in a good balance of minimal dimerisation and at the same time low levels of residual *iso*-butyl groups remaining. The presence of some insertion in Al–C bonds is evidenced by the observation of trace $C_{12}$ and $C_{16}$ olefins by GC analysis (octene insertion into Al–$^i$Bu and Al–Oct respectively). The $^1$NMR spectrum of [$Al(Oct)_3$] also contains two trace signals at 4.75 ppm and 4.80 ppm, characteristic of vinylidene groups expected from these reactions (Scheme 2).

These products do not interfere with later analyses, and no attempt was made to remove them (although they are effectively removed in the olefin elimination step, below). $^1H$ NMR spectroscopy also shows the presence of some remaining Al–$^i$Bu groups in the [Al(Oct)$_3$], corresponding to up to 7 mol% *iso*-butyl with respect to all alkyl groups (octyl plus *iso*-butyl), and also trace octenes (1-octene and internal octenes). The *iso*-butyl groups can be eliminated as *iso*-butene in subsequent reactions at elevated temperature, but again the vinylidene $^1H$ NMR signal at 4.68 ppm does not interfere with the octene signals of interest.



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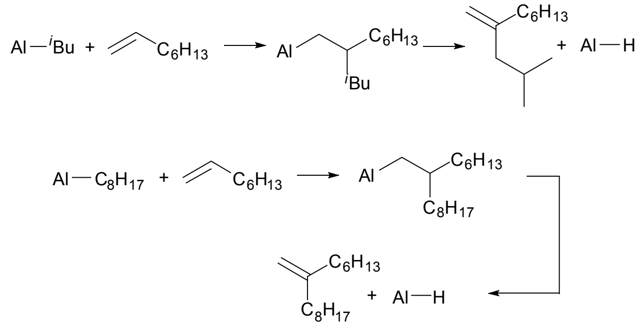


**Scheme 2.** *Iso*-butyl–octene and octyl–octene coupling (dimerization) reactions.

## Olefin elimination from tri-*n*-octylaluminium

The presence of free octene signals (4.92–5.02 and 5.70–5.80 ppm for 1-octene and 5.35–5.45 ppm for internal octenes), along with an aluminium hydride signal at 3.95 ppm, indicate a low equilibrium concentration of [HAl(Oct)$_2$] and octene in [Al(Oct)$_3$] at room temperature. Variable temperature NMR spectroscopy ([Al(Oct)$_3$] = 0.285 M in toluene-d$_8$) shows that the amount of free 1-octene increases as the temperature is increased, along with a concomitant increase in the intensity of the Al–H signal (Figure 1). The amount of 1-octene relative to [Al(Oct)$_3$], which is 0.6% at room temperature, reaches ca. 1.9% at 100 °C. The measured amount of internal octenes stays constant at ca. 1.0–1.3% as the temperature is raised, which indicates that these products are most likely formed by a much slower isomerisation process which converts free 1-octene to internal octenes. They do not appear to be formed during the time scale of the VT NMR experiment. At 100 °C the formation of *iso*-butene also becomes significant, and as a result the Al–H signal is larger than expected based on only the amount of 1-octene released.

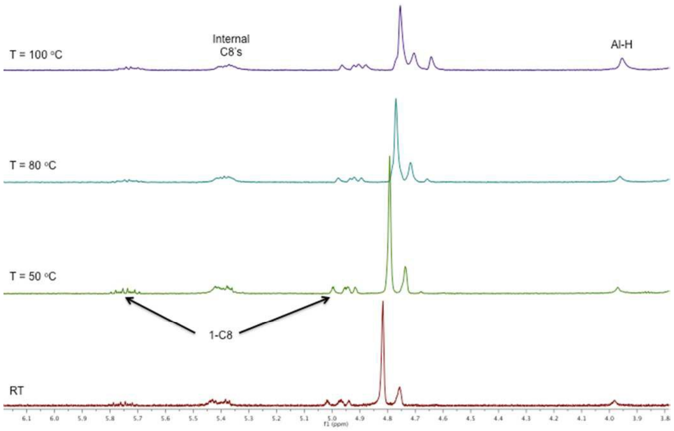


**Figure 1.** Variable temperature $^1H$ NMR of Al(Oct)$_3$ in the olefinic and Al–H region.

These results indicate a low but significant degree of 1-octene elimination as the temperature is increased. We therefore attempted to drive this reaction by heating neat [Al(Oct)$_3$] under vacuum (ca. $10^{-4}$ atm). At temperatures above 150 °C refluxing of [Al(Oct)$_3$] is observed and 1-octene begins to collect in a cold trap. The elimination reaction is more vigorous at 170 °C, where ca. 50% of the [Al(Oct)$_3$] is converted to [HAl(Oct)$_2$] and 1-octene in 1 hr. Some representative experiments are shown in Table 1. Entry 1 shows the results of elimination carried out on the initially prepared [Al(Oct)$_3$], which as discussed above contains some C$_{12}$ and C$_{16}$ impurities. These are carried over during elimination, but the product is still composed of 96% octenes, of which 97.6% is 1-octene. Entry 2 is more representative of the inherent selectivity of the process. For this sample, [Al(Oct)$_3$] was prepared by adding 1-octene to a mixture of [HAl(Oct)$_2$] and [Al(Oct)$_3$] from a previous elimination experiment (insertion of octenes into [HAl(Oct)$_2$] is discussed in detail below). As such, the C$_{12}$ and C$_{16}$ impurities have been removed in the first elimination reaction. In this case, the olefin collected is composed solely of octenes, again with an excellent selectivity to 1-octene. This experiment demonstrates that it is possible to strip 1-octene from tri-*n*-octylaluminium with high selectivity for α-olefin, and also that octene dimerization can be avoided under these conditions.

**Table 1.** 1-Octene elimination experiments

| Entry | Temp (°C) | Time (min) | Olefin yield (%)[a] | C$_8$ (mol%) | Selec 1-C$_8$ (%)[b] | C$_{12}$ (mol%) | C$_{16}$ (mol%) |
|---|---|---|---|---|---|---|---|
| 1 | 170 | 70 | 52 | 96.4 | 97.6 | 3.6 | 0.1 |
| 2[c] | 170 | 60 | 64 | 100 | 97.7 | - | - |
| 3[d] | 150-180 | 290 | 49 | 92.7 | 79.3 | 4.6 | 2.7 |

[a] Yield of olefins with respect to initial amount of Al(Oct)$_3$. [b] Selectivity to 1-octene within total C$_8$ fraction. [c] second cycle of elimination, see test for discussion. [d] Closed system (static vacuum, see text for discussion).

Entry 3 in Table 1 was carried out under a static vacuum; that is the elimination flask and cold trap were initially evacuated before being sealed. Under these conditions, distillation of the liberated olefin over to the cold trap is not expected to be as fast. The importance of rapid olefin removal after elimination is illustrated by this experiment through two effects. Firstly, 1-octene is partially isomerised to internal octenes, and secondly a small but significant amount of $C_{16}$ octene dimer is formed (corresponding to 5 wt% of the liberated olefin).

The degree of double bond movement in the isomerised octenes has been assessed by GC analysis. For an elimination experiment with a low level of isomerisation (Table 1, entry 1), the internal octenes are composed of 70% *cis*- and *trans*-2-octene, with the remaining 30% being the 3- and 4-octenes. This can be rationalised on the basis that the 2-octenes are the first products formed by 1-octene isomerisation, so will be formed before deeper internal octenes. In a run with more extensive isomerisation (Table 1, entry 3), the combined 2-octene content of the internals drops to 55%, due to a greater degree of isomerisation to 3- and 4-octenes.

It has been found that the elimination reaction can be taken to 70-80% conversion to [HAl(Oct)$_2$] with recovery of a clear and colourless mixture of [Al(Oct)$_3$] and [HAl(Oct)$_2$]. Above this level of conversion however, spontaneous decomposition and deposition of aluminium metal occurs. The decomposition of diethylaluminium hydride at elevated temperatures, to produce aluminium metal and hydrogen, has been reported.[13,18] The reaction is thought to be promoted by heterogeneous autocatalysis, which is certainly consistent with our observations; aluminium deposits do not slowly form over the course of the reaction, but rather the clear liquid rapidly drops aluminium once conversion increases above ca. 80%. Decomposition is thought to result from precipitation of alane, which is thermally unstable (the decomposition of alane has been the subject of more recent studies).[28] Presumably in our experiments some amount of $AlH_3$ is formed at high concentrations of the hydride. Decomposition does not continue however, unless the elimination reaction is also continued. A mixture of [Al(Oct)$_3$] and [HAl(Oct)$_2$] is quite stable in the presence of the aluminium deposits. The reaction is also not detrimental to the selectivity of elimination; 1-octene is still produced with high purity if elimination is continued in the presence of deposited aluminium. It does of course represent a loss of aluminium from the system however. We found that by restricting the conversion to around 50-60%, decomposition could be completely eliminated and the alkylaluminium hydride mixtures recycled.

## Alkylaluminium hydride speciation

Within the [HAl(Oct)$_2$]/[Al(Oct)$_3$] mixtures obtained through elimination, at low mole fractions of [HAl(Oct)$_2$] (less than ca. 10%), only a single hydride resonance is observed at 3.95 ppm, as seen in the variable temperature $^1$H NMR experiment above (Figure 1). However, as the percentage of [HAl(Oct)$_2$] increases, the signal at 3.95 ppm decreases in intensity and new hydride signals appear further upfield. The major new resonance is at 3.05 ppm, which is accompanied by shoulders either side (2.95 and 3.14 ppm) and another small peak at 3.26 ppm. The hydride region of the $^1$H NMR spectrum as a function of [HAl(Oct)$_2$] percentage is shown in Figure 2. As the temperature is raised these hydride signals broaden and finally converge at 100 °C to a single broad peak at 3.2 ppm (see Supplementary Information). This is indicative of exchange processes occurring between the different species, as are cross peaks between the main hydride signals in the EXSY NMR spectrum (Supplementary Information). Furthermore, if tetrahydrofuran is added in an amount equal to the total amount of aluminium, the various hydride species collapse to a single resonance at 4.05 ppm. This species is suggested to be [HAl(Oct)$_2$(thf)].

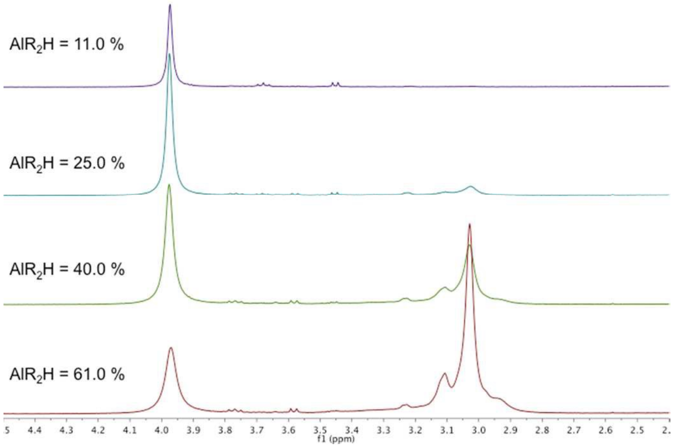
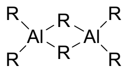


**Figure 2.** $^1$H NMR of the Al-H region at different percentages of [HAl(Oct)$_2$].

Tri-*n*-alkylaluminium compounds are known to exist as alkyl-bridged dimers in solution,[29-31] so in the absence of hydride, complex **1** will be the major species present. With only a small amount of hydride present, the mixed alkyl/hydride bridged dimer **2**[13,16] is suggested for the signal at 3.97 ppm. Pure dialkylaluminium hydrides are known to exist as trimers[30,32] (complex **3**), which may correspond to the signal at 3.05 ppm. A previous NMR study[33] of [$^i$Bu$_2$AlH] concluded that the main hydride signal (in this case at 2.72 ppm) was the trimer, while a similar upfield shoulder to that observed in our work was assigned to a pentamer. The downfield shoulder to the main signal was suggested to be the monomer [$^i$Bu$_2$AlH]. We assign the shoulder at 2.95 ppm to the pentamer **4**, but consider it unlikely that the non-bridging hydride in the monomer would have a shift so similar to bridging hydrides. As such, the signal at 3.14 ppm was initially unassigned. The signal at 3.27 ppm disappears at high percentages of [HAl(Oct)$_2$], which may indicate it is another species which contains [Al(Oct)$_3$] within its structure. Based on the calculated NMR spectrum (below), we tentatively assign it to the trimeric complex **5**.



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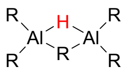

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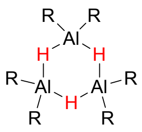

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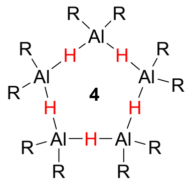

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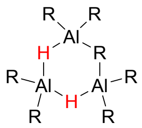

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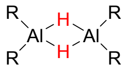

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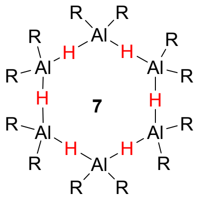


**7**

In support of these assignments, theoretical NMR shielding values have been calculated for each proposed complex (GIAO-DFT, *n*-butyl groups in place of *n*-octyl, see Theoretical methods section for details). In Figure 3, the calculated absolute shielding values (σ) are plotted against the assigned experimental $^{1}$H NMR chemical shifts (δ). A very good linear relationship exists, which lends support to these assignments. Another possibility for the signal at 3.26 ppm is the dimer **6**, which has a calculated shielding very similar to **5** (28.05 ppm for **5** cf. 27.97 ppm for **6**). The calculated shielding for monomeric [$R_2AlH$], together with the relationship derived in Figure 3, yields a predicted shift of 5.4 ppm for this complex. There is no sign of a hydride resonance in this region in any of our experiments.

The previous NMR study of [$^{i}Bu_2AlH$] also considered the hexamer, [$Al_6(\mu\text{-}H)_6R_{12}$] **7**, to be a possibility for the upfield shoulder.[33] Our calculations together with the relationship of Figure 3 predict a hydride chemical shift of 3.11 ppm for this species. As such, this may well be the identity of the hitherto unassigned downfield shoulder at 3.14 ppm. In contrast, the tetramer, [$Al_4(\mu\text{-}H)_4R_8$], is calculated to produce a hydride resonance at 2.79 ppm. We also attempted to study the speciation of Al by $^{27}$Al NMR, however this was unsuccessful‡.

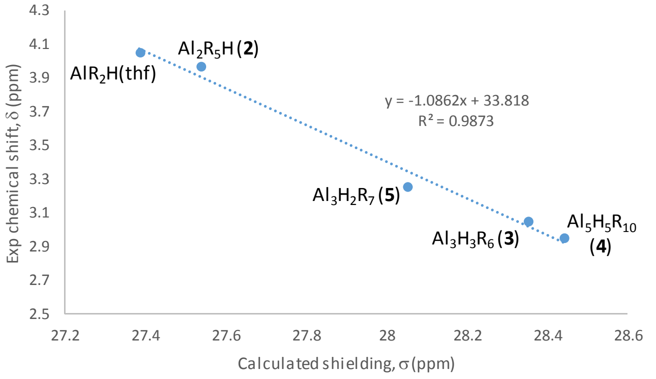


**Figure 3.** Experimental $^{1}$H NMR Al-H chemical shift versus calculated (B3LYP/6-311+G(2d,p)) shielding for proposed [$Al_xH_yR_z$] solution structures.

On the basis of these assignments, the speciation of aluminium as a function of the ratio of [$HAl(Oct)_2$] to [$Al(Oct)_3$] can be plotted as is shown in Figure 4 (RT, [Al] = 0.55–0.57 M in $C_6D_6$). In this plot, the amount of [$Al_2R_6$] (**1**) is calculated by difference (total aluminium minus all Al–H containing species). The change in speciation with hydride content is also evident in the $^{13}$C NMR spectrum, largely in the Al–octyl α–C signals, and adds further credence to our assignments. This is illustrated, along with some discussion of the proposed assignments, in the Supplementary Information.

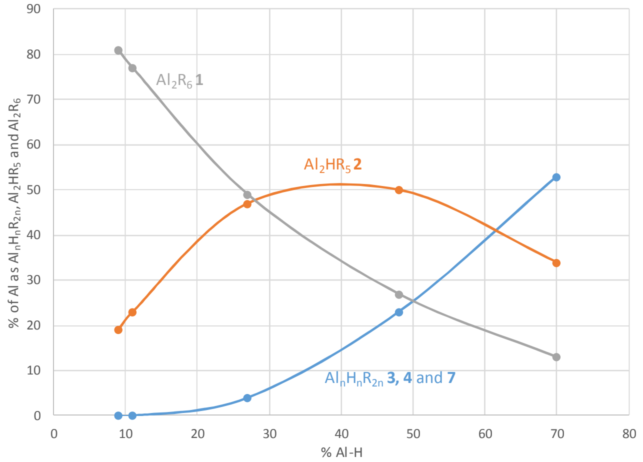


**Figure 4.** Aluminium speciation as a function of [$HAl(Oct)_2$] content at room temperature. [Al] = 0.55–0.57 M in $C_6D_6$.

### Theoretical treatment of olefin elimination

The effective removal of 1-octene from [$Al(Oct)_3$] is in contrast to our findings with tri-*n*-octylborane, [$B(Oct)_3$], which proved resilient to elimination.[14] The stability of [$B(Oct)_3$] could be rationalised on theoretical grounds, and we have likewise carried out calculations on the model compound [$Me_2Al^{n}Bu$] with the accurate CBS-QB3[34,35] method. Our previous work with boranes demonstrated that elimination of an *n*-butyl group is a reliable model for longer *n*-alkyl chains. The free energy profile for elimination from [$Me_2Al(\mu\text{-}Bu)]_2$ is shown in Figure 5a, along with elimination from [$Me_2B^{n}Bu$] for comparison (Figure 5b). In the aluminium system the bridging alkyl ligands of the dimer have been left as butyl groups, as methyl bridging leads to stronger binding and is therefore not a good model for higher alkyls. The reaction has been modelled as leading to the hydride/alkyl bridged dimer **2**, as this is the major form of Al–H at low conversions. In the case of boron, alkyl bridging is not favourable and hydride bridged dimers are the principal form of [$R_2BH$].[12] The overall barrier to elimination is somewhat higher for aluminium than for boron, but this is due solely to the energetic penalty associated with breaking the alkyl-bridged dimer (trialkylboranes are monomeric in solution). The major difference between the two cases lies in the stability of the products, hydride and free olefin. For aluminium, the reaction is endergonic, but considerably less so compared to boron. A higher equilibrium concentration of free olefin is therefore expected, as found experimentally. This appears to be the reason why removal of α-olefin from the aluminium system is possible, rather than being due to an inherently lower reaction barrier when compared to the boron system.

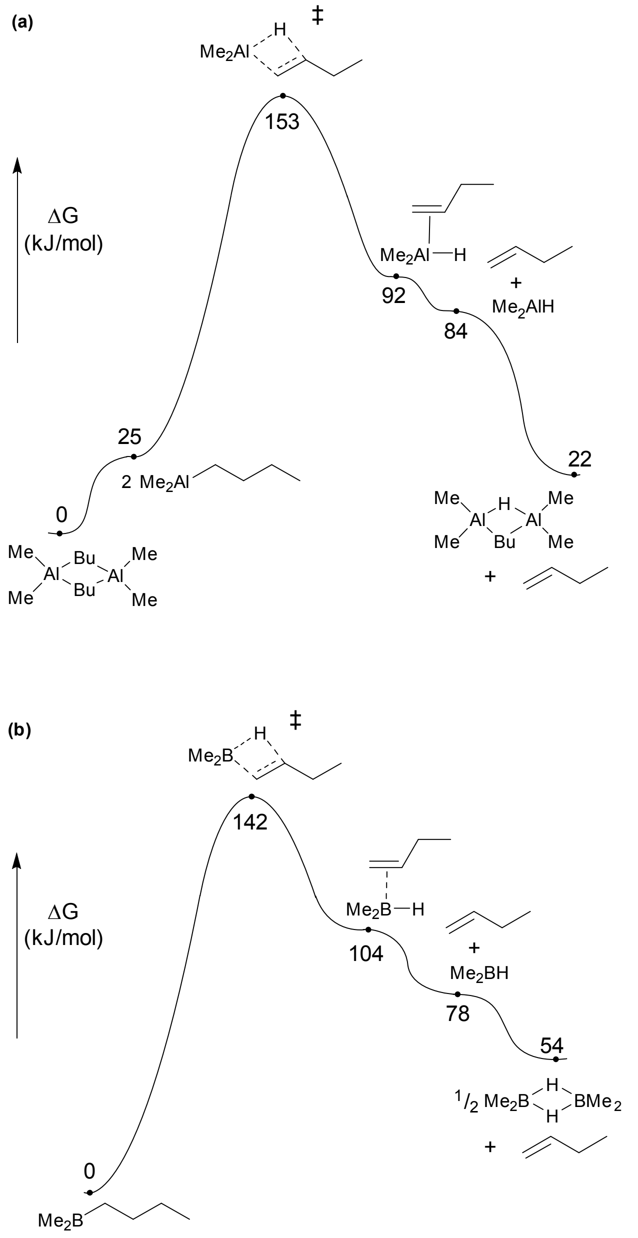


**Figure 5.** Gibbs free energy surface (kJ·mol$^{-1}$) for elimination of 1-butene from model Al and B alkyls (CBS-QB3 energies).

These calculations represent gas phase energetics, so in order to estimate a condensed phase equilibrium position, the calculated free energy (1 atm standard state concentration) has to be converted to a 1 M standard state. This transformation has been detailed previously.[14] At 100 °C, the free energy of reaction so obtained is 19 kJ·mol$^{-1}$. In neat [Al(Oct)$_3$] this corresponds to 2.3% free 1-octene relative to [Al(Oct)$_3$]. In comparison, the figure for [B(Oct)$_3$] is $9 \times 10^{-4}$ %. At the concentration of the variable temperature NMR experiment (Figure 1), theory predicts a free 1-octene content of 0.3% at room temperature, rising to 6% at 100 °C. While this appears to overestimate the amount of free 1-octene at higher temperatures, in comparison to the NMR experiment above (1.9% at 100 °C), considering the predicted value is derived by extrapolation of gas phase calculations to solution, we consider the agreement reasonable.

### Olefin insertion and isomerisation

We initially investigated the re-insertion of 1-octene into [HAl(Oct)$_2$]. This reaction serves to demonstrate that aluminium hydride obtained through elimination can be recycled and remains active toward olefin addition. Furthermore, it provides for comparisons with internal olefin insertion experiments. The insertion of 1-octene into the Al–hydride bond can be monitored by $^1$H NMR and a representative kinetic profile is shown in Figure 6a. An apparent half-life of ca. 30 minutes is observed for this reaction in toluene at 75 °C, which is in line with Ziegler's studies of α-olefin insertion into [HAlEt$_2$].[18] More detailed kinetic studies have been carried out previously ([HAl$^i$Bu$_2$] plus 1-butene) which show that the reaction is first order in olefin and approximately one-half order in aluminium hydride.[36] The order in hydride is thought to be due to the need for monomeric [HAlR$_2$] to form prior to insertion. We have not repeated these studies herein.

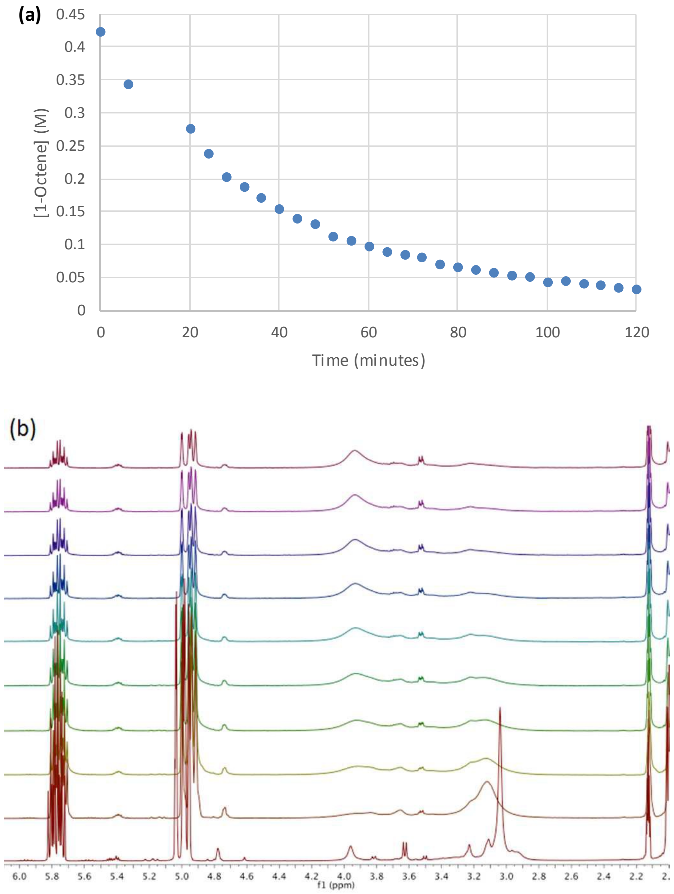


**Figure 6.** $^1$H NMR monitoring of 1-octene addition to [HAl(Oct)$_2$] (0.55 M in toluene-$d_8$, [1-octene]$_0$ = 0.42 M, 75 °C). (a) [1-octene] as a function of time, and (b) time series $^1$H NMR spectra of the hydride and olefin regions.

As $[HAl(Oct)_2]$ is consumed in the reaction, the speciation of aluminium changes as might be expected given the above observations. This is essentially the exact reverse of the changes observed upon increasing degrees of elimination. Time series $^1H$ NMR spectra of the hydride and olefinic region are illustrated in Figure 6b. Another aspect of note is that, under the relatively mild conditions required for 1-octene insertion, no competing insertion into the Al–carbon bond is observed. This is confirmed by the absence of $C_{16}$ olefin dimers following subsequent olefin elimination (Table 1, entry 2).

In order to study the insertion of internal olefins into $[HAl(Oct)_2]$, a thermodynamic mix of *n*-octenes was prepared by isomerising 1-octene with a catalytic amount of $[Ni(OAc)_2]/[AlEt_2Cl]$. This mix is composed of all possible isomers of *n*-octene in the following ratios (Table 2): 1-octene (1.5%), *trans*-4 (10.5%), *cis* and *trans*-3 and *cis*-4 (33.4%, co-elute in GC), *trans*-2 (40.5%) and *cis*-2 (14.1%). Reaction of this mixture with $[HAl(Oct)_2]$ at temperatures from 115–180 °C for 24 hr met with only partial success. At 115 °C, the highest level of insertion of octene achieved was 62% when an Al–H to octene ratio of 3:1 was employed (neat reagents). The figure was 51% insertion at a ratio closer to stoichiometric (Al–H:octene = 1.3:1). Prolonged reaction times do not increase the level of insertion, and it seems these results represent the equilibrium position of internal olefin insertion/elimination.

If the un-inserted octenes are removed under vacuum at room temperature, it is possible to analyse the mixture for preferential reactivity of certain isomers. This is illustrated in Table 2 (entry 2), and some slight changes to the composition are evident. 1-Octene is practically absent in the un-inserted olefins consistent with preferential insertion of the terminal olefin. The amount of *trans*-2 and *cis*-2-octene is decreased slightly, indicating they insert to a greater extent than 3- and 4-octene, which have increased somewhat in percentage terms.

**Table 2.** Octene composition before and during insertion experiments

| Entry | 1-octene (%) | *Trans*-4 (%) | *Cis*-2 (%) | *Trans*-2 (%) | Other[a] (%) |
|---|---|---|---|---|---|
| 1. Feed composition[b] | 1.5 | 10.5 | 14.1 | 40.5 | 33.4 |
| 2. Un-inserted[c] | trace | 15.0 | 10.4 | 34.3 | 40.3 |
| 3. Eliminated[d] | 32.3 | 8.3 | 9.4 | 20.9 | 29.1 |
| 3a[e] | - | 12.2 | 13.9 | 30.9 | 43.0 |

[a] *cis*- and *trans*-3 and *cis*-4-octene. [b] initial composition of internal octene mixture. [c] Composition of octenes which do not insert and are removed at room temperature. [d] composition of octenes collected by elimination (vacuum, 170 °C). [e] Entry 3a shows the composition of entry 3 with respect to internal octenes only (excluding 1-octene).

While *sec*-aluminium alkyls appear to be in equilibrium with free internal olefins, it was hoped that isomerisation (step 2 in Scheme 1) might lead to accumulation of the more stable primary aluminium alkyl and therefore lead to a greater degree of insertion. Unfortunately, there is no evidence for significant isomerisation to the primary alkyl even with prolonged (24 hr) heating. The composition of octenes eliminated (vacuum, 170 °C) after the insertion of internal olefins is shown in Table 2, entry 3. While the 1-octene content is considerably higher than in the octene mixture fed, this is simply because there is an abundance of pre-existing Al-*n*-octyl groups present in the $[HAl(Oct)_2]$ reactant. In fact, the percentage of primary *n*-octyl groups in the reactant was 87% of the total potential Al–octyl groups (Al reactant plus added octenes). The lower percentage of 1-octene eliminated (32%) therefore demonstrates Al–*sec*-alkyls are more reactive towards elimination, which is a known effect.[17] The composition of the internal octenes (excluding 1-octene, entry 3a) released by elimination is not markedly different to the composition reacted with $[HAl(Oct)_2]$, and does not indicate that *sec*-alkyls are isomerising to primary alkyls to an significant extent. The situation is not aided by increasing the temperature. After 9 hr at 170 °C a similar composition of octenes is obtained by elimination, but in this case along with 15 mol% (with respect to liberated olefins) octene dimers. Given the level of dimerization occurring at 170 °C, we did not attempt more forcing conditions for the isomerisation step.

The partial insertion of internal olefins is most evident in the hydride region of the $^1H$ NMR spectrum (Figure 7). The signals initially centred at 3.05 ppm broaden and split. This is likely due to the presence of a proportion of *sec*-octyl groups in complexes **3**, **4** and **7**. Interestingly, there is no change to the hydride signal at 3.95 ppm attributed to complex **2**. This seemingly indicates that the *sec*-alkyl groups reside on higher cyclic oligomers, and not the mixed alkyl/hydride bridged dimer. After high temperature elimination, peak splitting in the hydride region is largely removed, indicating that the majority of *sec*-alkyl groups have been eliminated, although the peak shape (shouldering) indicates a small amount of *sec*-alkyl remains. This is confirmed by quenching the reaction with $D_2O$ and analysis by $^{13}C$ NMR spectroscopy; in addition to deuterium coupling on carbon-1, there are also small deuterium coupled signals for carbon numbers 2, 3 and 4 (shown in the Supplementary Information).

~~*Cis*-2~~

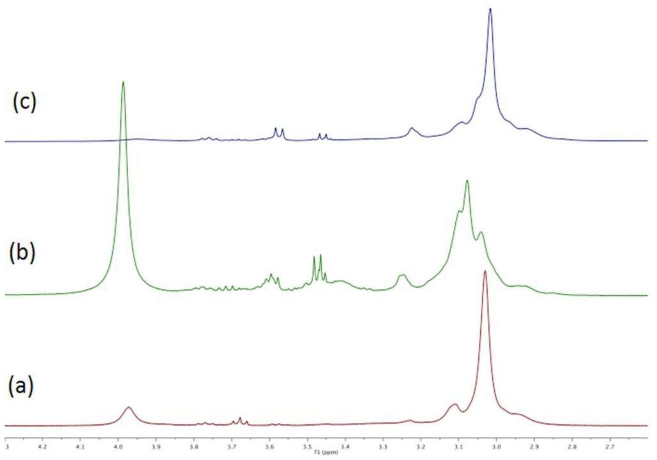


**Figure 7.** $^1H$ NMR spectrum of the Al–H region of $[HAl(Oct)_2]$ before (a) and after (b) insertion of internal octenes, and (c) after elimination. See text for discussion.

### Theoretical treatment of internal olefin insertion/elimination

A theoretical estimate of the energetics of internal olefin insertion and elimination has been obtained by studying a model involving *cis* and *trans*-2-butene elimination (Figure 8). In the direction of elimination, the activation barrier is slightly lower than the same barrier for 1-butene elimination (Figure 5a). Elimination of the *trans* isomer is slightly easier than *cis*. This probably accounts for the greater amount of *trans*-2-octene compared to *cis*-2-octene which is found in the elimination experiments (both are derived from a common *sec*-octylaluminium species, and selectivity in the elimination experiments should be under kinetic control rather than thermodynamic). The relative energy of the final products reveals why internal octene insertion does not proceed to completion. In fact, at 100 °C and in solution the reaction free energy, $\Delta G_{\text{react}}$, is estimated to be -2.8 kJ·mol$^{-1}$ for *trans*-2-butene elimination. The approximate free energy neutrality of the reaction is consistent with the equilibrium position observed experimentally.

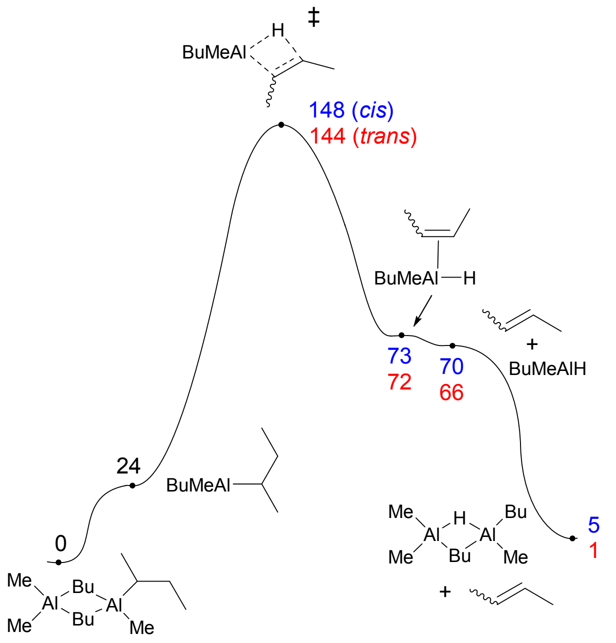
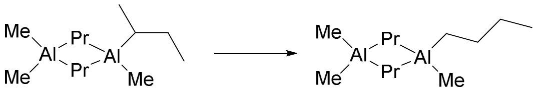


**Figure 8.** Gibbs free energy surface (kJ·mol$^{-1}$) for elimination of *cis*- and *trans*-2-butene from a model Al alkyl (CBS-QB3 energies).

### Comparison of alkylborane and alkylaluminium reactivity

While insertion and isomerisation of internal olefins at boranes, $R_2BH$, is well established, we previously found that elimination of LAOs is not practical.[14] The situation is reversed with aluminium, where LAOs are readily removed but insertion and isomerisation of internal olefins appears to be too slow to be of practical use. The thermodynamics of isomerisation from a sec-alkyl to a primary alkylaluminium are such that the reaction is favourable. For instance, the free energy change of Reaction 3 is calculated to be -11 kJ·mol$^{-1}$ at the CBS-QB3 level (in this case bridging propyl groups were modelled to reduce the computational expense). The problem therefore appears to be one of rate, and as we have shown, attempts to increase this at elevated temperature led to olefin dimerisation.



(3)

One further possibility investigated was the use of a mixed $R_2BH/R_2AlH$ system. The rationale here was that insertion and isomerisation could proceed at boron, followed by transfer of the primary alkyl to aluminium. This was attempted with a 5:1 mixture of $[HAl(Oct)_2]$ and $[HB(Oct)_2]$, but unfortunately there was no improvement in the degree of insertion or isomerisation. Furthermore, the elimination reaction from this mixture was sluggish and more prone to decomposition. The reason for this is currently unclear.

## Summary and Conclusions

Herein we have studied individual steps in the potential contrathermodynamic isomerisation of internal olefins with alkylaluminium according to Scheme 1. It has been shown that α-olefin may be liberated from tri-*n*-alkylaluminium on a preparative scale with very high selectivity. The energetics of this process, and the speciation of aluminium hydrides formed, has been elucidated with a combination of experimental and theoretical methods. It has been shown that α-olefin elimination is endergonic, but that the equilibrium concentration of free olefin is such that the reaction can be driven by rapid olefin removal.

Dialkylaluminium hydride formed through elimination can be effectively recycled, as demonstrated by re-insertion of 1-octene. However, insertion of internal olefins reaches an equilibrium position, where approximately half of the olefin remains uninserted. Unfortunately, isomerisation of *sec*-alkylaluminiums derived from 2-, 3-, and 4-octene appears to be too slow to drive the reaction toward the more stable primary alkylaluminium. The main hurdle to be overcome in the aluminium-based contrathermodynamic isomerisation cycle of Scheme 1 therefore appears to lie with Step 2, isomerisation. Our studies herein have focussed on the possibility of an uncatalysed process, with the exception of an unsuccessful attempt at isomerisation catalysis with a borane. We are currently investigating the use of transition metal catalysts to promote the isomerisation step and the effect of these on subsequent olefin elimination.

## Experimental and theoretical methods

### General

All manipulations were performed under an argon atmosphere using standard Schlenk techniques or carried out in a glovebox. Solvents were purified by passage through an Innovative Technologies solvent purification system and, where appropriate, were stored over a sodium mirror. 1-Octene was dried by distillation over sodium and stored over a sodium mirror. Tri-*iso*-butylaluminium was purchased from Sigma-Aldrich and used as received. NMR measurements were recorded on a Bruker Avance III HD NMR spectrometer with a 5 mm BBFO probe operating at 400 MHz ($^1$H) or 100 MHz ($^{13}$C). GC–MS analysis was carried out on a Varian 3800 GC coupled to a Varian 1200 triple quadrupole mass spectrometer in single quadrupole mode.

**Preparation of internal *n*-octenes.** To a flask containing $Ni(OAc)_2 \cdot 4H_2O$ (0.018g, 72 μmol), 1-octene (40.0 mL, 0.25 mol) and $[Al(Oct)_3]$ (0.40 mL, 0.91 mmol) were added and the mixture heated to 100 °C for 5 hr. After sitting over night the octene was vacuum distilled from the catalyst residue. The composition of octene isomers was as detailed in Table 2.

**Preparation of tri-n-octylaluminium $[Al(Oct)_3]$.** 1-Octene (28.0 mL, 178 mmol) was added to $Al^iBu_3$ (12.12 g, 61.11 mmol) and the reaction mixture was heated to 110 °C overnight. The flask was left open to an argon bubbler to allow isobutene to escape. The resultant clear liquid was placed under vacuum at room temperature for 2 hr to remove residual isobutene. The yield of trialkylaluminium is essentially quantitative by NMR, with the principal impurity being 7 mol% *iso*-butyl groups (relative to all alkyl groups) corresponding to a nominal $Al^iBu_3$ content of 4 wt%. Trace amounts of two vinylidene olefins ($C_{12}H_{24}$ and $C_{16}H_{32}$) are also detected by $^1$H NMR (4.75 and 4.80 ppm) and GC–MS. $^1$H NMR ($C_6D_6$): δ 0.56 (t, *J* = 8 Hz, 6H, Al$CH_2$); 0.92 (t, *J* = 8 Hz, 9H, $CH_3$); 1.2–1.5 (30H, $CH_2$); 1.62 (m, 6H, AlCH$_2$$CH_2$). $^{13}$C NMR ($C_6D_6$): δ 11.3 (Al$C$H$_2$); 14.4 ($C$H$_3$); 23.2, 25.9, 29.8, 29.9, 32.4, 36.2 ($C$H$_2$). $^1$H NMR Signals for *iso*-butyl: δ 0.34 (d, *J* = 8 Hz, 2H, Al$CH_2$); 1.10 (d, *J* = 4 Hz, 6H, $CH_3$); 2.02 (m, 1H, C$H$(CH$_3$)$_2$). Trace $^1$H NMR signals for free octenes and $[HAl(Oct)_2]$ are discussed in the text.

**1-Octene elimination from $[Al(Oct)_3]$.** A representative example corresponds to entry 1 in Table 1: A Schlenk flask connected to a liquid nitrogen cold trap was charged with $[Al(Oct)_3]$ (2.25 g, 6.14 mmol) and kept under vacuum while heated to 170 °C. 1-Octene distilled off and was collected in the cold trap. After 70 min at 170 °C the flask was cooled to room temperature and backfilled with argon. The contents of the cold trap were diluted with dichloromethane and analysed by GC–FID after addition of nonane as an internal standard. The remaining mixture of $[Al(Oct)_3]$ and $[HAl(Oct)_2]$ was analysed by $^1$H NMR. The yield of olefins obtained was 0.336 g of 1-octene, 8.2 mg of mixed internal octenes, 19.2 mg of $C_{12}H_{24}$ and 0.5 mg of $C_{16}H_{32}$, corresponding to an olefin yield of 52% with respect to $[Al(oct)_3]$. The yield according to $^1$H NMR, as measured by the amount of $[HAl(Oct)_2]$ formed, was 55%.

Heating under vacuum for ca. 1.5 hr leads to higher conversion, this being the upper limit before decomposition occurs: $[Al(Oct)_3]$ (1.82 g, 4.97 mmol) was heated under vacuum as above at 170 °C for 1.5 hr. There was obtained 0.417 g of 1-octene, 10.0 mg of mixed internal octenes and 15.1 mg of $C_{12}H_{24}$, corresponding to an olefin yield of 78%. The yield as measured by $^1$H NMR of the obtained $[HAl(Oct)_2]$ was 73%.

An example of a second cycle of elimination after re-insertion of 1-octene corresponds to entry 2 in Table 1: An aluminium hydride sample from a prior elimination experiment (1.10 g, 20% $[Al(Oct)_3]$, 80% $[HAl(Oct)_2]$ (3.47 mmol of hydride)) was treated with 1-octene (0.38 g, 3.38 mmol) and heated at 125 °C for 20 min. After removal of a sample for $^1$H NMR analysis there remained 3.79 mmol of $[Al(Oct)_3]$ along with $[HAl(Oct)_2]$ (93% $[Al(Oct)_3]$). Olefin elimination at 170 °C for 1 hr yielded 0.266 g of 1-octene and 6.3 mg of internal octenes, corresponding to a 64% yield (66% by $^1$H NMR).

$^1$H NMR of $[HAl(Oct)_2]$ ($C_6D_6$): δ 0.43 (m, 4H, Al$CH_2$); 0.93 (m, 6H, $CH_3$); 1.33-1.44 (br, 20H, $CH_2$); 1.63 (br, 4H, AlCH$_2$$CH_2$); 3.95, 3.26, 3.05 (br, 1H, Al$H$, see text for full assignment of aluminium hydride resonances). $^{13}$C NMR ($C_6D_6$): δ 8.5 (Al$C$H$_2$), 14.4 ($C$H$_3$), 23.2, 26.3, 29.9, 30.1, 32.5, 36.0 ($C$H$_2$).

**1-octene insertion into $[HAl(Oct)_2]$.** To a screw cap NMR tube containing aluminium hydride (100 μL, 20% $[Al(Oct)_3]$, 80% $[HAl(Oct)_2]$ (0.255 mmol of hydride)) was added toluene-$d_8$ (450 μL), 1-octene (30 μL, 0.19 mmol) and phenanthrene as internal standard (2.0 mg, 0.011 mmol). The sample was monitored by $^1$H NMR for 120 min with a probe temperature of 75 °C. After 120 min 0.18 mmol of 1-octene had been consumed (95%).

**Insertion of internal octenes into $[HAl(Oct)_2]$.** A representative example consists of adding a mixture of internal octenes (103 mg, 0.92 mmol), as prepared above, to a mixture of $[HAl(Oct)_2]$ and $[Al(Oct)_3]$ (70% hydride, 2.43 mmol). The solution was heated in a closed flask at 110 °C for 15 hr and 130 °C for a further 2 hr. The degree of octene insertion and aluminium speciation may be monitored by $^1$H NMR spectroscopy as detailed in the text. After cooling to room temperature, the free octenes (uninserted) were removed under vacuum and collected in a cold trap. The remaining alkylaluminium was then subjected to elimination conditions (vacuum, 170 °C) for 1 hr and the eliminated octenes collected in a cold trap. The volatiles collected were analysed by GC-FID analysis using nonane as an internal standard. The yield of olefin obtained was 23 mg (0.20 mmol) of octenes removed at low temperature (free octene) and 35 mg (0.31 mmol) at high temperature (eliminated). The typical composition of each fraction is as detailed in Table 2.

### Theoretical methods

All calculations throughout this paper were performed using Gaussian09,[37] utilising hardware from the National Computational Infrastructure (NCI) Australian national facility or the Tasmanian Partnership for Advance Computing (TPAC) facility. For the evaluation of Gibbs free energy changes, geometry optimisations were performed without symmetry constraints at 298 K and 1 atm, using the CBS–QB3[34,35] compound method (transition structures were located using the Berny algorithm[38] as implemented in Gaussian09). In some cases free energies were recalculated at elevated temperature as discussed in the text. We have previously demonstrated, through benchmarking against the W1BD[39-41] method, that the

CBS-QB3 method leads to accurate energies for insertion and elimination reactions of alkylboranes.[14] It is therefore expected that this method will likewise lead to accurate results for closely related reactions of alkylaluminiums. Analytical frequency calculations (included in the compound method) were employed to verify structural optimisations. All minima (ground–state) structures contained no imaginary frequencies, and all transition structures contained only one imaginary frequency that exhibited vibrational modes consistent with the anticipated reaction pathway. This was further verified by optimisation of slightly relaxed transition structures in both directions. The optimised geometries and energies for all stationary points are supplied in the Supporting Information.

NMR shielding tensors were computed with the Gauge-Independent Atomic Orbital (GIAO) method,[42,43] at the B3LYP/6-311+G(2d,p) level of density functional theory[44-47] (both geometry optimisations and NMR calculations). In cases where different Al-hydrides in the same molecule had slightly different calculated isotropic chemical shielding, an average value was employed. Rather than calculating a predicted chemical shift relative to tetramethylsilane, we have plotted the experimental chemical shifts against the absolute calculated isotropic shieldings. The merits of this approach have been discussed previously.[48]

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## Notes and references

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Electronic Supplementary Information (ESI) available: additional supporting NMR spectra and optimised geometries and energies of all stationary points. See DOI: 10.1039/b000000x/

‡ Multiple attempts to study the speciation of $[HAl(Oct)_2]/[Al(Oct)_3]$ mixtures by $^{27}Al$ NMR spectroscopy were unsuccessful, yielding no clear signals (from -50–75 °C). Successful acquisition of spectra for $[Al(H_2O)_6]^{3+}$ (standard) and $[Al^{i}Bu_3]$ (159 ppm) rule out instrumental problems. It may be that exchange between the multiple species present, together with dynamics of the long octyl chains, leads to broadening to the point that the signals are not observed.

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