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Action of Organoaluminum Reagents on Esters: Alkene Production and the Degradation of Synthetic Lubricants

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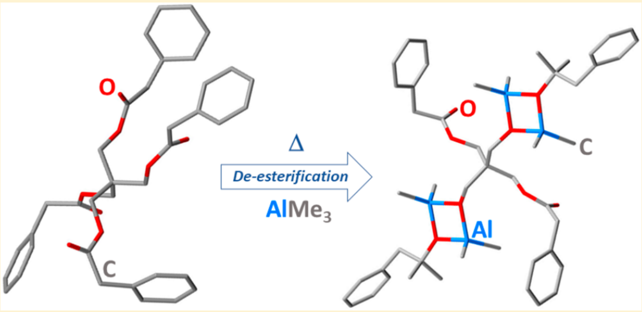
Supporting Information

ABSTRACT: Reactions of methylaluminum reagents with ester-based lubricating oils are mimicked through the reaction of trimethylaluminum (TMA) with tetraesters $C(CH_2OC(O)R)_4$ (R = C_5H_{11} $\mathbf{4}^{Pent}$, Bn $\mathbf{4}^{Bn}$). Using a 2:1 stoichiometry gave adduct $\mathbf{4}^{Pent}(TMA)_4$. NMR spectroscopy on 1:1−12:1 TMA/$\mathbf{4}^{Pent}$ systems suggested $\mathbf{4}^{Pent}$ gave dimethylated adduct $C_5H_{11}CMe_2OAlMe_2(TMA)$, $\mathbf{2}^{Pent}(TMA)$. Similar combination of TMA with $\mathbf{4}^{Bn}$ at raised temperatures transformed $\mathbf{4}^{Bn}$ into $C(CH_2OAlMe_2)_4(\mathbf{2}^{Bn})_4$ $\mathbf{5}(\mathbf{2}^{Bn})_4$ by sequential reaction of each ester group. Doubly reacted $\{BnC(O)OCH_2\}_2C(CH_2OAlMe_2)_2(\mathbf{2}^{Bn})_2$ $\mathbf{7}^{Bn}(\mathbf{2}^{Bn})_2$ was isolated and characterized. A Mitsubishi molecule could also be isolated, its formation rationalized by the elimination of $\mathbf{2}^{Bn}$ and TMA from $\mathbf{5}(\mathbf{2}^{Bn})_4$. The action of Me_nAlCl_{3-n} (n = 1, 1.5, 2) was studied initially on monoester BnC(O)OMe $\mathbf{1}^{Bn}$. Combining excess Me_2AlCl with $\mathbf{1}^{Bn}$ gave adduct $\mathbf{1}^{Bn}(Me_2AlCl)$ and small amounts of dimethylated $BnCMe_2OAlMe_2(Me_2AlCl)$, $\mathbf{2}^{Bn}(Me_2AlCl)$, and $MeOAlCl_2$ **10**. $\mathbf{2}^{Bn}(Me_2AlCl)$ was fully characterized and, in the presence of **10**, acted as a source of $\mathbf{2}^{Bn}(MeAlCl_2)$. From this species, a mixture of alkenes could be generated by formal elimination of $Me_3Al_2(OH)Cl_2$ **13**, the decomposition of which was presumed to also explain MeH observation. Replacing Me_2AlCl with aluminum sesquichloride or $MeAlCl_2$ led to progressively more sluggish but similar reactions. Using Me_nAlCl_{3-n} (n = 1, 1.5, 2) with tetraesters suggested similar reactivity to monoesters.



INTRODUCTION

The enormous interest that recent years have seen in hydrofluorocarbons (HFCs) has stemmed from the global move away from the use of ozone-depleting chlorofluorocarbons[1] as refrigerants. However, while the fact that these so-called F-gases had only indirect effects on the ozone layer led to their increased use,[2] so studies have revealed a more detailed picture of the real extent of their greenhouse effects.[3] This has led to successive regulations, the latest of which[4] outlawed products containing F-gases with a global warming potential (GWP)[5] > 150 as part of a worldwide strategy aimed at reducing HFC dependence.[6] Subsequently, the remit of regulations has been expanded to impact on most refrigeration and vapor compression systems for air conditioning,[7] leading to efforts to replace commonly used high-GWP refrigerants like R-134a (1,1,1,2-tetrafluoroethane).[8] Concurrent with the introduction of new regulatory frameworks, the illicit use of R-40 (chloromethane) in refrigeration systems has emerged as a major problem.[9] While R-40 has a GWP of just 13, the reaction of alkyl chlorides with aluminum (viz. components in industrial refrigeration units) promoted by aluminum halide catalyst is established.[10] Moreover, reports exist that reaction can proceed in the absence of a catalyst and that using heat only[11] alkyl chlorides can react with aluminum to give R_nAlCl_{3-n}. For R-40, this would yield methylaluminum chlorides, which can in turn react with ancillary organics. One such compound is RL 32H, a commonly used polyolester (POE) compound oil designed to be compatible with HFC refrigerants. While this has led to interest in the reactions of aluminum-based organometallics with esters,[11] the field has hitherto been dominated by the study of trialkylaluminums. Trimethylaluminum (TMA) has been used to generate reactive complexes,[12] hemialkoxides,[13] alkylated acetates,[14] and ketonized heteroaromatic esters,[15,16] to induce the reduction of cyclic ketones,[17] and to modify poly(methyl methacrylate).[18] Meanwhile, both TMA and triethylaluminum have been used to produce ketones,[16,19] aldehydes,[19] and amides[20] from esters.

Surprisingly, given the interest in alkylaluminum sesquichloride cocatalysts to the polymer industry,[21] reactions of Me_nAlCl_{3-n} (n = 1, 1.5, 2) with esters are difficult to find in the literature. Only limited work has been done on derivatizing methyl benzoate with methylaluminum chlorides. Adduct formation between the ester and Me_2AlCl has been recorded.[22] Thereafter, Me_2AlCl (but not TMA) was suggested to promote $PhCMe_2OAlMeCl$ formation, presumably alongside that of MeOAlMeCl, the subsequent reaction of which gave either alkene $PhC({=}CH_2)Me$, presumably alongside HOAlMeCl, or Ph(t-Bu), presumably alongside $O(AlMeCl)_2$.[23] The expected byproduct of methyl ester reaction with TMA itself,

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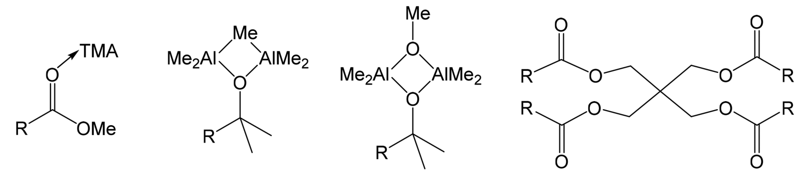

R = Et, Bn **1**(TMA) R = Et, Bn **2**(TMA) R = Et, Bn **2**(**3**) R = C_5H_{11}, Bn **4**

Figure 1. Adducts **1**(TMA), **2**(TMA), **2**(**3**), and pentaerythritol-based tetraester **4**.

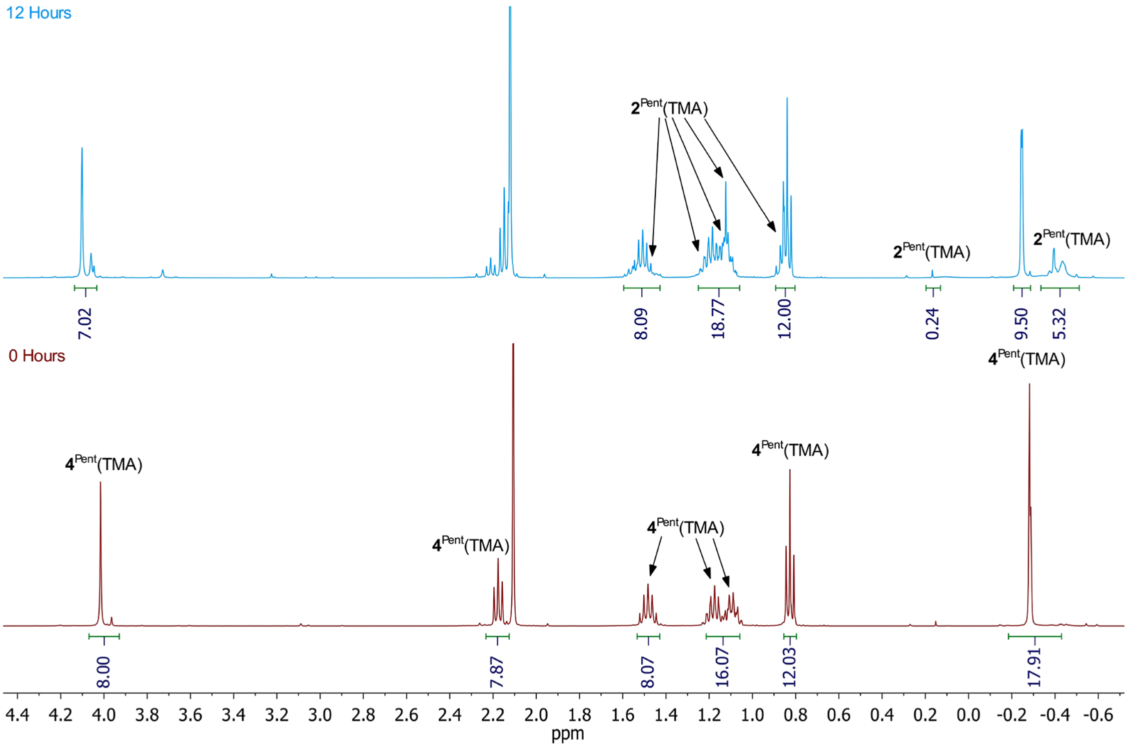

Figure 2. ^1H NMR spectra of aliquots from the introduction of TMA to 4^{Pent} in a 2:1 ratio at room temperature in toluene (visible at δ 2.11 ppm) after reagent combination (bottom) and 12 h (top). The solvent is benzene-d_6.

Me_2AlOMe, has been extensively studied.[24] However, whereas the byproducts of methylaluminum chloride reaction with esters proposed in ref 23 were reasonable, direct evidence for their formation was not presented. Indeed, while some aluminum hydroxides have been reviewed,[24,25] only a very few literature reports of AlCl-incorporating hydroxides[26] and oxides (aluminoxanes) exist.[27] More broadly, aluminoxanes have been extensively studied,[25] particularly as alkene polymerization cocatalysts.[28] Whereas most work has focused on the hydrolysis of alkylaluminum compounds,[29] anhydrous aluminoxane formation has been reported. Thus, TMA has been reacted with carboxylic acids[30] and alcohols,[31] and with Mg or Mn alkoxides.[32] DMSO has been used to oxidize $[\{(Me_3Si)_2CH\}_2Al]_2$,[33] and reaction of $(Mes^*AlH_2)_2$ with $(Me_2SiO)_3$ has given $(Mes^*AlO)_4$ (Mes^* = 2,4,6-(t-Bu)$_3$-C_6H_2).[34] Lastly, dual aluminum oxide−hydroxides have been investigated.[35]

Recently, reaction of TMA with POEs was modeled using methyl propionate and methyl phenylacetate.[11] Data pointed to the formation of adducts MeORC═O(TMA) (R = Et, Bn) **1**(TMA) that reacted, particularly in the presence of excess TMA, to give $Me_2RCOAlMe_2$ **2** and Me_2AlOMe **3**. The preference for reaction in the presence of excess TMA led to capture of this by **2**, with **2**(TMA) thereafter reacting with **3** at raised temperatures to give $Me_4Al_2(\mu^2\text{-}OMe)(\mu^2\text{-}OCRMe_2)$ **2**(**3**) while regenerating TMA (Figure 1).

We now extend the recent ester derivatization by TMA, using pentaerythritol-based tetraesters **4** (Figure 1) that closely mimic RL 32H.[36,37] The reaction of monoesters and tetraesters with methylaluminum chlorides, Me_nAlCl_{3-n} (n = 1, 2), and the sesquichloride $Me_{1.5}AlCl_{1.5}$ is explored. NMR spectroscopy suggests that the enhanced Lewis acidity of Me_nAlCl_{3-n} promotes the thermal elimination of alkenes, and even methane, presenting significant safety implications.

■ RESULTS AND DISCUSSION

Tetraester Reaction with TMA. To extend our recent analysis of ester derivatization by TMA using improved POE mimics, tetraesters $C(CH_2OC(O)R)_4$ 4^R (R = Bn 4^{Bn}, C_5H_{11} 4^{Pent}) were prepared (Figures S1−S5).[38] TMA was introduced to 4^{Pent} in 1:1, 2:1, 4:1, 8:1, and 12:1 ratios (Figures S6 and S7). While the first of these systems only yielded evidence for 1:1 adduct formation (^{13}C NMR δ 174.1 ppm, cf. δ 172.3 ppm for 4^{Pent}), the 2:1 system proved more variable. Immediately after combination at room temperature, NMR spectroscopy suggested empirically 2:1 adduct formation (i.e., formally half of the ester functions in all the 4^{Pent} were complexed), with exchange averaging the resulting ester signal to δ 177.0 ppm in

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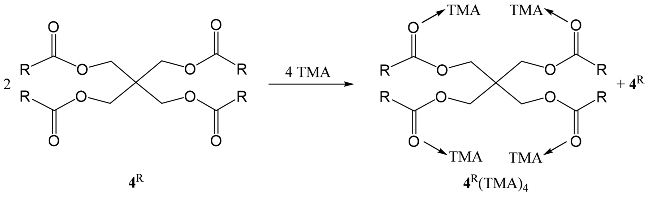
the ^{13}C NMR spectrum. However, after 12 h, ^{1}H NMR spectroscopy revealed the evolution of a singlet at δ 1.11 ppm characteristic of dimethylation (Figures 2 and S6). On the basis of this, attempts were made to isolate the initial species that resulted when TMA and $\mathbf{4}^{Pent}$ were combined. While spectroscopy suggested that the 2:1 combination of TMA with $\mathbf{4}^{Pent}$ gave a 2:1 adduct, chilling the mixture to −27 °C immediately after combination of the reagents led to crystallization of a material that suggested averaging of the ester ^{13}C NMR signal could be attributed not only to intra- but also to intermolecular exchange. This material proved highly reactive at room temperature and largely resisted thorough characterization. However, crystallographic determination suggested (tetra)adduct $\mathbf{4}^{Pent}(TMA)_4$ (Scheme 1 and Figure S10).

Scheme 1. Conversion of 4^{R} to the Corresponding TMA (Tetra)adduct[a]



[a] R = C_5H_{11}.

Aliquots from 8:1 and 12:1 reactions between TMA and $\mathbf{4}^{Pent}$ revealed that immediately after combining reagents there was an absence of ester groups, and $C_5H_{11}CMe_2OAlMe_2(TMA)$, $\mathbf{2}^{Pent}(TMA)$, itself could clearly be observed (δ 79.2, 44.3, 32.0, 28.4, 24.3, 22.6, 13.8, −4.5, and −7.0 ppm (^{13}C); δ 1.44, 1.22, 1.12, 1.11, 1.10, 0.87, 0.10, and −0.45 ppm (^{1}H), Figures 3, S6, and S7). In the analogous monoester work, dimethylation gave **2**(TMA) and eliminated Me_2AlOMe **3**. However, in the current case, spectroscopy revealed less clear evidence for the presence of the tetrolate-based elimination byproduct. A very broad signal centered at ca. 3.8 ppm in the ^{1}H NMR spectra could be tentatively attributed to the CH_2O region of the tetrolate-based elimination byproduct $C(CH_2OAlMe_2)_4$ **5** (Scheme 2). This broad feature showed the correct integration (2H per dimethylated $\mathbf{2}^{Pent}(TMA)$, Figure 3).

Repeated attempts to isolate products of reaction between TMA and $\mathbf{4}^{Pent}$ failed. This led us to investigate the use of the benzyl tetraester $\mathbf{4}^{Bn}$, in the hope that inclusion of the benzyl group would aid recrystallization. TMA was introduced to $\mathbf{4}^{Bn}$ in 2:1, 4:1, 8:1, and 12:1 ratios. NMR spectroscopic analysis of aliquots of the resulting mixtures suggested analogous behavior to that seen for $\mathbf{4}^{Pent}$ (Figures S11 and S12). This was evidenced by the observation of $\mathbf{2}^{Bn}(TMA)$ (δ 136.7, 130.3, 128.1, 126.7, 79.5, 50.8, 28.0, −4.5 and −7.0 ppm (^{13}C); δ 2.86, 1.11, 0.13, and −0.42 ppm (^{1}H)) and retention of a broad signal at ca. 4.0 ppm (Scheme 2).

To further investigate this broad central tetrolate core region, the TMA−$\mathbf{4}^{Bn}$ reactions were repeated but were heated to reflux for 2 h, as it had previously been shown that heating a TMA−monoester mixture resulted in the formation of an OMe-bridged species, **2**(**3**). The reaction was undertaken at 2:1, 4:1, 6:1, and 8:1 TMA/$\mathbf{4}^{Bn}$ ratios. This resulted in the appearance of a number of sharp signals in the δ 4.6−2.9 ppm region of the ^{1}H NMR spectrum that were attributable to CH_2O protons (Figure S13). The ^{13}C NMR spectrum (Figure S14) also revealed a number of new signals from the CH_2O carbons. Two types of dimethylaluminum alkoxide product of reaction were identified. The first was dimethylated $\mathbf{2}^{Bn}$, and the second was the tetrolate-based product of ester cleavage retaining 3, 2, 1, or 0 unreacted ester groups ($\mathbf{6}^{Bn}$, $\mathbf{7}^{Bn}$, $\mathbf{8}^{Bn}$, or **5**). These two types of alkoxide formed adducts based on 4-membered Al_2O_2 rings, all of which were identified spectroscopically (Scheme 3).

In fact, Figure S13 reveals that the 8:1 reaction of TMA with $\mathbf{4}^{Bn}$ yielded aliquots that comprised two tetrolate-containing species. In both of these, the ester groups had completely reacted. Data suggested the explanation for this to be the coexistence of $\mathbf{5}(\mathbf{2}^{Bn})_4$ alongside a species in which **5** had then undergone the elimination of 3 equiv of dimethylated $\mathbf{2}^{Bn}$ complexant and 1 equiv of TMA to form tetrolate product $\mathbf{9}(\mathbf{2}^{Bn})_2$ (δ 3.94, 2.96, 2.79, 1.07, −0.35, and −0.46 ppm (^{1}H)), 4 equiv of $\mathbf{2}^{Bn}$ (presumed to exist as two dimers; δ 3.00, 1.23, and −0.28 ppm (^{1}H)) and 2 equiv of $\mathbf{2}^{Bn}(TMA)$ (δ 2.86, 1.12, 0.13, and −0.42 ppm (^{1}H)) (Figure 4 and Scheme 4). Five further observations are relevant to extracting a structure for $\mathbf{9}(\mathbf{2}^{Bn})_2$: First, the tetrolate/free $\mathbf{2}^{Bn}$ ratio. Second, the nature of the tetrolate ligand, whereby the retention of 1 equiv of $\mathbf{2}^{Bn}$ per tetrolate suggests the availability of three alkoxide O-centers for further bonding. Third, consistent with this, replacement of

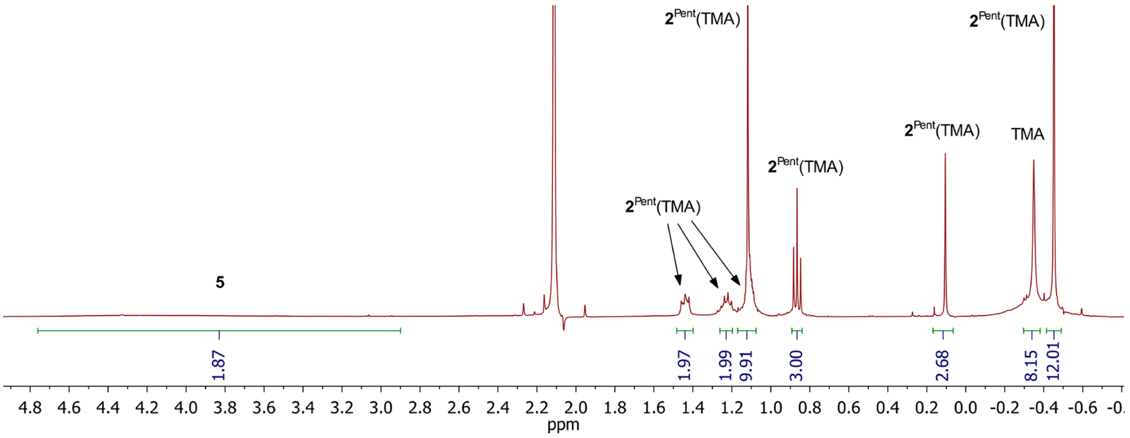
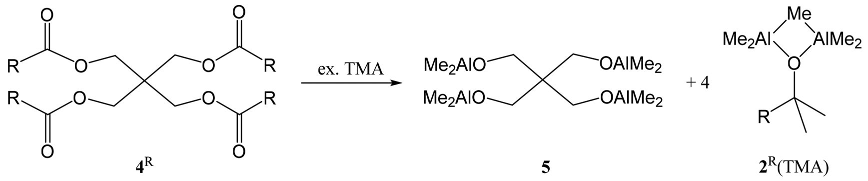


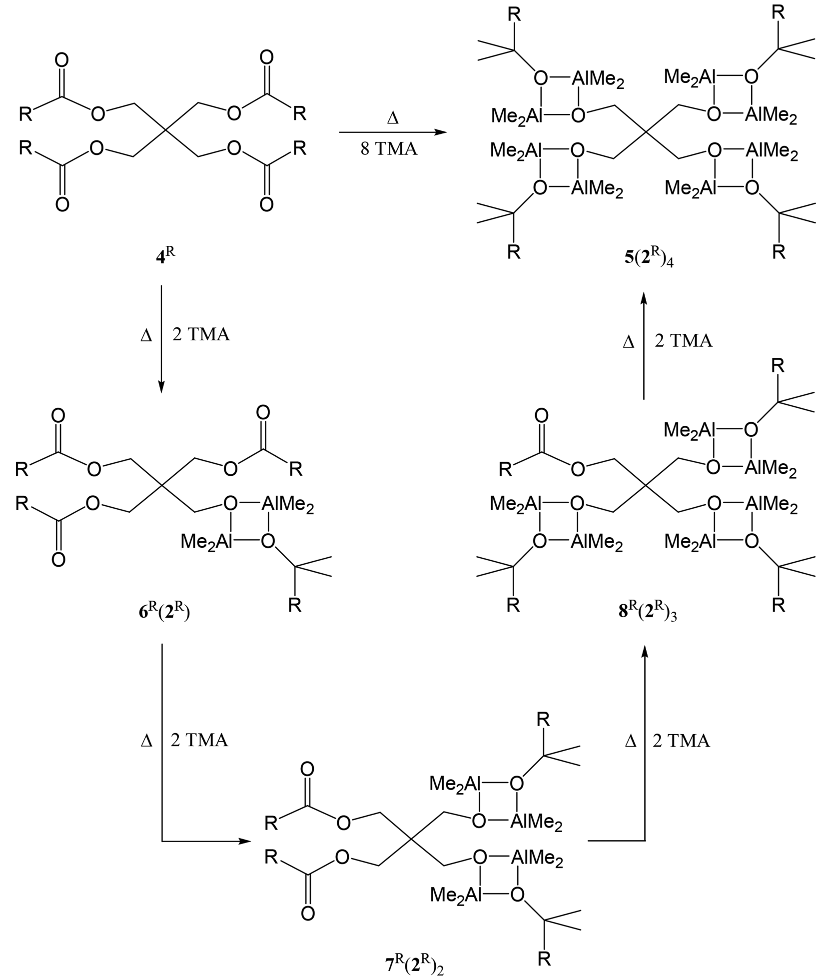
Figure 3. ^{1}H NMR spectrum of an aliquot from the 12:1 reaction of TMA with $\mathbf{4}^{Pent}$ at room temperature in toluene (δ 2.11 ppm) showing complete ester cleavage. The solvent is benzene-d_6.

Scheme 2. Generation of Tetrolate-Based C(CH$_2$OAlMe$_2$)$_4$ **5** from the Reaction of **4**^{R} with TMA[a]



[a]R = C$_5$H$_{11}$, Bn.

Scheme 3. Sequential De-Esterification of **4**^{R} to Finally Give **5**^{R} with the Concomitant Trapping of 1−4 equiv of **2**^{R}[a]



[a]R = Bn.

the CH$_2$ signal in the ^{1}H NMR spectrum of **5**(**2**^{Bn})$_2$ (δ 4.47 ppm) with signals at δ 3.93 and 2.94 ppm (6H and 2H, respectively). Fourth, the observation of two types of Al-bonded Me group in **9**(**2**^{Bn})$_2$ in the ratio of 4:3. Fifth, the ^{27}Al NMR spectrum reveals a sharp signal at δ 8.7 ppm ($W_{1/2}$ = 300 Hz) which is characteristic of 6-coordinate aluminum, along with a broad signal at δ 156.8 ppm ($W_{1/2}$ = 3500 Hz) due to 4-coordinate aluminum. Taken together, these data are consistent with the creation of a so-called Mitsubishi molecule,[39] which is based on an Al$_4$O$_6$ core in which a central Al^{3+} is coordinated by six O-centers, in this case provided by two tridentate alkoxide ligands that also capture three AlMe$_2$ moieties (Scheme 4).

The proportions of **4**^{Bn} and **5**(**2**^{Bn})$_4$−**9**(**2**^{Bn})$_2$ formed as a function of 1 equiv of TMA per molecule of **4**^{Bn} have been extracted from the ^{1}H NMR spectroscopic data and are given in Table 1. Data reveal that for every 2 equiv of TMA added approximately one ester group reacts. This observation replicates the reactivity of monoesters (see above). The binomial distribution of products seen indicates a lack of cooperativity.

Attempts to crystallize the products of reaction between TMA and **4**^{Bn} have met with mixed results. The addition of hexane to the reaction mixture of 4:1 TMA/**4**^{Bn} in toluene has allowed the isolation of crystalline material. X-ray diffraction confirmed this to be **7**^{Bn}(**2**^{Bn})$_2$ (Figure 5 and Scheme 3), the structure of which is consistent with the NMR spectroscopic formulation of the major component of the reaction mixture. The isolation of this material establishes two important points. First, two out of the four ester groups in **4**^{Bn} have undergone

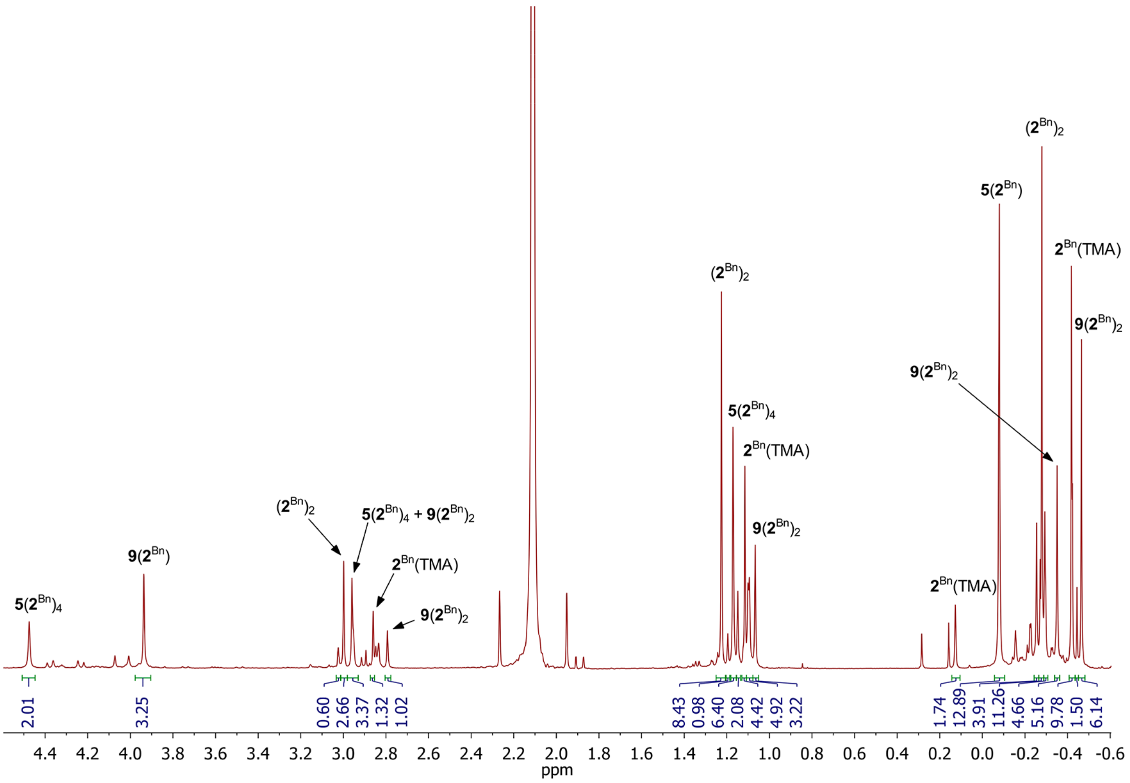


Figure 4. ^{1}H NMR spectrum of an aliquot from the reaction of TMA with 4^{Bn} in an 8:1 ratio after heating to reflux for 2 h in toluene (δ 2.11 ppm), showing the formation and subsequent reaction of $5(2^{Bn})_4$ to give $9(2^{Bn})_2$. The solvent is benzene-d_6.

Scheme 4. Formation of $9(2^{Bn})_2$, 2^{Bn}, and TMA from $5(2^{Bn})_4$

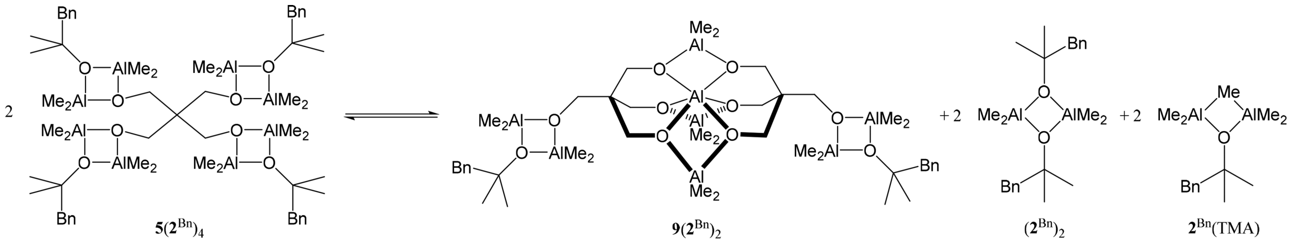


Table 1. Proportions of Substrate 4^{Bn} and Ester Cleavage Products $5(2^{Bn})_4$–$9(2^{Bn})_2$ as a Function of Equivalents of TMA Relative to 4^{Bn} from ^{1}H NMR Spectroscopic Integrals[a]

	No. ester groups reacted					
TMA (equiv) wrt 4^{Bn}	0 (4^{Bn})	1 ($6^{Bn}(2^{Bn})$)	2 ($7^{Bn}(2^{Bn})_2$)	3 ($8^{Bn}(2^{Bn})_3$)	4 ($5(2^{Bn})_4 + 9(2^{Bn})_2$)	total % ester groups reacted
0	100	0	0	0	0	0
2	35	50	15	0	0	20
4	0	25	54	21	0	49
6	0	0	16	50	34	80
8	0	0	0	0	100	100

[a] Analysis based on aliquots withdrawn after reflux in toluene for 2 h. Solvent: benzene-d_6.

dimethylation. Second, as for $2(3)$, the 4-membered Al_2O_2 metallacycles incurred by ester cleavage/alkoxide capture are symmetrical, based on $(AlMe_2)_2(\mu^2\text{-OR})_2$ metallacycles. The isolation of $7^{Bn}(2^{Bn})_2$ plainly verifies the cleavage of two esters en route to the production of two molecules of dimethylated $BnMe_2COAlMe_2$ 2^{Bn}, that could then be captured by eliminated $\{BnC(O)OCH_2\}_2C(CH_2OAlMe_2)_2$ 7^{Bn} (Scheme 3).

In a similar vein to the 4:1 TMA/4^{Bn} reaction, removal of solvent from the reaction mixture of 6:1 TMA/4^{Bn} produced a white solid, which could be redissolved in hexane. This solution yielded crystals that X-ray diffraction confirmed to be $9(2^{Bn})_2$ (Figure 6), establishing reaction of all four ester groups in 4^{Bn}. Rather than demonstrating the formation of $5(2^{Bn})_4$, diffraction supports the spectroscopic analysis of this reaction mixture, corroborating the exclusion of 2^{Bn} and TMA from $5(2^{Bn})_4$ to give $9(2^{Bn})_2$ (Scheme 4).

Monoester Reaction with Me_nAlCl_{3-n} (n = 1, 1.5, 2). Our interest in the role of alkyl chloride–aluminum combinations in the autocatalytic generation of alkylalumi-

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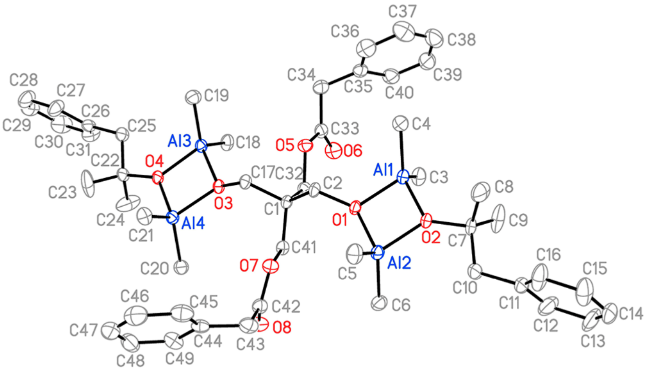


Figure 5. Molecular structure of $7^{Bn}(\mathbf{2}^{Bn})_2$. Thermal ellipsoids at 30% probability and hydrogen atoms omitted. Selected bond lengths (Å) and angles (deg): O1−Al1 1.851(2), O1−Al2 1.853(2), O2−Al1 1.848(2), O2−Al2 1.854(2), O1−Al2−O2 80.86(10), O1−Al1−O2 81.07(10), Al1−O1−Al2 99.00(10), Al1−O2−Al2 99.07(10).

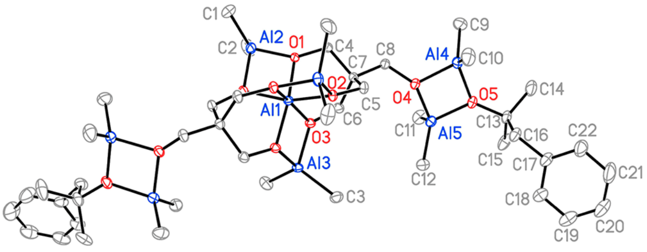
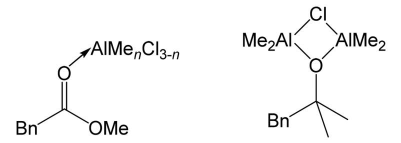


Figure 6. Molecular structure of $\mathbf{9}(\mathbf{2}^{Bn})_2$. Thermal ellipsoids at 30% probability and hydrogen atoms omitted. Selected bond lengths (Å) and angles (deg): O1/2/3−Al2/3 1.822(2)−1.828(2), O1/2/3−Al1 1.874(2)−1.888(2), O4−Al 1.851(3)−1.858(3), O5−Al 1.838(3)−1.848(3), O−Al1−O 77.96(10)−104.13(11), Al−O1/2/3−Al 99.21(12)−100.72(11), O−Al2/3−O 80.96(11)−81.15(15), O4−Al4−O5 81.07(11), O4−Al5−O5 81.00(11), Al4−O4−Al5 98.42(11), Al4−O5−Al5 99.21(12).

nums led us to recently test reactions of TMA with monoesters.[11] However, since this work aims to mimic the reactivity of organoaluminums generated through the attack of chloromethane on aluminum, it followed that reactions of Me_nAlCl_{3-n} warranted study. A hexane solution of Me_2AlCl was therefore added to methyl phenylacetate at −78 °C, after which the mixture was left to reach room temperature. A 3-fold excess of Me_2AlCl was used based on the observed preference for reaction of TMA with esters when the former was in excess.[11] However, in contrast to work in which 3:1 TMA/ester reacted to quantitatively give $\mathbf{2}^{Bn}$(TMA), work with Me_2AlCl was dominated by adduct formation, with ^{13}C NMR spectroscopy revealing a C═O signal at δ 182.3 ppm (cf. δ 170.9 ppm for $\mathbf{1}^{Bn}$)[11] for $\mathbf{1}^{Bn}(Me_2AlCl)$ (Figures 7 and S22). The same spectrum points to limited formation of a second species, with signals at δ 50.4 and 28.0 ppm tentatively attributed to CH_2 and C*Me* from a dimethylated product. ^{1}H NMR spectroscopy reinforces this message, pointing to 96% adduct formation through characteristic signals at δ 3.54 and 2.78 ppm (CH_2 and OMe, respectively). Meanwhile, 4% dimethylation is evidenced by minor signals for CH_2 and CMe in a 1:3 ratio at δ 2.85 and 1.08 ppm. These shifts are similar to those seen for $\mathbf{2}^{Bn}$(TMA) (δ 2.86 and 1.11 ppm)[11] and suggest 3:1 reaction of Me_2AlCl with ester, initially yielding BnMeC═O and MeClAlOMe **11**, before forming a dimethylated species. A signal at δ −0.27 ppm reveals an integral twice that of the resonance at δ 1.08 ppm. This suggests that although it might be expected that the dimethylation of $\mathbf{1}^{Bn}(Me_2AlCl)$ should yield $\mathbf{2}^{Bn}(MeAlCl_2)$ in the event (and akin to previous work with $\mathbf{2}^{Bn}$(TMA)), $\mathbf{2}^{Bn}$ traps unreacted Me_2AlCl to give $\mathbf{2}^{Bn}(Me_2AlCl)$. In this species, the chloride ligand bridges the two metals, leaving four identical Al-bonded methyl groups (Figures 7 and 8 and Scheme 5).



$\mathbf{1}^{Bn}(Me_nAlCl_{3-n})$ (*n* = 1, 2) $\mathbf{2}^{Bn}(Me_2AlCl)$

Figure 7. Methylaluminum chloride adducts of $\mathbf{1}^{Bn}$ and $\mathbf{2}^{Bn}$.

The temperature dependence of Me_2AlCl−$\mathbf{1}^{Bn}$ reaction was probed by heating the reaction mixture to reflux. Spectroscopic analysis of an aliquot then revealed significant growth of δ 50.4 and 28.0 ppm ^{13}C NMR peaks, pointing to increased formation of the dimethylated derivative (Figure S25). ^{1}H NMR spectroscopy corroborates this view and points to a mixture containing multiple components. A new set of peaks attributable to a dimethylated species were observed (^{1}H NMR δ 2.92 and 1.12 ppm), suggesting another adduct of $\mathbf{2}^{Bn}$. Using NOESY (Figure S27), this species was identified as the expected product of the dimethylation of $\mathbf{1}^{Bn}(Me_2AlCl)$ and $\mathbf{2}^{Bn}(MeAlCl_2)$. We propose this to be formed from $\mathbf{2}^{Bn}(Me_2AlCl)$ (see above and Scheme 5). The dominant species are adduct $\mathbf{1}^{Bn}(Me_2AlCl)$ (44%) and dimethylated $\mathbf{2}^{Bn}$ (54%). However, two minor components present are alkenes **12** in a 2% combined yield of **12a** (PhCH═CMe$_2$, singlet, δ 6.28 ppm) and **12b** (BnC(═CH$_2$)Me, singlets, δ 4.80 and 4.75 ppm) that arise from the formal elimination from $\mathbf{2}^{Bn}(MeAlCl_2)$ of $Me_3Al_2(OH)Cl_2$ **13** (Scheme 5). The same reaction was attempted at 100 °C for 24 h in toluene-d_8 in a sealed J. Young NMR tube. The resulting mixture now revealed signals consistent with MeH (^{1}H NMR δ 0.17 ppm, ^{13}C NMR −4.3 ppm, Figures S28 and S29),[40] leading us to propose that **13** converts to oxide $Me_2Al_2OCl_2$ **14**. Further attempts to study the effects of temperature on reaction in toluene proved not to be straightforward. While heating to reflux for 2 h yielded $\mathbf{1}^{Bn}(Me_2AlCl)$ (40%) and alkenes **12** (60% combined, 1:4 **12a**/**12b**), extended heating (24 h) gave also Friedel−Crafts reaction of the solvent[41] (Scheme S1). Notwithstanding, variable-temperature studies in toluene successfully revealed alkene formation from 60 °C and exhaustive methylation[29e,42] to give Bn(*t*-Bu) **15** from 80 °C with adducts of $\mathbf{2}^{Bn}$ eliminated at temperatures in excess of 70 °C (Figure S31 and Scheme S1). Lastly, investigation of reaction stoichiometry revealed data consistent with the mechanism in Scheme 5. $\mathbf{1}^{Bn}(Me_2AlCl)$ (42%) and alkenes **12** (58% combined) formed when using 2:1 Me_2AlCl/ester in toluene while a 1:1 ratio led to the dominance of $\mathbf{1}^{Bn}(Me_2AlCl)$.

Moving from Me_2AlCl to $MeAlCl_2$, the increased Lewis acidity of the Al-reagent led adduct formation to dominate, with ^{13}C NMR spectroscopy revealing a C═O signal at δ 184.2 ppm for $\mathbf{1}^{Bn}(MeAlCl_2)$ (cf. Scheme 5). Meanwhile, treatment of $\mathbf{1}^{Bn}$ with aluminum sesquichloride, ($Me_{1.5}AlCl_{1.5}$ from 1:1 $AlCl_3$/TMA), yielded activity intermediate between Me_2AlCl and $MeAlCl_2$. Data point to the enhanced Lewis acidity of the resulting systems, with 1:3 ester/aluminum

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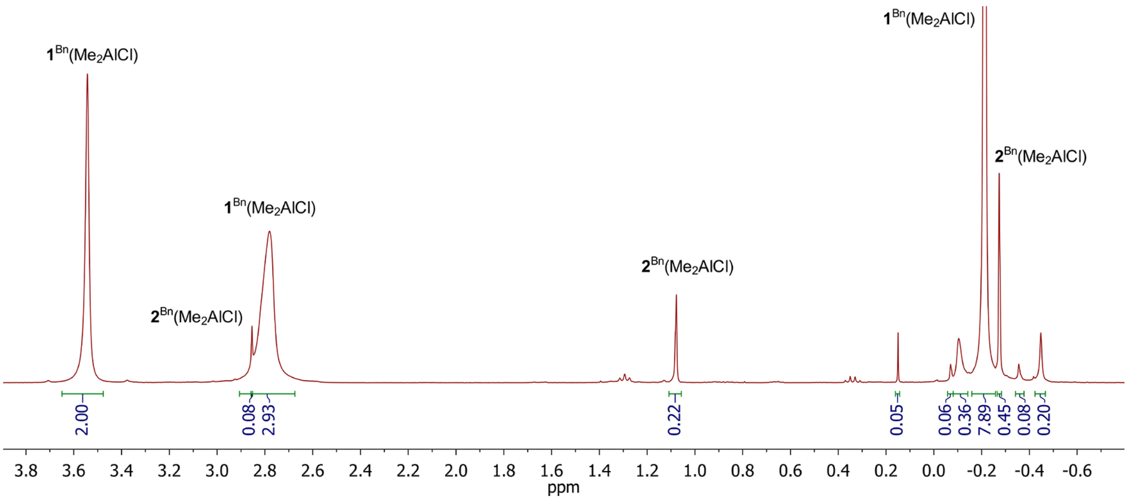
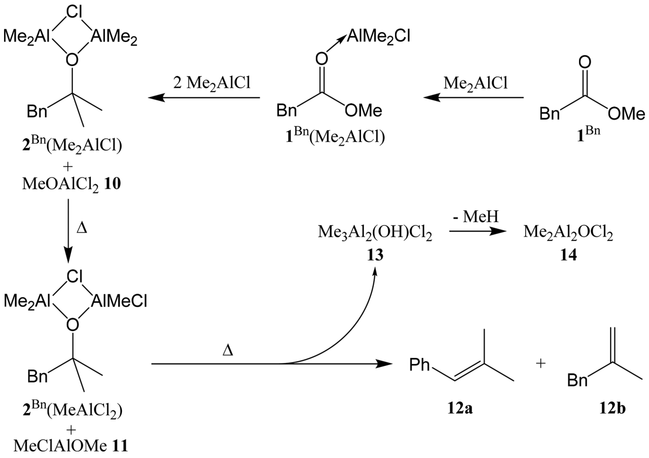


Figure 8. ^1H NMR spectrum from the room-temperature reaction between Me_2AlCl and methyl phenylacetate $\mathbf{1}^{Bn}$ employing a 3:1 ratio in hexane. The solvent is benzene-d_6.

Scheme 5. Generation of $\mathbf{2}^{Bn}(MeAlCl_2)$ and 11 En Route to the Production of Volatiles 12 and MeH



mixtures giving predominantly adduct $\mathbf{1}^{Bn}(Me_{1.5}AlCl_{1.5})$, which reveals a ^{13}C NMR C═O signal at δ 183.6 ppm (cf. δ 182.3 ppm for $\mathbf{1}^{Bn}(Me_2AlCl)$, δ 184.2 ppm for $\mathbf{1}^{Bn}(MeAlCl_2)$). At <60 °C, adduct formation is quantitative, and dimethylation is not observed. Evidence that dimethylation can proceed at high-temperature comes from the observation of alkenes **12** (5% combined) alongside $\mathbf{1}^{Bn}(Me_{1.5}AlCl_{1.5})$ (91%) after heating to 80 °C for 24 h. However, once again, present alongside these components is the product of reaction with toluene solvent (Scheme S2).

Attempts to isolate $\mathbf{2}^{Bn}(Me_2AlCl)$ and $\mathbf{2}^{Bn}(MeAlCl_2)$ were undertaken. The $\mathbf{1}^{Bn}$−Me_2AlCl reaction that was heated to 60 °C for 24 h was shown spectroscopically to yield the most dimethylation, and this system was therefore reduced *in vacuo* to remove toluene and alkenes. The remaining liquid yielded a solid, which could be melted and then left to cool slowly to give crystals. These were analyzed by X-ray crystallography (Figure 9). Diffraction revealed metallacyclic $Me_4Al_2(\mu^2\text{-}Cl)(\mu^2\text{-}OCBnMe_2)$, $\mathbf{2}^{Bn}(Me_2AlCl)$. This motif is similar to that seen recently for $\mathbf{2}^{Bn}(TMA)$[11] and is consistent with solution studies (see above) that pointed to a mixture of expected dimethylation product $\mathbf{2}^{Bn}(MeAlCl_2)$ and spectroscopically dominant $\mathbf{2}^{Bn}(Me_2AlCl)$, with the former complex becoming prominent at higher temperatures. It transpires that the structural motif demonstrated by $\mathbf{2}^{Bn}(Me_2AlCl)$ is highly unusual, with fully characterized $Al_2(\mu^2\text{-}O)(\mu^2\text{-}Cl)$ metallacycles being rare. To the best of our knowledge, only two other examples have been crystallographically characterized, both the result of $AlCl_3$ adduct formation.[43] The coexistence of $\mathbf{2}^{Bn}(MeAlCl_2)$ and $\mathbf{2}^{Bn}(Me_2AlCl)$ made it impossible to obtain accurate elemental analysis for the latter in spite of repeated attempts.

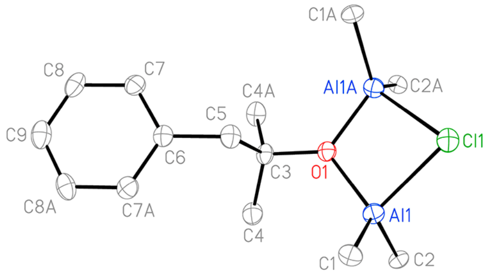


Figure 9. Molecular structure of $\mathbf{2}^{Bn}(Me_2AlCl)$. Thermal ellipsoids at 30% probability and hydrogen atoms omitted. Selected bond lengths (Å) and angles (deg): O1−Al1 1.837(3), C1−Al1 1.954(5), C2−Al1 1.982(5), Cl1−Al1 2.308(2), C3−O1 1.474(8), Al1−Cl1−Al1A 80.06(9), Al1−O1−Al1A 107.8(2), Cl1−Al1−O1 85.08(13), C1−Al1−C2 120.5(2).

To further investigate MeH production from the products of $\mathbf{1}^{Bn}$−Me_2AlCl reactions, attempts were made to separately isolate $\mathbf{2}^{Bn}(Me_2AlCl)$ and $\mathbf{2}^{Bn}(MeAlCl_2)$ via an alternative method. The reaction of phenylacetyl chloride **16** with 2 equiv of TMA resulted in complete conversion to $\mathbf{2}^{Bn}(Me_2AlCl)$ (Figure S32). This is believed to proceed by TMA first undergoing a chloride exchange with **16** to produce phenylacetone **17** (and Me_2AlCl), which then reacts with TMA to produce $\mathbf{2}^{Bn}(Me_2AlCl)$ (Scheme 6). Heating the toluene solution of $\mathbf{2}^{Bn}(Me_2AlCl)$ to reflux for 2 h formed a small amount (10%) of $(\mathbf{2}^{Bn})_2$ but failed to yield either alkenes or methane (Figure S35). Concentration of the room temperature reaction mixture resulted in the formation of crystalline material at −27 °C. These crystals were shown by X-ray crystallography to exhibit a unit cell the same as that of the product from the $\mathbf{1}^{Bn}$−Me_2AlCl reaction (Figure 9). Indeed, further analysis confirmed the crystals as $\mathbf{2}^{Bn}(Me_2AlCl)$.

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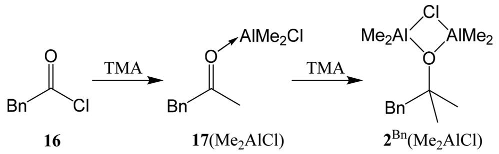
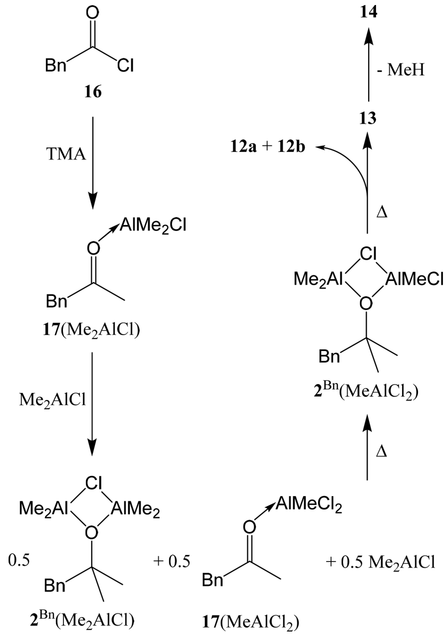
Scheme 6. Generation of Adduct $2^{Bn}(Me_2AlCl)$ from 16



Attempts to produce $2^{Bn}(MeAlCl_2)$ involved reacting **16** with TMA and Me_2AlCl (1 equiv of each). This initially formed **17** and 2 equiv of Me_2AlCl in a reaction which proved to be much slower (viz. the reduced nucleophilicity of Me_2AlCl compared to that of TMA). Stirring at room temperature for 2 h resulted in 49% **17**, 33% $\mathbf{2}^{Bn}(Me_2AlCl)$, and 18% $\mathbf{2}^{Bn}(MeAlCl_2)$ (Figure S41). Raising the reaction temperature to 60 °C led to an increase in the amount of $\mathbf{2}^{Bn}(MeAlCl_2)$ (8% **17**, 31% $\mathbf{2}^{Bn}(Me_2AlCl)$, and 61% $\mathbf{2}^{Bn}(MeAlCl_2)$). However, above 70 °C, the formation of alkenes **12a**/**b** was observed (Scheme 7), with reaction of toluene to form Friedel–Crafts products also seen. Heating the reaction mixture to 100 °C in toluene-d_8 in a sealed J. Young NMR tube for 2 h also resulted in the observation of MeH (^1H NMR δ 0.17 ppm, ^{13}C NMR −4.3 ppm, Figures S42 and S43), indicating that it is $\mathbf{2}^{Bn}(MeAlCl_2)$ and not $\mathbf{2}^{Bn}(Me_2AlCl)$ that represents a source of MeH. We attribute this to the greater number of chloride ligands increasing the Lewis acidity of $MeAlCl_2$ relative to that of Me_2AlCl.

Scheme 7. Generation of $2^{Bn}(MeAlCl_2)$ from 16 Yielding Volatiles 12 and MeH



Tetraester Reaction with Me_nAlCl_{3-n} (n = 1, 1.5, 2). The study of methylaluminum chlorides with monoesters was next extended to pentaerythritol-based tetraester mimics of POEs. In the first instance, the use of $\mathbf{4}^{Bn}$ with 12 equiv of Me_2AlCl (3 equiv per ester group) in toluene resulted in limited reactivity that was, nonetheless, similar to that of the monoester. ^1H NMR spectroscopy revealed that only 2% of the ester groups had reacted to form $\mathbf{2}^{Bn}(Me_2AlCl)$ after 2 h at room temperature (viz. Scheme 5). Heating to reflux in toluene for 2 h resulted in complete reaction of the tetraester to give alkenes **12a** and **12b**, while a small amount of exhaustive methylation gave Bn(t-Bu) **15** and Friedel–Crafts products were also noted (Figure S45). ^1H NMR spectroscopy revealed a broad signal, centered at ca. δ 3.9 ppm, which we tentatively attribute to the CH_2O region of the tetrolate-based byproduct of complete reaction, $C(CH_2OAlMe_mCl_n)_4$ **18** ($m + n = 2$, viz. **5** in Scheme 2). On the basis of observed monoester reactivity (see above), the reaction of Me_2AlCl with $\mathbf{4}^{Bn}$ was investigated by heating an identical 12:1 reaction mixture to 70 °C for 2 h (Figure S48). ^1H NMR spectroscopy of an aliquot of the reaction now revealed the conversion of 35% of the ester groups to give $\mathbf{2}^{Bn}(Me_2AlCl)$ and 16% to give $\mathbf{2}^{Bn}(MeAlCl_2)$. A very broad signal centered at ca. δ 3.8 ppm resulted from the remaining esters and various CH_2OAl groups present. In contrast to the monoester system, carefully raising the reaction temperature now resulted in an increase in the amount of $\mathbf{2}^{Bn}(Me_2AlCl)$ and $\mathbf{2}^{Bn}(MeAlCl_2)$ produced, with $\mathbf{2}^{Bn}(MeAlCl_2)$ becoming most abundant at 100 °C. Formation of alkenes **12a** and **12b** was now seen from 90 °C, which again contrasts with Me_2AlCl–monoester reactions, where alkene formation was seen from 60 °C (viz. Figure S31).

The use of $MeAlCl_2$ in place of Me_2AlCl resulted in the formation of a white precipitate when it was introduced to $\mathbf{4}^{Bn}$ in a 12:1 ratio. This material proved intractable. In contrast, use of an equimolar mixture of Me_2AlCl and $MeAlCl_2$ (i.e., aluminum sesquichloride) with $\mathbf{4}^{Bn}$ (6 equiv of each of Me_2AlCl and $MeAlCl_2$ per $\mathbf{4}^{Bn}$) resulted in similar reactivity to that seen using $MeAlCl_2$, with a white precipitate formed at lower temperatures but with heating of the reaction to reflux in toluene achieving a yellow solution. NMR spectroscopy of an aliquot revealed the presence of alkenes **12a** and **12b**, Friedel–Crafts products, trimethylated **15**, and a broad set of peaks at 4.5–3.5 ppm suggesting a mixture of unreacted ester groups and CH_2OAl units (Figure S49).

The observation that $\mathbf{4}^{Pent}(TMA)_4$ crystallized (Figure S10) but did so as a highly sensitive material that proved difficult to analyze led to attempts to produce the analogous Me_2AlCl and $MeAlCl_2$ structures. Pleasingly, the addition of 2 equiv of Me_2AlCl to $\mathbf{4}^{Pent}$ allowed the isolation of crystalline $\mathbf{4}^{Pent}(Me_2AlCl)_4$ (Figure 10). Relative to similarly structured $\mathbf{4}^{Pent}(TMA)_4$, the O–Al distances are shorter (mean 1.845 Å vs mean 1.920 Å in the TMA adduct). This is consistent with Me_2AlCl being a stronger Lewis acid, and appeared to impart additional stability that enabled more thorough characterization of the adduct.

■ CONCLUSIONS

The reaction of TMA has been extended from mono- to tetraester systems that are close relatives of industrial lubricants. Results revealed the ability of pentaerythritol-based $C(CH_2OC(O)R)_4$ to form adducts that could be isolated ($\mathbf{4}^{Pent}(TMA)_4$). Subsequent sequential reaction of each of the four ester functions was monitored, with spectroscopic observation of the stepwise conversion of each group corroborated by the isolation of twice-reacted $\{BnC(O)OCH_2\}_2C(CH_2OAlMe_2)_2(\mathbf{2}^{Bn})_2$ $\mathbf{7}^{Bn}(\mathbf{2}^{Bn})_2$, where $\mathbf{2}^{Bn}$ is $BnCMe_2OAlMe_2$. These data demonstrated that reactivity reported recently for monoesters can be extended to more complex, multifunctional polyolesters highly relevant to the refrigeration and transport industries. The reactions of methylaluminums with monoesters have also been extended beyond our recent report of the activity of TMA through the use of methylaluminum chlorides, Me_nAlCl_{3-n}. New results

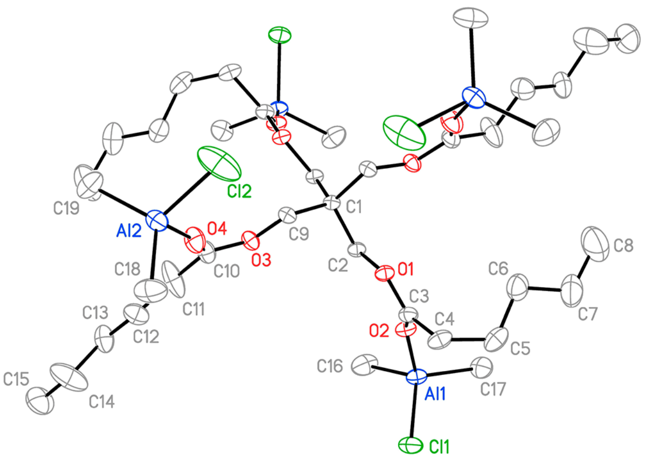


Figure 10. Molecular structure of $\mathbf{4}^{\mathrm{Pent}}(\mathrm{Me_2AlCl})_4$. Thermal ellipsoids at 30% probability, with hydrogen atoms and minor disorder omitted. Selected bond lengths (Å) and angles (deg): O2−Al1 1.8729(18), C16−Al1 1.944(3), C17−Al1 1.960(3), Cl1−Al1 2.1839(10), O4−Al2 1.817(9), C18−Al2 1.958(14), C19−Al2 1.974(12), Cl2−Al2 2.172(8), C3−O2−Al1 149.15(16), C10−O4−Al2 163.6(3).

point to similar but suppressed reactivity as *n* is decreased. The use of $\mathrm{Me_2AlCl}$ with BnC(O)OMe $\mathbf{1}^{\mathrm{Bn}}$ initially yielded a simple adduct but also provided evidence for dimethylation and the formation of a mixture of $\mathbf{2}^{\mathrm{Bn}}(\mathrm{Me_2AlCl})$ and $\mathbf{2}^{\mathrm{Bn}}(\mathrm{MeAlCl_2})$. In stark contrast to results obtained with TMA, this system proved capable of thermally eliminating alkenes (directly) and methane (indirectly). Replacing the monoesters with tetraesters showed similar reactivity, again seen with the production of alkenes and methane. These data, and the production of volatiles particularly, have significant health and safety implications for industry given the recently reported complications caused by the use of counterfeit additives in refrigeration technologies.

■ EXPERIMENTAL SECTION

General Synthetic and Analytical Details. Reactions and manipulations were carried out under dry nitrogen, using double manifold and glovebox methods. Solvents were distilled off sodium−potassium amalgam (hexane) or sodium (toluene) immediately prior to use. Methyl phenylacetate (Sigma-Aldrich) was stored over molecular sieve (4 Å). TMA (2.0 M in toluene) and $\mathrm{Me_2AlCl}$ (1.0 M in hexane) were purchased from Sigma-Aldrich and used as received. ***Caution:*** *TMA is pyrophoric and should only be handled under anaerobic conditions.* $\mathrm{AlCl_3}$ was purchased from Sigma-Aldrich and stored in a glovebox. Pentaerythritol was purchased from Alfa Aesar and stored in a glovebox. Phenylacetyl chloride and hexanoyl chloride were purchased from Fisher Scientific and used as received. For all new compounds and adducts we report elemental analysis, ^{1}H, $\{^1\mathrm{H}\}^{13}\mathrm{C}$, and (where appropriate) ^{27}Al NMR spectroscopy, and single crystal X-ray diffraction. Exceptions to this are $\mathbf{4}^{\mathrm{Pent}}$ (which lacks X-ray diffraction) and $\mathbf{4}^{\mathrm{Pent}}(\mathrm{TMA})_4$ (characterized only by X-ray diffraction). Elemental analysis was carried out on a PerkinElmer 240 Elemental Analyzer. NMR data were collected on a Bruker Avance III HD 400 MHz Smart Probe FT NMR spectrometer (400.130 MHz for ^{1}H, 100.613 MHz for ^{13}C, 104.261 for ^{27}Al). Spectra were obtained at 25 °C. ^{1}H and ^{13}C chemical shifts are internally referenced to deuterated solvent and calculated relative to TMS. ^{27}Al used an external reference (1 M $\mathrm{AlCl_3(H_2O)_6}$ in $\mathrm{D_2O}$). Chemical shifts are given in δ ppm. Abbreviations used are br = broad, d = doublet, m = multiplet, quin = quintet, s = singlet, t = triplet, F/C = Friedel−Crafts.

Crystallographic Details. Crystals were transferred from the mother liquor to a drop of perfluoropolyether oil mounted upon a microscope slide under cold nitrogen gas.[44] Suitable crystals were attached to the goniometer head via a MicroLoop, which was then centered on the diffractometer. Data were collected on a Bruker D8 Quest (Cu Kα, λ = 1.54184 Å), equipped with an Oxford Cryosystems low-temperature device. Structures were solved using SHELXT,[45] with refinement, based on F^2, by full-matrix least-squares.[46] Non-hydrogen atoms were refined anisotropically (for disorder, standard restraints and constraints were employed as appropriate) and a riding model with idealized geometry was employed for the refinement of hydrogen atoms. Compound $\mathbf{9}(\mathbf{2}^{\mathrm{Bn}})_2$ crystallized as a two-component nonmerohedral twin. Orientation matrices for the two components were found using the program Cell Now, and the two components were integrated with SAINT. The exact twin law determined by the integration program was (0.99997, −0.00021, 1.27249), (−0.00012, −1.00000, 0.00008), (0.00004, −0.00010, −0.99997). The data were corrected for absorption using Twinabs. 21800 reflections (3354 unique) involved domain 1 only (mean I/σ = 22.5), 21604 reflections (3344 unique) involved domain 2 only (mean I/σ = 20.1) and 15765 reflections (3230 unique) involved two domains (mean I/σ = 24.8). The structure was solved with SHELXT using data from domain 1 only (HKLF 4). For refinement, all observations involving domain 1 were included (HKLF 5); single reflections that also occurred in composites were omitted. R_{int} is based on agreement between observed single and composite intensities and those calculated from refined unique intensities and twin fractions. All crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC 1867820−1867825. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: + 44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Synthesis and Characterization of $\mathbf{7}^{\mathrm{Bn}}(\mathbf{2}^{\mathrm{Bn}})_2$. TMA (1.0 mL, 2.0 mmol, 2.0 M in toluene) was added dropwise to $\mathbf{4}^{\mathrm{Bn}}$ (304 mg, 0.5 mmol) in toluene (4 mL) under a $\mathrm{N_2}$ atmosphere at −78 °C and allowed to reach room temperature. The solution was heated to reflux for 2 h. Addition of hexane (6 mL) and storage at −27 °C resulted in the formation of colorless needle crystals. Yield 100 mg (22% wrt $\mathbf{4}^{\mathrm{Bn}}$). Mp 140−142 °C. ^{1}H NMR spectroscopy (400 MHz, benzene-d_6): δ 7.28−6.85 (m, 20H, Ph), 4.25 (s, 4H, $\mathrm{CH_2O}$), 3.84 (s, 4H, $\mathrm{CH_2O}$), 3.51 (s, 4H, $\mathrm{CH_2}$), 2.87 (s, 4H, $\mathrm{CH_2}$), 1.12 (s, 12H, Me), −0.37 (s, 24H, AlMe). ^{13}C NMR (100 MHz, benzene-d_6): δ 170.0 (C═O), 136.7, 133.5 (*i*-Ph), 130.3, 129.4 (*o*-Ph), 128.6, 128.0 (*m*-Ph), 127.2, 126.7 (*p*-Ph), 77.7 (CO), 62.1, 62.0($\mathrm{CH_2O}$), 51.1 ($\mathrm{CH_2}$), 44.2 ($\mathrm{C_{quat}}$), 40.9 ($\mathrm{CH_2}$), 28.4 (Me), −8.4 (AlMe). ^{27}Al NMR (104 MHz, benzene-d_6): Only see background signal; elemental analysis calculated (%) for $\mathrm{C_{49}H_{72}Al_4O_8}$: C 65.61, H 8.09. Found: C 65.46, H 8.01. X-ray crystal data: $\mathrm{C_{49}H_{72}Al_4O_8}$, M = 896.98, triclinic, space group $P\overline{1}$, a = 12.3772(4), b = 13.6608(5) c = 17.5106(6) Å, α = 68.249(2), β = 70.040(2), γ = 79.421(2), V = 2579.22(16) Å^3, Z = 2, ρ_{calcd} = 1.155 g cm^{-3}, μ = 1.222 mm^{-1}, T = 180(2) K. 74 742 data (9120 unique, R_{int} = 0.1304, θ < 66.810°) were collected. $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ = 0.1473, conventional R = 0.0609 on F values of 5198 reflections with $F^2 > 2\sigma(F^2)$, GoF = 1.017, 562 parameters. Max. peak/hole ±0.440 eÅ^{-3}.

Co-Synthesis and Characterization of $\mathbf{9}(\mathbf{2}^{\mathrm{Bn}})_2$ and $(\mathbf{2}^{\mathrm{Bn}})_2$. TMA (1.5 mL, 3.0 mmol, 2.0 M in toluene) was added dropwise to $\mathbf{4}^{\mathrm{Bn}}$ (304 mg, 0.5 mmol) in toluene (4 mL) under a $\mathrm{N_2}$ atmosphere at −78 °C and allowed to reach room temperature. The solution was heated to reflux for 2 h, and then the solvent was removed under vacuum. The solid was redissolved in hexane (8 mL), and storage at room temperature for 1 day resulted in the formation of colorless crystals. Yield 40 mg. Mp 221−224 °C. ^{1}H NMR spectroscopy (400 MHz, benzene-d_6): δ 7.08−6.83 (m, 12.5H, $\mathbf{9}(\mathbf{2}^{\mathrm{Bn}})_2$ + $(\mathbf{2}^{\mathrm{Bn}})_2$ Ph), 3.93 (s, 12H, $\mathbf{9}(\mathbf{2}^{\mathrm{Bn}})_2$ $\mathrm{CH_2O}$), 3.00 (s, 1H, $(\mathbf{2}^{\mathrm{Bn}})_2$ $\mathrm{CH_2}$), 2.94 (s, 4H, $\mathbf{9}(\mathbf{2}^{\mathrm{Bn}})_2$ $\mathrm{CH_2O}$), 2.79 (s, 4H, $\mathbf{9}(\mathbf{2}^{\mathrm{Bn}})_2$ $\mathrm{CH_2}$), 1.22 (s, 3H, $(\mathbf{2}^{\mathrm{Bn}})_2$ Me), 1.06 (s, 12H, $\mathbf{9}(\mathbf{2}^{\mathrm{Bn}})_2$ Me), −0.27 (s, 3H, $(\mathbf{2}^{\mathrm{Bn}})_2$ AlMe), −0.34 (s, 18H, $\mathbf{9}(\mathbf{2}^{\mathrm{Bn}})_2$ AlMe), −0.46 (s, 24H, $\mathbf{9}(\mathbf{2}^{\mathrm{Bn}})_2$ AlMe). ^{13}C NMR (100 MHz, benzene-d_6): δ 136.5 ($\mathbf{9}(\mathbf{2}^{\mathrm{Bn}})_2$ *i*-Ph), 130.3 ($\mathbf{9}(\mathbf{2}^{\mathrm{Bn}})_2$ *o*-Ph), 128.1 ($\mathbf{9}(\mathbf{2}^{\mathrm{Bn}})_2$ *m*-Ph), 126.8 ($\mathbf{9}(\mathbf{2}^{\mathrm{Bn}})_2$ *p*-Ph), 77.9 ($\mathbf{9}(\mathbf{2}^{\mathrm{Bn}})_2$ CO), 69.8 ($\mathbf{9}(\mathbf{2}^{\mathrm{Bn}})_2$ $\mathrm{CH_2O}$), 62.2 ($\mathbf{9}(\mathbf{2}^{\mathrm{Bn}})_2$ $\mathrm{CH_2O}$), 51.2 ($(\mathbf{2}^{\mathrm{Bn}})_2$ $\mathrm{CH_2}$), 51.0 ($\mathbf{9}(\mathbf{2}^{\mathrm{Bn}})_2$ $\mathrm{CH_2}$), 40.6 ($\mathbf{9}(\mathbf{2}^{\mathrm{Bn}})_2$ $\mathrm{C_{quat}}$), 28.5 ($(\mathbf{2}^{\mathrm{Bn}})_2$ Me), 28.3 ($\mathbf{9}(\mathbf{2}^{\mathrm{Bn}})_2$

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Me), −8.5 (**9**(**2**$^{\mathrm{Bn}}$)$_2$ AlMe), −12.1 (**9**(**2**$^{\mathrm{Bn}}$)$_2$ AlMe). ^{27}Al NMR (104 MHz, benzene-d_6): δ 8.7 ($W_{1/2}$ = 340 Hz); elemental analysis calculated (%) for $C_{50}H_{93.5}Al_{8.5}O_{10.5}$ (representing NMR spectroscopy): C 54.97, H 8.63. Found: C 52.33, H 8.48. X-ray crystal data: $C_{44}H_{84}Al_8O_{10}$, M = 988.95, monoclinic, space group $C2/c$, a = 26.8564(8), b = 16.9050(5) c = 13.6338(4) Å, β = 108.8420(10), V = 5858.1(3) Å^3, Z = 4, ρ_{calcd} = 1.121 g cm^{-3}, μ = 1.694 mm^{-1}, T = 180(2) K. 5149 data (5149 unique, R_{int} = 0.0614, $\theta < 66.623°$) were collected. $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2} = 0.1622$, conventional R = 0.0583 on F values of 4542 reflections with $F^2 > 2\sigma(F^2)$, GoF = 1.154, 291 parameters. Max. peak/hole ±0.487 eÅ^{-3}.

Spectroscopic Characterization of BnC(O)OMe 1$^{\mathrm{Bn}}$ + Me$_2$AlCl Reaction Mixtures. *Method 1.* Me$_2$AlCl (6 mL, 6 mmol, 1.0 M in hexane) was added dropwise at −78 °C to methyl phenylacetate **1**$^{\mathrm{Bn}}$ (0.28 mL, 2 mmol) and the mixture allowed to warm to room temperature. After stirring for 2 h, the solvent was removed *in vacuo* to give a clear residue which was analyzed by NMR spectroscopy. ^{1}H NMR spectroscopy (400 MHz, benzene-d_6) δ 7.09−6.76 (m, 4.5H, **1**$^{\mathrm{Bn}}$(Me$_2$AlCl) + **2**$^{\mathrm{Bn}}$(Me$_2$AlCl) Ph), 3.54 (s, 2H, **1**$^{\mathrm{Bn}}$(Me$_2$AlCl) CH$_2$), 2.85 (s, 0.08H, **2**$^{\mathrm{Bn}}$(Me$_2$AlCl) CH$_2$), 2.78 (s, br, 3H, **1**$^{\mathrm{Bn}}$(Me$_2$AlCl) OMe), 1.08 (s, 0.22H, **2**$^{\mathrm{Bn}}$(Me$_2$AlCl) Me), −0.21 (s, 7.9H, **1**$^{\mathrm{Bn}}$(Me$_2$AlCl) AlMe), −0.27 (s, 0.45H, **2**$^{\mathrm{Bn}}$(Me$_2$AlCl) AlMe). ^{13}C NMR (100 MHz, benzene-d_6): δ 182.3 (**1**$^{\mathrm{Bn}}$(Me$_2$AlCl) C═O), 130.2, 129.4, 128.8, 128.1 (**1**$^{\mathrm{Bn}}$(Me$_2$AlCl) + **2**$^{\mathrm{Bn}}$(Me$_2$AlCl) Ph), 56.1 (**1**$^{\mathrm{Bn}}$(Me$_2$AlCl) OMe), 50.4 (**2**$^{\mathrm{Bn}}$(Me$_2$AlCl) CH$_2$), 41.1 (**1**$^{\mathrm{Bn}}$(Me$_2$AlCl) CH$_2$), 28.0 (**2**$^{\mathrm{Bn}}$(Me$_2$AlCl) Me), −7.2 (**1**$^{\mathrm{Bn}}$(Me$_2$AlCl) + **2**$^{\mathrm{Bn}}$(Me$_2$AlCl) AlMe). ^{27}Al NMR (104 MHz, benzene-d_6): δ 170.5 ($W_{1/2}$ = 3800 Hz), 127.7 ($W_{1/2}$ = 1400 Hz).

Method 2. The above method was repeated, but after warming to room temperature, the reaction was heated to reflux for 24 h and then solvent removed *in vacuo* to give a clear residue which was analyzed by NMR spectroscopy. ^{1}H NMR spectroscopy (400 MHz, benzene-d_6) δ 7.09−6.76 (m, 9.7H, **1**$^{\mathrm{Bn}}$(Me$_2$AlCl) + **2**$^{\mathrm{Bn}}$(Me$_2$AlCl) + **2**$^{\mathrm{Bn}}$(MeAlCl$_2$) Ph), 6.28 (s, 0.01H, **12a** CH═C), 4.80 (s, 0.03H, **12b** C═CH$_2$), 4.75 (s, 0.03H, **12b** C═CH$_2$), 3.90−3.48 (m, 2.3H, **1**$^{\mathrm{Bn}}$(Me$_2$AlCl) CH$_2$), 3.30−2.96 (m, 4.7H, unassigned), 2.92 (s, 0.8H, **2**$^{\mathrm{Bn}}$(MeAlCl$_2$) CH$_2$), 2.85 (s, 0.8H, **2**$^{\mathrm{Bn}}$(Me$_2$AlCl) CH$_2$), 2.66 (s, br, 2.5H, **1**$^{\mathrm{Bn}}$(Me$_2$AlCl) OMe), 1.71 (s, 0.04H, **12a** Me), 1.68 (s, 0.03H, **12a** Me), 1.40−1.16 (m, 1.7H, unassigned), 1.12 (s, 2.1H, **2**$^{\mathrm{Bn}}$(MeAlCl$_2$) Me), 1.08 (s, 2H, **2**$^{\mathrm{Bn}}$(Me$_2$AlCl) Me), 0.22 to −0.20 (m, 3.5H, unassigned AlMe), −0.22 (s, 1.4H, **2**$^{\mathrm{Bn}}$(MeAlCl$_2$) AlMe), −0.27 (s, 5.4H, **2**$^{\mathrm{Bn}}$(Me$_2$AlCl) AlMe), −0.29 (s, 1H, **2**$^{\mathrm{Bn}}$(MeAlCl$_2$) AlMe), −0.30 to −0.70 (m, 8.9H, unassigned AlMe). ^{13}C NMR (100 MHz, benzene-d_6): δ 183.4 (**1**$^{\mathrm{Bn}}$(Me$_2$AlCl) C═O), 135.9, 135.4, 130.3, 130.2, 129.5, 128.8, 128.2 (**1**$^{\mathrm{Bn}}$(Me$_2$AlCl) + **2**$^{\mathrm{Bn}}$(Me$_2$AlCl) + **2**$^{\mathrm{Bn}}$(MeAlCl$_2$) Ph), 83.7 (**2**$^{\mathrm{Bn}}$(MeAlCl$_2$) CO), 81.1 (**2**$^{\mathrm{Bn}}$(Me$_2$AlCl) CO), 56.7 (**1**$^{\mathrm{Bn}}$(Me$_2$AlCl) OMe), 53.0−51.8 (unassigned OMe), 50.4 (**2**$^{\mathrm{Bn}}$(Me$_2$AlCl) CH$_2$), 50.1 (**2**$^{\mathrm{Bn}}$(MeAlCl$_2$) CH$_2$), 41.1 (**1**$^{\mathrm{Bn}}$(Me$_2$AlCl) CH$_2$), 28.0 (**2**$^{\mathrm{Bn}}$(Me$_2$AlCl) + **2**$^{\mathrm{Bn}}$(MeAlCl$_2$) Me), −6.1, −6.4, −8.5 (**1**$^{\mathrm{Bn}}$(Me$_2$AlCl) + **2**$^{\mathrm{Bn}}$(Me$_2$AlCl) + **2**$^{\mathrm{Bn}}$(MeAlCl$_2$) AlMe). ^{27}Al NMR (104 MHz, benzene-d_6): δ 164.8 ($W_{1/2}$ = 3800 Hz), 124.4 ($W_{1/2}$ = 1700 Hz).

Method 3. AlCl$_3$ (267 mg, 2 mmol), toluene (1 mL), and TMA (2 mL, 4 mmol, 2.0 M in toluene) were reacted to form Me$_2$AlCl (6 mmol, 2.0 M in toluene). Methyl phenylacetate **1**$^{\mathrm{Bn}}$ (0.28 mL, 2 mmol) was added dropwise at −78 °C and the mixture allowed to warm to room temperature to give a colorless solution. After stirring for 24 h at the desired temperature an aliquot of the solution was analyzed by NMR spectroscopy.

Room-Temperature Reaction. ^{1}H NMR spectroscopy (400 MHz, benzene-d_6) δ 7.09−6.76 (m, 5H, **1**$^{\mathrm{Bn}}$(Me$_2$AlCl) + **2**$^{\mathrm{Bn}}$(Me$_2$AlCl) Ph), 3.53 (s, br, 2H, **1**$^{\mathrm{Bn}}$(Me$_2$AlCl) CH$_2$), 2.86 (s, 0.24H, **2**$^{\mathrm{Bn}}$(Me$_2$AlCl) CH$_2$), 2.82 (s, br, 3H, **1**$^{\mathrm{Bn}}$(Me$_2$AlCl) OMe), 1.08 (s, 0.6H, **2**$^{\mathrm{Bn}}$(Me$_2$AlCl) Me), 0.01 to −0.25 (m, 1.2H, unassigned AlMe), −0.27 (s, 13.5H, **1**$^{\mathrm{Bn}}$(Me$_2$AlCl) + **2**$^{\mathrm{Bn}}$(Me$_2$AlCl) AlMe), −0.34 to −0.49 (m, 2.5H, unassigned AlMe). ^{13}C NMR (100 MHz, benzene-d_6): δ 181.5 (**1**$^{\mathrm{Bn}}$(Me$_2$AlCl) C═O), 130.2, 129.4, 128.8, 128.1 (**1**$^{\mathrm{Bn}}$(Me$_2$AlCl) + **2**$^{\mathrm{Bn}}$(Me$_2$AlCl) Ph), 56.2 (**1**$^{\mathrm{Bn}}$(Me$_2$AlCl) OMe), 50.4 (**2**$^{\mathrm{Bn}}$(Me$_2$AlCl) CH$_2$), 41.1 (**1**$^{\mathrm{Bn}}$(Me$_2$AlCl) CH$_2$), 27.9 (**2**$^{\mathrm{Bn}}$(Me$_2$AlCl) Me), −7.0 (**1**$^{\mathrm{Bn}}$(Me$_2$AlCl) + **2**$^{\mathrm{Bn}}$(Me$_2$AlCl) AlMe). ^{27}Al NMR (104 MHz, benzene-d_6): δ 174.1 ($W_{1/2}$ = 3500 Hz), 126.7 ($W_{1/2}$ = 1300 Hz).

50 °C Reaction. ^{1}H NMR spectroscopy (400 MHz, benzene-d_6) δ 7.09−6.76 (m, 5H, **1**$^{\mathrm{Bn}}$(Me$_2$AlCl) + **2**$^{\mathrm{Bn}}$(Me$_2$AlCl) + **2**$^{\mathrm{Bn}}$(MeAlCl$_2$) Ph), 3.57 (m, br, 2H, **1**$^{\mathrm{Bn}}$(Me$_2$AlCl) CH$_2$), 3.30−2.96 (m, 0.64H, unassigned), 2.93 (s, 0.26H, **2**$^{\mathrm{Bn}}$(MeAlCl$_2$) CH$_2$), 2.86 (s, 0.48H, **2**$^{\mathrm{Bn}}$(Me$_2$AlCl) CH$_2$), 2.85−2.62 (m, br, 3H, **1**$^{\mathrm{Bn}}$(Me$_2$AlCl) OMe), 1.13 (s, 0.49H, **2**$^{\mathrm{Bn}}$(MeAlCl$_2$) Me), 1.08 (s, 1.4H, **2**$^{\mathrm{Bn}}$(Me$_2$AlCl) Me), 0.01 to −0.20 (m, 2.2H, unassigned AlMe), −0.22 (s, 0.4H, **2**$^{\mathrm{Bn}}$(MeAlCl$_2$) AlMe), −0.27 (s, 9.5H, **2**$^{\mathrm{Bn}}$(Me$_2$AlCl) + **2**$^{\mathrm{Bn}}$(MeAlCl$_2$) AlMe), −0.36 (s, 0.4H, **2**$^{\mathrm{Bn}}$(MeAlCl$_2$) AlMe), −0.45 (s, 2.2H, unassigned AlMe). ^{13}C NMR (100 MHz, benzene-d_6): δ 182.5 (**1**$^{\mathrm{Bn}}$(Me$_2$AlCl) C═O), 135.9, 130.2, 129.5, 128.8, 128.1 (**1**$^{\mathrm{Bn}}$(Me$_2$AlCl) + **2**$^{\mathrm{Bn}}$(Me$_2$AlCl) Ph + **2**$^{\mathrm{Bn}}$(MeAlCl$_2$) Ph), 83.7 (**2**$^{\mathrm{Bn}}$(MeAlCl$_2$) CO), 81.1 (**2**$^{\mathrm{Bn}}$(Me$_2$AlCl) CO), 56.7, 56.5 (**1**$^{\mathrm{Bn}}$(Me$_2$AlCl) OMe), 50.4 (**2**$^{\mathrm{Bn}}$(Me$_2$AlCl) CH$_2$), 50.1 (**2**$^{\mathrm{Bn}}$(MeAlCl$_2$) CH$_2$), 41.1 (**1**$^{\mathrm{Bn}}$(Me$_2$AlCl) CH$_2$), 27.9 (**2**$^{\mathrm{Bn}}$(Me$_2$AlCl) + **2**$^{\mathrm{Bn}}$(MeAlCl$_2$) Me), −6.7 (**1**$^{\mathrm{Bn}}$(Me$_2$AlCl) + **2**$^{\mathrm{Bn}}$(Me$_2$AlCl) + **2**$^{\mathrm{Bn}}$(MeAlCl$_2$) AlMe). ^{27}Al NMR (104 MHz, benzene-d_6): δ 176.6 ($W_{1/2}$ = 3400 Hz), 127.2 ($W_{1/2}$ = 1300 Hz).

60 °C Reaction. ^{1}H NMR spectroscopy (400 MHz, benzene-d_6) δ 7.34−6.76 (m, **1**$^{\mathrm{Bn}}$(Me$_2$AlCl) + **2**$^{\mathrm{Bn}}$(Me$_2$AlCl) + **2**$^{\mathrm{Bn}}$(MeAlCl$_2$) + **12a** + **12b** Ph), 6.28 (s, 0.01H, **12a** CH═C), 4.80 (m, 0.02H, **12b** C═CH$_2$), 4.75 (m, 0.02H, **12b** C═CH$_2$), 3.59 (m, br, 2H, **1**$^{\mathrm{Bn}}$(Me$_2$AlCl) CH$_2$), 3.32−2.97 (m, 1.67H, unassigned), 2.93 (s, 0.57H, **2**$^{\mathrm{Bn}}$(MeAlCl$_2$) CH$_2$), 2.86 (s, 0.73H, **2**$^{\mathrm{Bn}}$(Me$_2$AlCl) CH$_2$), 2.83−2.58 (m, br, 2.6H, **1**$^{\mathrm{Bn}}$(Me$_2$AlCl) OMe), 1.72 (s, 0.02H, **12a** Me), 1.70 (s, 0.02H, **12a** Me), 1.55 (s, 0.06H, **12b** Me), 1.38−1.17 (m, 0.75H, unassigned), 1.13 (s, 1.2H, **2**$^{\mathrm{Bn}}$(MeAlCl$_2$) Me), 1.08 (s, 1.9H, **2**$^{\mathrm{Bn}}$(Me$_2$AlCl) Me), 0.01 to −0.20 (m, 2.9H, unassigned AlMe), −0.22 (s, 0.55H, **2**$^{\mathrm{Bn}}$(MeAlCl$_2$) AlMe), −0.27 (s, 4.1H, **2**$^{\mathrm{Bn}}$(Me$_2$AlCl) AlMe), −0.30 (s, 9.1H, **1**$^{\mathrm{Bn}}$(Me$_2$AlCl) + **2**$^{\mathrm{Bn}}$(MeAlCl$_2$) AlMe), −0.37 (s, 0.68H, **2**$^{\mathrm{Bn}}$(MeAlCl$_2$) AlMe), −0.45 (s, 2.8H, unassigned AlMe). ^{13}C NMR (100 MHz, benzene-d_6): δ 183.5 (**1**$^{\mathrm{Bn}}$(Me$_2$AlCl) C═O), 135.9, 135.4, 130.2, 129.5, 128.8, (**1**$^{\mathrm{Bn}}$(Me$_2$AlCl) + **2**$^{\mathrm{Bn}}$(Me$_2$AlCl) Ph + **2**$^{\mathrm{Bn}}$(MeAlCl$_2$) Ph), 83.7 (**2**$^{\mathrm{Bn}}$(MeAlCl$_2$) CO), 81.1 (**2**$^{\mathrm{Bn}}$(Me$_2$AlCl) CO), 56.7 (**1**$^{\mathrm{Bn}}$(Me$_2$AlCl) OMe), 50.4 (**2**$^{\mathrm{Bn}}$(Me$_2$AlCl) CH$_2$), 50.1 (**2**$^{\mathrm{Bn}}$(MeAlCl$_2$) CH$_2$), 41.1 (**1**$^{\mathrm{Bn}}$(Me$_2$AlCl) CH$_2$), 27.9 (**2**$^{\mathrm{Bn}}$(Me$_2$AlCl) + **2**$^{\mathrm{Bn}}$(MeAlCl$_2$) Me), −6.1, −6.7 (**1**$^{\mathrm{Bn}}$(Me$_2$AlCl) + **2**$^{\mathrm{Bn}}$(Me$_2$AlCl) + **2**$^{\mathrm{Bn}}$(MeAlCl$_2$) AlMe). ^{27}Al NMR (104 MHz, benzene-d_6): δ 171.7 ($W_{1/2}$ = 3000 Hz), 124.2 ($W_{1/2}$ = 1700 Hz).

70 °C Reaction. ^{1}H NMR spectroscopy (400 MHz, benzene-d_6) δ 7.34−6.76 (m, **1**$^{\mathrm{Bn}}$(Me$_2$AlCl) + **2**$^{\mathrm{Bn}}$(Me$_2$AlCl) + **2**$^{\mathrm{Bn}}$(MeAlCl$_2$) + **12a** + **12b** Ph), 6.28 (s, 0.02H, **12a** CH═C), 4.80 (m, 0.15H, **12b** C═CH$_2$), 4.75 (m, 0.15H, **12b** C═CH$_2$), 3.59 (m, br, 2H, **1**$^{\mathrm{Bn}}$(Me$_2$AlCl) CH$_2$), 3.32−2.97 (m, 4H, unassigned), 2.93 (s, 0.81H, **2**$^{\mathrm{Bn}}$(MeAlCl$_2$) CH$_2$), 2.86 (s, 0.91H, **2**$^{\mathrm{Bn}}$(Me$_2$AlCl) CH$_2$), 2.83−2.58 (m, br, 2.4H, **1**$^{\mathrm{Bn}}$(Me$_2$AlCl) OMe), 1.72 (s, 0.12H, **12a** Me), 1.69 (s, 0.11H, **12a** Me), 1.55 (s, 0.51H, **12b** Me), 1.38−1.17 (m, 1.9H, unassigned), 1.13 (s, 1.9H, **2**$^{\mathrm{Bn}}$(MeAlCl$_2$) Me), 1.08 (s, 2H, **2**$^{\mathrm{Bn}}$(Me$_2$AlCl) Me), 0.01 to −0.20 (m, 5H, unassigned AlMe), −0.22 (s, 1.3H, **2**$^{\mathrm{Bn}}$(MeAlCl$_2$) AlMe), −0.28 (s, 4.1H, **2**$^{\mathrm{Bn}}$(Me$_2$AlCl) AlMe), −0.32 (s, 10.8H, **1**$^{\mathrm{Bn}}$(Me$_2$AlCl) + **2**$^{\mathrm{Bn}}$(MeAlCl$_2$) AlMe), −0.37 (s, 1.4H, **2**$^{\mathrm{Bn}}$(MeAlCl$_2$) AlMe), −0.45 (s, 3.1H, unassigned AlMe). ^{13}C NMR (100 MHz, benzene-d_6): δ 135.9, 135.4, 130.2, 129.5, 128.8, (**1**$^{\mathrm{Bn}}$(Me$_2$AlCl) + **2**$^{\mathrm{Bn}}$(Me$_2$AlCl) Ph + **2**$^{\mathrm{Bn}}$(MeAlCl$_2$) Ph), 83.7 (**2**$^{\mathrm{Bn}}$(MeAlCl$_2$) CO), 81.1 (**2**$^{\mathrm{Bn}}$(Me$_2$AlCl) CO), 56.7 (**1**$^{\mathrm{Bn}}$(Me$_2$AlCl) OMe), 50.4 (**2**$^{\mathrm{Bn}}$(Me$_2$AlCl) CH$_2$), 50.1 (**2**$^{\mathrm{Bn}}$(MeAlCl$_2$) CH$_2$), 44.6 (**12b** CH$_2$), 41.1 (**1**$^{\mathrm{Bn}}$(Me$_2$AlCl) CH$_2$), 27.9 (**2**$^{\mathrm{Bn}}$(Me$_2$AlCl) + **2**$^{\mathrm{Bn}}$(MeAlCl$_2$) Me), −6.6 (**1**$^{\mathrm{Bn}}$(Me$_2$AlCl) + **2**$^{\mathrm{Bn}}$(Me$_2$AlCl) + **2**$^{\mathrm{Bn}}$(MeAlCl$_2$) AlMe). ^{27}Al NMR (104 MHz, benzene-d_6): δ 174.2 ($W_{1/2}$ = 3000 Hz), 124.5 ($W_{1/2}$ = 1600 Hz).

80 °C Reaction. ^{1}H NMR spectroscopy (400 MHz, benzene-d_6) δ 7.34−6.76 (m, **1**$^{\mathrm{Bn}}$(Me$_2$AlCl) + **12a** + **12b** Ph), 6.28 (s, 0.21H, **12a** CH═C), 4.80 (m, 0.93H, **12b** C═CH$_2$), 4.75 (m, 0.93H, **12b** C═CH$_2$), 3.59, 3.54 (m, br, 2H, **1**$^{\mathrm{Bn}}$(Me$_2$AlCl) CH$_2$), 3.32−2.97 (m, 4.7H, unassigned OMe), 3.15 (s, 2.3H, **12b** CH$_2$), 2.83−2.62 (m, br, 1.8H, **1**$^{\mathrm{Bn}}$(Me$_2$AlCl) OMe), 2.37 (s, 0.04H, **15** CH$_2$), 1.72 (s, 0.78H, **12a** Me), 1.69 (s, 0.78H, **12a** Me), 1.55 (s, 0.51H, **12b** Me), 0.84 (s, 0.26H, **15** Me), 0.01 to −0.60 (m, 20H, unassigned AlMe), −0.34 (s, 12.7H, **1**^{Bn}(Me_2AlCl) AlMe). ^{13}C NMR (100 MHz, benzene-d_6): δ 144.8, 139.6 (**12b** C), 129.5, 129.4 (**1**^{Bn}(Me_2AlCl) Ph), 128.9 (**12b** Ph), 125.6 (**12a**=CH), 111.8 (**12b**=CH_2), 57.9 (**1**^{Bn}(Me_2AlCl) OMe), 44.6 (**12b** CH_2), 41.5, 41.1 (**1**^{Bn}(Me_2AlCl) CH_2), 26.4 (**12a** Me), 21.6 (**12b** Me), 18.9 (**12a** Me), −6.8 (**1**^{Bn}(Me_2AlCl) AlMe). ^{27}Al NMR (104 MHz, benzene-d_6): δ 177.1 ($W_{1/2}$ = 2500 Hz), 124.3 ($W_{1/2}$ = 1800 Hz).

Reaction Heated to Reflux. ^{1}H NMR spectroscopy (400 MHz, benzene-d_6) δ 7.34−6.76 (m, **1**^{Bn}(Me_2AlCl) + **12a** + **12b** Ph), 6.28 (s, 0.39H, **12a** CH=C), 4.80 (m, 1H, **12b** C=CH_2), 4.75 (m, 1H, **12b** C=CH_2), 3.58 (s, 0.39H, **1**^{Bn}(Me_2AlCl) CH_2), 3.32−2.97 (m, 3H, unassigned OMe), 3.15 (s, 3.2H, **12b** CH_2), 2.99 (s, 1.1H, unassigned OMe), 2.81−2.72 (m, br, 1.2H, unassigned OMe), 2.37 (s, 0.16H, **15** CH_2), 1.72 (s, 1.5H, **12a** Me), 1.69 (s, 1.5H, **12a** Me), 1.55 (s, 3.2H, **12b** Me), 1.33 (s, 0.44H, F/C Me), 1.22 (s, 0.56, F/C Me), 0.91−0.78 (m, 2.2H, F/C Me), 0.84 (s, 0.82H, **15** Me), 0.11 to −0.60 (m, 21H, unassigned AlMe), −0.36 (s, 12.7H, **1**^{Bn}(Me_2AlCl) AlMe). ^{13}C NMR (100 MHz, benzene-d_6): δ 144.8, 139.6 (**12b** C), 134.7, 130.8, 129.4 (**1**^{Bn}(Me_2AlCl) Ph), 128.9 (**12b** Ph), 125.3 (**12a** = CH), 111.9 (**12b** = CH_2), 44.6 (**12b** CH_2), 29.1 (**15** Me), 26.4 (**12a** Me), 21.6 (**12b** Me), 18.9 (**12a** Me). ^{27}Al NMR (104 MHz, benzene-d_6): δ 190.6 ($W_{1/2}$ = 3100 Hz), 136.1 ($W_{1/2}$ = 3000 Hz), 94.9 ($W_{1/2}$ = 300 Hz), 93.5 ($W_{1/2}$ = 300 Hz).

Method 4. First, 0.1 mL of the 3:1 solution from Method 3 was placed in a sealed J. Young NMR tube with 0.6 mL of toluene-d_8 and heated to 100 °C for 24 h. ^{1}H NMR spectroscopy (400 MHz, toluene-d_8) δ 7.34−6.76 (m, **1**^{Bn}(Me_2AlCl) + **12a** + **12b** Ph), 6.22 (m, 1H, **12a** CH=C), 4.77 (m, 4.2H, **12b** C=CH_2), 4.72 (m, 4.2H, **12b** C=CH_2), 3.60, 3.56 (s, 4.5H, **1**^{Bn}(Me_2AlCl) CH_2), 3.27, 3.16, 2.79 (s, 5.9H, **1**^{Bn}(Me_2AlCl) OMe) 3.20, 2.86 (m, 6.6H, unassigned OMe), 3.13 (s, 9H, **12b** CH_2), 2.99 (s, 1.1H, unassigned OMe), 2.81−2.72 (m, br, 1.2H, unassigned OMe), 1.72 (d, 3.7H, **12a** Me), 1.68 (s, 3.7H, **12a** Me), 1.54 (s, 13.4H, **12b** Me), 0.17 (s, 4.1H, MeH), 0.11 to −0.64 (m, 52H, unassigned AlMe), −0.35 (s, 37H, Me_2AlCl AlMe). ^{13}C NMR (100 MHz, toluene-d_8): δ 184.5 (**1**^{Bn}(Me_2AlCl) C=O), 145.1, 139.9 (**12b** C), 134.9 (**12b** C), 129.8 (**1**^{Bn}(Me_2AlCl) Ph), 128.9 (**12b** Ph), 125.6 (**12a** = CH), 112.2 (**12b** = CH_2), 58.9, 57.2 (**1**^{Bn}(Me_2AlCl) OMe), 44.9 (**12b** CH_2), 41.8, 41.5 (**1**^{Bn}(Me_2AlCl) CH_2), 26.8 (**12a** Me), 22.0 (**12b** Me), 19.3 (**12a** Me), −4.3 (MeH), −6.3 (**1**^{Bn}(Me_2AlCl) AlMe). ^{27}Al NMR (104 MHz, toluene-d_8): δ 183.0 ($W_{1/2}$ = 2300 Hz), 129.9 ($W_{1/2}$ = 2000 Hz), 99.8 ($W_{1/2}$ = 300 Hz), 97.8 ($W_{1/2}$ = 400 Hz).

Spectroscopic Characterization of BnC(O)Cl 16 + TMA Reaction Mixtures. TMA (2 mL, 4 mmol, 2.0 M in toluene) was added dropwise to phenylacetyl chloride **16** (0.26 mL, 2 mmol) under a N_2 atmosphere at −78 °C and allowed to reach room temperature. After stirring for 2 h at the desired temperature an aliquot of the solution was analyzed by NMR spectroscopy.

Room-Temperature Reaction. ^{1}H NMR spectroscopy (400 MHz, benzene-d_6) δ 7.14−6.77 (m, 5H, **2**^{Bn}(Me_2AlCl) Ph), 2.85 (s, 2H, **2**^{Bn}(Me_2AlCl) CH_2), 1.08 (s, 6H, **2**^{Bn}(Me_2AlCl) Me), −0.28 (s, 12H, **2**^{Bn}(Me_2AlCl) AlMe). ^{13}C NMR (100 MHz, benzene-d_6): δ 135.9, 130.2, 128.2, 126.9 (**2**^{Bn}(Me_2AlCl) Ph), 81.1 (**2**^{Bn}(Me_2AlCl) C_{quat}), 50.4 (**2**^{Bn}(Me_2AlCl) CH_2), 27.9 (**2**^{Bn}(Me_2AlCl) Me), −6.1 (**2**^{Bn}(Me_2AlCl) AlMe). ^{27}Al NMR (104 MHz, benzene-d_6): δ 169.4 ($W_{1/2}$ = 5200 Hz).

Reaction Heated to Reflux. ^{1}H NMR spectroscopy (400 MHz, benzene-d_6) δ 7.15−6.77 (m, 5H, **2**^{Bn}(Me_2AlCl) Ph), 2.99 (s, 0.2H, (**2**^{Bn})$_2$ CH_2), 2.85 (s, 2H, **2**^{Bn}(Me_2AlCl) CH_2), 1.22 (s, 0.6H, (**2**^{Bn})$_2$ Me), 1.08 (s, 6H, **2**^{Bn}(Me_2AlCl) Me), −0.28 (s, 12.6H, **2**^{Bn}(Me_2AlCl) + (**2**^{Bn})$_2$ AlMe). ^{13}C NMR (100 MHz, benzene-d_6): δ 135.9, 130.2, 128.2, 126.9 (**2**^{Bn}(Me_2AlCl) Ph), 81.1 (**2**^{Bn}(Me_2AlCl) C_{quat}), 77.6 ((**2**^{Bn})$_2$ C_{quat}), 51.2 (((**2**^{Bn})$_2$ CH_2), 50.4 (**2**^{Bn}(Me_2AlCl) CH_2), 28.5 (((**2**^{Bn})$_2$ Me), 27.9 (**2**^{Bn}(Me_2AlCl) Me), −6.1 (**2**^{Bn}(Me_2AlCl) AlMe). ^{27}Al NMR (104 MHz, benzene-d_6): δ 173.6 ($W_{1/2}$ = 5300 Hz).

Spectroscopic Characterization of BnC(O)Cl 16 + TMA + Me_2AlCl Reaction Mixtures. *Method 1.* $AlCl_3$ (89 mg, 0.67 mmol), toluene (0.33 mL), and TMA (1.67 mL, 3.33 mmol, 2.0 M in toluene) were reacted to form $Me_{2.5}AlCl_{0.5}$ (4 mmol, 2.0 M in toluene). Phenylacetyl chloride (0.26 mL, 2 mmol) was added dropwise under a N_2 atmosphere at −78 °C and allowed to reach room temperature. After stirring for 2 h, at the desired temperature an aliquot of the solution was analyzed by NMR spectroscopy.

Room-Temperature Reaction. ^{1}H NMR spectroscopy (400 MHz, benzene-d_6) δ 7.15−6.61 (m, **17**($MeAlCl_2$) + **2**^{Bn}(Me_2AlCl) + **2**^{Bn}($MeAlCl_2$) Ph), 3.09 (s, 2H, **17**($MeAlCl_2$) CH_2), 2.93 (s, 0.8H, **2**^{Bn}($MeAlCl_2$) CH_2), 2.86 (s, 1.4H, **2**^{Bn}(Me_2AlCl) CH_2), 1.64 (s, 3H, **17**($MeAlCl_2$) Me), 1.13 (s, 2.3H, **2**^{Bn}($MeAlCl_2$) Me), 1.08 (s, 4.2H, **2**^{Bn}(Me_2AlCl) Me), −0.05 (s, 2H, **17**($MeAlCl_2$) AlMe), −0.22 (s, 1.3H, **2**^{Bn}($MeAlCl_2$) AlMe), −0.28 (s, 16.5H, **2**^{Bn}(Me_2AlCl) + **2**^{Bn}($MeAlCl_2$) AlMe), −0.38 (s, 1.1H, **2**^{Bn}($MeAlCl_2$) AlMe). ^{13}C NMR (100 MHz, benzene-d_6): δ 233.2 (**17**($MeAlCl_2$) C=O), 135.9, 135.4, 130.2, 129.2, 129.1, 128.2, 127.1, 127.0 (**2**^{Bn}(Me_2AlCl) + **2**^{Bn}($MeAlCl_2$) + **17**($MeAlCl_2$) Ph), 83.7 (**2**^{Bn}($MeAlCl_2$) CO), 81.1 (**2**^{Bn}(Me_2AlCl) C_{quat}), 51.0 (**17**($MeAlCl_2$) CH_2), 50.4 (**2**^{Bn}(Me_2AlCl) CH_2), 50.1 (**2**^{Bn}($MeAlCl_2$) CH_2), 29.6 (**17**($MeAlCl_2$) Me), 28.0 (**2**^{Bn}(Me_2AlCl) + **2**^{Bn}($MeAlCl_2$) Me), −6.1 (**2**^{Bn}(Me_2AlCl) + **2**^{Bn}($MeAlCl_2$) AlMe). ^{27}Al NMR (104 MHz, benzene-d_6): δ 173.7 ($W_{1/2}$ = 4000 Hz), 127.6 ($W_{1/2}$ = 2000 Hz).

50 °C Reaction. ^{1}H NMR spectroscopy (400 MHz, benzene-d_6) δ 7.15−6.61 (m, **17**($MeAlCl_2$) + **2**^{Bn}(Me_2AlCl) + **2**^{Bn}($MeAlCl_2$) Ph), 3.06 (s, 2H, **17**($MeAlCl_2$) CH_2), 2.93 (s, 5.4H, **2**^{Bn}($MeAlCl_2$) CH_2), 2.86 (s, 3.1H, **2**^{Bn}(Me_2AlCl) CH_2), 1.63 (s, 3H, **17**($MeAlCl_2$) Me), 1.13 (s, 16H, **2**^{Bn}($MeAlCl_2$) Me), 1.08 (s, 10H, **2**^{Bn}(Me_2AlCl) Me), −0.05 (s, 2.8H, **17**($MeAlCl_2$) AlMe), −0.22 (s, 8H, **2**^{Bn}($MeAlCl_2$) AlMe), −0.28 (s, 20H, **2**^{Bn}(Me_2AlCl) AlMe) − 0.29 (s, 7H, **2**^{Bn}($MeAlCl_2$) AlMe), −0.38 (s, 7H, **2**^{Bn}($MeAlCl_2$) AlMe). ^{13}C NMR (100 MHz, benzene-d_6): δ 233.2 (**17**($MeAlCl_2$) C=O), 135.9, 135.4, 130.2, 129.2, 129.1, 128.2, 127.1, 127.0 (**2**^{Bn}(Me_2AlCl) + **2**^{Bn}($MeAlCl_2$) + **17**($MeAlCl_2$) Ph), 83.7 (**2**^{Bn}($MeAlCl_2$) CO), 81.1 (**2**^{Bn}(Me_2AlCl) C_{quat}), 51.0 (**17**($MeAlCl_2$) CH_2), 50.4 (**2**^{Bn}(Me_2AlCl) CH_2), 50.1 (**2**^{Bn}($MeAlCl_2$) CH_2), 29.6 (**17**($MeAlCl_2$) Me), 27.9 (**2**^{Bn}(Me_2AlCl) + **2**^{Bn}($MeAlCl_2$) Me), −6.3 (**2**^{Bn}(Me_2AlCl) + **2**^{Bn}($MeAlCl_2$) AlMe). ^{27}Al NMR (104 MHz, benzene-d_6): δ 174.7 ($W_{1/2}$ = 4100 Hz), 128.2 ($W_{1/2}$ = 2700 Hz).

60 °C Reaction. ^{1}H NMR spectroscopy (400 MHz, benzene-d_6) δ 7.15−6.61 (m, **17**($MeAlCl_2$) + **2**^{Bn}(Me_2AlCl) + **2**^{Bn}($MeAlCl_2$) Ph), 3.04 (s, 0.3H, **17**($MeAlCl_2$) CH_2), 2.92 (s, 2H, **2**^{Bn}($MeAlCl_2$) CH_2), 2.85 (s, 1H, **2**^{Bn}(Me_2AlCl) CH_2), 1.61 (s, 0.4H, **17**($MeAlCl_2$) Me), 1.13 (s, 6H, **2**^{Bn}($MeAlCl_2$) Me), 1.08 (s, 3H, **2**^{Bn}(Me_2AlCl) Me), −0.04 (s, 0.4H, **17**($MeAlCl_2$) AlMe), −0.22 (s, 3H, **2**^{Bn}($MeAlCl_2$) AlMe), −0.28 (s, 6H, **2**^{Bn}(Me_2AlCl) AlMe), −0.29 (s, 3H, **2**^{Bn}($MeAlCl_2$) AlMe), −0.38 (s, 3H, **2**^{Bn}($MeAlCl_2$) AlMe). ^{13}C NMR (100 MHz, benzene-d_6): δ 233.2 (**17**($MeAlCl_2$) C=O), 135.9, 135.4, 130.2, 129.2, 129.1, 128.2, 127.1, 127.0 (**2**^{Bn}(Me_2AlCl) + **2**^{Bn}($MeAlCl_2$) + **17**($MeAlCl_2$) Ph), 83.7 (**2**^{Bn}($MeAlCl_2$) CO), 81.1 (**2**^{Bn}(Me_2AlCl) C_{quat}), 51.0 (**17**($MeAlCl_2$) CH_2), 50.4 (**2**^{Bn}(Me_2AlCl) CH_2), 50.1 (**2**^{Bn}($MeAlCl_2$) CH_2), 29.6 (**17**($MeAlCl_2$) Me), 27.9 (**2**^{Bn}(Me_2AlCl) + **2**^{Bn}($MeAlCl_2$) Me), −6.4 (**2**^{Bn}(Me_2AlCl) + **2**^{Bn}($MeAlCl_2$) AlMe). ^{27}Al NMR (104 MHz, benzene-d_6): δ 175.5 ($W_{1/2}$ = 4000 Hz), 129.4 ($W_{1/2}$ = 2700 Hz).

70 °C Reaction. ^{1}H NMR spectroscopy (400 MHz, benzene-d_6) δ 7.15−6.61 (m, **2**^{Bn}(Me_2AlCl) + **2**^{Bn}($MeAlCl_2$) + **12b** Ph), 4.80 (s, 0.03H, **12b** C=CH_2), 4.75 (s, 0.03H, **12b** C=CH_2), 2.92 (s, 2H, **2**^{Bn}($MeAlCl_2$) CH_2), 2.85 (s, 0.7H, **2**^{Bn}(Me_2AlCl) CH_2), 1.55 (s, 0.1H, **12b** Me), 1.13 (s, 6H, **2**^{Bn}($MeAlCl_2$) Me), 1.08 (s, 2.1H, **2**^{Bn}(Me_2AlCl) Me), −0.23 (s, 3H, **2**^{Bn}($MeAlCl_2$) AlMe), −0.28 (s, 5H, **2**^{Bn}(Me_2AlCl) AlMe) −0.29 (s, 3H, **2**^{Bn}($MeAlCl_2$) AlMe), −0.38 (s, 3H, **2**^{Bn}($MeAlCl_2$) AlMe). ^{13}C NMR (100 MHz, benzene-d_6): δ 135.9, 135.4, 135.0, 130.2, 128.2, 127.1, 127.0, 111.8 (**2**^{Bn}(Me_2AlCl) + **2**^{Bn}($MeAlCl_2$) + **12b** Ph), 111.8 (**12b** = CH_2), 83.7 (**2**^{Bn}($MeAlCl_2$) CO), 81.1 (**2**^{Bn}(Me_2AlCl) C_{quat}), 50.4 (**2**^{Bn}(Me_2AlCl) CH_2), 50.1 (**2**^{Bn}($MeAlCl_2$) CH_2), 44.6 (**12b** CH_2), 27.9 (**2**^{Bn}(Me_2AlCl) + **2**^{Bn}($MeAlCl_2$) Me), −6.4 (**2**^{Bn}(Me_2AlCl) + **2**^{Bn}($MeAlCl_2$) AlMe). ^{27}Al NMR (104 MHz, benzene-d_6): δ 174.1 ($W_{1/2}$ = 4100 Hz), 131.0 ($W_{1/2}$ = 3000 Hz).

80 °C Reaction. ^{1}H NMR spectroscopy (400 MHz, benzene-d_6) δ 7.15−6.61 (m, **2**^{Bn}($MeAlCl_2$) + **12a** + **12b** Ph), 6.27 (s, 0.1H, **12a**), 4.80 (s, 0.5H, **12b** C=CH_2), 4.75 (s, 0.5H, **12b** C=CH_2), 3.15 (s, 1.2H, **12b** CH_2), 2.92 (s, 2H, **2**^{Bn}($MeAlCl_2$) CH_2), 1.71 (s, 0.4H, **12a**

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Me), 1.69 (s, 0.4H, **12a** Me), 1.55 (s, 1.5H, **12b** Me), 1.13 (s, 6H, **2**$^{\mathrm{Bn}}$(MeAlCl$_2$) Me), −0.22 (s, 3H, **2**$^{\mathrm{Bn}}$(MeAlCl$_2$) AlMe), −0.27 (s, 3H, **2**$^{\mathrm{Bn}}$(MeAlCl$_2$) AlMe), −0.35 (s, 3H, **2**$^{\mathrm{Bn}}$(MeAlCl$_2$) AlMe). ^{13}C NMR (100 MHz, benzene-d_6): δ 135.9, 135.4, 135.0, 130.2, 128.2, 127.1, 127.0 (**2**$^{\mathrm{Bn}}$(MeAlCl$_2$) + **12a** + **12b** Ph), 111.8 (**12b** = CH$_2$), 83.7 (**2**$^{\mathrm{Bn}}$(MeAlCl$_2$) CO), 50.1 (**2**$^{\mathrm{Bn}}$(MeAlCl$_2$) CH$_2$), 44.6 (**12b** CH$_2$), 27.9 (**2**$^{\mathrm{Bn}}$(MeAlCl$_2$) Me), −6.4 (**2**$^{\mathrm{Bn}}$(Me$_2$AlCl) + **2**$^{\mathrm{Bn}}$(MeAlCl$_2$) AlMe). ^{27}Al NMR (104 MHz, benzene-d_6): δ 180.0 ($W_{1/2}$ = 3700 Hz), 133.3 ($W_{1/2}$ = 2700 Hz).

Reaction Heated to Reflux. ^{1}H NMR spectroscopy (400 MHz, benzene-d_6) δ 7.15−6.61 (m, **12a** + **12b** + F/C Ph), 6.27 (s, 0.2H, **12a**), 4.80 (s, 0.2H, **12b** C═CH$_2$), 4.75 (s, 0.2H, **12b** C═CH$_2$), 3.46 (d, 1H, F/C CH), 3.28 (d, 1.8H, F/C CH), 3.15 (s, 0.4H, **12b** CH$_2$), 2.96−2.70 (m, 11H, F/C CH$_2$), 1.71 (s, 0.8H, **12a** Me), 1.69 (s, 0.8H, **12a** Me), 1.55 (s, 1H, **12b** Me), 1.33 (s, 5.5H, F/C Me), 1.22 (s, 12H, F/C Me), 0.95−0.60 (m, 38H, F/C Me), −0.10 to −0.48 (m, 85H, unassigned AlMe). ^{13}C NMR (100 MHz, benzene-d_6): δ 145.8, 143.0, 139.2, 138.9, 130.8, 130.5, 130.2, 128.2, 127.1, 127.0, 124.0, 122.7 (**12a** + **12b** + F/C Ph), 60.5, 54.3 (F/C CH), 51.8, 51.0, 48.1, 47.8, 47.2, 46.7, 44.8 (F/C CH$_2$), 31.6, 30.3, 29.1, 28.2, 27.3 (F/C Me), −7.0 (unassigned AlMe). ^{27}Al NMR (104 MHz, benzene-d_6): δ 170.4 ($W_{1/2}$ = 4100 Hz), 131.7 ($W_{1/2}$ = 1500 Hz), 92.6 ($W_{1/2}$ = 300 Hz), 79.9 ($W_{1/2}$ = 300 Hz).

Method 2. First, 0.1 mL of the **16** + TMA + Me$_2$AlCl toluene solution from Method 1 was placed in a sealed J. Young NMR tube with 0.6 mL of toluene-d_8 and heated to 100 °C for 2 h. ^{1}H NMR spectroscopy (400 MHz, toluene-d_8) δ 7.15−6.95 (m, **12a** + **12b** + F/C Ph), 6.23 (s, 1H, **12a**), 4.77 (s, 3.3H, **12b** C═CH$_2$), 4.72 (s, 3.3H, **12b** C═CH$_2$), 3.40 (d, 0.3H, F/C CH), 3.23 (d, 0.8H, F/C CH), 3.13 (s, 7H, **12b** CH$_2$), 2.72 (s, 2.7H, F/C CH$_2$), 1.72 (s, 3.6H, **12a** Me), 1.68 (s, 3.6H, **12a** Me), 1.54 (s, 10.5H, **12b** Me), 1.30 (s, 3.7H, F/C Me), 1.19 (s, 7.7H, F/C Me), 0.89−0.77 (m, 15H, F/C Me), 0.17 (s, 8.3H, MeH), −0.10 to −0.45 (m, 100H, unassigned AlMe). ^{13}C NMR (100 MHz, toluene-d_8): δ 145.1, 139.9, 139.2, 131.1, 130.7, 130.2, 128.2, 127.1, 127.0, 124.9, 123.0 (**12a** + **12b** + F/C Ph), 112.2 (**12b** = CH$_2$), 52.1, 51.4, 48.4, 47.6, 47.1, 45.1, 38.7, 38.5 (F/C CH$_2$), 44.9 (**12b** CH$_2$), 32.0, 31.8, 30.4, 29.4, 28.6, 27.8, 17.1 (F/C Me), −4.3 (MeH), −6.6 (unassigned AlMe). ^{27}Al NMR (104 MHz, toluene-d_8): δ 183.8 ($W_{1/2}$ = 4100 Hz), 136.6 ($W_{1/2}$ = 1400 Hz), 93.0 ($W_{1/2}$ = 300 Hz), 80.0 ($W_{1/2}$ = 300 Hz).

Synthesis and Characterization of BnMe$_2$COAlMe$_2$(Me$_2$AlCl), 2$^{\mathrm{Bn}}$(Me$_2$AlCl). *Method 1.* AlCl$_3$ (267 mg, 2 mmol), toluene (1 mL), and TMA (2 mL, 4 mmol, 2.0 M in toluene) were reacted to form Me$_2$AlCl (6 mmol, 2.0 M in toluene). Methyl phenylacetate **1**$^{\mathrm{Bn}}$ (0.28 mL, 2 mmol) was added dropwise at −78 °C and the mixture allowed to warm to room temperature to give a colorless solution. The solution was heated to 60 °C for 24 h and then placed under vacuum to remove the solvent and stored at −27 °C to produce a white solid. The solid was melted by heating to 40 °C and then left at room temperature to produce crystalline blocks. Yield 40 mg (7% wrt **1**$^{\mathrm{Bn}}$). Mp decomposed to a yellow solid at 120 °C. ^{1}H NMR spectroscopy (400 MHz, benzene-d_6): δ 7.10−6.74 (m, **1**$^{\mathrm{Bn}}$(Me$_2$AlCl) + **2**$^{\mathrm{Bn}}$(Me$_2$AlCl) + **2**$^{\mathrm{Bn}}$(MeAlCl$_2$) Ph), 6.28 (s, 0.01H, **12a** CH═C), 4.80 (m, 0.02H, **12b** C═CH$_2$), 4.75 (m, 0.02H, **12b** C═CH$_2$), 3.57 (s, br, 2.8H, **1**$^{\mathrm{Bn}}$(Me$_2$AlCl) CH$_2$), 2.92 (s, 0.83H, **2**$^{\mathrm{Bn}}$(MeAlCl$_2$) CH$_2$), 2.85 (s, 2H, **2**$^{\mathrm{Bn}}$(Me$_2$AlCl) CH$_2$), 2.74−2.60 (m, br, 3.5H, **1**$^{\mathrm{Bn}}$(Me$_2$AlCl) OMe), 1.38−1.17 (m, 2.2H, unassigned), 1.12 (s, 2.6H, **2**$^{\mathrm{Bn}}$(MeAlCl$_2$) Me), 1.07 (s, 6H, **2**$^{\mathrm{Bn}}$(Me$_2$AlCl) Me), −0.22 (s, 1.4H, **2**$^{\mathrm{Bn}}$(MeAlCl$_2$) AlMe), −0.27 (s, 12H, **2**$^{\mathrm{Bn}}$(Me$_2$AlCl) AlMe), −0.28 (s, 1.4H, **2**$^{\mathrm{Bn}}$(MeAlCl$_2$) AlMe), −0.38 (s, 1.4H, **2**$^{\mathrm{Bn}}$(MeAlCl$_2$) AlMe). ^{13}C NMR (100 MHz, benzene-d_6): δ 135.9, 130.2, 129.5, 128.8, 128.2, 127.0(**1**$^{\mathrm{Bn}}$(Me$_2$AlCl) + **2**$^{\mathrm{Bn}}$(Me$_2$AlCl) + **2**$^{\mathrm{Bn}}$(MeAlCl$_2$) Ph), 81.1 (**2**$^{\mathrm{Bn}}$(Me$_2$AlCl) CO), 50.4 (**2**$^{\mathrm{Bn}}$(Me$_2$AlCl) CH$_2$), 50.1 (**2**$^{\mathrm{Bn}}$(MeAlCl$_2$) CH$_2$), 41.1 (**1**$^{\mathrm{Bn}}$(Me$_2$AlCl) CH$_2$), 27.9 (**2**$^{\mathrm{Bn}}$(Me$_2$AlCl) + **2**$^{\mathrm{Bn}}$(MeAlCl$_2$) Me), −6.1 (**1**$^{\mathrm{Bn}}$(Me$_2$AlCl) + **2**$^{\mathrm{Bn}}$(Me$_2$AlCl) + **2**$^{\mathrm{Bn}}$(MeAlCl$_2$) AlMe). ^{27}Al NMR (104 MHz, benzene-d_6): δ 163.6 ($W_{1/2}$ = 3900 Hz), 126.0 ($W_{1/2}$ = 1700 Hz); satisfactory elemental analysis could not be obtained. X-ray crystal data: C$_{14}$H$_{25}$Al$_2$ClO, M = 298.75, orthorhombic, space group *Pnma*, a = 7.4160(5), b = 14.3329(10) c = 16.3610(11) Å, V = 1739.1(2) Å^3, Z = 4, ρ_{calcd} = 1.141 g cm^{-3}, μ = 2.820 mm^{-1}, T = 180(2) K. 9242 data (1590 unique, R_{int} = 0.0955, θ < 66.789°) were collected. $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ = 0.2071, conventional R = 0.0725 on F values of 1025 reflections with $F^2 > 2\sigma(F^2)$, GoF = 1.042, 91 parameters. Max. peak/hole ±0.497 eÅ^{-3}.

Method 2. TMA (2 mL, 4 mmol, 2.0 M in toluene) was added dropwise to phenylacetyl chloride **16** (0.26 mL, 2 mmol) under a N$_2$ atmosphere at −78 °C and allowed to reach room temperature. After stirring for 2 h, the solution was concentrated *in vacuo* and stored at −27 °C to produce crystalline blocks. Yield 140 mg (23% wrt **16**). Mp 64−66 °C. ^{1}H NMR spectroscopy (400 MHz, benzene-d_6): δ 7.08−6.75 (m, 5H, Ph), 2.85 (s, 2H, CH$_2$), 1.07 (s, 6H, Me), −0.27 (s, 12H, AlMe). ^{13}C NMR (100 MHz, benzene-d_6): δ 135.9 (*i*-Ph), 130.2 (*o*-Ph), 128.2 (*m*-Ph), 126.9 (*p*-Ph), 81.1 (CO), 50.5 (CH$_2$), 27.9 (Me), −6.1 (br, AlMe). ^{27}Al NMR (104 MHz, benzene-d_6): δ 171.2 ($W_{1/2}$ = 4900 Hz); elemental analysis calculated (%) for C$_{14}$H$_{25}$Al$_2$ClO: C 56.28, H 8.43, Cl 11.87. Found: C 56.21, H 8.41, Cl 11.82. X-ray crystal data: verified to be **2**$^{\mathrm{Bn}}$(Me$_2$AlCl) by crystallographic cell check.

Synthesis and Characterization of 4$^{\mathrm{Pent}}$ (Me$_2$AlCl)$_4$. AlCl$_3$ (44 mg, 0.33 mmol), toluene (2 mL), and TMA (0.33 mL, 0.66 mmol, 2.0 M in toluene) were reacted to form Me$_2$AlCl (1 mmol). **4**$^{\mathrm{Pent}}$ (0.27 mL, 0.5 mmol) was added dropwise under a N$_2$ atmosphere at −78 °C and allowed to reach room temperature. Once the solution reached room temperature, it was stored at −27 °C for 1 day to produce colorless needle crystals. Yield 75 mg (33% wrt AlCl$_3$). Mp 120−123 °C. ^{1}H NMR spectroscopy (400 MHz, chloroform-d): δ 4.54 (s, 8H, CH$_2$O), 2.75 (t, 8H, CH$_2$), 1.74 (quin, 8H, CH$_2$), 1.40−1.31 (m, 16H, CH$_2$), 0.92 (t, 12H, Me), −0.63 (s, 24H, AlMe). ^{13}C NMR (100 MHz, chloroform-d): δ 182.6 (C═O), 65.8 (CH$_2$O), 42.1 (C$_{\mathrm{quat}}$), 35.2, 31.1, 24.6, 22.1 (CH$_2$), 13.8 (Me), −7.9 (br, AlMe). ^{27}Al NMR (104 MHz, chloroform-d): only background signal; elemental analysis calculated (%) for C$_{37}$H$_{76}$Al$_4$Cl$_4$O$_8$: C 49.45, H 8.52, Cl 15.78. Found: C 48.64, H 8.24, Cl 15.94. X-ray crystal data: C$_{37}$H$_{76}$Al$_4$Cl$_4$O$_8$, M = 898.69, monoclinic, space group *C*2/*c*, a = 31.4647(12), b = 8.2194(3) c = 20.7543(8) Å, β = 92.278(2), V = 5363.3(4) Å^3, Z = 4, ρ_{calcd} = 1.113 g cm^{-3}, μ = 2.957 mm^{-1}, T = 180(2) K. 53 023 data (4735 unique, R_{int} = 0.0420, θ < 66.699°) were collected. $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ = 0.1731, conventional R = 0.0580 on F values of 4271 reflections with $F^2 > 2\sigma(F^2)$, GoF = 1.049, 262 parameters. Max. peak/hole ±0.748 eÅ^{-3}.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.8b00763.

Synthetic and analytical (NMR spectroscopic) details (PDF)

Accession Codes

CCDC 1867820−1867825 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

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