Lubricant Degradation

Reactions of Trimethylaluminium: Modelling the Chemical Degradation of Synthetic Lubricants

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Abstract: In investigating and seeking to mimic the reactivity of trimethylaluminium (TMA) with synthetic, ester-based lubricating oils, the reaction of methyl propionate 1 was explored with 1, 2 and 3 equivalents of the organoaluminium reagent. Spectroscopic analysis points to the formation of the adduct 1(TMA) accompanied by the low level 1:1 production of Me₃AlOEtMe₂ 2 and Me₃AlOMe 3 when an equimolar amount of TMA is applied. The deployment of excess TMA favours reaction to give 2 and 3 over 1(TMA) adduct formation and spectroscopy reveals that in hydrocarbon solution substitution product 2 traps unreacted TMA to yield 2(TMA). The ¹H NMR spectroscopic observation of two Al–Me signals not attributable to free TMA and in the ratio 1:4 suggests the formation of a previously only postulated, symmetrical metallacycle in Me₃Al(µ₂-Me)(µ₂-OCEtMe₂). In the presence of 3, 2(TMA) undergoes thermally induced exchange to yield Me₃Al(µ₂-OMe)(µ₂-OCEtMe₂) 4 and TMA. The reaction of methyl phenylaceta 5 with TMA allows isolation of the crystalline product Me₃AlOOCBnMe₃(TMA) 6(TMA), which allows the first observation of the Me₃Al(µ₂-Me)(µ₂-OR) motif in the solid state. Distances of 2.133(3) Å (Al–Me₃bridge) and 1.951 Å (mean Al–Me₃terminal) are recorded. The abstraction of TMA from 6(TMA) by the introduction of Et₂O has yielded 6, which exists as a dimer.

Introduction

Ideas on the atmospheric reaction of chlorofluorocarbons (CFCs) have existed for more than 40 years¹ and are well documented.² Although legislation has been implemented aimed at eliminating their use,³ the effects of substitute refrigerants such as perfluorocarbons (PFCs) and hydrofluorocarbons (HFCs) have been the subject of subsequent scrutiny⁴ and regulation.⁵ More specifically, with emissions from (automobile) air conditioning units representing a growing climate control concern⁶ action has been initiated⁷ to avoid the use of refrigerants with a global warming potential > 150 (GWP = 100 year warming potential of one kg of a gas relative to one kg CO₂).⁸ This has had the effect of phasing out greenhouse gases such as R-134a (1,1,2-tetrafluoroethane, GWP = > 1000).⁹ However, illicit HFC use remains a problem, with R-40 (chloromethane; GWP = 13) having been used as a counterfeit refrigerant.¹⁰ This raises issues of reactivity with aluminium components in refrigeration units. Although the reaction of alkyl chlorides with aluminium under the influence of an aluminium halide catalyst is well established,¹⁰ it is known that reaction also proceeds in the absence of catalyst.¹⁰b,¹¹ In this vein, in our hands the autocatalytic formation of trialkylaluminium and (catalyst) AlCl, from an alkyl chloride–aluminium mixture has been initiated by heat only.¹² The products of reaction between R-40 itself and aluminium include trimethylaluminium (TMA), which is potentially reactive with respect to other chemicals present. These include proprietary compound oils (e.g. RL 32H)¹³ formulated for use in conjunction with HFC refrigerants. They comprise synthetic polyolesters (POEs) which, in RL 32H itself, have a pentaerythritol core.¹⁴

Although the interaction of organoaluminium compounds with esters has been studied¹⁵ the specifics of the mechanism remain surprisingly obscure and, in particular, reaction intermediates are incompletely understood. AlEt₃ has been reacted with esters in an equimolar ratio to give ‘ate complexes that rearrange to ketones and aldehydes.¹⁶ Studies using TMA have explored the formation of donor–acceptor complexes and their derivatization with excess aluminium reagent.¹⁷ Moreover, the deployment of excess TMA at high temperature has incurred double methylation and tertiary alcohol formation. However, mechanistic insights were limited to the alternative use of Me₂AlCl.¹⁸ Although the formation of hemialkoxides has been postulated based on the derivatization of ketones and aldehydes using alkylaluminiums,¹⁹ these species have not hitherto been recorded in ester-based systems. Meanwhile, the use of excess TMA has been reported in the alkyla- tion of acetates,²⁰ and the ketonization of heteroaromatic esters using 1 equivalent of TMA has been reported.²¹ Reaction selectivity has been investigated, with TMA used at low temperature²² in the stereoselective reduction of cyclic ke-
tones\textsuperscript{24} to give neoliacinic acid.\textsuperscript{25} The reaction was done in the presence of ancillary ester groups, with competing transesterification proving controllable.\textsuperscript{26}

The expected by-product of ester reaction with TMA, Me\textsubscript{2}AlOR, has been the subject of extensive study.\textsuperscript{27} However, this has tended to focus not upon its synthesis as a by-product of ketonization reactions but rather on the oxophilic derivatization of Al–C bonds\textsuperscript{28} by moisture\textsuperscript{29} or oxygen.\textsuperscript{30} From a structural point of view, aluminium organooxide formation\textsuperscript{31} and di-/trimerization is well established.\textsuperscript{32} For example, the simple aluminium alkoxide Me\textsubscript{2}AlOMe has been shown to be trimeric.\textsuperscript{33,34}

In this work we model the reaction of TMA with synthetic POEs and elucidate intermediates along the reaction pathway between TMA and esters in general for the first time. Structure and stability are monitored for intermediate complexes and solution data clarify the reaction stoichiometry.

Results and Discussion

The ability of alkylaluminium compounds to be autocatalytically generated through the action of alkyl chlorides on aluminium metal has led us to seek to model the potential reactivity of lubricant oils used in industrial refrigeration units with respect to TMA. Reactions involving a simple aliphatic ester were undertaken whereby TMA in toluene was initially added dropwise to methyl propionate\textsuperscript{1} (1:1) under a N\textsubscript{2} atmosphere at \textdegree-78\textdegree C. Though this system failed to readily produce isolable products, the observation of a pale-green colour upon heating, which disappeared when left to cool to room temperature, suggested the interaction of ester and TMA and led to further investigations. Accordingly, an excess of TMA (see the Supporting Information, Figure S1) was added to 1 (3:1 TMA:1) under N\textsubscript{2} at \textdegree-78\textdegree C. After reaching room temperature the solution was stirred for 2 hours, whereupon the NMR spectra of an aliquot were collected. \textsuperscript{1}H NMR spectroscopy and COSY suggested the formation of two species (Figure 1, top), with \textsuperscript{13}C NMR spectroscopy confirming the complete absence not only of ester but of C=O groups from each species (see Figure S3 in the Supporting Information). These data suggest that 2:1 reaction of TMA with ester has occurred, one equivalent of TMA expelling methoxide to induce the formation of a reactive EtMeC=O intermediate alongside Me\textsubscript{2}AlOMe\textsubscript{3} \textsuperscript{3} (\textdelta\textsubscript{1}H = 3.06, \textdelta\textsubscript{13}C = -0.59 ppm)\textsuperscript{30} before a second equivalent of TMA has reacted with the ketone to give the dimethylaluminium alkoxide Me\textsubscript{2}AlOCEtMe\textsubscript{2}. Integrals of peaks at \textdelta\textsubscript{1}H = 0.61 (2) and 3.06 ppm (3) suggest the two products to be present in a 1:1 ratio. Lastly, the observation that signals at \textdelta\textsubscript{1}H = -0.47 and \textdelta\textsubscript{13}C = -0.59 ppm reveal relative integrals of 2:1 leads us to speculate that 2 traps the final (unreacted) equivalent of TMA present to give Me\textsubscript{2}AlOCetMe\textsubscript{2}(TMA) 2(TMA) (Scheme 1). Based on these spectroscopic data we attribute what would be an unusual 4-membered Al\textsubscript{2}OC metallacycle to this adduct, in which four Me groups are equivalent, with the terminal groups (Me\textsubscript{t}) resonating.

Figure 1. The \textsuperscript{1}H spectra of aliquots from the reaction between TMA and methyl propionate 1 in toluene (\textdelta\textsubscript{1}H = 2.11 ppm) employing 3:1 (top), 2:1 (middle) and 1:1 (bottom) stoichiometries. The solvent is [D\textsubscript{6}]benzene. *Free TMA.
Evidence ratios (Figure 1, middle and bottom). The retention in a 3:1 ratio by the gradual replacement of esters with TMA to yield adduct at and TMA (Figure 1, bottom), with were retained in the 3:1 system reveals not only the interaction of this system. In contrast, the 2:1 TMA: (Scheme 1). In a similar vein, $^{13}$C NMR spectroscopy showed resonances at $\delta_C = -4.6$ and $-7.7$ ppm due to AlMe$_3$ and AlMe$_4$, respectively, the latter representing the superposition of signals attributable to both 1(TMA) and 2(TMA). Meanwhile, 3 was now clearly shown by the presence of a signal at $\delta_C = -11.1$ ppm. Both 2(TMA) and 3 were retained in the 3:1 system, with 1(TMA) now completely absent and a small amount of unretracted TMA identified at $\delta_C = -0.36$ ppm (Figure 1, top and Supporting Information Figure S3). $^{27}$Al NMR spectroscopy evidenced the trend from 1(TMA) towards the formation of 2(TMA) and 3 by the gradual replacement of a dominant signal at $\delta_{Al} = 185.0$ ppm in the 1:1 system (carbonyl-bonded 4-coordinate Al) with a signal at $\delta_{Al} = 156.2$ ppm in the 3:1 system (alkoxide-bonded 4-coordinate Al; Supporting Information Figures S3–S5).

Spectroscopy points to an Me$_3$Al$_2$(µ$^2$-Me)(µ$^2$-OEtMe$_2$) formulation based on a symmetrical OAl$_2$C metallacycle for 2(TMA). However, although this is similar to motifs previously proposed,[19] the thermal stability of such a motif has not hitherto been reported. With this in mind, the reaction mixture resulting from the introduction of TMA in toluene to 1 in a 3:1 ratio (spectroscopically characterized as ostensibly a 1:1 mixture of 2(TMA) and 3, Figure 1, top) was heated to reflux for 4 hours. NMR spectroscopic analysis of aliquots obtained after $t = 0$, 1, 2, 3 and 4 hours revealed a gradual thermal rearrangement (Figure 2 and Supporting Information Figure S6), with the spectra demonstrating the in situ reformation of free TMA ($\delta_{Al} = -0.36$ ppm ($^1$H after 4 hours)) alongside that of the new complex 2(3) = Me$_3$Al$_2$(µ$^2$-OMe)(µ$^2$-OEtMe$_2$) 4 (Scheme 2). Evidence bridging (AlMe$_4$) and four terminal (AlMe$_3$) AlMe groups, respectively, in a Me$_3$Al(µ$^2$-Me)AlMe$_4$ fragment and that 2(TMA) is symmetrical, metallacyclic Me$_3$Al$_2$(µ$^2$-Me)(µ$^2$-OEtMe$_2$) (Scheme 1). In a similar vein, $^{13}$C NMR spectroscopy showed resonances at $\delta_C = -4.6$ and $-7.7$ ppm due to AlMe$_3$ and AlMe$_4$, respectively, the latter representing the superposition of signals attributable to both 1(TMA) and 2(TMA). Meanwhile, 3 was now clearly shown by the presence of a signal at $\delta_C = -11.1$ ppm. Both 2(TMA) and 3 were retained in the 3:1 system, with 1(TMA) now completely absent and a small amount of unretracted TMA identified at $\delta_C = -0.36$ ppm (Figure 1, top and Supporting Information Figure S3). $^{27}$Al NMR spectroscopy evidenced the trend from 1(TMA) towards the formation of 2(TMA) and 3 by the gradual replacement of a dominant signal at $\delta_{Al} = 185.0$ ppm in the 1:1 system (carbonyl-bonded 4-coordinate Al) with a signal at $\delta_{Al} = 156.2$ ppm in the 3:1 system (alkoxide-bonded 4-coordinate Al; Supporting Information Figures S3–S5).

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for the symmetry of an O₆Al₃ ring in 4 comes from the development of a single Me₆ signal at δₖ = −0.48 ppm. Meanwhile, residual 2(TMA) (δₖ = −0.47 ppm) and 3 (δₖ = −0.59 ppm) remain clearly identifiable. Integrals suggest that thermal rearrangement of 2(TMA) + 3 to give 4 + TMA proceeds to around 54% completion after 4 hours under the conditions used.

Further investigation of the thermal rearrangement of 2(TMA) focused on the reaction mixtures resulting from the 1:1 and 2:1 reaction of TMA with 1 (spectroscopically characterized as ostensibly 1(TMA) (Figure 1, bottom) and a mixture of 1(TMA), 2(TMA) and 3 (Figure 1, middle), respectively) being heated to reflux for 2 hours. Data elucidate the processes in Equations 1 and 2:

\[ 1(TMA) + 2 TMA \rightarrow 2(TMA) + 3 \quad (1) \]

\[ 2(TMA) + 3 \rightarrow 4 + TMA \quad (2) \]

\[ 4 \rightarrow 2 + 3 \quad (3) \]

The use of 1:1 1:TMA without heating results in very limited reaction, with only traces of 2(TMA) and 3 existing alongside (dominant) 1(TMA) (δₖ = 2.98 ppm, Figure 1, bottom). Even heating fails to completely consume 1 and instead around 50% unreacted 1 can clearly be seen after 2 hours (δₖ = 3.32 ppm, Figure 3, bottom). This is explained by viewing 1 as reacting with 3 equivalents of TMA to yield 2(TMA) and 3, which then undergoes thermal exchange to give 4 + TMA. This latterly generated TMA can then react with remaining 1, eventually converting half the available 1 into 4. In the 1:2 1:TMA system, the greater amount of TMA present aids the formation of 2(TMA) + 3 [Eq. (1)] and Figure 3, top). These then act as a source of further 4 + TMA [Eq. (2)]. The eventual consequence of this cycle is the complete removal of both 1(TMA) and TMA from the system. This explains the formation of 4 only in this system. However, remnant 3 is also observed. This can be understood by the appearance of a further species (δₖ = 1.50, 1.15, 0.68, −0.40 ppm), which we attribute to 3. (We speculate that this product forms a dimer or trimer in solution based on the observation of a ²⁷Al NMR signal that, at δₖ = 155.1 ppm, is consistent with tetracoordinate metal.) It appears
then that 4 is in equilibrium with it constituents [Eq. (3)]; a fact most clearly suggested by noting the 1:1 ratio of the signals at δm = −0.40 and −0.59 ppm (2 and 3, respectively). Based on 1H NMR spectroscopy, this equilibrium lies heavily on the side of 4 (ca. 88:12 (2 + 3)).

Repeated attempts to isolate crystalline products of reaction between methyl propionate and TMA proved fruitless on account of a low melting point and led to the replacement of 1 with methyl phenylacetate 5 (Supporting Information, Figure S7) in an attempt to crystallographically verify the identities/structures of ester decomposition products. Hence, TMA in toluene was added dropwise to 5 (1:1, 2:1 or 3:1 TMA:5). NMR spectroscopic analysis of the resulting mixture revealed similar behaviour to that noted for the methyl propionate system, with the formation of initial adduct 5(TMA) in the presence of 1 equivalent of TMA followed by reaction to give 6(TMA) and 3 in the presence of more than 1 equivalent of TMA (Scheme 1 and Supporting Information Figures S8–S10). As with 2(TMA), the capture of excess TMA by 6 could be inferred from the 1H NMR spectroscopic observation of Al-bonded Me groups at high field (δm = −0.42 ppm (Mẽ)) and δm = 0.13 ppm (Mẽ)) in a 4:1 ratio alongside retention of the singlet at δm = −0.59 ppm due to 3 (see above). 13C NMR spectroscopy reinforced the co-presence of 3 alongside 6(TMA) through the observation of a broad high field resonance at δc = −11.1 ppm (3) alongside signals at δc = −4.5 (6(TMA), Mẽ) and −7.0 ppm (6(TMA), Mẽ). For the 3:1 TMA:5 combination, the liquid remaining after reaction was reduced in volume and stored at room temperature to produce colourless blocks. This reaction was repeated using a Lewis base returning just very similar results. Of these, only five show trapping TMA, demonstrating the highly unusual nature of this phenomenon. The nearest analogues of 6(TMA) are based on asymmetric bis(oxyphenyl) structures of type 1 (Figure 5) demonstrated by tetraaluminium bis(bis(oxyphenyl)-methyl)anthracene and -dibenzo-furan complexes[38] and the bisaluminium derivative of a 1,1′-bis-2,2′-oxynaphthyl ligand.[39] A type I motif has been recorded once also in heterobimetallic Al–Ti chemistry.[40]

The repeated observation that both 2(TMA) and 6(TMA) form alongside MeAlOMe 3 and that crystalline 6(TMA) is isolated contaminated by 3 led to attempts to separate the components. Efforts here took two forms. In one set of experiments, the solvent mixture was modified post-synthetically. Hence, the recrystallization of 6(TMA) (leading to the crystal structure shown in Figure 4) gave a crystalline material that analyzed by 1H NMR spectroscopy as an approximately 1:1 mixture of 6(TMA) and 3 (see Experimental Section, co-synthesis of 6(TMA) and 3, Method 1). This ratio accurately reflected that of the two products generated in the reaction, which point was simply evidenced by analysing an aliquot of the reaction mixture (see Experimental Section, spectroscopic characterization of 5 + 3 TMA). In contrast, the introduction of hexane prior to recrystallization vastly improved the purity with which crystalline 6(TMA) could be isolated (10:1 6(TMA):3 by 1H NMR spectroscopy; see Experimental Section, co-synthesis of 6(TMA) and 3, Method 2). An alternative approach involved attempting to solvate one component of the 3/6(TMA) mixture using a Lewis base. With this in mind, TMA in toluene was added to methyl phenylacetate in a 3:1 ratio under N2 at −78 °C. Removal of toluene was followed by the addition of excess Et2O. This resulted in the precipitation of a white solid, which was recrystallised by heating to give a solution and then storing at room temperature to produce colourless blocks. 1H NMR spectroscopic analysis suggested the presence of Ph but not of Et2O and high field signals previously attributed to TMA were absent. These data suggest the abstraction of TMA as an ether solvate,[41] leading to the crystallization of 6. This was confirmed crystallographically by the observation of a simple dimer based on an (AlO)₃ core of a type common in aluminium organooxide chemistry (Figure 6).[27b,28a]

**Conclusion**

In summary, the autocatalytic nature of the reaction between alkylchlorides and aluminium to give AlCl₃ and TMA has led us to study the reactions of TMA with model esters that mimic...
suitable crystals were attached to the goniometer in toluene) was purchased from Sigma–
were obtained at 25 °C. For 1H and 13C, chemical shifts are internally referenced to deuterated solvent and calculated relative to TMS. For 19Al, an external reference was used (1 mm AlCl3.H2O, in D2O). Chemical shifts are expressed in δ ppm. The following abbreviations are used: br = broad, m = multiplet, q = quartet, s = singlet, sh = shoulder, t = triplet.

Crystallographic details

Crystals were transferred from the mother liquor to a drop of perfluoropolyether oil mounted upon a microscope slide under cold nitrogen gas. Suitable crystals were attached to the goniometer head via a MicroLoopTM, which was then centred 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, with refinement, based on R, by full-matrix least squares. Non-hydrogen atoms were refined anisotropically and a riding model with idealized geometry was employed for the refinement of H-atoms. For 6, one BnMe3C group was modelled as disordered, though separate positions for the phenyl group could not be refined satisfactorily. The occupancy was refined, with restraints placed upon both the 1,2- and 1,3-distances and upon the anisotropic atomic displacement parameters. CCDC 1504652 and 1504653 contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

Spectroscopic characterization of EtC(O)OMe 1 + TMA reaction mixtures

TMA (1.5, 3.0 or 4.5 mL, 3, 6 or 9 mmol, 2.0 mL in toluene) was added dropwise to methyl propionate 1 (0.29 mL, 3 mmol) under a N2 atmosphere at −78 °C before being allowed to reach room temperature. The resulting solution was stirred for 2 hours at this temperature. An aliquot (0.1 mL) was mixed with [D6]benzene (0.7 mL) and analyzed by NMR spectroscopy, revealing 1(TMA), 2(TMA) and 3.

1: 1-TMA. 1H NMR spectroscopy (400 MHz, [D6]benzene): δ = 3.08 (s, 0.2H; 2 OMe), 2.98 (m, 3H; 1(TMA), OMe), 1.97 (m, 2H; 2(TMA) AlMe3), 1.42 (q, 0.1H; 2(TMA) CH2), 1.07 (s, 0.3H; 2(TMA) Me), 0.65 (m, 3.2H; 1(TMA)+2(TMA) CH2Me), 0.16 (s, 0.1H; 2(TMA) Me), −0.33 (m, 9H; 1(TMA), AlMe3), −0.49 (s, 0.3H; 2(TMA) Me), −0.60 ppm (s, 0.4H; 3 Me); 13C NMR (100 MHz, [D6]benzene): δ = −181.4 (17(TMA) CO), 79.5 (27(TMA) CO), 53.8 (17(TMA) OMe), 50.4 (13 OMe), 36.6 (2(TMA) CH2), 27.7 (17(TMA) CH2Me+2(TMA) Me), 8.8 (2(TMA) CH2Me), 8.2 (1(TMA) CH2Me), −7.7 ppm (11(TMA) AlMe); 29Al NMR (104 MHz, [D6]benzene): δ = 185.0 (1(TMA)), 157.7 ppm (2(TMA) + 3).

1: 2-TMA. 1H NMR spectroscopy (400 MHz, [D6]benzene): δ = 3.08 (s, 3H; 3 OMe), 2.94 (s, 2.4H; 1(TMA), OMe), 1.95 (q, 1.6H; 1(TMA) CH2), 1.42 (q, 2H; 2(TMA) CH2), 1.07 (s, 6H; 2(TMA) Me), 0.63 (t, 5.4H; 1(TMA)+2(TMA) CH2Me), 0.09 (br, s, 3H; 2(TMA) Me), −0.32 (s, 7.1H; 1(TMA), AlMe3), −0.49 (br, 12H; 2(TMA) Me), −0.60 ppm (s, 6H, 3 Me); 13C NMR (100 MHz, [D6]benzene): δ = −181.8 (1(TMA) CO), 79.5 (2(TMA) CO), 54.0 (1(TMA) OMe), 50.4 (3 OMe), 36.6 (2(TMA) CH2), 27.7 (1(TMA) CH2Me+2(TMA) Me), 8.8 (2(TMA) CH2Me), 8.2 (1(TMA) CH2Me), −4.6 (2(TMA) Me), −7.7 (br, 1(TMA)+2(TMA) Me), −11.1 ppm (3 Me); 29Al NMR (104 MHz, [D6]benzene): δ = −179.7 (sh., 1(TMA)), 153.9 ppm (2(TMA) + 3).

1: 3-TMA. 1H NMR spectroscopy (400 MHz, [D6]benzene): δ = 3.06 (s, 3H; 3 OMe), 1.41 (q, 2H; 2(TMA) CH2), 1.05 (s, 6H; 2(TMA) Me), 0.61 (t, 3H; 2(TMA) CH2Me), 0.09 (s, 3H; 2(TMA) Me), −0.36 (s, 3.5H; TMA), −0.47 (s, 12H; 2(TMA) Me), −0.59 ppm (s, 6H, 3 Me);
Thermal stability of 1:3 EtC(O)OMe 1:TMA reaction mixture

The reaction mixture at the end of the 1:3 reaction of 1 with TMA in toluene (to give 2(TMA) and 3; see above) was heated to reflux for 4 hours using an oil bath to form MeAlMe(OMe)2 and TMA. Aliquots (0.1 mL) were diluted with D2O benzene (0.7 mL) and analyzed by NMR spectroscopy after time, t = 0 (before heating), 1, 2, and 4 hours.

\[ t = 0 \text{ hr.} \quad \text{H NMR spectroscopy (400 MHz, [D6]benzene):} \quad \delta = 3.07 (s, 3H; 3 Me), 1.41 (s, 2H; 2(TMA) CH2), 1.06 (s, 7H; 2(TMA) Me), 0.62 (t, 3H; 2(TMA) CH2Me), 0.10 (s, 3H; 2(TMA) Me), -0.36 (s, br, 1.5H; TMA), -0.48 (s, 12H; 2(TMA) Me), -0.60 ppm (s, 6H; 3 Me); \]

\[ 1^1C \text{ NMR (100 MHz, [D6]benzene):} \quad \delta = 79.5 (2(TMA) CO), 50.4 (3 OMe), 36.6 (2(TMA) CH2), 27.7 (2(TMA) Me), 8.8 (2(TMA) CH2Me), -4.5 (2(TMA) Me), -7.4 (br, 4 Me + 2(TMA) Me), -9.5 ppm (3 Me). \]

\[ t = 2 \text{ hr.} \quad \text{H NMR spectroscopy (400 MHz, [D6]benzene):} \quad \delta = 3.07 (s, 1.7H; 3 OMe), 3.01 (s, 1.3H; 4 OMe), 1.43 (q, 0.8H; 4 CH2), 1.41 (q, 1.2H; 2(TMA) CH2), 1.09 (s, 2.5H; 4 Me), 1.06 (s, 3.5H; 2(TMA) Me), 0.66 (t, 1.3H; 4 CH2Me), 0.62 (t, 1.7H; 2(TMA) CH2Me), 0.10 (s, 1.5H; 2(TMA) Me), -0.36 (s, br, 4.5H; TMA), -0.48 (s, 7H; 2(TMA) Me), -0.49 (s, 9.5H; 4 Me), -0.60 ppm (3.5H; 3 Me); \]

\[ 1^13C \text{ NMR (100 MHz, [D6]benzene):} \quad \delta = 79.5 (2(TMA) CO), 77.0 (4 CO), 50.4 (3 OMe), 48.3 (4 OMe), 37.1 (4 CH) 36.6 (2(TMA) CH2), 28.1 (4 Me + 2(TMA) Me), 8.9 (4 CH2Me), 8.8 (2(TMA) CH2Me), -4.5 (2(TMA) Me), -7.4 (br, 4 Me + 2(TMA) Me), -9.5 ppm (3 Me). \]

\[ t = 3 \text{ hr.} \quad \text{H NMR spectroscopy (400 MHz, [D6]benzene):} \quad \delta = 3.07 (s, 1.5H; 3 OMe), 3.01 (s, 1.5H; 4 OMe), 1.44 (q, 1.4H; 4 CH2), 1.41 (q, 1.1H; 2(TMA) CH2), 1.10 (s, 3H; 4 Me), 1.06 (s, 3H; 2(TMA) Me), 0.66 (t, 1.5H; 4 CH2Me), 0.62 (t, 1.5H; 2(TMA) CH2Me), 0.10 (s, 1.5H; 2(TMA) Me), -0.35 (s, br, 4.5H; TMA), -0.47 (s, 6H; 2(TMA) Me), -0.48 (s, 6H; 4 Me), -0.59 ppm (s, 3H; 3 Me); \]

\[ 1^1C \text{ NMR (100 MHz, [D6]benzene):} \quad \delta = 79.5 (2(TMA) CO), 77.0 (4 CO), 50.4 (3 OMe), 48.3 (4 OMe), 37.1 (4 CH) 36.6 (2(TMA) CH2), 28.1 (4 Me + 2(TMA) Me), 8.9 (4 CH2Me), 8.8 (2(TMA) CH2Me), -4.5 (2(TMA) Me), -7.5 (br, 4 Me + 2(TMA) Me), -9.5 ppm (3 Me). \]

\[ t = 4 \text{ hr.} \quad \text{H NMR spectroscopy (400 MHz, [D6]benzene):} \quad \delta = 3.07 (s, 1.4H; 3 OMe), 3.02 (s, 1.6H; 4 OMe), 1.43 (q, 1.1H; 4 CH2), 1.41 (q, 0.9H; 2(TMA) CH2), 1.10 (s, 3.3H; 4 Me), 1.06 (s, 2.7H; 2(TMA) Me), 0.66 (t, 1.6H; 4 CH2Me), 0.62 (t, 1.4H; 2(TMA) CH2Me), 0.10 (s, 1.4H; 2(TMA) Me), -0.36 (s, br, 5H; TMA), -0.47 (s, 5.5H; 2(TMA) Me), -0.48 (s, 6.5H; 4 Me), -0.59 ppm (s, 2.8H; 3 Me); \]

\[ 1^13C \text{ NMR (100 MHz, [D6]benzene):} \quad \delta = 79.5 (2(TMA) CO), 77.0 (4 CO), 50.4 (3 OMe), 48.3 (4 OMe), 37.1 (4 CH) 36.6 (2(TMA) CH2), 28.1 (4 Me + 2(TMA) Me), 8.9 (4 CH2Me), 8.8 (2(TMA) CH2Me), -4.5 (2(TMA) Me), -7.5 (br, 4 Me + 2(TMA) Me), -9.5 ppm (3 Me). \]

Thermal stability of 1:1 and 1:2 EtC(O)OMe 1:TMA reaction mixtures

The reaction mixture at the end of the 1:1 and 1:2 reactions of 1 with TMA in toluene (to give 1(TMA), 2(TMA) and 3; see above) was heated to reflux for 2 hours using an oil bath. Aliquots (0.1 mL) were diluted with D2O benzene (0.7 mL) and analyzed by NMR spectroscopy.

\[ 1^1C \text{ NMR (100 MHz, [D6]benzene):} \quad \delta = 156.7 (2 + 3 + 4), 8.1 ppm (trace, unidentifed). \]

Spectroscopic characterization of BoC(O)OMe 5 + TMA reaction mixtures

As for 1:1-TMA but using methyl phenylacetate 5 (0.42 mL, 3 mmol) to give 5(TMA), 6(TMA) and 3. An aliquot (0.1 mL) was mixed with D2O benzene (0.7 mL) and analyzed by NMR spectroscopy.

\[ 1^3^1^S \text{ NMR spectroscopy (400 MHz, [D6]benzene):} \quad \delta = 7.13-8.66 (m, 5.5H; 5(TMA) + 6(TMA) Ph), 3.34 (s, 2H; 5(TMA) CH2), 3.07 (s, 0.4H; 3 OMe), 2.89 (s, 3H; 5(TMA) OMe), 2.86 (s, 0.2H; 6(TMA) CH2), 1.12 (s, 0.6H; 6(TMA) Me), -0.24 (m, 9H; 1(TMA), AlMe), -0.43 (s, 1.2H; 6(TMA) Me), -0.59 ppm (s, 0.8H; 3 Me); \]

\[ 1^3^1^C \text{ NMR (100 MHz, [D6]benzene):} \quad \delta = 178.5 (5(TMA) CO), 136.6, 131.7, 130.3, 128.1, 127.6 (5(TMA) + 6(TMA) Ph), 79.5 (6(TMA) CO), 54.0 (5(TMA) OMe), 50.7 (6(TMA) CH2), 50.4 (3 OMe), 40.7 (5(TMA) CH2), 28.0 (6(TMA) Me), -4.5 (6(TMA) Me), -7.0 (6(TMA) Me), -7.5 (5(TMA) Me), -11.2 ppm (3 Me); \]

\[ 2^1^H \text{ NMR (104 MHz, [D6]benzene):} \quad \delta = 180.5 (sh, 5(TMA)), 153.6 ppm (3 + 6(TMA)). \]

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Co-synthesis and characterization of BnMe$_2$COAIme(TMA) 6 (TMA) and 3

Method 1) TMA (4.5 mL, 9 mmol, 2.0 mol in toluene) was added dropwise to methyl phenylacetate (0.42 mL, 3 mmol) under a N$_2$ atmosphere at ~78 °C and allowed to reach room temperature. The resulting solution was stirred and generated heat. After 2 hours the solution was placed under vacuum to remove the toluene. The remaining liquid was stored at 4 °C for 1 day, producing colourless crystals of 6(TMA) and 3. Combined yield of 6(TMA) and 3: 910 mg (83% of the total mass expected); m.p. < 30 °C; H NMR spectroscopy (400 MHz, [D$_6$]benzene): δ = 7.05-6.84 (m, 5 H; 6(TMA) Ph), 3.06 (s, 3 H; 3 OMe), 2.86 (s, 2 H; 6(TMA) CH$_2$), 1.11 (s, 6 H; 6(TMA) Me). 0.13 (s, 3 H; 6(TMA) Me). –0.60 ppm (s, 6 H; 3 Me); 13C NMR (100 MHz, [D$_6$]benzene); δ = 136.7, 130.3, 128.0, 126.7 (6(TMA) Ph), 79.5 (6(TMA) CO), 50.7 (6(TMA) CH$_2$), 50.4 (3 OMe), 28.0 (6(TMA) Me). –4.5 (6(TMA) Me) –7.0 (6(TMA) Me); –11.1 ppm (3 Me); $^{31}$Al NMR (104 MHz, [D$_6$]benzene); δ = 154.0 ppm (3 + 6(TMA)).

Method 2) As for Method 1 but after stirring the reaction mixture for 2 hours the solution was placed under vacuum to remove the toluene. The remaining liquid was treated with hexane (1 mL) and the resulting solution stored at ~20 °C for 1 day, producing a small quantity of colourless crystals. Combined yield of 6(TMA) and 3: 240 mg (22% of the total mass expected); m.p. 68–70 °C; H NMR spectroscopy (400 MHz, [D$_6$]benzene): δ = 7.05–6.84 (m, 5 H; 6(TMA) Ph), 3.05 (s, 0.3 H; 3 OMe), 2.86 (s, 2 H; 6(TMA) CH$_2$), 1.11 (s, 6 H; 6(TMA) Me), 0.12 (s, 3 H; 6(TMA) Me), –0.42 (s, 12 H; 6(TMA) Me), –0.58 ppm (s, 0.6 H; 3 Me); $^{13}$C NMR (100 MHz, [D$_6$]benzene): δ = 136.7, 130.3, 128.1, 126.7 (6(TMA) Ph), 79.5 (6(TMA) CO), 50.7 (6(TMA) CH$_2$), 28.0 (6(TMA) Me), –4.5 (6(TMA) Me), –7.0 ppm (6(TMA) Me); $^{31}$Al NMR (104 MHz, [D$_6$]benzene); δ = 155.4 ppm (3 + 6(TMA)); satisfactory elemental analysis could not be achieved.

Synthesis and characterization of BnMe$_2$COAIme$_2$ 6

TMA (4.5 mL, 9 mmol, 2.0 mol in toluene) was added dropwise to methyl phenylacetate (0.42 mL, 3 mmol) under a N$_2$ atmosphere at ~78 °C before being allowed to attain room temperature. The resulting solution was stirred and generated heat. After 2 hours the solution was placed under vacuum to remove the toluene. The remaining liquid was treated with EtO (3 mL) to give a white precipitate that dissolved upon gentle heating. Colourless prismatic crystals formed as the mixture cooled to room temperature and over a period of 1 day produced a large crop of 6. Yield 417 mg (67% w/w TMA); m.p. 124–126 °C; H NMR spectroscopy (400 MHz, [D$_6$]benzene): δ = 7.07–6.92 (m, 5H; Ph), 3.00 (s, 2H; CH$_2$), 1.22 (s, 6H; Me), –0.28 ppm (s, 6H; AlMe); $^{13}$C NMR (100 MHz, [D$_6$]benzene); δ = 137.1 (1–Ph), 130.4 (o-Ph), 128.3 (m-Ph), 126.6 (p-Ph), 77.6 (CO), 51.2 (CH$_2$), 28.5 (Me), –5.7 ppm (AlMe); $^{31}$Al NMR (194 MHz, [D$_6$]benzene); δ = 179.8 ppm; elemental analysis calcd (%) for C$_{22}$H$_{18}$Al$_2$: C 69.88, H 9.29; found: C 68.73, H 9.70; X-ray crystal data: C$_{30}$H$_{24}$Al$_2$: M = 412.50, monoclinic, space group P2$_1$/c; a = 11.9568(5), b = 8.7121(4), c = 23.7485(10) Å, β = 98.5772(2) °; V = 2446.19(18) Å$^3$, Z = 4, $\rho_{calc}$ = 1.120 cm$^{-1}$, $\mu$ = 1.182 mm$^{-1}$, T = 180(2)K, 34603 data (4334 unique, R$_p$ = 0.0301, R = 0.6637) were collected. wrR = $\Sigma$(w$F^2$/F$^2$) = 0.0994, conventional R = 0.0340 on F values of 4013 reflections with F$^2$ > 2σ(F$^2$). GoF = 1.063, 282 parameters. Max. peak/hole = 0.281 eÅ$^{-3}$.

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