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# Reaction of trimethylaluminium with main group hydroxides: a non-hydrolysis route to methylalumoxane †

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**Reaction of $AlMe_3$ with $[(^tBu)_2Ga(\mu\text{-}OH)]_3$ or $Ph_3EOH$ (E = Sn, Pb) yields catalytically active MAO, $[MeAlO]_n$, along with $(^tBu)_2GaMe$ and $Ph_3EMe$, respectively, in contrast, the reaction with $Ph_3EOH$ (E = C, Si, Ge) yields $[Me_2Al(\mu\text{-}OEPh_3)]_2$; the formation of MAO is proposed to occur *via* hydroxide exchange and the formation of unstable $[Me_2Al(\mu\text{-}OH)]_n$; the propensity towards alkane elimination *versus* hydroxide exchange is controlled by the relative Brønsted acidity of the main group hydroxide.**

Gaining insight into the mechanism of formation for methylalumoxane ($[MeAlO]_n$, MAO) is an important step in the development of synthetic strategies to yield MAO with high and (perhaps more importantly) consistent catalytic activity. The most common method for formation of MAO is the reaction of $AlMe_3$ with water.[1] Unfortunately, the complex nature of this reaction has made it difficult to study in detail. However, through the study of model systems, some understanding of the mechanism has been gained. [2–4] The hydrolysis of $AlMe_3$ is not the only reported method for the synthesis of alkylalumoxanes.[5–7] One of the more unusual methods for the synthesis of an alkylalumoxane involves the reaction of the trimeric hydroxide $[(^tBu)_2Ga(\mu\text{-}OH)]_3$ with $Al(^tBu)_3$.[3] It was proposed that the formation of $Ga(^tBu)_3$ as the major gallium-containing product indicates that hydroxide exchange between gallium and aluminium occurs (eqn. (1)) preferentially to the condensation elimination reaction between the gallium hydroxide and aluminium alkyl.

$$Al(^tBu)_3 + 1/3\,[(^tBu)_2Ga(\mu\text{-}OH)]_3 \rightarrow 1/n\,[(^tBu)_2Al(\mu\text{-}OH)]_n + Ga(^tBu)_3 \quad (1)$$

Subsequent condensation of the aluminium hydroxide, $[(^tBu)_2Al(\mu\text{-}OH)]_n$, yielded the alumoxane, $[(^tBu)Al(\mu_3\text{-}O)]_8$. It would be reasonable to expect that the reaction of $[(^tBu)_2Ga(\mu\text{-}OH)]_3$ with $AlMe_3$ would yield MAO. Precedent for this proposal is found in the exchange reactions observed between $AlR_3$ and aluminium tris-alkoxides[8] or $(Ph_3Sn)_2O$.[9] We have undertaken an investigation into the reactivity of $AlMe_3$ with $[(^tBu)_2Ga(\mu\text{-}OH)]_3$ as well as the main group hydroxides, $Ph_3EOH$ (E = C, Si, Ge, Sn, Pb).

The reaction of $[(^tBu)_2Ga(\mu\text{-}OH)]_3$ with $AlMe_3$ in toluene solution at room temperature yields MAO and $(^tBu)_2GaMe$. The formation of MAO was confirmed by $^1H$ NMR spectroscopy which exhibits a broad featureless resonance between 0.5 and −0.5 ppm indicative of MAO.[10] The identity of $(^tBu)_2GaMe$ was also confirmed by comparison of the known $^1H$ and $^{13}C$ NMR shifts.[11] In addition, an examination of the polymerization of ethylene using $Cp_2ZrCl_2$ as a catalyst showed that the catalytic activity of the MAO formed from this reaction is comparable to that of commercial samples under similar Al : Zr ratios.‡ The formation of $(^tBu)_2GaMe$ in almost quantitative yield (based upon $^1H$ NMR) suggests that hydroxide/methyl exchange occurs between $[(^tBu)_2Ga(\mu\text{-}OH)]_3$ and $AlMe_3$, resulting in the formation of $[Me_2Al(\mu\text{-}OH)]_n$, which has been previously shown to be unstable, even at low temperatures, with regard to methane elimination and MAO formation.[12]

MAO formation is also observed for the reaction of $Ph_3SnOH$ and $Ph_3PbOH$ with $AlMe_3$, along with the associated exchange product, eqn. (2).

$$AlMe_3 + Ph_3EOH \rightarrow Ph_3EMe + [MeAlO]_n + MeH \quad (2)$$
$$E = Pb, Sn$$

As described above, the presence of MAO is confirmed by NMR and catalysis measurements,‡ while $Ph_3SnMe$ and $Ph_3PbMe$ were confirmed by comparison to the known NMR chemical shifts.[13,14] In addition, $Ph_3SnMe$, and $Ph_3PbMe$ may be isolated in essentially quantitative yield by hydrolysis of the reaction mixture followed by extraction with $Et_2O$.

In contrast to the tin and lead derivatives, the reaction of $Ph_3EOH$ (E = C, Si, Ge) with $AlMe_3$ in toluene at room temperature did not yield MAO, but rather dimeric $[Me_2Al(\mu\text{-}OEPh_3)]_2$ [E = C,[6] Si (**1**), Ge (**2**)] eqn. (3). All the dimethylaluminium compounds, $[Me_2Al(\mu\text{-}OEPh_3)]_2$, may be purified by recrystallization from $CH_2Cl_2$ and characterized by $^1H$, $^{13}C$, and $^{27}Al$ NMR spectroscopy.§

$$AlMe_3 + Ph_3EOH \rightarrow 1/2\,[Me_2Al(\mu\text{-}OEPh_3)]_2 + MeH \quad (3)$$
$$E = C,\ Si\ (\mathbf{1}),\ Ge\ (\mathbf{2})$$

The reaction of $Ph_3EOH$ (E = C, Si, Ge) with $AlMe_3$ occurs preferentially through an alkane elimination, in a similar manner to that observed for simple alcohols,[15] whereas the tin and lead analogs appear to undergo a reaction *en route* to MAO that is analogous to the hydroxide/methyl exchange observed for $[(^tBu)_3Ga(\mu\text{-}OH)]_3$. This observation poses the following question: *what property of the Group 14 hydroxide determines its reactivity?*

We have observed that C-methylation of aluminium alkoxides occurs with increasing ease for derivatives of stable carbocations in the presence of suitable Lewis acid catalysts.[16] Although the stability of the cations, $[Ph_3E]^+$ (E = Sn, Pb), are lower than the analogous carbocation, it may be reasonable to suggest that the reaction of $Ph_3EOH$ (E = Sn, Pb) with $AlMe_3$ results in the formation of $[Me_2Al(\mu\text{-}OEPh_3)]_2$, which subsequently decomposes *via* the formation of $[Ph_3E]^+$. Oliver and co-workers, however, have reported that $[Me_2Al(\mu\text{-}OSnPh_3)]_2$ may be isolated from the reaction of $(Ph_3Sn)_2O$ with $AlMe_3$.[9] We have prepared $[Me_2Al(\mu\text{-}OSnPh_3)]_2$ by this route, and found that it is not converted to MAO and $Ph_3SnMe$ under the conditions employed for the reaction of $Ph_3EOH$ (E = Sn, Pb) with $AlMe_3$. Furthermore, no decomposition of $[Me_2Al(\mu\text{-}OSnPh_3)]_2$ is observed after refluxing in toluene (110 °C) for 6 hours in the presence of 1 molar equivalent of $AlMe_3$. Thus, the formation of MAO using $Ph_3EOH$ (E = Sn, Pb) does not involve the formation of $[Me_2Al(\mu\text{-}OEPh_3)]_2$ intermediates.

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† Electronic supplementary information (ESI) available: full experimental details and listings of spectral data. See http://www.rsc.org/suppdata/dt/b1/b104578b/

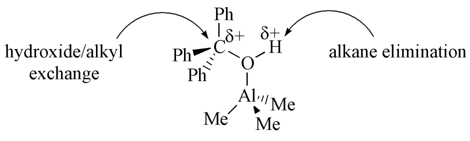
**Table 1** Relationship between the $^1H$ NMR chemical shift of the hydroxide in $Ph_3EOH$ and the reaction products

| Hydroxide | $^1H$ NMR $\delta$ O$H$ | Product | Reaction |
|---|---|---|---|
| $Ph_3COH$ | 2.36 | $[Me_2Al(\mu-OCPh_3)]_2$ | Alkane elimination |
| $Ph_3SiOH$ | 1.82 | $[Me_2Al(\mu-OSiPh_3)]_2$ | Alkane elimination |
| $Ph_3GeOH$ | 1.45 | $[Me_2Al(\mu-OGePh_3)]_2$ | Alkane elimination |
| $[(^tBu)_2Ga(OH)]_3$ | 0.78 | MAO + $(^tBu)_2GaMe$ | Hydroxide exchange |
| $Ph_3SnOH$ | 0.56 | MAO + $Ph_3SnMe$ | Hydroxide exchange |
| $Ph_3PbOH$ | 0.42 | MAO + $Ph_3PbMe$ | Hydroxide exchange |

Alkane elimination for $AlMe_3$ is ordinarily associated with the reaction of Brønsted acids, while the alkoxide/alkyl exchange (*cf.*, eqn. (1)) is associated with the Lewis basic properties of the alkoxide ligand. Since the Lewis basicity of the hydroxide oxygen should be similar, the defining property for $Ph_3EOH$ would be the acidity of the hydroxide hydrogen. We have previously shown that a good correlation exists between the Brønsted acidity of a hydroxide and the $^1H$ NMR chemical shift of the O$H$.[17] A down field hydroxide proton correlates with an acidic hydroxide. Since all the $Ph_3EOH$ compounds are structurally equivalent, with the exception of the central metal, a change in the $\delta$ O$H$ should reflect the relative acidity of the hydroxide. The hydroxide $^1H$ NMR chemical shifts for $Ph_3EOH$ and the products of the reaction of $AlMe_3$ are given in Table 1, along with the relative position of $[(^tBu)_2Ga(OH)]_3$. In moving down the Group 14 period from E = C to Pb, there is a partition in the relative acidity of the hydroxide O$H$ that occurs between $Ph_3GeOH$ ($\delta = 1.45$) and $Ph_3SnOH$ ($\delta = 0.56$). This partition coincides with the change in observed reactivity. Thus, the more acidic hydroxides undergo alkane elimination, whereas the more basic hydroxides undergo hydroxide exchange.

The Brønsted acidity *per se* does not appear to be the only factor that determines whether $Ph_3EOH$ undergoes hydroxide/methyl exchange or methane elimination in the presence of $AlMe_3$. As noted above, if $AlMe_3$ is reacted with $Ph_3COH$ at room temperature the alkane elimination product, $[Me_2Al(\mu-OCPh_3)]_2$ is formed. When this reaction is carried out at −78 °C, however, a bright yellow solution is observed, which dissipates as the temperature is raised. Analysis of the reaction products by $^1H$ NMR shows that, in addition to $[Me_2Al(\mu-OCPh_3)]_2$, the presence of $Ph_3CMe$ and MAO is observed. The fraction of the products associated with hydroxide/methyl exchange increases the longer the reaction mixture is held at −78 °C. The relative fraction of the hydroxide exchange reaction increases from 5 to 13% as the reaction time increases from 1 to 48 hours. Thus, it appears that at low temperatures the two reactions are competing.

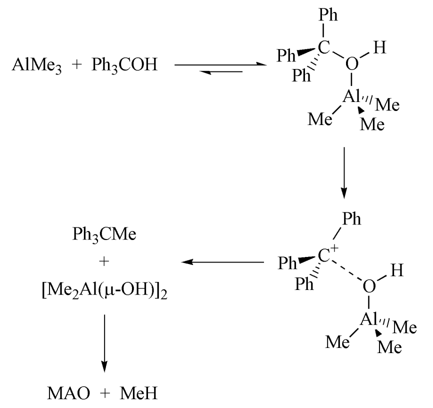
It is known that Lewis acid–base complexes of $AlMe_3$ are formed at low temperature and that adduct formation is a "dead-end" to alkane elimination.[18] Furthermore, we have shown that the coordination of an alcohol to $AlR_3$ increases the acidity of the OH significantly (**I**).[4] Clearly a similar effect will be felt by the carbon, resulting in the carbon becoming more electrophilic, allowing for alkylation by $AlMe_3$ (**I**).



**I**

Alternatively, placing increased positive charge on the carbon would stabilize the formation of the $[Ph_3C]^+$ cation, the presence of which is indicated by the distinctive yellow color of the solution.[19] The formation of a $[Ph_3C]^+[AlMe_3(OH)]^-$ ion pair by heterolytic cleavage of the C–O bond, followed by alkyl transfer to the $[Ph_3C]^+$ cation, would yield $[Me_2Al(\mu-OH)]_n$, which decomposes to MAO.[12] A summary of the proposed reaction is shown in Scheme 1.

The temperature dependent partition between hydroxide exchange and alkane elimination is also observed for aluminium hydrides. The reaction of $Ph_3COH$ and $(^iBu)_2AlH$ was carried out at both room temperature and −78 °C. The reaction at −78 °C yielded $Ph_3CH$ and isobutylalumoxane (IBAO) in quantitative yield. The resulting $Ph_3CH$ was identified by comparison with a genuine sample, while the IBAO was found to be catalytically active by polymerization testing. In contrast, the reaction at room temperature yielded $(^iBu)_2Al(OCPh_3)$ (**3**)§ and hydrogen.



**Scheme 1** Proposed low temperature reaction of $AlMe_3$ with $Ph_3COH$.

We have demonstrated that $AlMe_3$ reacts with low acidity main group hydroxides to yield MAO *via* a proposed hydroxide/alkyl exchange reaction. Furthermore, MAO may be formed from the reaction with acidic hydroxides if the reaction is carried out at sufficiently low temperatures to inhibit alkane elimination. The presence of a bright yellow color and UV-vis absorption characteristic of the $[Ph_3C]^+$ cation suggests that the hydroxide exchange is promoted by the stability of the carbocation. The absence of this bright yellow color or the hydroxide exchange products during the room temperature reaction indicates that hydroxide exchange is favored at low temperature and that alkane elimination is favored at high temperature. We are continuing our investigation of alternative routes to MAO, as well as a full investigation as to the relative catalytic activity of MAO prepared by various routes.

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## Notes and references

‡ To a sample of MAO solution (*ca.* 7 mmol Al) was added $Cp_2ZrCl_2$ (*ca.* 0.1 mol%), and the resulting mixture stirred for 30 minutes. Ethylene was then bubbled through the reaction mixture for 10 minutes at room temperature. Quenching with methanol and filtration resulted in the isolation of polyethylene as characterized by $^{13}C$ CPMAS NMR and TGA analysis. Polymerization activities were in the range of 1300–1600 kg PE (mol Zr)$^{-1}$.

§ **$[Me_2Al(\mu-OSiPh_3)]_2$ (1).** $^1H$ NMR: $\delta$ 7.62 (12H, m, *o*-C$H$), 7.15 (18H, m, *m*-, *p*-C$H$), −0.63 (12H, s, Al–C$H_3$). $^{13}C$ NMR: $\delta$ 136.5 (Si–$C$), 133.3 (*o*-CH), 130.9 (*p*-CH), 128.3 (*m*-CH), −6.6 (Al–$C$H$_3$). $^{27}Al$ NMR: $\delta$ 138 ($W_{1/2}$ = 9,800 Hz).

**$[Me_2Al(\mu\text{-}OGePh_3)]_2$ (2).** $^1$H NMR: $\delta$ 7.72 (12H, m, *o*-C*H*), 7.15 (18H, m, *m*-, *p*-C*H*), −0.59 (12 H, s, Al–C*H*$_3$). $^{13}$C NMR: $\delta$ 135.4 (Ge–*C*), 133.7 (*o*-*C*H), 131.2 (*p*-*C*H), 128.1 (*m*-*C*H), −7.2 (Al–*C*H$_3$). $^{27}$Al NMR: $\delta$ 140 ($W_{1/2}$ = 7,900 Hz).

**$(^iBu)_2Al(OCPh_3)$ (3).** $^1$H NMR: $\delta$ 7.55 [6H, d, *J*(H–H) = 8.15 Hz, *o*-C*H*], 7.19 (6H, m, *o*-CH), 7.06 [3H, t, *J*(H–H) = 7.3 Hz, *p*-C*H*], 1.66 [1H, sept, *J*(H–H) = 6.4 Hz, C*H*(CH$_3$)$_2$], 0.80 [6H, d, *J*(H–H) = 6.8 Hz, CH(C*H*$_3$)$_2$], 0.01 [2H, d, *J*(H–H) = 6.3 Hz, Al–C*H*$_2$]. $^{13}$C NMR: $\delta$ 145.0 (OC*C*), 128.8 (*o*-*C*H), 131.1 (*p*-*C*H), 131.3 (*m*-*C*H), 90.7 (OC), 28.7 [CH(*C*H$_3$)$_2$], 25.4 [*C*H(CH$_3$)$_2$]. Full charactrisation details are available as ESI.†

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