Modification of aluminium alkoxides with dialkylmalonates

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Monatsh Chem (2010) 141:717–727
DOI 10.1007/s00706-010-0317-1

Abstract Depending on the reaction conditions, different aluminium dialkylmalonate derivatives were obtained by reaction of aluminium alkoxides Al(OR)₃ (R = Et, iPr, tBu) with dialkylmalonates, viz. Al(malonate)₃ (malonate = dimethyl, diethyl, di-i-propyl and di-t-Butyl malonate), Al₂(OiPr)₄(malonate)₂ (malonate = di-i-propyl and di-t-Butyl malonate), Al₂(OiPr)₂(dii-propylmalonate)₄ and Al₃(OH)(OEt)₃(diethylmalonate)₅. All compounds were characterized by NMR spectroscopy, and single crystal structure analyses are reported for each type of compound. An Al₂(OiPr)₂(dialkylmalonate)₄ derivative was only obtained by disproportionation of Al₂(OiPr)₄(di-i-propylmalonate)₂, but not by reaction of Al(OiPr)₃ with dialkylmalonates in the corresponding molar ratio. Reactions of Al(OiBu)₃ only resulted in Al(malonate)₃ derivatives, but no transesterification was observed, contrary to the reaction of Al(OiPr)₃ with dimethyl or diethyl malonate.

Keywords Aluminium alkoxides · Dialkylmalonates · ²⁷Al NMR spectroscopy

Introduction

Substitution of one or more alkoxo groups of metal alkoxides by bi- or multidentate ligands is a well known and frequently used method to lower the reactivity of the metal alkoxides upon hydrolysis and to avoid formation of precipitates instead of gels during sol–gel processing [1]. This is achieved by reducing the number of hydrolysable alkoxo groups, blocking of coordination sites at the metal centre and lowering the Lewis acidity of the metal centre [2].

A consequence of the Lewis acidity of the metal centres is the strong tendency of metal alkoxides to form alkoxo-bridged oligomers to attain higher coordination numbers. The degree of oligomerization is inversely correlated to the steric demand of the alkoxo group. Taking aluminium alkoxides as an example, dimeric [Al(OtBu)₃]₂ is formed with tert-butoxo groups, tetrameric [Al(OiPr)₃]₄ with iso-propoxo groups, and even larger oligomeric, linear species [Al(OEt)₃]ₙ with ethoxo groups [3–7]. This tendency to form oligomers is retained after modification with organic ligands. For example, Al alkoxides and siloxides are known to form mono-, di-, tri- or oligomeric species after modification with β-diketones [8–10].

Various ligand classes have been used for the modification of metal alkoxides, e.g. β-diketonates, β-ketoesters, amines, aminoalcoholates or oximates [11]. A systematic study on reactions of Al(OiPr)₃ with β-ketoesters recently showed a dependence of the formed species on the reaction temperature. Formation of trisubstituted Al(β-ketoesterate)₃ is favoured at room temperature, independent of the applied stoichiometric ratio. To obtain monosubstituted Al₂(OiPr)₄ (β-ketoesterate)₂ (i.e. Al/ketoesterate ratio = 1) higher reaction temperatures had to be applied or alternatively Al(OiPr)₃ had to be thermally de-oligomerized prior to the reaction. No influence of the β-ketoester OR groups was observed, except for the reaction with tert-butyl acetacetate, where transesterification was observed [12]. Based on these results, we investigated the modification of aluminium alkoxides with dialkylmalonates. To the best of our knowledge, no structural investigations on dialkylmalonate-
substituted aluminium alkoxides were reported until the present work. Only the modification of some metal chlorides or amides with malonates for use as metal-organic chemical vapour deposition (MOCVD) precursors or polymerization catalysts has been reported [13–19].

The use of dialkylmalonates also opens an opportunity to introduce functional groups, e.g. polymerizable groups for the use as precursors for inorganic–organic hybrid materials with dual network structures [20]. Compared to \( \beta \)-ketoesters, where ligands such as allyl acetooxime (aaa-H) or 2-(methacryloyloxy)ethyl acetooxime (meaa-H) are coordinated to Ti, Zr or Al alkoxides [12, 21–24], dialkylmalonates can accommodate two functional groups per ligand and therefore introduce twice as many functionalities. Compared to \( \beta \)-ketoesterate ligands, a further benefit is that owing to the symmetric nature of malonates, the number of possible stereoisomers is reduced and spectroscopic characterization therefore is eased. For example, one \( C_3 \)- and three \( C_1 \)-symmetric isomers coexist for the \( \beta \)-ketoester derivatives Al(\( \beta \)-ketoesterate). This gives rise to four sets of signals in the NMR spectra, complicating their interpretation [12].

In this contribution, we report our results on the modification of Al(OR)\(_3\) (R = tBu, iPr, Et) with dimethyl (dmem-H), diethyl (detm-H), di-iso-propyl (diprm-H) and di-tert-butyl (dtbum-H) malonate (Fig. 1).

Formation, structure and stability of dialkylmalonate derivatives were studied, including investigation of transesterification as a possible side reaction, depending on the OR groups of the malonate ligand, the Al(OR)\(_3\) precursor and the reaction conditions. The results are compared to analogous reactions with \( \beta \)-diketones and \( \beta \)-ketoesters.

**Results and discussion**

**Al(dialkylmalonate)\(_3\)** complexes

As expected, dialkylmalonates had a lower reactivity towards aluminium alkoxides compared to \( \beta \)-ketoesters due to the presence of a second OR substituent. No reaction with [Al(OiPr)\(_3\)]\(_4\) was observed at room temperature.

Reaction at higher temperatures led to the desired products, although longer reaction times were necessary.

Monomeric complexes Al(dialkylmalonate)\(_3\) (1) were prepared by reacting Al(OiPr)\(_3\) or Al(OtBu)\(_3\) with the corresponding dialkylmalonates in a 1:3 stoichiometric ratio (Eq. 1). The complexes 1 lack Al–OR groups and are therefore not standard sol–gel precursors, but they are important for the complete characterization of the other products with a lower degree of substitution (see below) and also prove the possibility to directly replace OiPr groups at the Al centre by dialkylmalonate without requiring additional reagents for deprotonation of the malonate.

\[
\text{Al(OiPr)\(_3\)} + 3 \text{RO} \rightarrow \text{Al} - \begin{array}{ccc}
\text{O} & \text{OR} & \text{O} \\
\text{OR} & \text{OR} & \text{OR}
\end{array} + 3 \text{iPrOH}
\]

The complexes Al(diprm)\(_3\) (1c) and Al(dtbum)\(_3\) (1d) were obtained by reacting Al(OiPr)\(_3\) with diprm-H or dtbum-H in toluene at 60 or 80 °C. The reactions with dmem-H and detm-H were less straightforward and resulted in products giving NMR spectra with multiple, broad and overlapping resonances. A closer look revealed that transesterification, i.e. exchange of the malonate OR’ groups with OiPr groups, had taken place concomitantly, which was inter alia indicated by the formation of free diprm-H and coordinated diprm, but formation of 1a or 1b could not be confirmed. Transesterification was not quantitative, and malonate species with both OiPr and OMe/OEt groups as well as Al(OEt)\(_3\)/Al(OMe), species were spectroscopically identified. Furthermore, there was no complete substitution and formation of Al(dialkylmalonate)\(_3\) species.

Since the degree of oligomerization of Al(OiPr)\(_3\) in solution is known to be temperature-dependent [25], [Al(OiPr)\(_3\)]\(_4\) was de-oligomerized prior to the reaction with the dialkylmalonates. This strategy was proven successful in the reaction with \( \beta \)-ketoesters [12]. A solution of [Al(OiPr)\(_3\)]\(_4\) in toluene was thus heated to reflux for 3 days and, after cooling to room temperature, dmem-H or detm-H was added. After stirring overnight at room temperature coordination of the malonate was confirmed by NMR spectroscopy, but again transesterification was observed to a large extent. These results demonstrate that (1) de-oligomerization accelerates substitution of alkoxo groups and enables the reaction at room temperature, but (2) does not prevent transesterification.

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**Fig. 1** Dialkylmalonates used for the modification of Al(OR)\(_3\)**
Compound 1c also was prepared by an alternative solvent-free reaction procedure, in which Al(OiPr)₃ was reacted with ten equivalents of diprm-H. Since neither [Al(OiPr)₃]₄ nor Al(diprm)₃ are very soluble in diprm-H and the reaction mixture stayed heterogeneous at 120 °C, it is supposed that thermally de-oligomerized Al(OiPr)₃ species were dissolved in diprm-H, where they reacted to give Al(diprm)₃, which then precipitated. Of course, mono- and disubstituted intermediates also have to be soluble in diprm-H.

To study the influence of the OR groups of Al(OR)₃, analogous reactions were carried out starting from Al(OrBu)₃. As a consequence of the bulkier tert-butoxo groups, dimeric [Al(OrBu)₃]₂ is the predominant species at room temperature and elevated temperatures, also in solution. As for de-oligomerized Al(OiPr)₃, coordination of malonate can already be observed at room temperature, although the reaction is slow. To accelerate the reaction, the temperature was raised to 50 °C and all Al(malonate)₃ complexes 1a–1d were obtained under these conditions. This reveals that the bulkiness of the OrBu is overcome by the easier accessibility of the tetrahedral Al centre in [Al(OrBu)₃]₂. Compared to Al(OiPr)₃, transesterification was not observed for Al(OrBu)₃ in any case, showing that the tendency to undergo transesterification depends on the steric demand of the alkoxy groups.

NMR spectroscopic characterization of 1a–1d in solution (C₆D₆, toluene-d₈) confirmed the expected symmetric octahedral structure showing only one signal for COC in the 1H (4.81–4.99 ppm) and 13C (66.2–69.0 ppm) NMR spectra as well as for CO (175.5–175.9 ppm). Interestingly, the signals for OCH(CH₃)₂ in 1c split into two doublets, whereas only one signal for COOCH(CH₃)₂ was observed. No significant influence on the 1H and 13C NMR shifts upon variation of the ester alkoxo group was found. 27Al NMR spectroscopy of 1c additionally confirmed the structure, showing only one sharp signal for octahedrally coordinated Al at 5.3 ppm [7].

Single crystal X-ray diffraction (XRD) of 1a and 1d (Fig. 2) revealed nearly ideal octahedral coordination around the central aluminium atom, with negligible differences in Al–O bond distances (186.9(1)–189.3(1) pm) and bite angles of the malonates very close to 90° (90.39(4)–91.36(4)°). Interestingly, the bond distances are distinctly shorter than those observed for Al–O ester bonds in Al(tet-buty1 acetoacetate)₃ [26] (193.0(2)–195.1(2) pm) and are more in the range of the Al–O keto distances (185.7(2)–186.8(2) pm) in the same complex [27] or in Al(acac)₃ (acac = acetylacetonate) (188.0(2) pm) [27].

In both complexes, two of the metallacycles formed by the coordination of the malonate ligand exhibit an envelope-like conformation with Al deviating from the O–C–CH–C–O plane, whereas the third metallacycle exhibits a nearly planar or slightly twisted conformation. The same combination of ligand conformations was observed for the mentioned β-diketonate and β-ketoesterate derivatives [26, 27].

**Fig. 2** Molecular structure of 1d (hydrogen atoms omitted for clarity)

Modification of Al(OiPr)₃ with dmem-H and detm-H in a stoichiometric ratio of Al/malonate = 1:1 also gave product mixtures through transesterification at the ester group as well as the Al centre. For the reaction with one equivalent of diprm-H or dbrum-H per Al, complexes of the composition Al₂(OiPr)₃(malonate)₂ (2c, malonate = diprm; 2d, malonate = dbrum) were obtained. Similar to analogous β-ketoesterate-substituted complexes [12], higher reaction temperatures and longer reaction times had to be applied.

The structure of 2 consists of one tetrhedrally coordinated Al centre surrounded by two terminal and two bridging OiPr groups, whereas the second Al centre is octahedrally coordinated by two bridging OiPr groups and two chelating malonate ligands (Fig. 3).

Contrary to β-ketoesterate-substituted complexes only one isomer is expected because of the symmetric dialkylmalonate ligands. This was confirmed by NMR spectroscopy, showing only one signal for the COCHCO proton at 4.83 (2c) and 4.68 (2d) ppm, respectively. The methine protons for the terminal (t) and bridging (b) AlOiPr groups are clearly distinguished at 4.26 (t) and 4.52 (b) ppm (2c) and 4.34 (t) and 4.52 (b) ppm (2d),
respectively. The $^{13}$C NMR resonances (63.5 (t) and 66.3 (b) for $2c$, 63.5 (t) and 65.8 (b) for $2d$) also confirm the binuclear structure. The methyl protons of the bridging OiPr groups give rise to two signals. This splitting might result from different environments caused by hindered rotation, viz. being directed to the octahedrally or tetrahedrally coordinated Al centre.

The signals for the malonate–OiPr ($2c$) and OtBu ($2d$) methyl protons also split into four and two signals, respectively. This indicates different environments of the malonate ester groups trans to another carboxylic group or trans to a bridging OiPr group. For $2c$ two signals for the malonate methine protons were also observed (4.96 and 5.41 ppm). Additionally, the OCHC(CH$_3$)$_2$ methyl protons in $2c$ for each of these two types of ester OiPr groups further give two doublets, indicating a preferential orientation of the OiPr groups which results in two non-equivalent environments for each methyl group.

Exchange spectroscopy (EXSY) spectra show exchange of the signals for the bridging/terminal OiPr groups and additionally for the two OiPr (in $2c$) or OtBu (in $2d$) groups of the malonate ligands (Fig. 4). Exchange between Al–OiPr and malonate–OR groups was not observed.

$^{27}$Al NMR spectra of $2c$ and $2d$ (Fig. 5) additionally supported the structure. Both spectra showed a broad signal assigned to tetrahedrally coordinated Al between 130 and 20 ppm with maxima at about 65 and 80 ppm, respectively, and one sharp signal at 5.1 or 4.8 ppm, assigned to octahedrally coordinated Al [7]. Integration of the signals revealed almost the expected 1:1 ratio, although integration is somewhat difficult because of the broad signal for tetrahedrally coordinated Al.

The single crystal structure analysis of $2d$ was in agreement with that derived from NMR spectra in solution (Fig. 6). The bite angles for the two malonate ligands at the octahedral Al centre are 90.29(7)$^\circ$ and 90.39(7)$^\circ$. One of the malonate ligands again shows a slightly envelope-like conformation, whereas the other one is nearly planar. Interestingly, no trans influence on the Al–O bond distances (188.26(15)–188.98(17) pm) was observed for the malonate ligands. The angle between the two bridging OiPr groups O(3)–Al(2)–O(4) at the octahedral Al centre is only 76.61(7)$^\circ$ and leads to a distortion of the coordination octahedron. As expected, the bond distances Al(2)–O(3) and Al(2)–O(4) between the octahedral Al centre and the bridging OiPr are significantly longer than those from the tetrahedral Al centre to the bridging units, viz. 190.34(17) and 190.21(16) pm vs. 179.78(16) (Al(1)–O(3)) and 179.13(17) (Al(1)–O(4)) pm.

![Fig. 3 Schematic structure of Al$_2$(OiPr)$_4$(malonate)$_2$ (malonate = diprm ($2c$) and dbum ($2d$))](image-url)
In addition, the O(3)–Al(1)–O(4) angle at the tetrahedral Al centre (82.17(7)°) is larger than that at the octahedral centre, as expected due to the different coordination geometry. Both bond distances to the terminal OPr groups Al(1)–O(1) and Al(1)–O(2) of 169.82(19) and 169.78(18) pm, respectively, are significantly shorter than those to the bridging OPr groups. Comparison with \( \text{Al}_2(\text{OiPr})_2(\text{diprm})_4(\text{tert-butyl acetoacetate})_2 \) shows similar bond distances and angles, with the bond distances Al–O \(^{\text{malonate}} \) lying between those for Al–O \(^{\text{ester}} \) (190.4(4)–192.6(4) pm) and Al–O \(^{\text{keto}} \) (185.0(4)–187.2(4) pm). The ketoesterate ligands in this structure also show both envelope and twisted conformation [12].

The structure of \( 2d \) shows two different environments for the methyl groups of the bridging OPr groups, which correlates with the observation of two signals in the solution \(^1\text{H} \) NMR spectrum and therefore indicates that these OPr groups do not rotate freely in solution.

\( \text{Al}_2(\text{OiPr})_2(\text{diprm})_4 \)

Storage of \( 2c \), a colourless oil, resulted in the formation of colourless crystals. Single crystal XRD surprisingly revealed that \( \text{Al}_2(\text{OiPr})_2(\text{diprm})_4(\text{3e}) \) had crystallized rather than \( 2c \) (Fig. 7). This is of special interest, since attempts to prepare \( 3c \) directly from Al(OiPr)\(_3\) with two equivalents of diprm-H at 100 °C had failed and only mixtures of \( \text{Al}_2(\text{OiPr})_6(\text{diprm})_2(\text{2c}) \) and Al(diprm)\(_3\) (1c) had been obtained. \( \text{Al}_2(\text{OR})_2(\beta\text{-diketonate})_4 \) derivatives were also reported to disproportionate to \( \text{Al}_2(\text{OR})_4(\beta\text{-diketonate})_2 \) and Al(\( \beta\text{-diketonate})_3 \) [8]. Only one structure analysis has been reported, viz. that of \( \text{Al}_2(\text{OiPr})_2(3.5\text{-heptandionate})_4 \) [10]. \( \beta\text{-Ketoesterate} \) derivatives of the general formula \( \text{Al}_2(\text{OR})_2(\beta\text{-ketoesterate})_4 \) were not obtained [12].

Other products formed during this rearrangement could not be identified by means of the used spectroscopic or crystallographic methods. The rearrangement occurred only upon storage of isolated \( 2c \), whereas storage of a solution of \( 2c \) in toluene did not show any changes after 1 month. Therefore the rearrangement could not be monitored by NMR spectroscopy.

The structure of \( 3c \) can formally be derived from that of \( 2 \) by substituting the two terminal OPr ligands with two malonate ligands and thus converting the tetrahedral aluminium centre in an octahedrally coordinated. Al–O bond distances to the malonate ligands are 190.1(4)–192.5(4) pm and the bite angles 88.8(2)–89.3(2)°. At each Al centre, one coordinated malonate ligand has an envelope-like conformation, whereas the other is nearly planar (as in \( 1c \)). The angles between the Al centre and the bridging OPr groups are 77.6(2)° (O(9)–Al(1)–O(10)) and 77.9(2)° (O(9)–Al(2)–O(10)) and the corresponding Al–O bond distances 186.7(4)–188.7(4) pm. Both C–O bonds of the bridging OPr groups are bent towards the same side of the Al\(_2\)O\(_2\) plane, resulting in one methyl group being closer and the other more distant to the plane, supporting the observation of two methyl signals in the \(^1\text{H} \) and \(^{13}\text{C} \) NMR spectra. EXSY spectroscopy reveals signals corresponding to exchange between the two AlOCHMe\(_2\) protons, indicating a fluctuating behaviour of these groups.

It is also interesting to mention that from the two possible geometric isomers, viz. \( \text{meso} \) and \( d,l \) (Fig. 8), the \( d,l \) form crystallizes at room temperature, in contrast to the
known structure of \( \text{Al}_2(\text{OiPr})_2(3,5\text{-heptandionate})_4 \), which crystallized in the meso form \([8, 10]\).

NMR spectroscopy confirmed the conversion of \(2\text{c}\) into \(3\text{c}\). The spectra of \(3\text{c}\) were completely different compared to that of \(2\text{c}\). The \(^1\text{H}\) NMR signals for COCHCO and AlOCH(CH\(_3\))\(_2\) were both shifted to higher ppm values, viz. 4.91 and 4.76 ppm, and only one quintet for AlOCH(CH\(_3\))\(_2\) was observed. The signals for COOCH(CH\(_3\))\(_2\) split into two slightly overlapping quintets at 5.17 and 5.28 ppm, caused by the different environments of the malonate OPr groups directed to and away from the second Al centre. Analogous to \(2\text{c}\), the signals for the malonate methyl groups split into four doublets (two of them overlapping), again indicating preferential orientation of the malonate OPr groups with non-equivalent environments for the methyl groups. The methyl proton resonances for the bridging AlOPr groups also split into two doublets, indicating hindered rotation of these groups and two different environments for the methyl groups. This confirms that the dimeric structure with two Al centres, each coordinated by two malonate ligands and bridged by two OPr groups, is retained in solution, further supported by the \(^{27}\text{Al}\) NMR data, showing only a signal for octahedrally coordinated Al centres at 3.5 ppm.

\[ \text{Al}_3(\text{OH})(\text{OE}t)_3(\text{detm})_5 \]

Since the preparation of Al(detm)\(_3\) (1b) from Al(OiPr)\(_3\) and detm-H failed due to transesterification, an alternative preparative route was explored to avoid transesterification. Since Al(OEt)\(_3\) is oligomeric, it is only sparingly soluble in most organic solvents, including toluene. However, at least partial thermal de-oligomerization and subsequent partial solubility was expected, as for Al(OiPr)\(_3\), and therefore Al(OEt)\(_3\), dispersed in toluene, was reacted with three equiv. of detm-H at 90 °C. The solution immediately cleared upon heating. Monitoring of the reaction by \(^1\text{H}\) NMR spectroscopy clearly revealed coordination of the malonate, but significant differences to the spectrum of \(1\text{b}\) were observed and greater proportions of unreacted detm-H were detected. Removal of all volatiles and storage of the obtained oil for a few days at room temperature yielded crystals, which turned out to be Al\(_3\)(OH)(OEt)\(_3\)(detm)\(_5\) (4) (Fig. 9).

The crystal structure of 4 shows three octahedrally coordinated Al centres. The two terminal Al centres are coordinated by two malonate ligands each, whereas the central one is coordinated only by one malonate, leading to an overall Al/malonate ratio of 3:5. One terminal Al centre (Al(1)) is connected to the central one (Al(2)) by bridging OEt groups, while the second terminal Al centre (Al(3)) is connected by only one bridging OEt group and a bridging hydroxo group. Again, one of the malonates at each terminal Al centre has an envelope conformation and the other is nearly planar, as is the malonate ligand at the central Al atom. No trans influence was observed, resulting in Al–O(malonate) bond distances of 188.57(11)–191.45 (11) pm, except for Al(1)–O(1), which is 194.76(11) pm. This slight elongation is traced back to a hydrogen bond between the hydroxo hydrogen H(16) and O(1) of 220.8(16) pm. The bite angles of the malonates are between 88.29(5)° and 89.56(5)°. The bond distances between the Al centres and the bridging O atoms are in the range 184.42(11)–189.57(11) pm, not showing significant differences for the hydroxo group compared to the OEt groups.

All resonances of the \(^1\text{H}\) and \(^{13}\text{C}\) NMR spectra could be assigned based on the structure, but no resonance for Al–OH was observed. Only one resonance for the methyl groups of the AlOEt groups were observed at 1.33 and 3.72–4.60 ppm in the \(^1\text{H}\) NMR spectrum. The \(^{13}\text{C}\) NMR spectrum showed only two signals at 18.4 and 56.6 ppm for the methyl and methylene carbons of the AlOEt groups. The methyl groups of the five detm ligands resulted in two triplets of equal intensity at 0.99 and 1.14 ppm in the \(^1\text{H}\) NMR spectrum. In the \(^{13}\text{C}\) NMR spectrum, the malonate OEt groups exhibited two resonances each for the methyl

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**Fig. 8** Schematic representation of meso and \(d,l\) geometries for Al\(_2\)(OR)\(_2\)(malonate)\(_4\) complexes

**Fig. 9** Molecular structure of 4 (C-bonded hydrogen atoms omitted for clarity)
and methylene carbon at 14.4/14.6, and at 60.0/60.1 ppm. Single resonances were observed for COCHCO in the $^1$H (4.91 ppm) and $^{13}$C (66.4 ppm) NMR spectra as well as for CO (175.4 ppm). EXSY spectra indicate exchange between the signals at 3.72–3.84 and 3.92–4.12 ppm and between the signals at 3.92–4.12 and 4.43–4.60 ppm. Since the signal at 3.72–3.84 ppm originates only from AlOCH$_2$Me and the signal at 4.43–4.60 ppm only from COOCH$_2$Me, whereas the signals at 3.92–4.12 ppm results from overlapping signals of both types of OEt groups and no exchange between the signals at 3.72–3.84 and 4.43–4.60 ppm was observed, it is assumed that exchange happens only between Al–OEt groups or between malonate–OR groups, but not between Al– and malonate–OR groups. $^{27}$Al NMR spectroscopy showed only one signal at 5.9 ppm, in line with the existence of only octahedrally coordinated Al $[^7]$. A slight broadening of the signal compared to those for octahedral Al in 1c, 2c, and 2d was observed and is probably caused by the coexistence of three different Al centres.

At present, the origin of the hydroxo group is not clear, but it is strongly believed that it results from cleavage of an OEt group with transfer of a proton to the oxygen and release of ethylene. The other possibility, partial hydrolysis during the reaction of only octahedrally coordinated Al $[^7]$. A slight broadening of the signal compared to those for octahedral Al in 1c, 2c, and 2d was observed and is probably caused by the coexistence of three different Al centres.

**Conclusions**

In this work it was shown that dialkylmalonates are versatile ligands for the modification of Al alkoxides and are a good alternative to $\beta$-diketone or $\beta$-ketoester derivatives, although ligand substitution requires higher reaction temperatures and longer reaction times due to the fact that deprotonation of the malonic esters is less favourable.

Products with an Al/malonate ratio of 1:3 (1c), 1:2 (3c) and 1:1 (2c) were obtained for the reaction of Al(OiPr)$_3$ with diprm-H. However, 3c was not obtained by the direct reaction of Al alkoxide with two equivalents of malonate but formed spontaneously from 2c upon storage. This is of particular interest, since analogous $\beta$-diketonate or $\beta$-ketoester derivatives were reported to be unstable and to decompose to give Al($\beta$-diketonate)$_3$ and Al$_2$(OiPr)$_4$(($\beta$-diketonate)$_2$ upon storage in solution at room temperature $[^8]$. Complexes 2c and 2d with an Al/malonate ratio of 1:1 have analogous structures to the corresponding $\beta$-ketoester derivatives $[^12]$, i.e. they are binuclear complexes with one octahedrally coordinated Al centre bearing two malonate ligands connected by two bridging OiPr groups to the second, tetrahedrally coordinated Al centre, bearing additional OiPr groups. Al$_2$(OiPr)$_2$(diprm)$_4$ (3c) is a C$_2$-symmetric dimer, again analogous to a known $\beta$-diketonate derivative $[^10]$, with two octahedrally coordinated Al centres.

Modification with dmem-H or detm-H resulted in partial transesterification in the case of Al(OiPr)$_3$, but not with Al(OBu)$_3$. This leads to the conclusion that the tendency to undergo transesterification depends on the malonate as well as on the alkoxo groups. The use of Al(OBu)$_3$ also allowed us to obtain Al(malonate)$_3$ complexes for all ligands used (1a–1d), but no products with a stoichiometric ratio of Al/malonate = 1:1 or 1:2 were obtained. This indicates that the OBu group is sterically too demanding to enable formation of Al–OBU–Al bridges, which are necessary to stabilize substitution products by means of coordination expansion.

Finally, the unexpected product Al$_3$(OH)(OEt)$_3$(detm)$_5$ (4) was obtained, bearing an AlOH group, most likely formed by scission of an OEt group. This is supported by the fact that 4 was obtained by two independent experiments.

**Experimental**

All operations were carried out in moisture- and oxygen-free atmosphere of dry argon by using standard Schlenk or glove box techniques. Al(OEt)$_3$ (Aldrich, 97%), Al(OiPr)$_3$ (Aldrich, 98% +), Al(OBu)$_3$ (Aldrich, techn.), dimethyl malonate (dmem-H, Aldrich, 98%), diethyl malonate (detm-H, Fluka, ≥99%), di-iso-propyl malonate (diprm-H, Aldrich, 99%) and di-tert-butyl malonate (dbum-H, Aldrich, 98%) were used as received. All solvents were dried and purified by standard techniques $[^29]$. C$_6$D$_6$ (euroiso-top, 99.5%) and toluene-d$_8$ (euroiso-top, 99.6%) used for NMR experiments were dried over 3-Å molecular sieves and degassed.

1D $^1$H and $^{13}$C NMR spectra were recorded on a Bruker AVANCE 250 spectrometer (250.13 MHz ($^1$H), 62.86 MHz ($^{13}$C)) and $^{27}$Al and 2D NMR spectra on a Bruker
AVANCE 300 spectrometer (300.13 MHz (1H), 75.47 MHz (13C), 78.21 MHz (27Al)). Both spectrometers were equipped with a 5-mm broadband probe head and a z-gradient unit. Correlated spectroscopy (COSY), heteronuclear single quantum correlation (HSQC), heteronuclear multiple-bond correlation (HMBC, evolution delay for long range coupling 100 ms) and exchange spectroscopy (EXSY, $t_{\text{mix}}$ = 1.2 s) were measured with Bruker standard pulse sequences. $J$ values are given in Hz. The $^{27}\text{Al}$ NMR signals were referenced externally against a 2 M solution of $\text{AlCl}_3$ in water (0 ppm). Superscript (t) and (b) are used to indicate terminal or bridging binding of OR groups.

As a result of the instability of compounds 2–4 towards moisture, elemental analyses were not meaningful and were not included. Purity of the compounds was determined by NMR spectroscopy and confirmed by single crystal XRD if suitable crystals were obtained.

**Tris(dimethylmalonato)aluminium**

(1a. $\text{Al}[(\text{COOMe})_2\text{CH}_2]_3$)

$\text{Al}(\text{OrBu})_3$ (0.498 g, 2.02 mmol) was dissolved in 7 cm$^3$ of toluene at room temperature and 0.69 cm$^3$ (0.798 g, 6.04 mmol) of dmem-H was added under stirring. The reaction mixture was stirred at room temperature for 6 days and at 50 °C for 2 days. $\text{Al}($dmem)$_3$ (0.801 g, 94%) was obtained as a colourless crystalline precipitate after removal of volatiles and drying in vacuo. $^1\text{H}$ NMR (toluene-$d_8$, 20 °C): $\delta$ = 4.91 (s, 3 H, COC$_2$O), 3.48 (s, 18 H, COOCH$_2$C$_2$H$_5$), 4.96 (s, 3 H, COOHCO), 3.48 (s, 18 H, COOCH$_2$C$_2$H$_5$) ppm; $^{13}\text{C}$ $^{1\text{H}}$ NMR (toluene-$d_8$, 20 °C): $\delta$ = 175.8 (CO), 66.2 (CO), 67.9 (CO), 68.0 (CO) ppm.

**Tris(diethylmalonato)aluminium**

(1b. $\text{Al}[(\text{COCOCMe})_2\text{CH}]_3$)

$\text{Al}(\text{OrBu})_3$ (0.498 g, 2.02 mmol) was dissolved in 5 cm$^3$ of toluene at room temperature and 0.92 cm$^3$ (0.971 g, 6.06 mmol) of dmem-H was added under stirring. The reaction mixture was stirred at room temperature for 11 days and at 50 °C for 3 days. $\text{Al}($dmem)$_3$ (0.967 g, 95%) was obtained as a colourless solid after removal of volatiles and drying in vacuo. $^1\text{H}$ NMR (toluene-$d_8$, 20 °C): $\delta$ = 4.91 (s, 3 H, COC$_2$O), 4.18–3.96 (m, 12 H, COOCMe$_2$C$_2$H$_5$), 1.00 (t, $J$ = 7.0 Hz, 18 H, COOCH$_2$C$_2$H$_5$) ppm; $^{13}\text{C}$ $^{1\text{H}}$ NMR (toluene-$d_8$, 20 °C): $\delta$ = 175.9 (CO), 67.1 (CO), 60.8 (CO) ppm.

**Tris(di-isopropylmalonato)aluminium**

(1c. $\text{Al}[(\text{COCOCMe}_2)\text{CH}]_3$)

$\text{Al}(\text{OrBu})_3$ (0.502 g, 2.04 mmol) was dissolved in 7 cm$^3$ of toluene at room temperature and 1.16 cm$^3$ (1.150 g, 6.11 mmol) of diprm-H was added under stirring. The reaction mixture was stirred at room temperature for 3 days and at 50 °C for 7 days. The solvent volume was reduced and $\text{Al}(\text{diprm})_3$ (0.804 g, 67%) obtained as colourless crystals after recrystallization and storage for few days at room temperature.

**Method A:** $\text{Al}(\text{OrPr})_3$ (0.994 g, 4.86 mmol) was dissolved in 10 cm$^3$ of toluene at room temperature and 2.77 cm$^3$ (2.745 g, 14.58 mmol) of diprm-H was added under stirring. The reaction mixture was stirred at 120 °C for 3 days. $\text{Al}(\text{diprm})_3$ (2.651 g, 93%) was obtained as a colourless solid after removal of volatiles and drying in vacuo.

**Method B:** $\text{Al}(\text{OrPr})_3$ (0.992 g, 4.86 mmol) and the mixture was stirred at 120 °C for 3 days. Toluene (2 cm$^3$) was added, resulting in dissolution of the colourless solid. After cooling to room temperature, $\text{Al}(\text{diprm})_3$ (2.102 g, 74%) was obtained as colourless crystals upon storage for few days.

$^1\text{H}$ NMR (C$_6$D$_6$, 20 °C): $\delta$ = 5.09 (sept, $J$ = 6.1 Hz, 6 H, COOCHMe$_2$), 4.96 (s, 3 H, COOCHCO), 1.18 (d, $J$ = 6.1 Hz, 18 H, COOCH(CH$_3$)$_2$), 1.07 (d, $J$ = 6.1 Hz, 18 H, COOCH(CH$_3$)$_2$) ppm; $^{13}\text{C}$ $^{1\text{H}}$ NMR (C$_6$D$_6$, 20 °C): $\delta$ = 175.5 (CO), 68.0 (CO), 67.9 (CO) ppm.

**Method C:** Diprm-H (9.18 cm$^3$, 9.097 g, 48.33 mmol) was added to $\text{Al}(\text{OrPr})_3$ (0.992 g, 4.86 mmol) and the mixture was stirred at 120 °C for 3 days. Toluene (2 cm$^3$) was added, resulting in dissolution of the colourless solid. After cooling to room temperature, $\text{Al}(\text{diprm})_3$ (2.102 g, 74%) was obtained as colourless crystals upon storage for few days.

$^1\text{H}$ NMR (C$_6$D$_6$, 20 °C): $\delta$ = 5.09 (sept, $J$ = 6.1 Hz, 6 H, COOCHMe$_2$), 4.96 (s, 3 H, COOCHCO), 1.18 (d, $J$ = 6.1 Hz, 18 H, COOCH(CH$_3$)$_2$), 1.07 (d, $J$ = 6.1 Hz, 18 H, COOCH(CH$_3$)$_2$) ppm; $^{13}\text{C}$ $^{1\text{H}}$ NMR (toluene-$d_8$, 20 °C): $\delta$ = 5.3 ppm.

**Tris(di-tert-butylmalonato)aluminium**

(1d. $\text{Al}[(\text{COCOCMe}_2)\text{CH}]_3$)

**Method A:** $\text{Al}(\text{OrBu})_3$ (0.506 g, 2.05 mmol) was dissolved in 7 cm$^3$ of toluene at room temperature and 1.36 cm$^3$ (1.314 g, 6.08 mmol) of dbum-H was added under stirring. The reaction mixture was stirred at 80 °C for 4 days. The solvent volume was reduced to approx. 3 cm$^3$, and $\text{Al}(\text{dbum})_3$ (0.822 g, 59%) was obtained as colourless crystals after recrystallization and storage for a few days at room temperature.

**Method B:** $\text{Al}(\text{OrPr})_3$ (0.995 g, 4.87 mmol) was dissolved in 10 cm$^3$ of toluene at room temperature and 3.27 cm$^3$ (3.159 g, 14.61 mmol) of dbum-H was added under stirring. The reaction mixture was stirred at 80 °C for 5 days. $\text{Al}(\text{dbum})_3$ (3.144 g, 96%) was obtained as a colourless solid after removal of volatiles and drying in vacuo. Colourless crystals suitable for single crystal XRD were obtained upon recrystallization from toluene at room temperature.

$^1\text{H}$ NMR (C$_6$D$_6$, 20 °C): $\delta$ = 4.81 (s, 3 H, COOCHCO), 1.50 (s, 54 H, COOC(CH$_3$)$_3$) ppm; $^{13}\text{C}$ $^{1\text{H}}$ NMR (C$_6$D$_6$, 20 °C): $\delta$ = 175.6 (CO), 79.9 (COOCMe$_3$), 69.0 (COOCHCO), 29.0 (COOC(CH$_3$)$_3$) ppm.

**Bis(di-isopropylmalonato)bisis(iso-propanolato)bisis(iso-propanolato)dialuminium**

(2c. $\text{Al}_2[(\text{COCOCMe}_2)\text{CH}]_2(\text{COOCH(CH}_3)_2\text{)}_2$)

$\text{Al}(\text{OrPr})_3$ (1.020 g, 4.99 mmol) was dissolved in 10 cm$^3$ of toluene at room temperature and 0.95 cm$^3$ (0.941 g, 5.00 mmol) of diprm-H was added under stirring. The reaction mixture was stirred at 100 °C for 3 days.
Al₂(OiPr)₃(diprm)₂ (1.577 g, 95%) was obtained as a colourless oil after removal of volatiles and drying in vacuo. ¹H NMR (C₆D₆, 20 °C): δ = 5.41 (quint, J = 6.2 Hz, 2 H, COOCHMe₂), 4.96 (quint, J = 6.2 Hz, 2 H, COOCHMe₂), 4.83 (s, 2 H, COCHCO), 4.52 (quint, J = 6.2 Hz, 2 H, AIOCHMe²(b)), 4.26 (quint, J = 6.2 Hz, 2 H, AIOCHMe²(b)), 1.49 (d, J = 6.2 Hz, 6 H, AIOCH(CH₃)₂(b)), 1.45–1.35 (m, 18 H, AIOCH(CH₃)₂(b) + AIOCH(CH₃)₂(b)), 1.28 (d, J = 6.2 Hz, 6 H, COOCH(CH₃)₂), 1.23 (d, J = 6.2 Hz, 6 H, COOCH(CH₃)₂), 1.10 (d, J = 6.2 Hz, 6 H, COOCH(CH₃)₂), 1.05 (d, J = 6.2 Hz, 6 H, COOCH(CH₃)₂) ppm; ¹³C {¹H} NMR (C₆D₆, 20 °C): δ = 175.1 (CO), 174.5 (CO), 68.4 (COCHCO), 67.2 (COOCHMe₂), 67.1 (COOCHMe₂), 64.4 (AIOCHMe²(b)), 25.4 (AIOCH(CH₃)₂(b)), 24.0 (AIOCH(CH₃)₂(b)), 23.2 (COOCH(CH₃)₂), 22.6 (COOCH(CH₃)₂), 22.5 (COOCH(CH₃)₂) ppm; ²⁷Al NMR (toluene-d₈, 20 °C): δ = 3.5 (octahedral) ppm.

Pentakis(diethylmalonato)tris(µ-ethanolato)-µ-hydroxo)trialuminium (4. Al₂(Oh)(COOCH₂CH₃)₃[CH(COOCH₂CH₃)₂]₃)

Toluene (10 cm³) and subsequently 2.80 cm³ of demt-H (2.954 g, 18.44 mmol) were added to Al(OEt)₃ (1.007 g, 6.21 mmol) at room temperature. The mixture was stirred at 90 °C for 4 days, whereupon it cleared. Removal of the volatiles in vacuo gave a slightly greenish oil which crystallized upon storage at room temperature for several days to give Al₂(Oh)(OEt)(diprm)₅ (1.874 g, 88%) as colourless crystals suitable for single crystal XRD. ¹H NMR (C₆D₆, 20 °C): δ = 4.91 (s, 2 H, COCHCO), 4.52 (quint, J = 5.9 Hz, 2 H, AIOCHMe²(b)), 4.34 (quint, J = 6.3 Hz, 2 H, AIOCHMe²(b)), 1.62 (s, 18 H, COOCH(CH₃)₃), 1.55 (d, J = 6.3 Hz, 6 H, AIOCH(CH₃)₂(b)), 1.51 (s, 6 H, COOC(CH₃)₂), 1.40 (s, 12 H, COOC(CH₃)₂), 1.40–1.32 (m, 18, AIOCH(CH₃)²(b) + AIOCH(CH₃)₂(b)) ppm; ¹³C {¹H} NMR (toluene-d₈, -60 °C): δ = 175.5 (CO), 174.5 (CO), 80.5 (COOCH₂Me), 79.9 (COOCH₂Me), 69.8 (COCHCO), 65.8 (AIOCHMe²(b), 63.5 (AIOCHMe²(b), 29.1 (COOCH(CH₃)₃), 28.7 (COOCH₂CH₃), 28.3 (COOC(CH₃)₂), 27.4 (AIOCH(CH₃)²(b)), 25.9 (AlOCH(CH₃)²(b)), 24.5 (AlOCH(CH₃)²(b)) ppm; ²⁷Al NMR (toluene-d₈, 20 °C): δ = 5.9 ppm.

X-ray structure analyses

Crystals of 1a, 1d-0.5toluene, 2d, 3c, and 4 suitable for single crystal XRD were mounted on a Bruker AXS KAPPA diffractometer fitted with an APEX II CCD area detector, using graphite-monochromated Mo-Kα radiation (λ = 71.073 pm). Data collection at 100 K covered a hemisphere of the reciprocal space by recording three sets of exposures, each of them exhibiting a different Φ angle. Each exposure covered 0.3° in ω (Table 1). The data were corrected for polarization and Lorentz effects, and an empirical absorption correction (SADABS) was applied. The cell dimensions were refined with all unique reflections. The structures were solved with direct methods (SHELXS97) and refinement to convergence was carried out with the full-matrix least squares method based on F₂ (SHELXL97) with anisotropic structure parameters for all non-hydrogen atoms. The hydrogen atoms were placed on calculated positions and refined riding on their parent atoms. Selected bond lengths and angles are compared in Table 2.
In the crystal structure of 2d one O/Pr, in 3c two O/Pr, and in 4 two malonate and two aluminium-bound OEt groups are disordered.

CCDC-742538 (for 1a), 742539 (for 1d), 742540 (for 2c), 742541 (for 3c), and 742542 (for 4) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments This work was supported by the Fonds zur Förderung der wissenschaftlichen Forschung (FWF), Austria (Project P20750). The authors thank R. Hellein and M. Schwabl for their supporting experimental work.

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