Modification of aluminum alkoxides with β -ketoesters: new insights into formation, structure and stability

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Abstract $[\text{Al}(\text{O}^i\text{Pr})_2(\beta\text{-ketoesterate})]_2$ and $\text{Al}(\beta\text{-ketoesterate})_3$ ($\beta\text{-ketoesterate}$ = methyl, ethyl, *iso*-propyl, *tert*-butyl, allyl and 2-(methacryloyloxy)ethyl acetoacetate) were prepared by reaction of $[\text{Al}(\text{O}^i\text{Pr})_3]_4$ with the corresponding β -ketoesters. $\text{Al}(\beta\text{-ketoesterate})_3$ derivatives were exclusively formed at room temperature, whereas elevated reaction temperatures, causing thermal de-oligomerization of $[\text{Al}(\text{O}^i\text{Pr})_3]_4$, were necessary for the formation of $[\text{Al}(\text{O}^i\text{Pr})_2(\beta\text{-ketoesterate})]_2$. All compounds were characterized by NMR spectroscopy, and $[\text{Al}(\text{O}^i\text{Pr})_2(\text{tert-butyl acetoacetate})]_2$ by a single crystal structure analysis. The $[\text{Al}(\text{O}^i\text{Pr})_2(\beta\text{-ketoesterate})]_2$ derivatives are asymmetrically substituted dimers with one octahedrally and one tetrahedrally substituted aluminum atom, bridged by two *iso*-propoxo groups, whereas the $\text{Al}(\beta\text{-ketoesterate})_3$ derivatives are monomers with octahedrally coordinated aluminum. Transesterification as a possible side reaction was only observed at elevated temperatures for $\text{Al}(\text{tert-butyl acetoacetate})_3$ in the presence of liberated *iso*-propanol.

Keywords Aluminum alkoxide derivatives · β -Ketoesterates · Transesterification · Ligand exchange

1 Introduction

One problem in the sol–gel chemistry of metal alkoxides is their high reaction rates during hydrolysis and condensation, compared to silicon alkoxides, and the resulting tendency to form precipitates instead of gels. Lowering of their reactivity can be achieved by substitution of one or more alkoxo groups by bi- or even multidentate ligands which are bound more strongly to the metal as a consequence of the chelate effect. Since the number of hydrolysable alkoxo groups is thus reduced and additional coordination sites at the metal centers are blocked, the rate of hydrolysis and the degree of cross-linking in the formed network are lowered [1].

Another consequence of the higher Lewis acidity of metal alkoxides is their tendency to form oligomers $[\text{M}(\text{OR})_x]_n$ via alkoxo bridges. The chemical and physical properties of the alkoxides strongly depend on the degree of oligomerization, which in turn is a result of the electronic and steric properties of the metal center and the alkoxo group. For example, aluminum *iso*-propoxide is tetrameric $[\text{Al}(\text{O}^i\text{Pr})_3]_4$ [2, 3], whereas the *tert*-butoxide $[\text{Al}(\text{O}^t\text{Bu})_3]_2$ is dimeric [4] in the solid state as well as in solution at room temperature. This example shows the inverse correlation between steric demand of the alkoxo group and degree of oligomerization. This tendency of metal alkoxides to oligomerize is retained after modification with bidentate organic ligands. Thus, aluminum alkoxides and siloxides are known to form mono-, di-, tri-, or oligomeric species upon modification with β -diketones [5, 6].

Modification of metal alkoxides with bidentate organic ligands also opens the possibility to introduce additional functionalities by using ligands bearing a functional organic group, e.g. polymerizable groups for the formation of class II inorganic–organic hybrid polymers. As a matter

Dedicated to David Avnir on the occasion of his 60th birthday.

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Fig. 1 β -Ketoesters used for modification of $\text{Al}(\text{O}^i\text{Pr})_3$

of fact, allyl (aaa-H) and 2-(methacryloyloxy)ethyl acetoacetate (meaa-H) (see Fig. 1) have often been used in sol-gel chemistry for this purpose for various metal alkoxides. Own previous work was mainly focused on the modification and functionalization of titanium and zirconium alkoxides by nitrogen-containing ligands [7]. In this work, we expand this work on aluminum alkoxides modified by reaction with β -ketoesters. Whereas the influence of the alkoxo or siloxo group on the oligomerization and structure of acac-substituted (acac = acetylacetonate) aluminum alkoxides or siloxides was studied in detail [5], this is not the case for variations of the ester OR groups in β -ketoesterate derivatives (β -ketoesterate = anion of β -ketoester). Since the bonding of β -ketoesterate ligands to the metal center is inherently asymmetrical (contrary to β -diketonate derivatives), because of the different electronic influence of the alkyl and OR substituents at the carbonyl carbon atoms, differences can be anticipated. In this article we report the results of our investigations on the formation and stability of aluminum *iso*-propoxide derivatives modified by methyl (meac-H), ethyl (etac-H), *iso*-propyl (*i*'prac-H) and *tert*-butyl (*t*'buac-H) acetoacetate as model ligands, as well as allyl (aaa-H) and 2-(methacryloyloxy)ethyl (meaa-H) acetoacetate as ligands with polymerizable groups (Fig. 1), including investigation of transesterification as possible side reaction. The influence of variation the ester group is reported as well as differences in coordination behavior of β -ketoesters compared to β -diketonates.

2 Experimental

All operations were carried out in a moisture and oxygen free atmosphere of dry argon using standard Schlenk or glove box techniques. $\text{Al}(\text{O}^i\text{Pr})_3$ (Aldrich, 98 + %), methyl acetoacetate (Aldrich, 99%) ethyl acetoacetate (Fluka,

p.a.), *iso*-propyl acetoacetate (Alfa Aesar, 98%), *tert*-butyl acetoacetate (Aldrich, 98%), allyl acetoacetate (Aldrich, 98%) and 2-(methacryloyloxy)ethyl acetoacetate (Aldrich, 95%) were used as received. All solvents were dried and purified by standard techniques. C_6D_6 (99.5%, euriso-top) and d_8 -toluene (99.6%, euriso-top) used for NMR experiments were dried over 3 Å molecular sieve and degassed. 1D ^1H and ^{13}C NMR spectra were recorded on a Bruker AVANCE 250 (250.13 MHz $\{^1\text{H}\}$, 62.86 MHz $\{^{13}\text{C}\}$) spectrometer. ^{27}Al and 2D NMR spectra were recorded on a Bruker AVANCE 300 (300.13 MHz $\{^1\text{H}\}$, 75.47 MHz $\{^{13}\text{C}\}$, 78.21 MHz $\{^{27}\text{Al}\}$) spectrometer. Both spectrometers were equipped with a 5 mm broadband probe head and a z-gradient unit. COSY (Correlated Spectroscopy), HSQC (Heteronuclear Single Quantum Correlation), HMBC (Heteronuclear Multiple-Bond Correlation, evolution delay for long range coupling 100 ms), and EXSY (Exchange Spectroscopy, $t_{\text{mix}} = 1.2$ s) were measured with Bruker standard pulse sequences. The ^{27}Al NMR signals were referenced externally against a 2 M solution of AlCl_3 in water (0 ppm).

2.1 $[\text{Al}(\text{O}^i\text{Pr})_2(\text{meac})]_2$

An amount of 1.003 g (4.91 mmol) of $\text{Al}(\text{O}^i\text{Pr})_3$ was dissolved in 10 mL of toluene at room temperature followed by slow addition of 0.570 g (4.91 mmol) of methyl acetoacetate under stirring. The clear reaction solution was stirred at 120 °C for 18 h. The volatiles were then removed *in vacuo*. The crude product was washed with 2 mL of *n*-pentane and a colorless oil obtained. Yield 1.217 g (95%).

^1H NMR (δ [ppm], C_6D_6 , 20 °C): 5.07 (s, 2H, COCHCO), 4.45 (sept, $J = 5.9$ Hz, 2H, $\text{OCH}(\text{CH}_3)_2$), 4.16 (sept, $J = 6.2$ Hz, 2H, $\text{OCH}(\text{CH}_3)_2$), 3.59 (s, 6H, COOCH_3), 1.66 (s, 6H, CH_3CO) 1.49–1.30 (m, 24H, $\text{OCH}(\text{CH}_3)_2$). ^{13}C $\{^1\text{H}\}$ NMR (δ [ppm], d_8 -toluene, 20 °C): 186.8 (CO), 175.2 (COO), 85.5 (COCHCO), 66.0 ($\text{OCH}(\text{CH}_3)_2$), 63.1 ($\text{OCH}(\text{CH}_3)_2$), 51.8 (COOCH_3), 28.0 ($\text{OCH}(\text{CH}_3)_2$), 25.5 (CH_3CO), 25.3 ($\text{OCH}(\text{CH}_3)_2$).

2.2 $[\text{Al}(\text{O}^i\text{Pr})_2(\text{etac})]_2$

An amount of 0.999 g (4.89 mmol) of $\text{Al}(\text{O}^i\text{Pr})_3$ was dissolved in 20 mL of toluene at room temperature followed by slow addition of 0.638 g (4.90 mmol) of ethyl acetoacetate under stirring. The clear reaction solution was stirred at room temperature for 12 h and then at 120 °C for additional 18 h. The volatiles were removed *in vacuo* and a colorless oil was obtained. Yield 1.297 g (97%).

^1H NMR (δ [ppm], C_6D_6 , 20 °C): 5.10 (s, 2H, COCHCO), 4.60–4.00 (m, 8H, $\text{OCH}(\text{CH}_3)_2/\text{COOCH}_2\text{CH}_3$), 1.68 (s, 6H, CH_3CO), 1.48 (d, $J = 6.2$ Hz, 12H, $\text{OCH}(\text{CH}_3)_2$), 1.39 (d, $J = 5.9$ Hz, 12H, $\text{OCH}(\text{CH}_3)_2$),

1.10 (t, $J = 7.1$ Hz, 6H, $\text{COOCH}_2\text{CH}_3$). ^{13}C { ^1H } NMR (δ [ppm], d_8 -toluene, 20 °C): 186.5 (CO), 174.6 (COO), 86.0 (COCHCO), 65.9 (OCH(CH₃)₂), 63.1 (OCH(CH₃)₂), 61.1 (COOCH₂CH₃), 28.0 (OCH(CH₃)₂), 25.5 (CH₃CO), 25.2 (OCH(CH₃)₂), 14.1 (COOCH₂CH₃).

2.3 [Al(OⁱPr)₂(ⁱprac)]₂

An amount of 1.006 g (4.93 mmol) of Al(OⁱPr)₃ was dissolved in 10 mL of toluene at room temperature followed by slow addition of 0.708 g (4.91 mmol) of *iso*-propyl acetoacetate under stirring. The clear reaction solution was stirred at 120 °C for 18 h. The volatiles were removed *in vacuo* and a colorless oil was obtained. Yield 1.388 g (98%).

^1H NMR (δ [ppm], C₆D₆, 20 °C): 5.39 (quint, $J = 6.2$ Hz, 2H, COOCH(CH₃)₂), 5.06 (s, 2H, COCHCO), 4.50 (quint, $J = 5.8$ Hz, 2H, OCH(CH₃)₂), 4.21 (quint, $J = 6.2$ Hz, 2H, OCH(CH₃)₂), 1.66 (s, 6H, CH₃CO), 1.48 (d, $J = 6.2$ Hz, 12H, OCH(CH₃)₂), 1.39 (d, $J = 5.8$ Hz, 12H, OCH(CH₃)₂), 1.30 (d, $J = 6.2$ Hz, 6H, COOCH(CH₃)₂), 1.12 (d, $J = 6.2$ Hz, 6H, COOCH(CH₃)₂). ^{13}C { ^1H } NMR (δ [ppm], d_8 -toluene, 20 °C): 186.2 (CO), 174.6 (COO), 86.5 (COCHCO), 68.6 (COOCH(CH₃)₂), 65.8 (OCH(CH₃)₂), 63.2 (OCH(CH₃)₂), 28.0 (OCH(CH₃)₂), 25.5 (CH₃CO), 25.2 (OCH(CH₃)₂), 21.8 (COOCH(CH₃)₂).

2.4 [Al(OⁱPr)₂(^tbuac)]₂

An amount of 1.006 g (4.93 mmol) of Al(OⁱPr)₃ was dissolved in 10 mL of toluene at room temperature followed by slow addition of 0.709 g (4.92 mmol) *tert*-butyl acetoacetate under stirring. The clear reaction solution was stirred at 120 °C for 18 h. The volatiles were then removed *in vacuo* and a white microcrystalline precipitate was obtained. Crystals suitable for single crystal XRD analysis were obtained upon crystallization from toluene at 4 °C. Yield 1.331 g (89%).

^1H NMR (δ [ppm], C₆D₆, 20 °C): 5.06/5.05/4.98 (s, 2H, COCHCO), 4.65–4.45 (m, 2H, OCH(CH₃)₂), 4.35–4.15 (m, 2H, OCH(CH₃)₂), 1.67 (s, 6H, CH₃CO), 1.62–1.25 (m, 42H, OCH(CH₃)₂/COOC(CH₃)₃). ^{13}C { ^1H } NMR (δ [ppm], d_8 -toluene, 20 °C): 189.9/185.3 (CO), 175.0 (CO), 86.2/87.4 (COCHCO), 81.5/80.5/80.0 (COOC(CH₃)₃), 65.8 (OCH(CH₃)₂), 63.1 (OCH(CH₃)₂), 28.5 (COOC(CH₃)₃), 28.0 (OCH(CH₃)₂), 25.3 (CH₃CO), 25.2 (OCH(CH₃)₂).

2.5 [Al(OⁱPr)₂(aaa)]₂

An amount of 0.998 g (4.89 mmol) of Al(OⁱPr)₃ was dissolved in 10 mL of toluene at room temperature followed by slow addition of 0.695 g (4.89 mmol) of allyl

acetoacetate under stirring. The slightly turbid reaction solution was stirred at 120 °C for 18 h. The volatiles were removed *in vacuo*, the crude product washed with 5 mL of dichloromethane and a pale yellow, slightly turbid oil was obtained. Yield 1.300 g (93%).

^1H NMR (δ [ppm], C₆D₆, 20 °C): 6.05–5.85 (m, 2H, COOCH₂CH=CH₂), 5.10 (s, 2H, COCHCO), 5.30–5.00 (m, 4H, COOCH₂CH=CH₂), 4.95–4.55 (m, 4H, COOCH₂CH=CH₂), 4.48 (quint, $J = 5.9$ Hz, 2H, OCH(CH₃)₂), 4.18 (quint, $J = 6.2$ Hz, 2H, OCH(CH₃)₂), 1.66 (s, 6H, CH₃CO), 1.50–1.25 (m, 24H, OCH(CH₃)₂). ^{13}C { ^1H } NMR (δ [ppm], d_8 -toluene, 20 °C): 188.0 (CO), 174.0 (COO), 132.8 (COOCH₂CH=CH₂), 117.5 (COOCH₂CH=CH₂), 86.0 (COCHCO), 66.1 (OCH(CH₃)₂), 66.0 (COOCH₂CH=CH₂), 63.1 (OCH(CH₃)₂), 28.0 (OCH(CH₃)₂), 25.5 (CH₃CO), 25.0 (OCH(CH₃)₂).

2.6 [Al(OⁱPr)₂(meaa)]₂

A solution of 1.009 g (4.94 mmol) of Al(OⁱPr)₃ dissolved in 10 mL of toluene was stirred at 120 °C for 18 h. After cooling to room temperature 1.055 g (4.92 mmol) of 2-(methacryloyloxy)ethyl acetoacetate was slowly added under stirring. The clear reaction solution was stirred at room temperature for additional 18 h. The volatiles were then removed *in vacuo* and a colorless oil was obtained. Yield 1.696 g (96%).

^1H NMR (δ [ppm], C₆D₆, 20 °C): 6.12 (s, 2H, OC(O)C(CH₃)=CH₂), 5.18 (s, 2H, OC(O)C(CH₃)=CH₂), 5.05 (s, 2H, COCHCO), 4.80–3.90 (m, 12H, OCH(CH₃)₂/OCH₂CH₂O), 1.79 (s, 6H, OC(O)C(CH₃)=CH₂), 1.63 (s, 6H, CH₃CO), 1.55–1.25 (m, 24H, OCH(CH₃)₂). ^{13}C { ^1H } NMR (δ [ppm], d_8 -toluene, 20 °C): 187.5 (CO), 174.4 (COO), 166.3 (OC(O)C(CH₃)=CH₂), 136.2 (OC(O)C(CH₃)=CH₂), 125.0 (OC(O)C(CH₃)=CH₂), 85.8 (COCHCO), 66.0 (OCH(CH₃)₂), 63.1 (OCH(CH₃)₂), 62.3 (OCH₂CH₂O), 27.9 (OCH(CH₃)₂), 25.4 (CH₃CO), 25.0 (OCH(CH₃)₂) 17.8 (OC(O)C(CH₃)=CH₂).

2.7 Al(meac)₃

An amount of 1.004 g (4.92 mmol) of Al(OⁱPr)₃ was dissolved in 10 mL of toluene at room temperature followed by slow addition of 1.710 g (14.71 mmol) of methyl acetoacetate under stirring. The clear reaction solution was then stirred at room temperature for 18 h. The volatiles were removed *in vacuo* and the resulting colorless solid washed with *n*-pentane.

^1H NMR (δ [ppm], C₆D₆, 20 °C): 5.17 (s, 3H, COCHCO), 3.43/3.38/3.34/3.33 (s, 9H, OCH₃), 1.83/1.82/1.80/1.79/1.77 (s, 9H, CH₃CO). ^{13}C { ^1H } NMR (δ [ppm], d_8 -toluene, 20 °C): 188.3/188.2/187.9/187.8 (CO), 174.8/

174.6 (COO), 85.0/84.7/84.5 (COCHCO), 51.0/50.9/50.8/50.7 (OCH₃), 25.8 (CH₃CO).

2.8 Al(etac)₃

An amount of 1.001 g (4.90 mmol) of Al(OⁱPr)₃ was dissolved in 20 mL of toluene at room temperature and 1.914 g (14.71 mmol) of ethyl acetoacetate was slowly added under stirring. The clear reaction solution was stirred at room temperature for 18 h. The volatiles were removed *in vacuo* and a white solid was obtained.

¹H NMR (δ [ppm], C₆D₆, 20 °C): 5.18/5.17 (s, 3H, COCHCO), 4.15–3.85 (m, 6H, OCH₂CH₃), 1.85/1.84/1.81/1.80 (s, 9H, CH₃CO), 1.00/0.99/0.91/0.90 (t, *J* = 7.1 Hz, 9H, OCH₂CH₃). ¹³C {¹H} NMR (δ [ppm], d₈-toluene, 20 °C): 188.1/188.0/187.7/187.6 (CO), 174.5/174.3/174.2 (COO), 85.2/85.0/84.8 (COCHCO), 60.4/60.3/60.2/60.1 (OCH₂CH₃), 25.9 (CH₃CO), 14.1/13.9 (OCH₂CH₃). ²⁷Al NMR (δ [ppm], d₈-toluene, 20 °C): 4.78 ppm.

2.9 Al(ⁱprac)₃

An amount of 1.005 g (4.92 mmol) of Al(OⁱPr)₃ was dissolved in 10 mL of toluene at room temperature and 2.125 g (14.74 mmol) of *iso*-propyl acetoacetate was slowly added under stirring. The clear reaction solution was stirred at room temperature for 18 h. The volatiles were removed *in vacuo* and a white, partially crystalline solid was obtained.

¹H NMR (δ [ppm], C₆D₆, 20 °C): 5.16 (s, 3H, COCHCO), 5.12–4.94 (m, 3H, OCH(CH₃)₂), 1.86/1.84/1.81/1.79 (s, 9H, CH₃CO), 1.20–0.95 (m, 18H, OCH(CH₃)₂). ¹³C {¹H} NMR (δ [ppm], d₈-toluene, 20 °C): 187.9/187.6/187.4/187.3 (CO), 175.1/175.0/173.9/173.8 (COO), 85.6/85.4/85.1 (COCHCO), 67.9/67.8/67.7/67.6 (OCH(CH₃)₂), 25.8/25.7 (CH₃CO), 21.7/21.6/21.5/21.4 (OCH(CH₃)₂).

2.10 Al(^tbuac)₃

An amount of 0.999 g (4.89 mmol) of Al(OⁱPr)₃ was dissolved in 10 mL of toluene at room temperature and 2.318 g (14.65 mmol) *tert*-butyl acetoacetate was slowly added under stirring. The clear reaction solution was stirred at room temperature for 18 h. The volatiles were then removed *in vacuo* and the resulting white, partially crystalline solid washed with dichloromethane. Yield 2.278 g (93%).

¹H NMR (δ [ppm], C₆D₆, 20 °C): 5.13/5.10/5.08 (s, 3H, COCHCO), 1.83/1.82/1.79 (s, 9H, CH₃CO), 1.46/1.45 (s, 27H, OC(CH₃)₃). ¹³C {¹H} NMR (δ [ppm], d₈-toluene, 20 °C): 187.2/187.0/186.9/186.6 (CO), 174.5/174.4/174.3/174.1 (COO), 86.4/86.2/86.1/86.8 (COCHCO), 80.6/80.3/

80.2/80.0 (OC(CH₃)₃), 28.8/28.3 (OC(CH₃)₃), 26.0/25.9/25.7 (CH₃CO).

2.11 Al(aaa)₃

An amount of 0.999 g (4.89 mmol) of Al(OⁱPr)₃ was dissolved in 10 mL of toluene at room temperature and 2.084 g (14.66 mmol) of allyl acetoacetate was slowly added under stirring. The slightly turbid reaction solution was stirred at room temperature for 18 h. The volatiles were then removed *in vacuo* and the resulting orange oil washed with dichloromethane. Yield 2.167 g (98%).

¹H NMR (δ [ppm], C₆D₆, 20 °C): 5.95–5.55 (m, 3H, OCH₂CH=CH₂), 5.15 (s, 3H, COCHCO), 5.10–4.85 (m, 6H, OCH₂CH=CH₂), 4.60–4.30 (m, 6H, OCH₂CH=CH₂), 1.81/1.79/1.78/1.76 (s, 9H, CH₃CO). ¹³C {¹H} NMR (δ [ppm], d₈-toluene, 20 °C): 188.6/188.4/188.2/188.0 (CO), 174.1/174.0/173.9/173.8 (COO), 132.7/132.6/132.5/132.4 (OCH₂CH=CH₂), 117.8/117.6/117.4/117.3 (OCH₂CH=CH₂), 85.1/84.9/84.8/84.7 (COCHCO), 65.2/65.0/64.8 (OCH₂CH=CH₂), 25.9/25.8 (CH₃CO).

2.12 Al(meaa)₃

An amount of 1.001 g (4.90 mmol) Al(OⁱPr)₃ was dissolved in 10 mL of toluene at room temperature and 3.153 g (14.72 mmol) of 2-(methacryloyloxy)ethyl acetoacetate was slowly added under stirring. The clear reaction solution was stirred at room temperature for 18 h. The volatiles were removed *in vacuo*, the crude product washed with dichloromethane and a colorless rubber-like mass was obtained. Yield 3.114 g (95%).

¹H NMR (δ [ppm], C₆D₆, 20 °C): 6.12/6.08 (s, 3H, OC(O)C(CH₃)=CH₂), 5.25–5.15 (m, 3H, OC(O)C(CH₃)=CH₂), 5.14 (s, 3H, COCHCO), 4.40–3.90 (m, 12H, OCH₂CH₂O), 1.85–1.75 (m, 18H, OC(O)C(CH₃)=CH₂), 1.85 (s, 9H, CH₃CO). ¹³C {¹H} NMR (δ [ppm], d₈-toluene, 20 °C): 189.2/189.0/188.6/188.5 (CO), 174.2/174 (COO), 166.3/166.2/166.1 (OC(O)C(CH₃)=CH₂), 136.1 (OC(O)C(CH₃)=CH₂), 125.3/125.0/124.8 (OC(O)C(CH₃)=CH₂), 85.1/84.9/84.8 (COCHCO), 62.5/62.4/62.3/62.2 (OCH₂CH₂O), 25.9/15.1 (CH₃CO), 17.9 (OC(O)C(CH₃)=CH₂).

3 Results and discussion

First attempts to prepare compounds [Al(OⁱPr)₂(β-ketoesterate)]_n by reaction of [Al(OⁱPr)₃]₄ with one molar equivalent of β-ketoester per Al at room temperature according to literature procedures for the modification of aluminum alkoxides with acetylacetone [5] and of titanium alkoxides with β-ketoesters [8, 9] did not yield the desired products. Even after prolonged reaction times at room

temperature, only a mixture of $\text{Al}(\beta\text{-ketoesterate})_3$ and unsubstituted $[\text{Al}(\text{O}^i\text{Pr})_3]_4$ was obtained for all esters used (Eq. 1).

Coordination of the β -ketoesterate ligand during this reaction was monitored by ^1H NMR spectroscopy, showing the disappearance of the signals of the CH_2 group between the two carbonyl groups of the non-coordinated esters (2.92–3.02 ppm) and the appearance of the signals for the corresponding CH proton of the deprotonated and coordinated ligand (5.18–5.08 ppm).

The exclusive formation of $\text{Al}(\beta\text{-ketoesterate})_3$ indicates that intermediate $[\text{Al}(\text{O}^i\text{Pr})_x(\beta\text{-ketoesterate})_{3-x}]_n$ species react more rapidly with β -ketoesters than $[\text{Al}(\text{O}^i\text{Pr})_3]_4$.

Heating the reaction solution, containing $\text{Al}(\beta\text{-ketoesterate})_3$ and $[\text{Al}(\text{O}^i\text{Pr})_3]_4$ along with liberated *iso*-propanol, to 120 °C overnight resulted in the formation of the anticipated $[\text{Al}(\text{O}^i\text{Pr})_2(\beta\text{-ketoesterate})]_n$ derivatives (Eq. 2). Reaction of isolated $\text{Al}(\beta\text{-ketoesterate})_3$ and $[\text{Al}(\text{O}^i\text{Pr})_3]_4$ in appropriate stoichiometric ratios in toluene (without free alcohol) gave the same results. After cooling to room temperature no redistribution to $\text{Al}(\beta\text{-ketoesterate})_3$ and $[\text{Al}(\text{O}^i\text{Pr})_3]_4$ occurred. This proves, that the monosubstituted dimer is the most stable species for this Al/β -ketoester ratio and the formation of $\text{Al}(\beta\text{-ketoesterate})_3$ at room temperature is due to a kinetic effect.

The same result was also obtained for an alternative preparation route, where a toluene solution of $[\text{Al}(\text{O}^i\text{Pr})_3]_4$ was thermally pre-treated. This is known to cause de-oligomerization of the tetrameric units [2, 10, 11]. According to literature, the solution consists mainly of dimeric and trimeric species after fast cooling to room temperature, but some tetrameric $[\text{Al}(\text{O}^i\text{Pr})_3]_4$ is still present or reformed. This was confirmed by ^{27}Al NMR spectroscopy, showing a broad signal for pentacoordinate Al of trimeric species in the range from about 45 to 15 ppm

[12], as well as a sharp signal at about 0 ppm for hexacoordinate Al of the tetramer, besides signals from about 80 to 50 ppm for tetracoordinate Al of di-, tri-, and tetrameric species (Fig. 2). ^1H NMR and EXSY spectroscopy additionally shows fast exchange between the alkoxo groups of all species present in the solution. After de-oligomerization of tetrameric $[\text{Al}(\text{O}^i\text{Pr})_3]_4$, the solution was cooled to room temperature, the β -ketoester was added and allowed to react for several hours. The resulting product was identified as $[\text{Al}(\text{O}^i\text{Pr})_2(\beta\text{-ketoesterate})]_2$, which means that pre-heating of the parent alkoxide and subsequent addition of ligand results in the same products as the in-situ heating of a mixture of the metal alkoxide and the ligand. This result shows (i) that reformation of $[\text{Al}(\text{O}^i\text{Pr})_3]_4$ from the dimer and trimer is slow at room temperature and (ii) that the dimer and trimer react faster with the β -ketoesters than the tetramer, and also faster than intermediate $[\text{Al}(\text{O}^i\text{Pr})_x(\beta\text{-ketoesterate})_{3-x}]_n$, giving directly the monosubstituted compounds.

The alternative synthetic pathway, i.e. thermal pre-treatment of the alkoxide, also opens the possibility to use temperature-sensitive ligands for modification. For example, gelation occurs when 2-(methacryloyloxy)ethyl acetoacetate (meaa-H), with its polymerizable methacrylic double bond, is reacted with $\text{Al}(\text{O}^i\text{Pr})_3$ at elevated temperatures, and no defined product could be isolated. In contrast, thermal de-oligomerization of the metal alkoxide tetramer and coordination of the ester under mild conditions (room temperature) yielded a well defined product, useable as precursor for inorganic–organic hybrid materials. Characterization by NMR spectroscopy showed the expected coordination of the β -ketoester giving rise to a signal at 5.05 ppm for the COCHCO proton. Signals for the $=\text{CH}_2$ protons of the methacrylate at 6.12 and 5.18 ppm showed preservation of the polymerizable double bond (Fig. 3). The small signal at 6.06 ppm results from minor impurities of $\text{Al}(\text{meaa})_3$, which is formed because in the pre-treated $\text{Al}(\text{O}^i\text{Pr})_3$ solution still some tetrameric $[\text{Al}(\text{O}^i\text{Pr})_3]_4$ is present, as mentioned above. Additional signals at about 7.10–7.00 ppm and at 2.10 ppm result from residual toluene.

The allyl acetoacetate derivative as an alternative compound bearing a polymerizable group can be

Fig. 2 Tetra-, tri- and dimeric form of $[\text{Al}(\text{OR})_3]_n$ ($n = 2\text{--}4$)

Fig. 3 ^1H NMR spectrum of $[\text{Al}(\text{O}^i\text{Pr})_2(\text{meaa})]_2$ in C_6D_6

synthesized by the “conventional” route because the ligand has a sufficient thermal stability.

All $\text{Al}(\text{OR})_2(\beta\text{-ketoesterate})$ derivatives show two ^1H NMR signals for the methine protons of the *iso*-propoxo groups, indicating the existence of two chemically different ligands. According to the X-ray analysis reported below, the derivatives are asymmetrically substituted, alkoxo-bridged dimers (Fig. 4). The structure type is the same as that of $[\text{Al}(\text{OSiMe}_3)_2(\text{acac})]_2$ [5]. In this structure, one aluminum center is tetrahedrally coordinated by two bridging and two terminal alkoxo groups, whereas the other aluminum center is octahedrally coordinated by two chelating β -ketoesterate ligands and the two bridging alkoxo groups. Given the asymmetric nature of the β -ketoesterate ligands, this results in three possible isomers, one C_1 and two C_2 symmetric (Fig. 4), each forming a pair of enantiomers, giving 6 stereoisomers overall. In the NMR spectrum, the C_2 symmetric complexes should show one set of signals for the ester ligands and two sets for the *iso*-propoxo groups (one for the bridging and one for the terminal) and splitting of these signals in two sets each for the C_1 symmetric complex. Since, in some cases, more than two signals were observed for the β -ketoesterate ligands and only two signals for the methine protons of the *iso*-propoxo groups, different isomers coexist in solution for which the *iso*-propoxo signals are not distinguishable. All signals were assigned by COSY, HSQC and HMBC NMR

Fig. 4 Possibly isomers of $[\text{Al}(\text{OR})_2(\beta\text{-ketoesterate})]_2$ (only one enantiomer shown for each geometry)

spectroscopy, showing the coexistence of more than one species in solution, but with one clearly dominating form. The methine signals of the *iso*-propoxo are clearly assigned to bridging and terminal groups, but in the CH_3 region multi signal overlap was observed and thus a definite assignment is difficult. The $[\text{Al}(\text{O}^i\text{Pr})_2(\beta\text{-ketoesterate})]_2$ complexes also show small signals beside a sharp main signal for the COCHCO proton. Only $[\text{Al}(\text{O}^i\text{Pr})_2(\text{t}^i\text{buac})]_2$ gave three signals of almost equal intensity.

Intermolecular ligand exchange between the different species was observed in EXSY experiments for all complexes. For the complexes $[\text{Al}(\text{O}^i\text{Pr})_2(\text{meac})]_2$, $[\text{Al}(\text{O}^i\text{Pr})_2(\text{t}^i\text{prac})]_2$, and $[\text{Al}(\text{O}^i\text{Pr})_2(\text{t}^i\text{buac})]_2$ splitting of the CH_3 protons of the methoxo, *iso*-propoxo and *tert*-butoxo ester groups, respectively, was also observed in the ^1H NMR spectra. Whereas this results in two signals of equal intensity for the t^iprac and t^ibuac derivative, one main signal at 3.59 ppm was found for the meac derivative, along with three smaller signals at 3.71, 3.52, and 3.24 ppm. In Fig. 5

Fig. 5 EXSY spectrum of $[\text{Al}(\text{O}^i\text{Pr})_2(\text{meac})]_2$ in $d_8\text{-toluene}$, OCH_3 -region

Table 1 ^1H NMR shifts of *iso*-propoxo groups of $[\text{Al}(\text{O}^i\text{Pr})_2(\beta\text{-ketoesterate})]_2$ ($\beta\text{-ketoesterate}$ = meac, etac, $^i\text{prac}$, $^t\text{buac}$) compared to $[\text{Al}(\text{O}^i\text{Pr})_3]_4$ (in C_6D_6)

	$\text{OCH}(\text{CH}_3)_2$ (bridging)	$\text{OCH}(\text{CH}_3)_2$ (terminal)	$\text{OCH}(\text{CH}_3)_2$ (bridging)	$\text{OCH}(\text{CH}_3)_2$ (terminal)
$[\text{Al}(\text{O}^i\text{Pr})_3]_4$	4.69	4.41	1.68/1.39 ^a	1.32
$[\text{Al}(\text{O}^i\text{Pr})_2(\text{meac})]_2$	4.45	4.16	1.49–1.30 ^b	1.49–1.30 ^b
$[\text{Al}(\text{O}^i\text{Pr})_2(\text{etac})]_2$	4.48	4.18	1.48	1.39
$[\text{Al}(\text{O}^i\text{Pr})_2(^i\text{prac})]_2$	4.50	4.21	1.48	1.39
$[\text{Al}(\text{O}^i\text{Pr})_2(^t\text{buac})]_2$	4.55	4.28	1.62–1.25 ^c	1.62–1.25 ^c

^a Splitting of bridging *iso*-propoxo groups [2]^b Overlap of bridging and terminal $\text{OCH}(\text{CH}_3)_2$ ^c Overlap with $\text{OC}(\text{CH}_3)_3$

the corresponding region of the EXSY spectrum is reproduced, showing exchange between all of these four signals.

In accordance with the NMR spectra of $[\text{Al}(\text{O}^i\text{Pr})_3]_4$ (see below), the signals for the bridging groups are shifted to lower field. The shifts of the O^iPr methine protons for the non-functional $\text{Al}(\text{OR})_2(\beta\text{-ketoesterate})$ derivatives are compared with that of $[\text{Al}(\text{O}^i\text{Pr})_3]_4$ in Table 1. The methine proton signals for all complexes are upfield shifted, corresponding to the reduced Lewis acidity of the substituted aluminum center. A slight trend to higher ppm values with increasing size of the ester OR groups for the ^1H NMR signals of the methine protons is observed. Corresponding ^{13}C NMR signals are not influenced by the ester OR group.

Crystals were obtained for the complex $[\text{Al}(\text{O}^i\text{Pr})_2(^t\text{buac})]_2$, and an X-ray crystal structure analysis was carried out. Although the quality of the data set was affected by formation of thin platelets and partial decomposition of the crystal during the measurement, the dimeric nature of the compound with one octahedrally and one tetrahedrally coordinated aluminum atom was confirmed (Fig. 6), and the C_1 isomer (Fig. 4) with the two ester groups occupying an equatorial and an axial position was found (“equatorial position” refers to the $\text{Al}_2(\mu\text{-OR})_2$ plane). Selected bond distances and angles are given in Table 2.

The Al–O distances of the chelating $^t\text{buac}$ are longer for the “ester” oxygen compared to that of the “keto” oxygen.

Fig. 6 Molecular structure of $[\text{Al}(\text{O}^i\text{Pr})_2(^t\text{buac})]_2$ in the crystalline state

Table 2 Selected bond distances [pm] and angles [deg] of $[\text{Al}(\text{O}^i\text{Pr})_2(^t\text{buac})_2]$

Al(1)–O(1)	171.4(5)	Al(2)–O(6)	190.4(4)
Al(1)–O(2)	171.5(4)	Al(2)–O(8)	185.0(4)
Al(1)–O(3)	180.4(4)	Al(2)–O(9)	192.6(4)
Al(1)–O(4)	180.0(4)	O(5)–C(14)	128.1(6)
Al(2)–O(3)	190.1(4)	O(6)–C(16)	126.9(6)
Al(2)–O(4)	191.7(4)	O(8)–C(22)	129.7(7)
Al(2)–O(5)	187.2(4)	O(9)–C(24)	125.7(7)
O(1)–Al(1)–O(2)	113.5(2)	O(4)–Al(2)–O(6)	93.9(2)
O(3)–Al(1)–O(4)	113.2(2)	O(4)–Al(2)–O(9)	87.4(2)
Al(1)–O(3)–Al(2)	100.4(2)	O(5)–Al(2)–O(6)	91.0(2)
Al(1)–O(4)–Al(2)	99.9(2)	O(5)–Al(2)–O(8)	89.4(2)
O(3)–Al(2)–O(4)	77.1(2)	O(6)–Al(2)–O(8)	92.9(2)
O(3)–Al(2)–O(5)	89.9(2)	O(6)–Al(2)–O(9)	86.0(2)
O(3)–Al(2)–O(8)	96.2(2)	O(8)–Al(2)–O(9)	90.8(2)
O(3)–Al(2)–O(9)	93.1(2)	O(3)–Al(2)–O(6)	170.9(2)
O(4)–Al(2)–O(5)	92.8(2)	O(4)–Al(2)–O(8)	172.9(2)
		O(5)–Al(2)–O(9)	177.0(2)

An additional trans effect from the bridging alkoxo groups causes shorter bond lengths for the equatorial bonds. The Al–O bond distances of the $^t\text{buac}$ ligands decrease in the order Al–O_{ester,ax} (192.6(4) pm) > Al–O_{ester,eq} (190.4(4) pm) > Al–O_{keto,ax} (187.2(4) pm) > Al–O_{keto,eq} (185.0(4) pm). Vice versa, the different substituents trans to the bridging alkoxo groups result in an asymmetric bridging situation (Al(2)–O(3) 190.1(4) pm and Al(2)–O(4) 191.7(4) pm).

The bridging Al–O distances Al(2)–O(3) and Al(2)–O(4) are significantly longer than Al(1)–O(3) (180.4(4) pm) and Al(1)–O(4) (180.0(4) pm), showing the bond distances from the bridging oxygen atoms to the octahedral aluminum center to be significantly longer than to the tetrahedral center. As expected, the distances Al(1)–O(1) 171.4(5) and Al(1)–O(2) 171.5(4) of the terminal alkoxo groups are distinctly shorter than that of the bridging groups.

For a better understanding of the coordination behavior of the β -ketoesterate ligands and their above mentioned formation at room temperature, the trisubstituted monomeric $\text{Al}(\beta\text{-ketoesterate})_3$ complexes were also studied for all ligands. The complexes were prepared by addition of three molar equivalents of the β -ketoester to the alkoxide. The structure of $\text{Al}(^t\text{buac})_3$ was previously determined [13]. The ^{27}Al chemical shift of 4.78 ppm in the NMR spectrum of $\text{Al}(\text{etac})_3$ is in line with the octahedral coordination of the aluminum atom. ^1H and ^{13}C NMR spectra of the $\text{Al}(\beta\text{-ketoesterate})_3$ compounds showed up to 4 signal sets for the ester groups. This is a result of the coexistence of different isomers in solution, viz. a C_3 symmetric isomer with the keto and ester oxygen atoms

Fig. 7 Different isomers of $\text{Al}(\beta\text{-ketoesterate})_3$ complexes

respectively in *fac* arrangement and a C_1 symmetric isomer with *mer* arrangement. In the C_3 symmetric complex, all ligands are symmetrically equivalent giving rise to one set of signals in the NMR spectra, whereas for the C_1 symmetric complex all ligands are non-equivalent, causing one set of signals for each ligand (Fig. 7). As a matter of fact each isomer forms a pair of enantiomers, which in the context of the NMR studies has no further consequences. Although the signals could not be assigned to the C_1 or C_3 isomer, the observation of four signal sets of equal intensity in the ^1H NMR spectra corresponds to a 1:3 ratio of C_3 and C_1 symmetric species. Variable temperature NMR showed that the isomers can transform into each other. Coalescence was observed above 80 °C, causing an averaged signal set (Fig. 8). EXSY experiments confirmed exchange of the β -ketoesterate signals between the different isomers. The CH_3 region of the EXSY spectrum of $\text{Al}(\text{etac})_3$ is given in Fig. 9, showing exchange for the CH_3CO (1.90–1.80 ppm) and OCH_2CH_3 (1.12–0.92 ppm) signals.

The ^1H chemical shifts of the β -keto protons of the coordinated ligands for the mono- and trisubstituted complexes are compared in Table 3. The signals for the trisubstituted species are shifted to somewhat higher ppm values for all complexes (5.18–5.08 ppm compared to 5.10–4.98 ppm for $[\text{Al}(\text{OR})_2(\beta\text{-ketoesterate})_2]$). No correlation between the chemical shifts of β -keto protons and carbons and the size of the ester OR groups was observed. The ^{13}C NMR shift differences between the mono- and trisubstituted complexes were not significant.

It is known that transesterification can occur as a possible side reaction during the reaction of metal alkoxides with esters [8] or can be used selectively as a preparative synthetic method [14]. Transesterification would change the structural and chemical properties of the metal alkoxides; for β -ketoesters with a functional OR group this would also result in the loss of the organic functionality. Transesterification as possible side reaction was studied for the reaction of the β -ketoesters with $[\text{Al}(\text{O}^i\text{Pr})_3]_4$ by NMR spectroscopy. If transesterification would occur, *iso*-propyl acetoacetate derivatives would be formed. ^1H NMR

Fig. 8 Temperature dependent ^1H NMR OCH_2CH_3 resonances of $\text{Al}(\text{etac})_3$ (d_8 -toluene)

Fig. 9 EXSY spectrum of $\text{Al}(\text{etac})_3$ at 20°C in d_8 -toluene, CH_3 -region

spectroscopy allows easy monitoring of the transesterification because the signal of the methine proton of the formed *iso*-propylacetoacetate at 5.15–4.85 ppm (in the monosubstituted complex) and 5.35 ppm (in the trisubstituted complex) is considerably shifted to higher ppm

Table 3 Comparison of ^1H NMR shifts of β -keto protons of $[\text{Al}(\text{O}^i\text{Pr})_2(\beta\text{-ketoesterate})]_2$ and $\text{Al}(\beta\text{-ketoesterate})_3$ complexes (in C_6D_6)

	$[\text{Al}(\text{O}^i\text{Pr})_2(\beta\text{-ketoesterate})]_2$	$\text{Al}(\beta\text{-ketoesterate})_3$
meac-H	5.07 (5.06) ^a	5.17
etac-H	5.10 (5.08) ^a	5.18/5.17
ⁱ prac-H	5.06 (5.04) ^a	5.16
^t buac-H	5.06/5.05/4.98	5.13/5.10/5.08
aaa-H	5.10	5.15
meaa-H	5.05	5.14

^a Values in brackets: signals of minor components with different coordination geometry

values compared with the signals of all the other esters. Additional evidence was obtained from HMBC experiments which show long range coupling between the methine proton and a carbonyl carbon if the *iso*-propyl ester was formed.

In no case was transesterification observed, neither at room temperature nor at 120°C , except for the reaction of $[\text{Al}(\text{O}^i\text{Pr})_3]_4$ with *three* equivalents of ^tbuac-H at 120°C . $\text{Al}(\text{buac})_3$, formed at room temperature, reacts at 120°C overnight with the liberated *iso*-propanol still present in the reaction solution to give $\text{Al}(\text{buac})_{3-x}(\text{prac})_x$. This reaction was studied in more detail by NMR spectroscopy, recording spectra in situ at 80°C in intervals of 2 and 4 h, respectively. Figure 10 shows the time dependence of the ratio between free *iso*-propanol and *tert*-butanol only could originate from the transesterification reaction. Longer reaction times finally led to complete substitution of all *tert*-butoxo groups by *iso*-propanol, giving $\text{Al}(\text{prac})_3$. Interestingly, for the reaction of $[\text{Al}(\text{O}^i\text{Pr})_3]_4$ with *one* equivalent of ^tbuac-H, after heating for 18 h to 120°C , no transesterification was observed and crystalline $[\text{Al}(\text{O}^i\text{Pr})_2(\text{buac})]_2$ was the only product. From the results it is assumed that the steric demand of the

Fig. 10 Time dependence of $^1\text{PrOH}/\text{BuOH}$ ratio at 80°C in d_8 -toluene

tert-butoxo group in $\text{Al}(\text{t}^{\text{buac}})_3$ favors transesterification and formation of sterically less demanding $\text{Al}(\text{t}^{\text{buac}})_{3-x}(\text{t}^{\text{prac}})_x$ species. Since one t^{buac} ligand in $[\text{Al}(\text{O}^{\text{iPr}})_2(\text{t}^{\text{buac}})]_2$ is replaced by two *iso*-propoxo groups, the steric constraint might be low enough to not cause transesterification in this case.

4 Conclusions

The substitution of $[\text{Al}(\text{O}^{\text{iPr}})_3]_4$ with one or three equivalents of the β -ketoesters meac-H, etac-H, t^{prac} -H, t^{buac} -H, aaa-H and meaa-H per Al resulted in derivatives $[\text{Al}(\text{O}^{\text{iPr}})_2(\beta\text{-ketoesterate})]_2$ and $\text{Al}(\beta\text{-ketoesterate})_3$, respectively, although special synthesis protocols are required to obtain $[\text{Al}(\text{O}^{\text{iPr}})_2(\beta\text{-ketoesterate})]_2$ derivatives. The monosubstituted derivatives $[\text{Al}(\text{O}^{\text{iPr}})_2(\beta\text{-ketoesterate})]_2$ are asymmetric dimers with one octahedrally coordinated Al center substituted by two ester ligands and one tetrahedrally coordinated Al atom surrounded by two bridging and two terminal *iso*-propoxo groups. The trisubstituted compounds $\text{Al}(\beta\text{-ketoesterate})_3$ are mononuclear octahedral complexes, giving rise to C_1 and C_3 symmetric isomers due to the asymmetric chelating ligand.

The alkoxo group of the esters had no influence on the structure of the products and only minor influence on the electronic properties, reflected in slightly different ^1H NMR shifts of the bridging and terminal *iso*-propoxo groups of the monosubstituted dimers.

Only in two cases the type of ligand used had consequences on the preparation and stability of the substituted aluminum alkoxide derivatives: (i) The complex $\text{Al}(\text{t}^{\text{buac}})_3$ undergoes transesterification in the presence of *iso*-propanol, giving $\text{Al}(\text{t}^{\text{prac}})_x(\text{t}^{\text{buac}})_{3-x}$. This behavior is attributed to the steric bulk of the *tert*-butoxo groups. (ii) Due to the thermal reactivity of the methacrylate substituent of meaa-H, direct reaction of $[\text{Al}(\text{O}^{\text{iPr}})_3]_4$ with meaa-H is not possible. However, $[\text{Al}(\text{O}^{\text{iPr}})_2(\text{meaa})]_2$ can be prepared by thermal de-oligomerization of $[\text{Al}(\text{O}^{\text{iPr}})_3]_4$ followed by addition of the ligand at room temperature.

Contrary to analogous reactions with acetylacetone [5, 6], the monosubstituted complexes $[\text{Al}(\text{O}^{\text{iPr}})_2(\beta\text{-ketoesterate})]_2$ were not formed when the compounds are reacted at room temperature. Mixtures of trisubstituted $\text{Al}(\beta\text{-ketoesterate})_3$ and non-reacted $[\text{Al}(\text{O}^{\text{iPr}})_3]_4$ were instead obtained. Formation of the monosubstituted complexes $[\text{Al}(\text{O}^{\text{iPr}})_2(\beta\text{-ketoesterate})]_2$ was achieved by heating this mixture at 120 °C, and they are stable after cooling to room temperature, indicating $[\text{Al}(\text{O}^{\text{iPr}})_2(\beta\text{-ketoesterate})]_2$ has a higher thermodynamic stability. Compared to $[\text{Al}(\text{O}^{\text{iPr}})_2(\text{acac})]_2$ [5], no aging to trimeric $[\text{Al}(\text{O}^{\text{iPr}})_2(\beta\text{-diketonate})]_3$ was observed for the β -ketoesterate derivatives. Thus, significant differences in reactivity of β -ketoesters and

β -diketones with $[\text{Al}(\text{O}^{\text{iPr}})_3]_4$ are noticed, since the structures of the formed derivatives may be different depending on the side conditions (temperature, time). This may have important consequences if those ligands are used to modify aluminum alkoxides for sol–gel processing.

5 X-Ray Structure Analysis

A plate-like crystal of $[\text{Al}(\text{O}^{\text{iPr}})_2(\text{t}^{\text{buac}})]_2$ was mounted on a Siemens SMART diffractometer with an area detector and measured in a nitrogen stream. Mo- K_α radiation ($\lambda = 71.069$ pm, graphite monochromator) was used for all measurements. The data collection (Table 4) at 100 K covered a hemisphere of the reciprocal space, by a combination of three sets of exposures. Each set had a different ϕ angle for the crystal, and each exposure took 25 sec and covered 0.3° in ω . The crystal-to-detector distance was 5 cm. The crystal partially decomposed during measurement. The data were corrected for polarization and Lorentz effects, and an empirical absorption correction (SADABS) was employed. The cell dimensions were refined with all unique reflections.

The structure was solved by direct methods (SHELXS97). Refinement was performed by the full-matrix least-squares method based on F^2 (SHELXL97) with anisotropic

Table 4 Crystallographic and structural parameters of $[\text{Al}(\text{O}^{\text{iPr}})_2(\text{t}^{\text{buac}})]_2$

Empirical formula	$\text{C}_{28}\text{H}_{54}\text{Al}_2\text{O}_{10}$
Formula weight	604.7
Crystal system	Monoclinic
Space group	$P2_1/n$
<i>a</i> [pm]	9.553(4)
<i>b</i> [pm]	18.029(7)
<i>c</i> [pm]	20.475(9)
α [°]	90.00
β [°]	91.825(8)
γ [°]	90.00
Volume [10^6 pm ³]	3525(3)
<i>Z</i>	4
Calcd. density [g cm^{-3}]	1.139
μ [mm^{-1}]	0.129
Crystal size [mm]	$1.60 \times 1.40 \times 0.10$
2θ range [°]	2.41–28.45
Reflections collected/unique	12759/6606
Data/parameters	6606/377
GOF on F^2	0.991
<i>R</i> [$I > 2\sigma(I)$]	0.1165
wR_2	0.3253
Largest peak/hole [$\text{e \AA}^{-3}$]	0.581/−0.375

thermal parameters for all non-hydrogen atoms. Hydrogen atoms were inserted in calculated positions and refined riding with the corresponding atom.

CCDC-694178 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

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