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Dramatic structural changes of donor-functionalized alkoxides of aluminium upon replacement of the ester functionality by ketone

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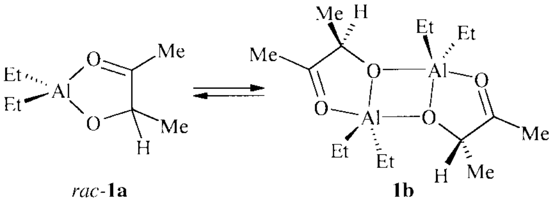
Upon replacement of the ester functionality by ketone functionality in α-hydroxy carbonyl compounds dramatic structural changes of donor-functionalized alkoxides of aluminium are observed: complete reversal of the stereochemistry of the aluminium alkoxide adduct formation, dissociation of the five-coordinate dimer to a monomeric four-coordinate chelate complex; the first example of an aluminium Cram-type chelate complex derived from the reaction of Et_3Al with an equimolar amount of *rac*-acetoin is reported.

Organometallic chelate compounds have been considered as intermediates in the often highly stereoselective reactions of nucleophilic addition to carbonyl compounds and more recently for radical reactions.[1,2] Recently, organoaluminium compounds have emerged as useful reagents for radical reactions,[2] including controlling the stereoselectivity of reactions of hydroxy ester enolate and hydroxy ether radicals.[3] In several cases the formation of monomeric four-coordinate aluminium chelate complexes have been proposed to account for the observed stereoselectivity,[2] which contrast with the well-known tendency of dialkylaluminium compounds derived from donor-functionalized alcohols (HO,X) to form dimeric five-coordinate complexes, $[R_2Al(O,X)]_2$.[4,5] It is worth noting that although five-coordination is almost exclusively observed in the solid state, this group of compounds exhibits a considerably greater structural variety in solution depending on the nature of the bifunctional ligand. For example, dialkylaluminium derivatives of saturated α- and β-hydroxy carbonyls maintain a dimeric five-coordinate structure in solution, however, they are nonrigid and dissociation of the Al–O chelate bonds gives rise to the rapid interchange of the chelating groups between two aluminium centres whilst the central Al_2O_2 bridging ring remains intact.[5–7]

As a part of our research program directed towards the understanding of factors controlling the structure and reactivity of organoaluminium complexes, we have become interested in the synthesis of aluminium alkoxides derived from chiral donor-functionalized alcohols. Very recently, we have shown that the formation of the $[R_2Al(O,O')]_2$ adduct is a highly stereoselective reaction, *e.g.*, in the equimolar reaction of ethyl *rac*-lactate (elacH) with Me_3Al only monomeric units of the same configuration as the chiral centre in the chelating ligand join with each other forming only the (*R*,*R*)- and (*S*,*S*)-$[Me_2Al(elac)]_2$ diastereomers.[5,7] This paper presents our initial findings on the synthesis and structural characterisation of the dialkylaluminium derivative of *rac*-acetoin (acetH), a chiral α-hydroxy ketone. The replacement of the ester group by ketone in the α-hydroxy carbonyl compounds studied leads to a complete reversal of the stereochemistry of the aluminium alkoxide adduct formed. A particularly significant point of the resulting product is its occurrence in an equilibrium mixture of monomer *rac*-Et_2Al(acet) **1a** and dimer (*R*,*S*)-$[Et_2Al(acet)]_2$ **1b** in solution (Scheme 1). Furthermore, **1a** represents a rare example of a stable Cram-type chelate.[1]

The interaction of Et_3Al with an equimolar amount of *rac*-acetoin (acetH) in CH_2Cl_2 at −78 °C results in ethane evolution and the quantitative formation of *rac*-$[Et_2Al(acet)]_n$ **1** (were *n* = 1, **1a**, or 2, **1b**). After a standard work up at room temperature, compound **1** is obtained initially as a liquid, changing over several hours to the solid state. ^1H, ^{13}C and ^{27}Al NMR and IR spectroscopic data in combination with cryoscopic molecular weight determination provide an insight into the structural features of compound **1** both in solution and in the solid state.† Thus, both the ^1H NMR spectrum of the post reaction mixture and cryoscopic determination of the liquid crude product revealed that initially the reaction product consists essentially of monomer **1a**, whereas the solid product, dissolved in benzene, was identified as the dimer **1b**. For example, the ^1H NMR spectrum of **1b** in a freshly prepared C_6D_6 solution (4.7% by weight) at 20 °C shows a quartet and a doublet for the CH proton and its adjacent methyl group, respectively, both associated with the chiral centre, as well as two well separated resonances for both methylene and methyl protons of the Al–CH_2CH_3 groups. After several minutes at 20 °C a new set of signals appears in the spectrum: a doublet of quartets for the Al–$C\mathit{H}_2CH_3$ protons, a triplet associated with the Al–$CH_2C\mathit{H}_3$ protons and a quartet and doublet of the protons associated with the chiral centre. The new signals were assigned to the monomeric chelate complex **1a**. It should be noted that the observed ^1H NMR patterns are simpler than expected due to the diastereotopic methylene protons of the Al–CH_2CH_3 groups, which in our opinion reflect a dynamic behaviour of the studied species in solution (see below). In time the resonances associated with **1b** decrease and those from **1a** increase, and the monomer–dimer equilibrium (Scheme 1) is established within three days. The dissociation of **1b** to the monomeric species was verified by cryoscopic molecular weight investigations in benzene solution which gave results fully consistent with the ^1H NMR measurements. The rate for the dissociation of dimer to monomers and the equilibrium constant at 20 °C, based upon ^1H NMR measurements, are $k_1 = 0.026\ h^{-1}$ and $K_{eq} = 0.73$ mol dm^{-3}, respectively. The plot of ln K_{eq} *vs.* $1/T$ yields $\Delta H° = -4.0 \pm 1.3$ kJ mol^{-1} and $\Delta S° = -16.7 \pm 4.3$ J K^{-1} mol^{-1}.



rac-**1a** **1b**

Scheme 1

Furthermore, the ^{13}C NMR spectra of **1a** and **1b** at ambient temperature compliment the ^1H NMR data. For example, the spectrum of **1a** shows one type of carbon resonance each for the methylene and methyl carbons of the ethyl groups of the Al–CH_2CH_3 groups, while in **1b** they appear as two resonances each. Furthermore, the presence of two well separated ethyl resonances in the ^1H and ^{13}C NMR spectra of **1b** even at higher temperature (up to 60 °C) indicates the *trans* structure for this adduct, *i.e.*, only monomeric units of the opposite configuration as the chiral centre in the chelating ligand associate with

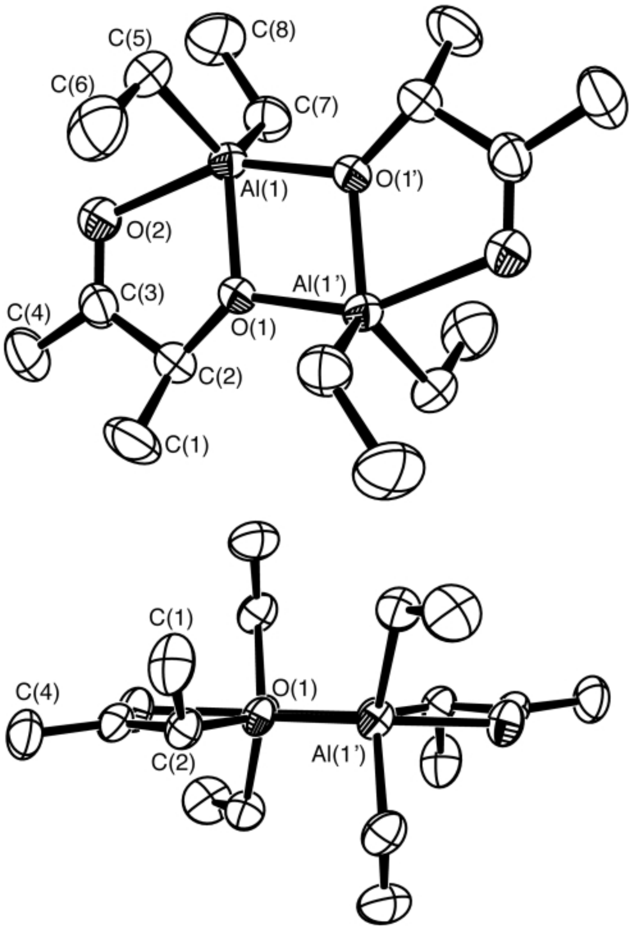


Fig. 1 ORTEP[10] plot of the molecular structure of (*R*,*S*)-[$Et_2Al(acet)]_2$ **1b** with thermal ellipsoids drawn at 30% probability level. Bottom: view of the molecule along a mean plane formed by the heterocyclic rings. Hydrogen atoms are omitted for clarity. Atoms labelled with prime belong to the centrosymmetric counterparts of the dimeric unit. Selected bond lengths (Å) and angles (°): Al(1)–O(1) 1.8452(18), Al(1)–O(1′) 1.9328(19), Al(1)–O(2) 2.166(2), Al(1)–C(5) 1.971(3), Al(1)–C(7) 1.987(3); O(1)–Al(1)–C(5) 119.11(12), O(1)–Al(1)–C(7) 117.12(13), C(5)–Al(1)–C(7) 122.26(15), O(2)–Al(1)–O(1′) 152.63(9), O(1)–Al–O(1′) 75.88(8), Al(1)–O(1)–Al(1′) 104.12(8).

each other. Very recently we have revealed a nonrigid structure for the analogous five-coordinate adduct derived from an α-hydroxy ester, (R^*,R^*)-[$Me_2Al(elac)]_2$,[7] and therefore it is reasonable to assume dynamic behaviour for dimer **1b** in solution. However, in the case of the *R*,*S* adduct the interchange of the coordinated carbonyl groups between the two aluminium atoms leads to no interchange of ethylaluminium environments and the *trans* complex will display different ethyl group resonances over a wide temperature range. According to our findings for the diethylaluminium derivative of ethyl *rac*-lactate, a different NMR pattern at ambient temperature should be expected for the nonrigid *R*,*R* and *S*,*S* dimers.[7] Additionally, it is interesting to note that an upfield shift of the ^{27}Al NMR resonance is observed with the rearrangement of the five-coordinate adduct **1b** (δ 131) to the four-coordinate complex **1a** (δ 122); thus, the shift is opposite to the expected coordination number effects.[8]

We conducted a crystal structure analysis of **1b** to further substantiate the geometrical molecular arrangement.‡ The structure determination reveals that **1b** crystallises in the $P\bar{1}$ space group with two unique dinuclear molecules in the unit cell, which reside on the centres of inversion. The two independent molecules have almost identical geometry, but in one molecule some disorder in the region of the methyl group was observed. Therefore we discuss here the geometric parameters of the non-disordered molecule. The oxygen-bridged dimeric molecule wherein the aluminium atoms are five-coordinate (Fig. 1) show C_i point group symmetry and the methyl group bonded to the chiral C-atom in the μ,η^2 bridging acetoinato ligands lie on the opposite side of the plane outlined by three fused heterocyclic rings. Thus, in the case of the dialkylaluminium derivative of acetoin adduct formation leads exclusively to the (*R*,*S*)-[$R_2Al(O,O')]_2$-type diastereomer, contrary to the result mentioned above for the five-coordinated adduct derived from a chiral α-hydroxy ester.[5,7] The observed change in stereoselectivity upon sterically neutral substitution of saturated donor-functionalized alcohols indicate a unique stereoelectronic control in adduct formation and the nature of this phenomena is a subject of further study. Additionally, the solid structure of **1b** is of the same morphology as related dialkylaluminium alkoxides derived from donor-functionalized alcohols.[4,5] The aluminium atoms adopt a distorted trigonal bipyramidal geometry with the most significant distortion found for the angle defined by axial substituents [O(2)–Al(1)–O(1′), 152.63(9)°]. For **1b** corresponding Al–O distances [1.845(2), 1.933(2) and 2.166(2) Å] are roughly the same as for the related hydroxy ester derivative, (R^*,R^*)-[$Me_2Al(elac)]_2$ [1.848(2), 1.936(2) and 2.157(2) Å, respectively].[7]

In conclusion, our study unambiguously shows that replacement of the ester functional group by ketone can have a profound effect on the aggregation behaviour of donor-functionalized alkoxides of aluminium. Therefore, when one considers the mechanism of reaction involving an organoaluminium reagent–donor-functionalized alcohol system then the aggregation state of the intermediates has to be considered. Further, the subject of this investigation gives potentially unique opportunities for a facile comparison of the Cram cyclic model for nucleophilic additions (especially for mild C-nucleophiles which do not destroy chelation) based on the monomeric four-coordinate and dimeric five-coordinate chelate complexes.[9]

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Notes and references

† Synthesis and selected data for **1a** and **1b**. To a suspension of *rac*-acetoin (7.0 mmol) in CH_2Cl_2 (15 cm^3) was added dropwise Et_3Al (7.0 mmol) at −78 °C. After the addition was complete the reaction mixture was allowed to warm to room temperature. The solvent was then removed under vacuum, leaving a colourless viscous liquid, and ^{1}H NMR spectroscopy showed it to consist of predominantly monomeric species. After dissolution of the crude product in hexane at room temperature and gradual cooling of the solution to −10 °C, the crystals formed were collected by filtration. Calc. for $C_{16}H_{34}Al_2O_4$: C, 55.80; H, 9.95. Found: C, 55.9; H, 9.8%. ^{1}H NMR (C_6D_6, 20 °C): **1a** δ 0.24 (4H, m, Al-CH_2CH$_3$), 1.08 (3H, d, CH-CH_3), 1.24 (3H, s, CH$_3$), 1.44 (6H, t, Al-CH$_2$$CH_3$), 4.22 (1H, q, CH); **1b** δ 0.16 (q, 4H, Al-CH_2CH$_3$), 0.34 (4H, q, Al-CH_2CH$_3$), 1.065 (6H, d, CH-CH_3), 1.27 (6H, s, CH$_3$), 1.33 (6H, t, Al-CH$_2$$CH_3$), 1.55 (6H, t, Al-CH$_2$$CH_3$), 4.14 (2H, q, CH). ^{13}C NMR (C_6D_6, 20 °C): **1a** δ 2.03 (br, Al-CH$_2$CH$_3$), 10.74 (Al-CH$_2$$CH_3$), 19.51 (CH$_3$), 22,47 (CH$_3$), 74.67 (OCH), 217.87 (CO); **1b** δ 0.78 (br, Al-CH$_2$CH$_3$), 3.95 (br, Al-CH$_2$CH$_3$), 10.65 (Al-CH$_2$$CH_3$), 10.78 (Al-CH$_2$$CH_3$), 19.51 (CH$_3$), 22.52 (CH$_3$), 74.97(OCH), 217.51 (CO). ^{27}Al NMR: δ 122 and 131 for **1a** and **1b**, respectively. IR (CH_2Cl_2, $\nu_{C=O}$): 1692 cm^{-1} (**1a**); 1694 cm^{-1} (**1b**). Equilibrium studies: a benzene-d_6 solution of **1b** (4.7% by weight) in a NMR tube was placed in a water bath maintained at 20 °C. A series of ^{1}H NMR spectra were collected over four days. The integration of the proton resonances of the methyl groups bonded to the carbonyl carbon atoms was used to determine the relative quantity of dimeric and monomeric species. Molecular weight measurements (cryoscopically in benzene, 4.7% by weight): Calc: 344.4 (dimer) and 172.2 (monomer). Found: 323 (after dissolution of the solid), 205 (after 70 h at 20 °C).

‡ Crystal data for **1b**: $C_{16}H_{34}Al_2O_4$, $M = 344.39$, triclinic, space group $P\bar{1}$ (no. 2), $Z = 2$, $a = 7.3458(18)$, $b = 8.8850(17)$, $c = 16.789(3)$ Å, $\alpha = 84.371(16)$, $\beta = 86.844(18)$, $\gamma = 78.253(17)°$, $U = 1068.3(4)$ Å^3, $T = 20$ °C, μ(Mo-Kα) = 0.149 mm^{-1}, 7403 reflections collected, 3785 unique ($R_{int} = 0.022$) which were used in all calculations. The structure was refined to final values of $R1 = 0.059$, $wR(F^2) = 0.163$ for 2947 reflections with $F_o > 4\sigma(F_o)$. CCDC reference number 186/1579. See http://www.rsc.org/suppdata/dt/1999/2909/ for crystallographic files in .cif format.

1 For reviews of chelation controlled nucleophile addition reactions see: M. T. Reetz, *Angew. Chem.*, *Int. Ed. Engl.*, 1984, **23**, 556; M. T. Reetz, *Acc. Chem. Res.*, 1993, **26**, 462; A. Mengel and O. Reiser, *Chem. Rev.*, 1999, **99**, 1191.

2 For a review of Lewis acids used in free radical reactions see: P. Renaud and M. Gerster, *Angew. Chem.*, *Int. Ed.*, 1998, **37**, 2562.

3 H. Urabe, K. Yamashita, K. Suzuki, K. Kobayashi and F. Sato, *J. Org. Chem.*, 1995, **60**, 3576; M. Gerster, K. Schenk and P. Renaud, *Angew. Chem.*, *Int. Ed. Engl.*, 1996, **35**, 2396; M. Gerster, L. Audergon, N. Moufid and P. Renaud, *Tetrahedron Lett.*, 1996, **37**, 6335.

4 *Coordination Chemistry of Aluminium*, ed. G. H. Robinson, VCH, New York, 1993; R. Benn, E. Janssen, H. Lehmkuhl and A. Rufińska, *J. Organomet. Chem.*, 1987, **333**, 169.

5 J. Lewiński, J. Zachara and I. Justyniak, *Organometallics*, 1997, **16**, 3859.

6 See also: E. A. Jeffery, A. Meisters and T. Mole, *J. Organomet. Chem.*, 1974, **74**, 373.

7 J. Lewiński, J. Zachara and I. Justyniak, *Chem. Commun.*, 1997, 1519.

8 It is generally assumed that the observed ^{27}Al NMR chemical shift is diagnostic of the compound coordination state and an upfield shift is expected with increasing coordination number for a given class of compounds. R. Benn, A. Rufińska, H. Lehmkuhl, E. Janssen and C. Kruger, *Angew. Chem.*, *Int. Ed. Engl.*, 1983, **22**, 779; R. Benn, E. Janssen, H. Lehmkuhl and A. Rufińska, *J. Organomet. Chem.*, 1987, **333**, 152.

9 Very recently this concept was successfully used with titanium reagents, see G. Bartoli, M. C. Bellucci, M. Bosco, E. Marcantoni and L. Sambri, *Chem. Eur. J.*, 1998, **4**, 2154.

10 M. N. Burnett and C. K. Johnson, ORTEPIII, Report ORNL-6895, Oak Ridge National Laboratory, Oak Ridge, TN, 1996.

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