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Electronic Factors Determining the Rearrangement of Dialkylaluminum *O,O′*-Chelate Compounds from Dimeric Five- to Monomeric Four-Coordinated Complexes on Dissolution. Structure Investigations of Dialkylaluminum Chelate Derivatives of α- and *β*-Hydroxy Carbonyl Compounds

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The synthesis and the structure characterization of dialkylaluminum *O,O′*-chelate complexes derived from α- and *β*-hydroxy carbonyl compounds: α-tropolone (tropH), ethyl *rac*-lactate (elacH), and 2-acetyl-4-chlorophenol (*Cl*-acphH), with saturated and conjugated unsaturated bond systems, are reported. The reaction of R_3Al with an equimolar amount of the hydroxy carbonyl compound leads to the formation of $[R_2Al(O,O')]_n$ chelate complexes [where *O,O′* = *Cl*-acph, R = Me (**1a**); trop, R = Et (**2b**); elac, R = Me (**3**)]. According to the X-ray study these compounds are dimeric in the solid state. The aluminum atoms adopt a distorted trigonal bipyramidal geometry with a long internal (in **1a** and **2b**) or external (in **3**) Al−O axial bond. In addition, complex **3** posseses a C_2 symmetry, which indicates that the five-coordinated $[R_2Al(O,O')]_2$-type adduct is formed in a highly stereoselective manner. In solution **1a** and **2b** adducts rearrange to the monomeric four-coordinated chelate complexes, while **3** remains a dimeric structure found in the solid state, as confirmed by cryoscopic molecular weight determination and ^1H and ^{27}Al NMR and IR spectroscopy. The influence of the nature of the *O,O′*-bifunctional ligand on the structure of dialkylaluminum chelate complexes in the solid state and in solution and the geometry of the aluminum coordination sphere are discussed on the basis of the results reported and structural data of related compounds.

Introduction

Organoaluminum derivatives of *O,O′*-bifunctional ligands have been investigated for many years due to their practical and fundamental importance. For example, these compounds have been reported as catalysts or precursors of catalysts in polymerization processes[1,2] or as organometallic intermediates in carbon−carbon bond formation reactions.[2,3] However, fully characterized organoaluminum *O,O′*-chelate complexes are surprisingly rare. Despite the fact that the $[R_2Al(O,O')]_2$-type adduct, the $[Me_2Al(\mu\text{-}OC(CH_3)N(Ph)CO(Ph))]_2$ compound derived from the condensation reaction, has been reported to be the first crystallographically characterized five-coordinated organoaluminum compound as early as in 1972,[2a] to date there have been only few related compounds, derivatives of hydroxy ethers and methoxyphenols, studied by both NMR spectroscopy and by X-ray diffraction, to provide details concerning their structures.[4−6] We have recently synthesized and structurally characterized the first monomeric five-coordinated $RAl(O,O')_2$-type complex [MeAl(mesal)$_2$, where mesal = methyl salicylate anion],[7] although the first attempts to isolate this type of compound were made in the late 1960s.[8] Further, structurally characterized monomeric four-coordinated organoaluminum *O,O′*-chelate complexes are also very rare, and recent examples are derived from the sterically crowded aluminum aryloxide compounds.[3b,c] It is also noteworthy that structure investigations of dichloro- and dialkoxyaluminum derivatives of unsaturated hydroxy ketones have revealed that these compounds may occur as monomeric molecules as well as molecules rearranged to multinuclear ionic or neutral complexes.[9,10]

Although the reported examples of structurally characterized dialkylaluminum *O,O′*-chelate complexes in-

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[2] (a) Kai, Y.; Yasuoka, N.; Kasai N.; Kakudo, M. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 3397. (b) Kai, Y.; Yasuoka, N.; Kasai N.; Kakudo, M. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 3403.

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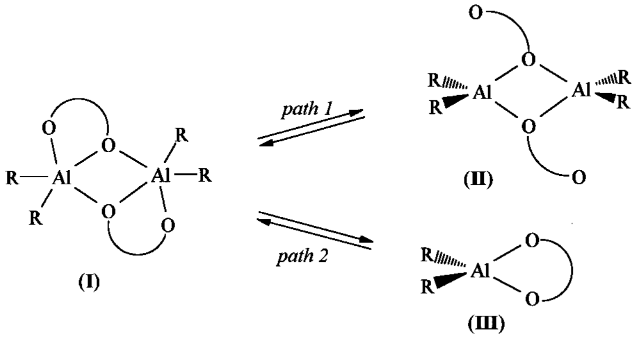
Scheme 1[a]



[a] O⌢O = deprotonated donor-functionalized hydroxy compound.

dicate that $R_2Al(O,O')$-type compounds have a tendency to occur in the form of oxygen-bridged dimer **I** with a five-coordinated metal center in the solid state (Scheme 1), the question about their structure in solution cannot be answered unequivocally. It has been reported that the structure of dialkylaluminum derivatives of aliphatic hydroxy ethers is dependent on the length of the aliphatic chain separating the two oxygen functional centers.[4,11] It has been proposed on the basis of NMR studies that the adduct **I** with five-membered chelates remains in solution as the five-coordinated structure at a wide range of temperatures and that the four-coordinated dimeric complex **II** with dangling *O,O'*-ligands is formed in the case of longer aliphatic chains separating the oxygen centers.[4,11] However other spectroscopic studies have indicated the existence of a nonrigid structure of the $[R_2Al(O,O')]_2$ adducts containing a five-membered ring system and the occurrence of intramolecular rearrangements with dissociation of the Al−O chelate bonds.[5] While rearrangements according to path 1 have been studied extensively, there is a lack of conclusive evidence for rearrangements occurring by dissociation of the bridging $Al_2(\mu\text{-}O)_2$ ring (path 2).

Due to the potential high utility of organoaluminum chelate complexes, it becomes important to know what ligands should be chosen to obtain monomeric or higher aggregated chelate derivatives. This should be based on an intimate understanding of the electronic and steric effects that control the coordination abilities and the degree of association of these compounds. From this point of view we have undertaken a comprehensive investigation on the synthesis and structure of alkylaluminum chelate compounds. Here we report the synthesis and structure characterization of dialkylaluminum *O,O'*-chelate complexes derived from α- and β-hydroxy carbonyl compounds: α-tropolone (tropH), ethyl *rac*-lactate (elacH), and 2-acetyl-4-chlorophenol (*Cl*-acphH), with saturated and conjugated unsaturated bond systems, respectively. The influence of the nature of the *O,O'*-chelating ligand on the structure of dialkylaluminum chelate complexes in the solid state and in solution and the geometry of the aluminum coordination sphere are discussed on the basis of the results obtained and structural data of related compounds.

Results

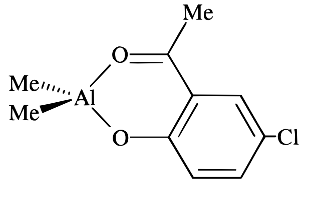
Synthesis of Dialkylaluminum Derivatives of Hydroxy Carbonyl Compounds. The reaction of R_3Al with equimolar amounts of the corresponding hydroxy carbonyl compound (*O,O'*-H) leads to the formation of dialkylaluminum *O,O'*-chelate complexes and alkane evolution according to eq 1. The compounds are

$$n\mathrm{R_3Al} + n(O,O')\mathrm{H} \rightarrow [\mathrm{R_2Al}(O,O')]_n + n\mathrm{RH} \quad (1)$$

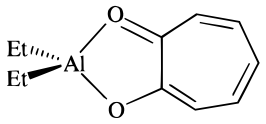
$n = 1$ or 2; *O,O'*-H = 2-acetyl-4-chlorophenol, R = Me (**1a**), Et (**1b**); *O,O'*-H = α-tropolone, R = Me (**2a**), Et (**2b**); *O,O'* = ethyl *rac*-lactate, R = Me (**3**)

obtained in the form of pale yellow or white solids in moderate to high yields, except **1b**, which we were not able to isolate out of the mixture of products. They are stable as solids or in solution under an inert atmosphere. Compound **2a** is not soluble in common organic solvents and was not structurally characterized, while **2b** is soluble in methylene chloride and very scarcely soluble in aromatic solvents. The other compounds are readily soluble in aromatic solvents.

Structure in Solution. Cryoscopic molecular weight measurements have revealed that compound **1a** occurs in the form of a monomeric complex in solution. Due to the low solubility of **2b** in benzene, a similar measurement could not be performed. The IR spectra of **1a** in CH_2Cl_2 solution show a decrease in the carbonyl stretching frequency (1619 cm^{-1}) compared to that of free *Cl*-acphH (1652 cm^{-1}), which is consistent with the coordination of the carbonyl group to aluminum. Similarly, the IR spectra of **2b** in CH_2Cl_2 solution show the existence of bands characteristic of a chelating tropolonate ligand (1572 and 1506 cm^{-1}).[12] The ^{27}Al NMR spectra of **1a** and **2b** consist of a single resonance at 149 and 155 ppm, respectively, corresponding to four-coordinate aluminum atoms.[4] The ^{1}H NMR spectrum of **1a** shows single resonances of $Al-CH_3$ and $C-CH_3$ protons and multiplets of aromatic protons, and in the spectrum of **2b** three well-separated multiplets of tropolonate protons and a triplet and quartet of ethyl protons occur. Thus, the above data are consistent with the monomeric tetrahedral chelate structures **IV** and **V** proposed for **1a** and **2b**, respectively.



(**IV**)



(**V**)

The dimethylaluminum derivative of ethyl *rac*-lactate has a dimeric structure in solution, contrary to the analogous derivatives of α- and β-hydroxy carbonyl compounds with unsaturated bond systems, which was confirmed on the basis of cryoscopic molecular weight investigation. In the IR spectra of **3** in CH_2Cl_2 solution the frequencies of the carbonyl group stretching vibrations band are consistent with the coordination of the ester group to the aluminum atom. The ^{27}Al NMR spectrum of **3** consists of a single resonance at 114 ppm, indicative of five-coordinated aluminum atoms.[4] The ^{1}H NMR spectrum of **3** in CD_2Cl_2 solution at 20 °C consists of a single resonance of the $Al-CH_3$ protons, a doublet and quartet of $C-CH_3$ and $C-H$ protons associated with

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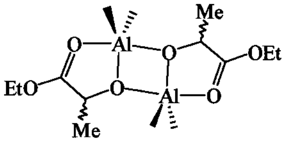
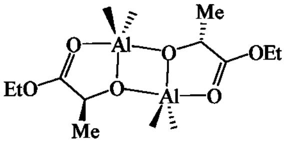
the chiral center, and two resonances of the ester ethyl group; the methylene protons of the ethyl group are diastereotopic, giving rise to an eight-line pattern. As the temperature is decreased, the resonance associated with Al−CH_3 protons broadens (about −80 °C) and splits into two well-separated resonances at −93 °C (an increase of temperature to −90 °C causes a coalescence back). The observed inequivalence of the Al−CH_3 groups indicates the presence of only *RR* and *SS* diastereoisomers (structure **VI**) in solution, and this is consistent with the structure found in the solid state (vide infra); for the dialkylaluminum derivative of ethyl *rac*-lactate the two dimeric five-coordinated structures **VI** and **VII** may be formed. Furthermore, the variable-temperature ^{1}H NMR spectra show that the five-coordinated adduct **3** is nonrigid in solution, and a dynamic behavior of this compound can be best interpreted in terms of a dissociative process in which the Al−O chelate bond undergoes cleavage, giving rise to the interchange of the chelating groups between the two aluminum centers and permitting the Al−CH_3 groups to become equivalent on the NMR time scale. The process is reversible, and the rate of exchange is concentration independent. Our recent structure investigation of the (*R*,*S*)-[R_2Al(benzoinato)]$_2$ adduct, the dialkylaluminum derivative of another racemic hydroxy carbonyl compound, rather precludes an equilibrium with dimeric four-coordinated species with rapid rotation of the bridging dangling ligand as responsible for the observed changes in temperature-dependent NMR spectra. The latter confirm that the formation of the [R_2-Al(*O*,*O*′)]$_2$-type adducts proceeds in a highly stereoselective manner and the interchange of chelating groups between the two aluminum centers does not lead to an exchange of the Al−CH_3 group environments [we observed exclusively the formation of the (*R*,*S*) diastereoisomer with mirror image chelate ligands].[13]



(*S**,*S**)

(**VI**)



(*R*,*S*)

(**VII**)

Table 1. Selected Bond Distances (Å) and Bond Angles (deg) in the [Me_2Al(2-acetyl-4-chlorophenolato)]$_2$ Adduct (1a)

molecule 1

Al(1)−O(11)	1.852(2)	O(11)−C(12)	1.347(4)
Al(1)−O(12)	1.964(2)	C(12)−C(17)	1.409(3)
Al(1)−O(11b)	2.103(2)	C(17)−C(18)	1.453(4)
Al(1)−C(10)	1.959(5)	O(12)−C(18)	1.242(4)
Al(1)−C(11)	1.955(5)		
O(11)−Al(1)−O(12)	88.5(1)	O(11b)−Al(1)−C(11)	94.3(2)
O(11)−Al(1)−C(10)	115.3(2)	C(10)−Al(1)−C(11)	129.7(2)
O(11)−Al(1)−C(11)	114.8(2)	Al(1)−O(11)−C(12)	131.7(2)
O(12)−Al(1)−C(10)	90.9(1)	Al(1)−O(12)−C(18)	132.8(2)
O(12)−Al(1)−C(11)	93.7(2)	O(12)−C(18)−C(17)	121.7(3)
O(11b)−Al(1)−O(11)	76.2(1)	C(12)−C(17)−C(18)	122.2(3)
O(11b)−Al(1)−O(12)	164.6(1)	O(11)−C(12)−C(17)	122.8(3)
O(11b)−Al(1)−C(10)	94.1(1)		

molecule 2

Al(2)−O(21)	1.854(2)	O(21)−C(22)	1.354(3)
Al(2)−O(22)	1.975(2)	C(22)−C(27)	1.408(4)
Al(2)−O(21a)	2.088(2)	C(27)−C(28)	1.457(5)
Al(2)−C(20)	1.955(5)	O(22)−C(28)	1.240(4)
Al(2)−C(21)	1.954(4)		
O(21)−Al(2)−O(22)	88.2(1)	O(21a)−Al(2)−C(21)	94.4(2)
O(21)−Al(2)−C(20)	115.8(2)	C(20)−Al(2)−C(21)	129.0(2)
O(21)−Al(2)−C(21)	115.1(2)	Al(2)−O(21)−C(22)	131.7(2)
O(22)−Al(2)−C(20)	92.8(2)	Al(2)−O(22)−C(28)	133.1(2)
O(22)−Al(2)−C(21)	91.8(2)	O(22)−C(28)−C(27)	121.6(3)
O(21a)−Al(2)−O(21)	76.0(1)	C(22)−C(27)−C(28)	122.3(3)
O(21a)−Al(2)−O(22)	164.2(1)	O(21)−C(22)−C(27)	122.9(3)
O(21a)−Al(2)−C(20)	94.5(2)		

[a] Atoms labeled with a and b belong to the centrosymmetric counterparts of the dimeric units with the symmetry codes (−*x* + 1, −*y* + 1, −*z* + 1) and (−*x* + 1, −*y*, −*z*), respectively.

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) in the [Et_2Al(tropolonato)]$_2$ Adduct (2b)

Al(1)−O(1)	1.903(1)	C(1)−C(2)	1.378(2)
Al(1)−O(1a)	2.094(1)	C(1)−C(7)	1.453(2)
Al(1)−O(2)	1.936(1)	C(2)−C(3)	1.400(2)
Al(1)−C(8)	1.969(2)	C(3) −C(4)	1.361(2)
Al(1)−C(10)	1.973(2)	C(4)−C(5)	1.395(3)
O(1)−C(1)	1.324(1)	C(5)−C(6)	1.367(2)
O(2)−C(7)	1.273(2)	C(6)−C(7)	1.412(2)
C(10)−C(11)	1.510(4)	C(8)−C(9)	1.525(4)
O(1)−Al(1)−O(2)	79.9(1)	Al(1)−C(8)−C(9)	114.5(2)
O(1)−Al(1)−O(1a)	72.1(1)	Al(1)−C(10)−C(11)	116.1(2)
O(1)−Al(1)−C(8)	118.3(1)	O(1)−C(1)−C(2)	121.2(1)
O(1)−Al(1)−C(10)	116.6(1)	O(1)−C(1)−C(7)	111.5(1)
O(1a)−Al(1)−O(2)	151.9(1)	O(2)−C(7)−C(6)	119.7(1)
O(1a)−Al(1)−C(8)	95.8(1)	O(2)−C(7)−C(1)	114.4(1)
O(1a)−Al(1)−C(10)	96.0(1)	C(1)−C(2)−C(3)	129.8(2)
O(2)−Al(1)−C(8)	95.9(1)	C(2)−C(3)−C(4)	129.6(2)
O(2)−Al(1)−C(10)	98.1(1)	C(3)−C(4)−C(5)	127.5(2)
C(8)−Al(1)−C(10)	124.8(1)	C(4)−C(5)−C(6)	129.8(2)
Al(1)−O(1)−Al(1a)	108.0(1)	C(5)−C(6)−C(7)	130.0(2)
Al(1)−O(1)−C(1)	117.5(1)	C(6)−C(7)−C(1)	125.8(1)
Al(1)−O(2)−C(7)	116.7(1)	C(7)−C(1)−C(2)	127.4(1)

[a] Atoms labeled with a belong to the centrosymmetric counterpart of the dimeric unit with the symmetry code (−*x* + 1, −*y* + 1, −*z* + 1).

Crystal Structure Data for 1a, 2b, and 3. Due to the differences observed in the solution structures of the dialkylaluminum derivatives of hydroxy carbonyl compounds described above, it was interesting to compare their structures in the solid state, and with this aim X-ray crystallographic studies were undertaken. A summary of crystallographic data for **1a**. **2b**, and **3** is given in Table 5. Selected bond Lengths and angles are given in Tables 1−3. Molecular structures and atom-numbering schemes are shown in Figures 1, 3, and 4. The results of the crystallographic investigation show that the dialkylaluminum chelate complexes studied share many common structural features. All of the compounds have a dimeric structure in the solid state where the monomeric units are held together by bridging aryloxide (or alkoxide) oxygen atoms. The aluminum atoms are five-coordinated in a distorted trigonal bipyramidal geometry. The two carbon atoms bound to the aluminum atom and the covalently bound oxygen atom of the chelating ligand outline an equatorial plane. The external axial position is occupied by a carbonyl oxygen atom and the internal axial position by the alkoxide (aryloxide) bridgingoxygen atom of the second

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Table 3. Selected Bond Distances (Å) and Bond Angles (deg) in the $[Me_2Al(ethyl\ lactato)]_2$ Adduct (3)

Al(1)–O(1)	1.848(2)	Al(1)–O(2)	2.157(2)
Al(1)–O(1a)	1.936(2)	O(2)–C(3)	1.224(3)
Al(1)–C(6)	1.954(4)	O(1)–C(2)	1.405(3)
Al(1)–C(7)	1.956(4)	C(2)–C(3)	1.509(4)
O(1)–Al(1)–O(1a)	75.60(11)	O(2)–Al(1)–C(6)	92.07(13)
O(1)–Al(1)–C(6)	117.9(2)	O(2)–Al(1)–C(7)	90.73(13)
O(1a)–Al(1)–C(6)	99.08(13)	Al(1)–O(2)–C(3)	111.4(2)
O(1)–Al(1)–C(7)	117.0(2)	Al(1)–O(1)–C(2)	122.9(2)
O(1a)–Al(1)–C(7)	102.13(12)	Al(1a)–O(1)–C(2)	130.5(2)
C(6)–Al(1)–C(7)	124.3(2)	O(2)–C(3)–C(2)	120.4(3)
O(1)–Al(1)–O(2)	78.20(9)	O(1)–C(2)–C(3)	106.0(3)
O(1a)–Al(1)–O(2)	153.77(10)	Al(1)–O(1)–Al(1a)	104.19(11)

[a] Atoms labeled with a belong to the counterpart of the dimeric unit with the symmetry code (*y*, *x*, −*z*).

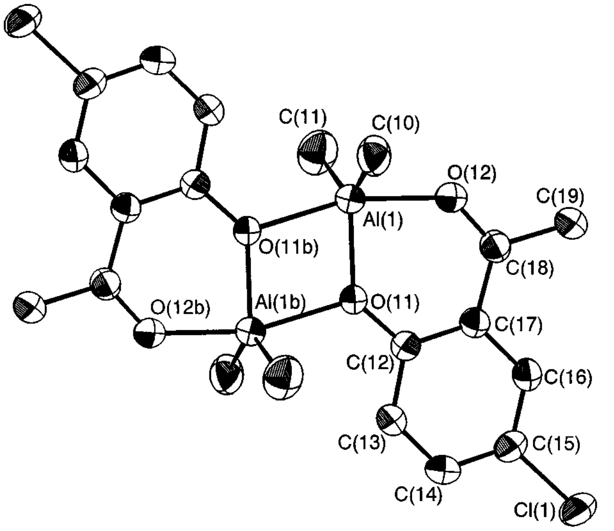


Figure 1. ORTEP diagram of $[Me_2Al(2\text{-aceto-4-chlorophenolato})]_2$ (**1a**) showing 50% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity.

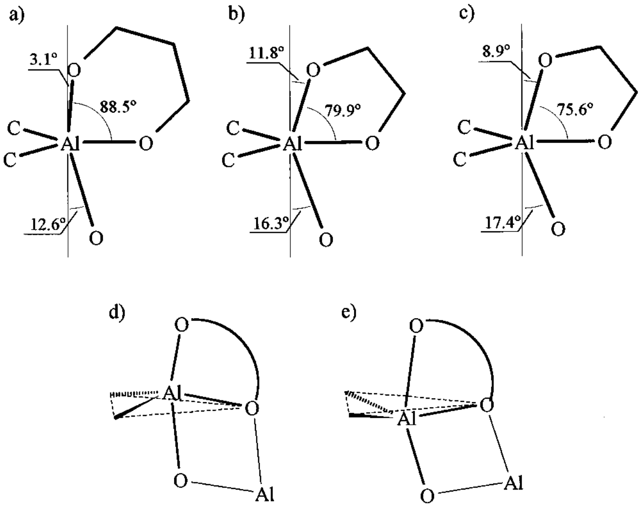


Figure 2. The geometry of the aluminum atom coordination sphere in (a) **1a**, (b) **2b**, and (c) **3**. Schematic representation of the aluminum atom displacement from the equatorial plane for (d) **1a** and **2b** and (e) **3**.

chelating ligand. The structures of **1a** and **2b** are centrosymmetric, whereas compound **3** adopts a noncentrosymmetric point group C_2. This and other observed differences in intramolecular geometry are discussed in detail below.

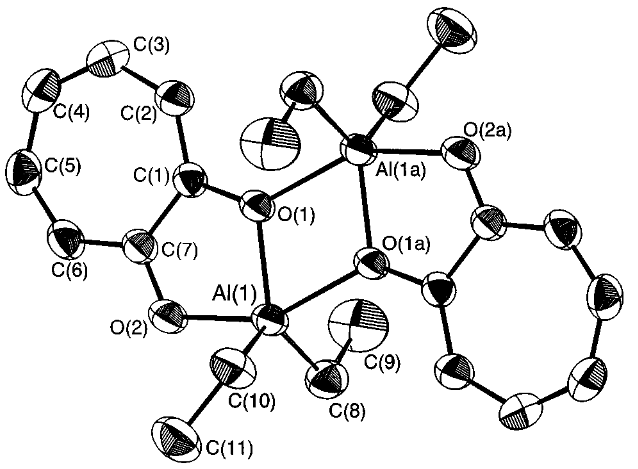


Figure 3. ORTEP diagram of $[Et_2Al(tropolonato)]_2$ (**2b**) showing 50% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity.

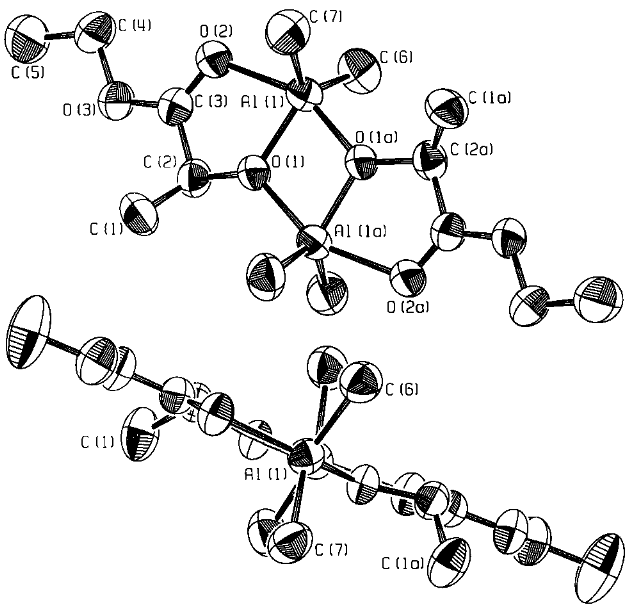
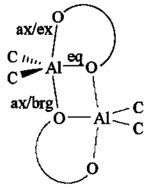
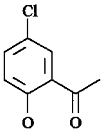
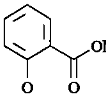
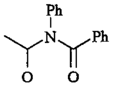
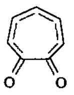
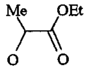
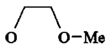
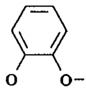
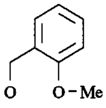


Figure 4. ORTEP diagram of (*S*,*S*)-$[Me_2Al(ethyl\ lactato)]_2$ (**3**) showing 50% probability thermal ellipsoids; views (top) perpendicular and (bottom) parallel to the Al_2O_2 plane. Hydrogen atoms are omitted for clarity.

The unit cell of **1a** contains two independent molecules with almost identical geometry. Corresponding parameters of bond distances for the two molecules agree within 2 esd of their mean except the Al–O bridging bonds (Table 1). The *Cl*-acph ligand in **1a** is coordinated to the aluminum atom via both the aryloxide oxygen and the acyl group and forms a planar six-membered $\overline{\mathrm{AlOCCCO}}$ ring. The participation of the O(11) atom in the formation of bridging bonds and the chelation of the carbonyl O(12) atom to the five-coordinated Al(1) atom result in significant lengthening of the Al(1)–O(11) [1.852(2) Å] and Al(1)–O(12) [1.964(2) Å] distances, respectively, when compared to those in the monomeric four-coordinated chelate complex with the related hydroxyacetophenone ligand, [MeAl(dbmp)(bhmap), 1.765(5) and 1.836(4) Å, respectively, where bhmap = 3-*tert*-butyl-2-hydroxy-5-methylacetophenone].[3c] The Al–O bridging bonds in **1a** are significantly longer than those observed in the related five-coordinated

Table 4. Selected Bond Distances (Å) and Angles (deg) for the Five-Coordinated $[R_2Al(O,O')]_2$-type Complexes Studied and Reported in the Literature[b]

	**1a** 	4[15] 	5[2a] 	**2b** 	**3** 	6[4] 	7[5] 	8[6] 
$Al-O_{eq}$	1.852(2)	1.850(2)	1.858	1.903(1)	1.848(2)	1.827	1.859(3)	1.821(1)
$Al-O_{ax/brg}$	2.103(2)	2.082(2)	1.985	2.094(1)	1.936(2)	1.892	1.952(3)	1.880(1)
$Al-O_{ax/ex}$	1.964(2)	2.003(2)	2.045	1.936(1)	2.157(2)	2.269	2.249(3)	2.572(2)
$\overline{Al-O_{brg}}$[a]	1.977	1.966	1.922	1.999	1.892	1.860	1.906	1.850
$\overline{Al-O}$	1.973	1.978	1.963	1.978	1.980	1.996	2.020	2.091
$\overline{Al-C}$	1.957	1.952	1.96	1.971	1.955	1.951	1.955	1.956
$O_{ax}-Al-O_{ax}$	164.4(1)	161.74(6)	158.3	151.9(1)	153.8(1)	152.1	150.4(1)	156.1(1)
C-Al-C	129.7(2)	129.4(2)	119.4	124.8(1)	124.3(2)	120.8	123.2	122.3(1)

[a] The mean value of the Al−O distances in the Al_2O_2 ring. [b] Designations of bonds as well as monoanionic ligands used in complex formations are shown in the column headings.

dialkylaluminum alkoxides (Table 4), which is undoubtedly due to the reduced Lewis basicity of the bridging aryloxide oxygen atoms resulting from the conjugation of the oxygen lone pair with the extended π-system. An important feature of structure **1a** is that the internal axial Al(1)−O(11b) bond [bridging one, 2.103(2) Å] is longer than the external axial Al(1)−O(12) bond. Thus, the internal axial bond joining two monomeric units is the weakest Al−O bond, and this bond is cleaved upon dissolution. It is interesting to note that the most important differences observed between independent molecules **1a** and **1a′** concern essentially this labile bond. The resulting dimer **1a** features a nearly planar system of five fused rings. The coordination geometry around the aluminum centers is shown in Figure 2a. The equatorial C_2AlO plane is almost planar with bond angles involving Al in this plane close to 120° [114.8(2)−129.7(2)°]. Some displacement (0.040 Å) is observed of the Al(1) atom from the equatorial plane toward the O(12) carbonyl oxygen atom (Figure 2d). The angle outlined by the axial bonds, O(12)−Al(1)−O(11b), is 164.6(1)°. The main distortion from ideal TBP geometry arises from the displacement of the Al(1)−O(11b) bond being a part of the $Al_2(\mu\text{-}O)_2$ four-membered ring from the normal to equatorial least-squares plane (12.6°) and is imposed by constraints in this central ring. The Al(1)−O(11) bond (external axial one) occupies an almost ideal axial position with a small bend of 3.1° (Figure 2a). Thus, the presence of a rigid six-membered AlOCCCO chelate ring in a dimeric five-coordinated dialkylaluminum chelate complex does not affect in principle the deformation of the aluminum atom coordination sphere.

In compound **2b** in the solid state the two tropolonate ligands chelate one aluminum atom each, to give two five-membered AlOCCO rings, and share one oxygen atom, forming oxygen bridges between two aluminum atoms. The resulting dimer features a nearly planar system of five fused rings, similarly as in the structure of **1a**. The bond angles involving an aluminum atom in the equatorial plane are close to 120° [116.6(1)−124.8(1)°]. The aluminum atom is displaced 0.055 Å from the equatorial plane toward the O(2) chelating atom (Figure 2d). The apical positions occupy oxygen atoms of two different chelating ligands [O(2) and O(1a)] with a bond angle of O(2)−Al(1)−O(1a) equal to 151.9(1)°. The observed bend of the O−Al−O axial skeleton results from the displacement of both Al(1)−O(1) and Al(1)−O(1a) axial bonds from the normal to equatorial least-squares plane, which is due to the constraints in the five-membered AlOCCO chelate rings and in the four-membered $Al_2(\mu\text{-}O)_2$ bridging ring (Figure 2b). The displacement is smaller for the $Al-O_{ax}$ bond of the five-membered ring (11.8°) in comparison to that of the four-membered ring (16.3°).

The observed Al−O and also the C−O and C−C bond distances in **2b** are consistent with the involvement of the oxygen atoms in a conjugated bond system within the chelate ligand, and as was observed for **1a**, the internal axial bond, Al(1)−O(1a) [2.094(1) Å], is significantly longer than the external axial bond Al(1)−O(2) [1.936(1) Å]. Thus, adduct **2b** easily rearranges in solution to the monomeric four-coordinated chelate complex **V** with disruption of the bridging bonds. Indeed, the equatorial Al(1)−O(1) bond [1.903(1) Å] in **2b** is significantly longer, and the axial chelating Al(1)−O(2) distance shorter, than the corresponding distances in **1a**, which suggests that the extended π-interaction is stronger in a tropolonate as compared with a hydroxyacetophenolate ligand.

The formation of bridging bonds by one oxygen atom of each chelating tropolonate ligand in **2b** causes a very slight bond alteration in the tropolonate ring (average values for single−double bond alteration are 1.402 and 1.369 Å, respectively). None of the single−double bond alteration in the ring was observed for tris(tropolonato)aluminum.[14] Small differentiation of C−O bridging and C−O nonbridging is observed as well. The C(1)−C(7) bond distance is longer than other C−C distances of the tropolonate ligand, and it is a feature of all metal tropolonates.

The monomeric units in **3** are bonded via alkoxide oxygen atoms O(1) and O(1a) with the formation of a central four-membered $Al_2(\mu\text{-}O)_2$ ring. The ethyl lactate anions form two five-membered chelate rings with aluminum atoms. The most interesting feature of structure **3** is the fact that the methyl groups bonded to the chiral C atom in the chelating ligand lie on the same side of the plane outlined by three fused heterocyclic rings, and indeed the dimer molecules have a C_2 symmetry. This indicates that only monomeric units of the same configuration as the chiral center in the chelating ligand associate with each other. Thus, the formation of the five-coordinated $[R_2Al(O,O')]_2$ adducts is a stereoselective reaction.

The coordination geometry of aluminum atoms in **3** is similar to that observed in **2b**. The angle outlined by the axial bonds is 153.8(1)°, and the deformation from the ideal value of 180° is due to the stresses occurring in both the central four-membered and chelating five-membered heterocyclic rings (Figure 2c). The angles between the bonds in the equatorial plane are close to 120°. However, the aluminum atoms stand out slightly from the equatorial plane [0.094(1) Å] (Figure 2e) toward the oxygen bridging atoms (*i.e.*, toward the opposite direction than is observed in **1a** and **2b**). It should be emphasized that in compound **3** the average Al−O external axial bond distance of 2.157(2) Å is significantly longer and the Al−O distances within the central $Al_2(\mu\text{-}O)_2$ ring [Al(1)−O(1) (1.848(2) Å) and Al(1)−O(1a) (1.936(2) Å)] are significantly shorter than the corresponding Al−O distances in related derivatives of unsaturated hydroxy carbonyl compounds **1a** and **2b**. These differences within the Al−O distances correlate well with the dimeric structure of the former and the monomeric structure of the latter in solution (vide infra).

Discussion

The dialkylaluminum derivatives of hydroxy carbonyl compounds reported here confirm that the $R_2Al(O,O')$-type chelate complexes have a tendency to occur in the solid state as dimers with a five-coordinated metal center. Furthermore, they contribute to a remarkable extension of the representative examples of the latter complexes. At present a detailed analysis of structural data of the known five-coordinated $[R_2Al(O,O')]_2$ adducts leads to interesting conclusions on the influence of the nature of chelating ligands on their structure in the solid state and in solution. Selected bond lengths and geometrical data of the coordination sphere in the structurally characterized dimeric five-coordinated dialkylaluminum *O,O'*-chelate complexes are summarized in Table 4.

Several points are worthy of note regarding the bond distances in compounds **1a**, **2b**, **3**, $[Me_2Al(\mu\text{-}OC_6H_4\text{-}2\text{-}CO_2CH_3)]_2$ (**4**),[15] $[Me_2Al(\mu\text{-}OC(CH_3)N(Ph)CO(Ph))]_2$ (**5**),[2a] $[Me_2Al(\mu\text{-}OC_2H_4OCH_3)]_2$ (**6**),[4] $[Et_2Al(\mu\text{-}OC_6H_4\text{-}2\text{-}OCH_3)]_2$ (**7**),[5] and $[Me_2Al(\mu\text{-}OCH_2C_6H_4\text{-}2\text{-}OCH_3)]_2$ (**8**)[6] (Table 4). The aluminum atoms in this set of complexes have the same C_2AlO_3 core, and as could be expected, the mean Al−O bond lengths differ only slightly and range from 1.963 to 2.091 Å. However, a considerable differentiation is observed for axial bridging ($Al{-}O_{ax/brg}$ = 1.880−2.103 Å) and axial external bonds ($Al{-}O_{ax/ex}$ = 1.936−2.572 Å): the longer the $Al{-}O_{ax/ex}$ distance, the shorter the $Al{-}O_{ax/brg}$ bond; thus the structural trans effect of the axial substituents is evident for the five-coordinated $[R_2Al(O,O')]_2$ chelate complexes. Generally, the values of Al−O distances depend on the nature of the chelate ligand, *i.e.*, essentially on the Lewis basicity of the bridging and chelating oxygen atoms, and three groups of the $[R_2Al(O,O')]_2$-type adducts may be distinguished.

Within the first group (compounds **1a**, **2b**, **4**, and **5**) the conjugation of the alkoxide oxygen lone electron pair with the extended π-system of the chelate ligand considerably weakens the Lewis basicity of the bridging oxygen and simultaneously strengthens the basicity of the chelating carbonyl oxygen. As a result, the $Al{-}O_{ax/brg}$ distance is longer than the $Al{-}O_{ax/ex}$ one. This type of conjugation is the strongest in a tropolonate ligand, and the average $Al{-}O_{brg}$ bond length in **2b** is the largest (1.999 Å) and the $Al{-}O_{ax/ex}$ bond length is the smallest [1.936(1) Å], compared with corresponding values of the other reported adducts (Table 4). Thus, when the $Al{-}O_{ax/brg}$ bond (bridging one) is longer than the $Al{-}O_{ax/ex}$ bond (chelating one), then the $[R_2Al(O,O')]_2$-type adduct easily rearranges to the monomeric four-coordinated chelate complex with cleavage of the bridging bonds.

A completely different situation occurs within the second group, compounds **6** and **8**, dialkylaluminum derivatives of saturated hydroxy ethers, where the "pure" alkoxide oxygen (strong Lewis base center) is the bridging oxygen atom and chelation occurs via the ethereal oxygen (weak Lewis base center). Hence, the average $Al{-}O_{brg}$ bond length is the smallest (1.850 and 1.860 Å, respectively), and the $Al{-}O_{ax/ex}$ distance is the largest [2.269 and 2.572(2) Å, respectively], among the $[R_2Al(O,O')]_2$ adducts discussed. Thus, for compounds with this type of chelate ligand the $Al{-}O_{ax/brg}$ bonds are significantly shorter than the $Al{-}O_{ax/ex}$ bonds, and they retain the dimeric structure in solution.

Within the third group (compounds **3**, **5**, and **7**), the formation of bridging bonds and chelation occur via relatively strong Lewis base centers (alkoxide and carbonyl oxygen atoms, respectively) or, on the contrary, this is due to the two significantly weaker base centers (methoxy and aryloxide oxygen atoms in **7**, respectively). Despite the reverse Lewis basicity of the bridging and chelating oxygen atoms in **3** and **5** versus **7**, the corresponding Al−O bridging bond ($Al{-}O_{eq}$ and $Al{-}O_{ax/brg}$) lengths are comparable and their average value falls within the range determined by the corresponding average $Al{-}O_{brg}$ bond distances of the first and second groups of compounds distinguished. Thus, the relatively strong electron donation by chelating groups, likewise the π-interaction of the bridging oxygen lone electron pair with the unsaturated bond system, may significantly weaken the bridging bonds in the dimeric $[R_2Al(O,O')]_2$-type complexes. However, within the third group of compounds the $Al{-}O_{ax/ex}$ bonds are still longer

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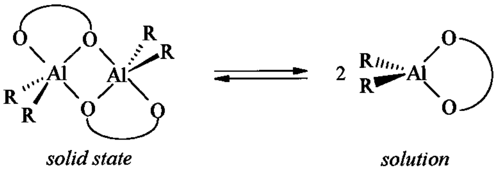
[14] Muetterties, E. L.; Guggenberger, L. J. *J. Am. Chem. Soc.* **1972**, *94*, 8046.

[15] Lewiński, J.; Zachara, J.; Starowieyski, K. B. *J. Chem. Soc., Dalton Trans.*, in press.

Scheme 2



than the Al−O$_{ax/brg}$ bonds joining two monomeric units, and these complexes remain dimeric in solution. Finally, in fact both factors, the weakening of the Lewis basicity of the bridging centers and the relatively large basicity of the chelating atoms, must occur simultaneously for the five-coordinated [R$_2$Al(*O*,*O*′)]$_2$ adduct to dissociate in solution to the monomeric four-coordinated dialkylaluminum chelate complex (Scheme 2).

It is noteworthy that the Al−O distances within the central four-membered Al$_2$(μ-O)$_2$ ring in the dimeric five-coordinated compounds **1**−**8** differ significantly despite the fact that the same bridging oxygen atoms are bonded to the equivalent aluminum atoms; the stronger the bridging Lewis base center, the smaller the difference in bond length observed. It is apparent that this results from the geometry of dimeric five-coordinated molecules, which imposes that each oxygen atom is in the equatorial position of one aluminum atom and in the axial position with respect to the second one. Although nonequivalence of M−O distances in asymmetric bridges is usually noted in the description of structural data, it is commonly interpreted as resulting from a different character of these bridging bonds.[16,17] We would like to emphasize at this point that the Al−O bonds in the Al$_2$(μ-O)$_2$ ring are of the same character (2c−2e σ-bonds) and the differences in the bridging Al−O bond lengths are due to the different geometrical locations in the aluminum atom coordination sphere.

In all structurally characterized dimeric five-coordinated dialkylaluminum *O*,*O*′-chelate complexes the geometry of the coordination sphere of the aluminum center may be described as a distorted TBP with a bent O−Al−O axial skeleton (Table 4) and almost planar C$_2$-AlO equatorial plane. It is interesting to note that the aluminum atom is always slightly displaced from the equatorial plane toward the stronger Lewis base center situated in the axial position (see Figure 2d,e). For compounds **2b**, **5**, and **8** consisting of five-membered chelates, the values of the angle defined by two apical substituents are similar and range from 150.4 to 152.1° and the distortion from ideal TBP geometry is imposed by constraints in both the central four-membered and chelate five-membered rings. This deformation is well illustrated for **2b** and **3** mentioned above (Figure 2). We note that, in the case of the corresponding compounds with six-membered chelates, the bending of the O−Al−O axial skeleton depends on the rigidity of the chelating ligand. As we have observed for **1a** (Figure 2a) and **4**,[15] the rigid six-membered ring imposed by the conjugated bond system within the chelates almost does not affect the deformation and the observed bend is caused by constraints in the four-membered central bridging ring (with a corresponding O−Al−O angle of ca. 164.5°). For **5** and **8**, the compounds consisting of partly stiffened chelates, the angle defined by axial bonds is significantly smaller (158.3 and 156.1°, respectively). Thus, an increase of rigidity of the *O*,*O*′-chelating ring enables the formation of a six-membered-ring system and five-coordinated aluminum centers in the solid state, although the structures in solution of the dialkylaluminum derivative may be different and depend on the nature of the *O*,*O*′-bifunctional ligand. It should be noted that a comparison of the Al−O chelating bond distance in **3** [2.157(2) Å] with the corresponding values in related dimeric dialkylaluminum derivatives of hydroxy ethers [2.249(3)−2.572(2) Å][4,6] indicates that the former is the strongest one. Thus taking into account that **3** is nonrigid in solution, it is reasonable to conclude that the latter is also nonrigid in solution, contrary to the earlier suggestions.[4]

It is interesting to note that the C−Al−C angles and Al−C bond distances in five-coordinated compounds **1**−**8** are not sensitive to changes in geometrical constraints imposed by different heterocyclic rings and as well as the Lewis basicity of the bridging and chelating oxygen atoms. This is indicated by the very small differences of the corresponding values given in Table 4.

It should be noted that alkylaluminum compounds derived from chiral bidentate ligands are very rare and, to the best of our knowledge, only the dialkylaluminum derivatives of optically active amine alcohols have been crystallographically characterized.[18] Our structure investigations of the dialkylaluminum derivatives of racemic hydroxy carbonyl compounds indicate that the formation of the [R$_2$Al(*O*,*O*′)]$_2$-type adducts is stereoselective. The observed exclusive formation of the (*S**,*S**) or (*R*,*S*)[13] diastereoisomers requires that only monomeric units of the same or different, respectively, configuration of the chiral center in the bidentate ligand associate with each other. However, further studies are required in order to determine the nature of the five-coordinated [R$_2$Al(*O*,*O*′)]$_2$ adduct formation in a highly stereoselective manner.

A detailed examination of the structure and reactivity of organoaluminum compounds with bidentate ligands is underway in our laboratory.

Experimental Section

All operations were carried out under nitrogen. Trimethylaluminum and triethylaluminum were freshly distilled, and α-tropolone and 2-aceto-4-chlorophenol were used as supplied. Solvents were dried and distilled prior to use. NMR spectra were recorded on a Varian 300 VXL spectrometer. IR spectra (1800−350 cm^{-1}) were recorded on a Specord-75IR spectrophotometer.

Synthesis of Me$_2$Al(2-aceto-4-chlorophenolato) (1a). A solution of 2-aceto-4-chlorophenol (1.34 g, 8.0 mmol) in toluene (10 cm^3) was cooled to −78 °C, and Me$_3$Al (0.58 g, 8.0 mmol) was added dropwise. After the addition was completed, the reaction mixture was warmed up to room temperature and stirred for 0.5 h. The removal of the volatiles under vacuum gave a yellow solid. Yield: 97%. Anal. Calcd for C$_{10}$H$_{12}$AlO$_2$-Cl: C, 53.00; H, 5.34; Cl, 15.64. Found: C, 53.1; H, 5.4; Cl,

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[16] Haaland, A. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 992. Haaland, A. *Coordination Chemistry of Aluminum*; VCH: New York, 1993; pp 1−56.

[17] The appropriate description of M−O differentiation in asymmetric bridges is really the subject of the discussion for other metal alkoxides; see, for example: Matchett, M. A.; Chiang, M. Y.; Buhro, W. E. *Inorg. Chem.* **1990**, *29*, 360.

[18] Sierra, M. L.; de Mel, V. S. J.; Oliver, J. P. *Organometallics* **1989**, *8*, 2486. Kumar, R.; Sierra M. L.; Oliver, J. P. *Organometallics* **1994**, *13*, 4285. Atwood, D. A.; Gabbai, F. P.; Lu, J.; Remington, M. P.; Rutheford, D.; Sibi, M. P. *Organometallics* **1996**, *15*, 2308.

Table 5. Data Collection and Structure Analysis Parameters for 1a, 2b, and 3

	compd		
	1a	**2b**	**3**
empirical formula	$C_{20}H_{24}Al_2Cl_2O_4$	$C_{22}H_{30}Al_2O_4$	$C_{14}H_{30}Al_2O_6$
cryst size, mm	0.15 × 0.35 × 0.35	0.22 × 0.34 × 0.42	0.14 × 0.14 × 0.36
cryst syst	triclinic	triclinic	tetragonal
space group	$P\bar{1}$	$P\bar{1}$	$P4_12_12$
a, Å	8.9516(12)	7.4327(17)	7.6188(7)
b, Å	10.6265(11)	9.1982(15)	7.6188(7)
c, Å	13.9648(16)	9.4303(18)	35.055(6)
α, deg	101.596(9)	104.345(14)	90
β, deg	102.507(10)	106.957(16)	90
γ, deg	113.705(9)	106.765(15)	90
V, Å^3	1124.1(2)	550.3(2)	2034.8(4)
Z	2	1	4
calc density, g/cm^3	1.339	1.244	1.137
abs coeff, mm^{-1}	0.39	0.15	0.16
radiation	Mo Kα ($\lambda = 0.710\ 73$ Å) graphite monochromator		
temp, K	298	298	293
$F(000)$	472	220	752
2θ range, deg	4.0−50.1	4.0−55.1	4.6−50.1
no. of reflns collected	4172	2723	4171
no. of unique data	3905 ($R_{int} = 0.0099$)	2527 ($R_{int} = 0.0118$)	1801 ($R_{int} = 0.0694$)
no. of obs data	2936 [$\lvert F_o \rvert > 3\sigma(F_o)$]	2152 [$\lvert F_o \rvert > 3\sigma(F_o)$]	945 [$I > 2\sigma(I)$]
no. of data/params	2936/349	2149/187	1697/112
R, R_w^{a}	0.0367, 0.0370	0.0359, 0.0387	
R_1, wR_2^{b}			0.0477, 0.1082
weighting scheme,^{c} w^{-1}	$\sigma^2(F_o) + 0.00051(F_o)^2$	$\sigma^2(F_o) + 0.00010(F_o)^2$	$\sigma^2(F_o^2) + (0.0280P)^2$
largest residuals, e Å^{-3}	+0.23/−0.22	+0.25/−0.14	+0.17/−0.16

[a] R and R_w based on observed data. [b] R_1 based on observed data, wR_2 on all unique data. [c] $P = {}^1/_3[\max(F_o^2,0) + 2F_c^2]$.

15.4. ^{1}H NMR (CH_2Cl_2/C_6D_6, 20 °C): δ −0.27 (s, 6H, Al−CH_3), 1.44 (s, 3H, COCH_3), 6.53−6.92 (m, 3H$_{arom}$). ^{27}Al NMR (CH_2Cl_2/C_6D_6): δ 149 ppm. IR (CH_2Cl_2): 1619 (s), 1589 (s), 1519 (s), 1559 (w), 1444 (m), 1379 (m), 1328 (s), 1233 (s), 1193 (w), 1143 (w), 1062 (w), 1022 (w), 977 (m), 897 (w), 877 (w), 842 (m), 646 (w), 586 (w), 571 (w), 511 (w), 430 (w), 395 (w), 350 (w) cm^{-1}. Molecular weight (cryoscopically in benzene): found 227, calcd 226.6.

Reaction of 2-Aceto-4-chlorophenol with Et_3Al. The reaction was carried out by using the same procedure as described for **1a**, using 2-aceto-4-chlorophenol (0.70 g, 4.1 mmol) in toluene (9 cm^3) and Et_3Al (0.47 g, 4.1 mmol). ^{1}H NMR of the resulting reaction products indicated a complex mixture difficult for identification.

Synthesis of Me_2Al(tropolonato) (2a). A stirred suspension of α-tropolone (0.427 g, 3.5 mmol) in Et_2O (5 cm^3) was cooled to −78 °C and treated dropwise with a solution of Me_3Al (0.252 g, 3.5 mmol) in Et_2O (4 cm^3). After the addition was completed, the solution became homogeneous and bright yellow. The reaction mixture was allowed to warm up to room temperature. Above −30 °C, gas evolution was observed and a yellow precipitate was formed. The solvent was evaporated under vacuum to give a yellow-brown solid. Anal. Calcd for $C_9H_{11}AlO_2$: C, 60.67; H, 6.22. Found: C, 60.5; H, 6.3. The resulting product was insoluble in common organic solvents.

Synthesis of Et_2Al(tropolonato) (2b). The procedure for this reaction is the same as described for **2a**, using α-tropolone (1.47 g, 12.0 mmol) and Et_3Al (1.37 g, 12.0 mmol), yielding a yellow solid. The yield of the crude product was essentially quantitative. The solid yellow residue was redissolved in dichloromethane. Crystals were grown from a dichloromethane solution at 0 °C. Anal. Calcd for $C_{11}H_{15}AlO_2$: C, 64.07; H, 7.33. Found: C, 64.0; H, 7.5. ^{1}H NMR (CH_2Cl_2/C_6D_6, 20 °C): δ = 0.48 (4H, q, Al−CH_2CH$_3$), 1.42 (6H, t, Al−CH$_2$CH_3), 6.22 (1H, t, C−H), 6.55 (2H, t, C−H), 7.08 (2H, d, C−H). ^{27}Al NMR (CH_2Cl_2/C_6D_6): δ 155 ppm. IR (CH_2Cl_2): 1572 (s), 1506 (s), 1404 (s), 1340 (s), 1204 (m), 1084 (w), 936 (w), 888 (w), 660 (m), 484 (w), 436 (w) cm^{-1}. Cryoscopic molecular weight measurements were not performed due to the poor solubility of **2b** in benzene.

Synthesis of [Me_2Al(ethyl lactato)]$_2$ (3). Ethyl *rac*-lactate (0.83 g, 7.0 mmol) was dissolved in toluene (10 cm^3), and Me_3Al (0.50 g, 7.0 mmol) was added dropwise at −78 °C. After the addition was completed, the reaction mixture was allowed to warm up to room temperature. The solvent was then removed under vacuum, leaving a white solid, which was crystallized from a toluene/hexane solution at 0 °C. The yield was essentially quantitative. Anal. Calcd for $C_{14}H_{30}Al_2O_6$: C 48.27; H, 8.68; Al, 15.49. Found: C, 48.3; H, 8.8; Al, 15.3. ^{1}H NMR (CD_2Cl_2, 20 °C): δ −0.72 (12H, s, Al−CH_3), 0.94 (6H, t, CH$_2$−CH_3), 1.35 (6H, d, CH−CH_3), 3.90 (4H, qd, CH_2−CH$_3$), 4.40 (1H, q, CH−CH$_3$); (−93 °C) −0.62 (6H, s, Al−CH_3), −0.56 (6H, s, Al−CH_3), 0.78 (6H, t, CH$_2$−CH_3), 1.32 (6H, d, CH−CH_3), 3.61 (4H, qd, CH_2−CH$_3$), 4.33 (1H, q, CH−CH$_3$). ^{27}Al NMR (C_6D_6, 20 °C) δ 114 ($\Delta H_{1/2}$ = 5780 Hz). IR (CH_2Cl_2, cm^{-1}): 1690 (s), 1477 (w), 1468 (w), 1456 (m), 1410 (m), 1384 (m), 1373 (w), 1348 (w), 1316 (w), 1188 (m), 1142 (s), 1080 (w), 1068 (w), 1032 (w), 946 (w), 884 (w), 860 (w), 610 (w). Molecular weight (cryoscopically in benzene): found 350, calcd 348.4.

X-ray Crystallographic Studies. Single crystals of **1a**, **2b**, and **3** suitable for X-ray diffraction studies were placed in a thin-walled capillary tube (Lindemann glass 0.5 mm) in an inert atmosphere. The tube was plugged with grease, then flame-sealed, and mounted on a goniometer head of a four-circle P3 (Siemens AG) diffractometer. The selected crystallographic data, the parameters of data collections, and refinement procedures are presented in Table 5. The crystal classes and the orientation matrices were obtained by the least-squares refinement of well-centered reflections randomly selected in the 2θ range 12−31° (32 reflections) for **1a**, 5−28° (25 reflections) for **2b**, and 15−23° (34 reflections) for **3**. The intensities were collected in the $\omega-2\theta$ mode and corrected for Lorentz-polarization effects and crystal decomposition (11% for **1a**, 2.5% for **2b**, and 2.2% for **3**). Gaussian absorption correction based on crystal shape was applied for a crystal of **3**, which resulted in transmission factors ranging from 0.953 to 0.982. The structures were solved by direct methods using the SHELXS 86 program.[19] The distribution of the peaks showed that compound **1a** crystallizes with two independent molecules in the asymmetric unit. The structures of **1a** and **2b** were refined against F (SHELX 76 program[20]) by full-

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(19) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *46*, 467.

(20) Sheldrick, G. M. *SHELX 76, Program for Crystal Structure Determination*; University of Cambridge: Cambridge, U.K., 1976.

matrix least-squares methods on data with $|F_o| > 3\sigma(F_o)$. Subsequent difference Fourier maps revealed the positions of all atoms. In both cases, all non-hydrogen atoms were refined anisotropically and isotropic thermal parameters were used for hydrogen atoms. The structure of **3** was refined by full-matrix least-squares on F^2 using the program SHELXL 93.[21] Hydrogen atoms were included in idealized positions and refined isotropically. The absolute structure of **3** could not be determined reliably from the X-ray data due to the high esd for the refined Flack χ parameter 0.3(4).[22] The final atomic coordinates and equivalent (isotropic) temperature factors with their esd's for **1a**, **2b**, and **3** are listed in the Supporting Information.

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Supporting Information Available: Listings of atomic coordinates and anisotropic thermal parameters for all non-hydrogen atoms, hydrogen positional and isotropic displacement parameters, and complete bond lengths and angles for **1a**, **2b**, and **3** (15 pages). Ordering information is given on any current masthead page.

OM961054D

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[21] Flack, H. D. *Acta Crystallogr., Sect. A* **1983**, *39*, 876.

[22] Sheldrick, G. M. *SHELXL 93, Program for Refinement of Crystal Structures*, University of Göttingen: Göttingen, Germany, 1993.