The synthesis and structure of bis(acetylacetonato)(2-hydroxyphenolato)aluminum : a stable dimer

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THE SYNTHESIS AND STRUCTURE OF BIS(ACETYLACETONATO)(2-HYDROXYPHENOLATO)- ALUMINIUM: A STABLE DIMER

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Abstract—The dimeric structure of bis(acetylacetonato)(2-hydroxyphenolato)aluminium (**I**) has been elucidated using NMR spectroscopy and vapour phase osmometry. It has been shown that in solution the three geometrical isomers of the dimer are in equilibrium with monomeric species. At high concentrations even trimeric and/or polymeric species have to be considered in the equilibrium.

The homopolymerization of epoxides is catalysed by the combination of tris(acetylacetonato)aluminium (**II**) and phenols.^{1,2} Catechol (**III**) has proved to be the most effective phenol. We have observed by NMR and HPLC the formation of a reactive intermediate in the homopolymerization of cyclohexene oxide.³ This intermediate proves to be the actual catalytic species and is the reaction product of **II** and **III**.³

Although a long history exists on the structure, properties, and chemistry of aluminium alkoxides⁴ and β -diketonates,⁵ knowledge of the reactions of **II** with phenols is limited to monodentate ligands.⁶ Bidentate ligands are only studied in reactions with aluminium alkoxides⁴ and aluminium salts.⁷ Most studies are dealing with the complexation of aluminium alkoxides or mixed alkoxide- β -diketonates. In a recent paper Wengrovius *et al.* described the synthesis of several dimeric complexes of $\text{Al}(\text{OR})(\beta\text{-diketonate})_2$.⁸ These dimers are thermally unstable in solution and decompose via ligand disproportionation. No monomer-dimer equilibrium is observed, probably due to the unfavourable five-coordinated aluminium in the monomer. We have synthesized bis(acetylacetonato)(2-hydroxyphenolato)aluminium (**I**) from **II** and **III** as an example of $\text{Al}(\text{OR})(\beta\text{-diketonate})_2$, in which the OR group is provided with a hydroxy functionality. We have studied in detail the dimeric structure of this effective catalyst for ring-opening polymerization by NMR spectroscopy.

EXPERIMENTAL

Preparation of bis(acetylacetonato)(2-hydroxyphenolato)aluminium (I)

Catechol (5.0 g, 45 mmol) was added to a solution of 9.6 g (29 mmol) tris(acetylacetonato)aluminium in 500 cm³ of diethylether and the mixture was refluxed for 48 h. The product precipitated during the reaction and was collected by filtration, thoroughly washed with diethylether and dried at reduced pressure, affording 2.4 g (10.2 mmol, 35%) spectroscopically pure bis(acetylacetonato)(2-hydroxyphenolato)aluminium, m.p. 192–194°C (dec.). An analytically pure sample was obtained upon crystallization from benzene, m.p. 195°C. Found: C, 56.9; H, 5.5; Al, 8.0. Calc. for $(\text{C}_{32}\text{H}_{38}\text{O}_{12}\text{Al}_2)$: C, 57.5; H, 5.7; Al, 8.1%. HPLC analysis of the raw reaction mixture showed the presence of **II**, **III**, acetylacetone, and a product with the same retention time as **I**.

Measurements

The ¹H- and ¹³C-NMR spectra were recorded at 80 and 20 MHz respectively with a Bruker WP-80-SY spectrometer. ²⁷Al-NMR spectra were recorded at 52 MHz with a Nicolet NT200. Solid state ¹³C-NMR spectra were recorded at 100 MHz with a Bruker MSL 400 using CP/MASS and TOSS for side band reduction. The two-dimensional NOE

Fig. 1. ^1H -NMR spectrum of a freshly prepared sample of **I** in CDCl_3 ; the connectivities indicated at the bottom are NOE interactions as measured with a mixing time of 1.4 s.

(NOESY) and COSY spectra were recorded at 250 MHz with a Bruker AM 250, using mixing times of 0.9, 1.4, and 1.9 s, respectively. The chemical shifts are reported in δ units (parts per million) relative to CHCl_3 and converted to δ TMS values using $\delta \text{CHCl}_3 = 7.25$ ppm. The vapour phase osmometric measurements were performed at the analytical department of the university of Groningen using 0.5% solutions in CHCl_3 at a temperature of 37°C .

RESULTS AND DISCUSSION

The reaction of **II** and **III** in ether at reflux temperature for 48 h yields **I** as a white precipitate in

35% yield. The substitution of a second acetylacetonate ligand is not observed despite a high ratio **III** over **II**. The ^1H -NMR spectrum of a freshly prepared sample of **I** in CDCl_3 is depicted in Fig. 1. The difference in chemical shift for the methyl groups of the acetylacetonate moiety ($\delta = 2.2$ – 2.0 vs $\delta = 1.3$ – 1.1 ppm) is remarkable. The three resonances at $\delta = 8.3$, 8.5 and 8.55 ppm indicate the presence of three isomers. This is supported by the observation that the relative intensities of the three isomers are dependent on the history of the sample (twice vs not recrystallized). The proximity of protons within **I** is assessed in a two-dimensional nuclear Overhauser enhancement (NOE) exper-

Fig. 2. ^{13}C -NMR spectrum of **I** in the solid state using CP/MASS.

iment. The NOE connectivities are indicated in Fig. 1. Besides the expected connectivities on the basis of adjacent hydrogens in the molecule, the experiment indicates a remarkable short distance between the acidic phenol hydrogens and the downfield CH_3 group of the acetylacetonate ligand. A solid state ^{13}C -NMR spectrum of **I** shows four resonances for both the carbonyl carbons and the methyl carbons of the acetylacetonate moiety (Fig. 2).

The NMR data cannot be explained by a simple monomeric structure of bis(acetylacetonato)(2-hydroxyphenolato)aluminium. However, the data are in complete accordance with a dimeric structure of **I**, in which the catechol ligands are responsible for the bridging (see Scheme 1). A CPK model of the dimer shows that the two benzene rings are located perpendicular to each other and that three geometrical isomers are possible, in which the four acetylacetonate ligands are all orientated longitudinally, all transversally, or in a combination of two longitudinal and two transverse dentations with respect to the Al–Al axis, respectively. Furthermore and most striking, the two phenolic hydroxyl groups are forced to close proximity at the same site of the dimer molecule offering a very acid proton by hydrogen bonding of these two hydroxyl groups. The model also clearly demonstrates that one CH_3 group of each acetylacetonate moiety is located in the shielding zone of the benzene ring, while the other is situated in the deshielding zone. Models of monomer and trimer do not show these (de)shielding effects.

We propose that the first step in the reaction of

Scheme 1.

II and **III** consists of a ligand exchange equilibrium between catechol and acetylacetone. This equilibrium has been confirmed by HPLC analysis.³ The primary monomeric product bis(acetylacetonato)(2-hydroxyphenolato)aluminium is in equilibrium with its dimer **I**, which separates from the reaction mixture. The ratio **II** over **III** and their concentrations determine the yield of **I**. Dimer **I** is an amorphous mixture of three isomers and is stable in air.

Dynamic NMR spectroscopy

When a sample of **I** in CDCl_3 was stored for several hours at room temperature the ^1H -NMR spectrum (see Fig. 3) deviated from that of a freshly prepared sample (Fig. 1). Apparently the dimer partially dissociates into monomeric species, to which the resonances at $\delta = 1.94$ and $\delta = 5.42$ ppm can

Fig. 3. ^1H -NMR spectrum of a sample of **I** in CDCl_3 after 2 h storing at room temperature; the resonances indicated with * correspond to dimer and with O to monomer.

Fig. 4. The change in molecular weight in time of a solution of **I** in CHCl_3 using VPO (*) and in CDCl_3 using ^1H -NMR (●).

be assigned. The spin-lattice relaxation times for all hydrogens of the dimer are shorter than the T_1 values of the corresponding atoms in the monomer. The information obtained from ^{27}Al -NMR spectroscopy is scarce. The singlet for dimer and monomer of **I** are indistinguishable, while the resonance is shifted 2 ppm upfield and broadened by a factor of 1.5 with respect to the tris(acetylacetonato)-aluminium resonance.

The dissociation of **I** is confirmed by vapour phase osmometry. The changes in molecular weight during the dissociation of the dimer **I** were measured using a dilute solution of CHCl_3 at 37°C (Fig. 4). At these low concentrations a simple dimer-monomer equilibrium was observed in which the equilibrium constant is high. The observed decrease in molecular weight in time is in full agreement with the NMR kinetic measurements in CDCl_3 under the same conditions (Fig. 4).

The equilibrium constant of the dimer-monomer interchange proved to be dependent on concentration, solvent and temperature. Lowering the concentration of **I** furnishes a higher degree of dissociation. Variable temperature ^1H -NMR spectroscopy of **I** in ODCB-d_4 were performed to study the dynamics of the geometrical isomerization in the dimer and of the dimer-monomer equilib-

rium. The results are presented in Fig. 5. As the temperature was raised the resonances due to the acidic phenol hydrogens of the three isomers of the dimer were shifted upfield and coalesced at 138°C . This coalescence corresponds to an isomerization of the acetylacetonate ligands. The $\Delta G^\ddagger$ of isomerization of the three isomers is established at 21.7 ± 0.7 kcal/mol. This free energy of activation is similar to those found for the isomerization of the octahedral tris(β -diketonato) complexes,⁹ but significantly higher than found for the $\text{Al}(\text{OR})(\beta\text{-diketonate})_2$ dimers.⁸ This observation is consistent with a normal β -diketonate octahedral isomerization, without going through a transition state in which one of the catecholate-aluminium bonds is broken. Furthermore, no coalescence was observed for the intermolecular dimer-monomer interchange.

At the high concentrations of **I**, used in this experiment, no linear correlation was found for the logarithm of the equilibrium constant (K) and the reciprocal temperature when K was calculated on the basis of a dissociation of the dimer alone (Fig. 5). Satisfactory fits could only be obtained when it was assumed that at high dimer concentrations trimeric or even polymeric species were involved.

The results presented above force us to propose that the reaction of **II** and **III** furnishes the dimer of bis(acetylacetonato)(2-hydroxyphenolato)aluminium (**I**). The dimer is present in three geometrical isomers and in solution these isomers are

Fig. 5. (a) The chemical shift of the acid phenolic hydrogens of the dimer as a function of temperature. (b) The calculated equilibrium constant as a function of temperature.

in equilibrium with monomeric and polymeric species. The unique structure of the dimer, with the close proximity of the acidic phenol hydrogens and both catechol ligands attached to two aluminium atoms, makes **I** an active catalytic species. Investigations concerning the catalytic role of **I** in the ring-opening of epoxides is in progress.³

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