Reactions of Dichloroaluminium Acetylacetonate with Lewis Bases. 1. Ionic Complex of $Cl_2Alacac$ with Tetrahydrofurane*

J. LEWIŃSKI and S. PASYNKIEWICZ**

Faculty of Chemistry, Warsaw Technical University (Politechnika), Koszykowa 75, 00-662 Warsaw, Poland

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Abstract

The reaction of dichloroaluminium acetylacetonate with THF has been studied. The ionic complex $[(acac)_2Al{\cdot}2THF]^+[AlCl_4]^-$ was found to result from the reaction. The structure of the complex has been investigated by the variable temperature ^1H NMR technique, as well as by ^{13}C and ^{27}Al NMR spectroscopy. The cation complex $[(acac)_2Al{\cdot}2THF]^+$ is predominantly *trans* in dichloromethane solution (75% *trans* and 25% *cis*). In the presence of an excess of THF a fast exchange proceeds at room temperature in the cation complex between the free THF molecules and those present in the complex, which is accompanied by a stereochemical rearrangement of the cation complex.

Introduction

The reactions of dialkylaluminium acetylacetonates with Lewis bases have been decided in our previous paper [1]. $R_2Alacac$ was found to form with Lewis bases (B) unstable five-coordinative complexes $R_2Alacac{\cdot}B$, which decompose forming $R_3Al{\cdot}B$ and $Al(acac)_3$. The results of studies on the reaction of dichloroaluminium acetylacetonate with THF are now presented. During these studies it appeared that $Cl_2Alacac$ has a more complicated composition than would result from earlier reports and that it does not correspond fully to a monomeric symmetric chelate $R_2Alacac$ structure. Studies on the structure of $Cl_2Alacac$ and of its reactions with other Lewis bases will be the subject of further papers.

Experimental

All reactions were carried out under an atmosphere of dry, deoxidized nitrogen. Commercial aluminium triacetylacetonate and aluminium trichloride were used. CH_2Cl_2 and THF, commercially available, were carefully dried and distilled before use. Dichloroaluminium acetylacetonate was obtained from $Al(acac)_3$ and $AlCl_3$ by the method described in the literature [2].

Measurements

^{27}Al NMR spectra were recorded on a Bruker WM 250 spectrometer, ^{13}C NMR spectra on a Varian XL 100 and Bruker WM 250 spectrometers and ^1H NMR spectra on a Tesla 80 MHz spectrometer.

Synthesis of $Cl_2Alacac$

11.83 g (88.6 mmol) of $AlCl_3$ and 14.35 g (44.3 mmol) of $Al(acac)_3$ were introduced into a Schlenk vessel, then 30 cm^3 of CH_2Cl_2 were added while stirring at 0 °C. The temperature was gradually raised to room temperature and the reaction was carried out for 3 h. $Cl_2Alacac$ was isolated from the reaction mixture by distillation at 103 °C/1 torr, yield 85%. Found: Al, 13.66. Calc.: Al, 13.70%.

Synthesis of the $[(acac)_2Al{\cdot}2THF][AlCl_4]$ Complex

A solution of 2.70 g (13.7 mmol) of $Cl_2Alacac$ in 8 cm^3 of CH_2Cl_2 was introduced into a Schlenk vessel, to which 2.20 g (26.8 mmol) of THF was dropped in while stirring at room temperature. The reaction was carried out for 20 min. The unreacted THF and CH_2Cl_2 were distilled off under an oil pump vacuum. The $[(acac)_2Al{\cdot}2THF][AlCl_4]$ complex obtained as a white crystalline solid is very soluble in CH_2Cl_2, quite soluble in THF, but insoluble in toluene and diethylether. The complex was crystallized from THF. Found: Al, 10.02; C, 39.90; H, 5.85. Calc. for $C_{18}H_{30}Al_2Cl_4O_6$: Al, 10.04; C, 40.15; H, 5.58%. The synthesis of the complex with deuterated THF was carried out analogously using THF-d_8 with 99% minimum isotopic purity (Merck).

Results

Dichloroaluminium acetylacetonate reacts with THF at room temperature at a 1:1 mole ratio yielding

*Dedicated to Prof. H. Lehmkuhl on the occasion of his 60th birthday.

**Author to whom correspondence should be addressed.

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a stable ionic complex, irrespective of whether THF is added in a stoichiometric amount or an excess.

$$2Cl_2Alacac + 2THF \longrightarrow [(acac)_2Al\cdot 2THF]^+[AlCl_4]^-$$

I

The complex I is a white crystalline solid, quite soluble in THF, very soluble in methylene chloride but insoluble in benzene and diethylether.

Nuclear Magnetic Resonance Measurements

NMR studies permitted the determination of the structure of the complex formed. On the basis of chemical shifts of the ^{27}Al NMR signals the coordination number of the aluminium atoms in the molecules can be assigned with considerable probability, and the character of the signal indicates the symmetry of the aluminium atom surroundings [3]. A sharp signal is observed in the spectrum for a symmetric surrounding. Disturbance of symmetry causes a widening of the signal.

In the ^{27}Al NMR spectrum of complex I in CH_2Cl_2 (Fig. 1) two signals appear of an identical intensity ratio determined on the basis of the integration of signals. The sharp signal at 102.6 ppm is a well known typical feature of $[AlCl_4]^-$, and the broad signal at 4.10 ppm has been attributed to the aluminium atom in an octahedral surrounding. The signal of the $[(acac)_2Al\cdot 2THF]^+$ cation is broadened with a decreasing of temperature and at −50 °C becomes practically diffused. The character of the sharp signal of the $[AlCl_4]^-$ ion does not change. In Fig. 2 two possible structures of the $[(acac)_2Al\cdot 2THF]^+$ cation are given. The surrounding of the aluminium atoms in each of the structures is different and separated signals of the aluminium atoms could be expected in the ^{27}Al NMR spectrum in the case of the presence of both isomers. In the spectra of the studied compound only a single signal appears at room temperature in the region of a six-coordinative aluminium.

The stereochemistry of the octahedral cation $[(acac)_2Al\cdot 2THF]^+$ was determined on the basis of variable temperature ^1H and ^{13}C NMR spectra.

Variable temperature ^1H NMR spectra of complex I in methylene chloride are presented in Fig. 3. The chemical shifts corresponding to particular protons are presented in Tables I and II. The ^1H NMR spectrum of complex I recorded at room temperature contains two singlets of the acetylacetonate protons,

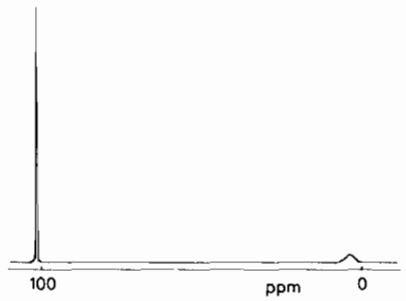


Fig. 1. ^{27}Al NMR spectrum of $[(acac)_2Al\cdot 2THF][AlCl_4]$ in CH_2Cl_2 solution at 27 °C; values relative to $[Al(H_2O)_6]^{3+}$ external.

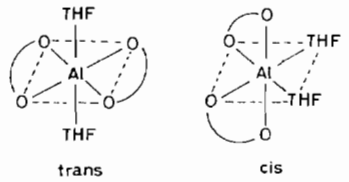


Fig. 2. Two possible structures for $[(acac)_2Al\cdot 2THF]^+$.

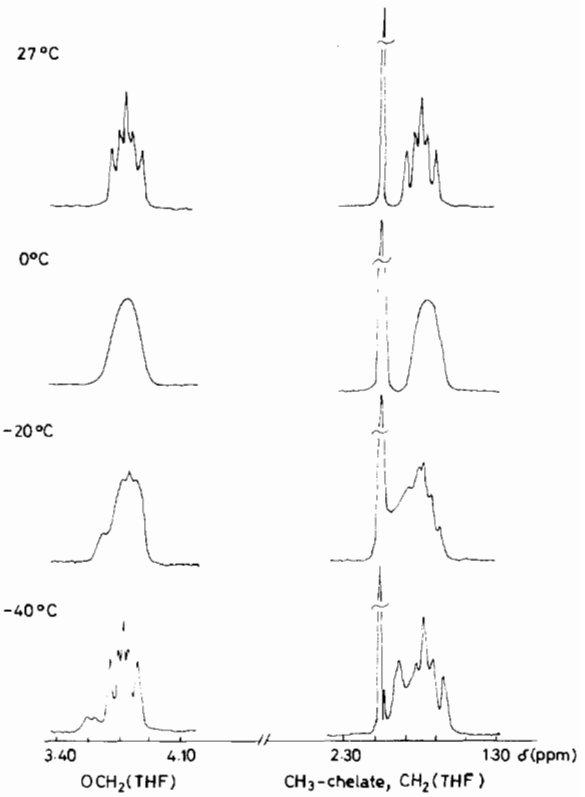


Fig. 3. Temperature dependence ^1H NMR 80 MHz spectra of $[(acac)_2Al\cdot 2THF][AlCl_4]$ in CH_2Cl_2 solution.

TABLE I. ^1H NMR Chemical Shifts in acac Proton Region for $[(acac)_2Al\cdot 2THF][AlCl_4]$ in CH_2Cl_2 as an Internal Standard $\delta(H) = 5.33$

Temperature (°C)	CH-ring	CH_3-chelate
27	5.71	2.06
−50	5.71	2.07, 2.03, 191

δ values in ppm.

TABLE II. ^{1}H NMR Chemical Shifts of THF Protons for Cl_2Alacac and THF Solution in CH_2Cl_2 as an Internal Standard δ(H) = 5.33, 27 °C

Solution	O-CH_2	CH_2
THF	3.68	1.77
$[(acac)_2Al{\cdot}2THF][AlCl_4]$ I	3.79	1.90
I + 2 THF	3.74	1.84
I + 4 THF	3.71	1.81
I + 2 THF[a]	3.89, 3.64, 3.57	1.92, 1.84, 1.74

δ values in ppm. [a]Shifts at −50 °C.

CH_3-chelate and CH-ring. The CH_3-chelate signal broadens when decreasing the temperature to 0 °C. With a further decrease of temperature the base line in the spectrum between the CH_3-chelate and CH_2(THF) protons considerably heightens. At −20 °C a new signal of CH_3-chelate protons can be distinguished at the side of the wavy broad signal of CH_2(THF) protons, while the most intense signal of those protons still remains broadened. Only at −40 °C does this signal become sharper and a third signal of the CH_3-chelate protons appears beside it from the higher field side. At the same time the base line between the signals lowers to the scale base. The signal of the CH-ring protons does not show such behaviour and its image remains unchanged within the temperature range studied. Such a course of change in the ^{1}H NMR spectrum with a decrease of temperature was attributed to the occurrence of the $[(acac)_2Al{\cdot}2THF]^+$ cation in the form of two isomers, *trans* and *cis*. The presence in the spectrum of a single sharp signal of CH_3-chelate protons at room temperature results from a fast exchange between the *trans* and *cis* forms. The rate of the stereochemical exchange decreases with a lowering temperature and is stopped within the NMR scale at −40 °C, which causes an initial broadening of that signal and then a splitting into three individual signals. The most intense signal occurring on the lower field side is attributed to the CH_3-chelate protons in the *trans* structure, and the remaining two ones to the magnetically non-equivalent protons in the *cis* structure. No clear splitting in the spectra of the CH_3-chelate protons for both isomers is observed with a change of temperature. The signals of the *cis* isomer appear gradually in the region between the *trans* and CH_2(THF) signals (as was already mentioned, a heightening of the spectrum base line between these signals, results from that). The reason for this is probably the fact that the differences of chemical shifts between the *trans* isomer signal and the middle of the doublet of the *cis* isomer signals are approximately equal. Since the variable temperature spectra analysis in the region of the CH_3-chelate protons signals is difficult due to the proximity of the CH_2(THF) protons signals, analogues studies for the complex using deuterated THF were carried out to confirm the correctness and assignment of changes observed in the spectra. Complete conformability with the description discussed above was obtained. On the basis of the integration of signals in the spectrum it was calculated that the *trans* isomer of the $[(acac)_2Al{\cdot}2THF]^+$ cation constitutes about 75% and the *cis* one about 25%.

The signals of two multiplets at complexed THF broaden with a lowering of temperature and at 0 °C they collapse into two broad bands. A further decreasing of temperature causes those signals to split again at about −20 °C up to −40 °C. No further changes of the spectra were observed below −40 °C. The appearance of new signals in the lower field indicates a different placing of THF in the *trans* and *cis* structure. However, the signals of THF protons lying in a higher field overlap with the CH_3-chelate signals in the *cis* structure.

On the basis of ^{1}H NMR studies it was found that in complex **I** a fast exchange of the donor molecules occurs at an excess of THF in a CH_2Cl_2 solution. Only two signals of the THF protons are present in the spectrum at room temperature. The chemical shifts of these signals are arithmetic weighted mean value of the free and complexed THF (Table II). By gradually decreasing the temperature, changes of the signals are observed in the spectra similar to those for the complex without an excess of THF. The only difference is that below 0 °C the additional signals of free THF slowly appear in the higher field. The exchange of THF is practically stopped, similarly to the stereochemical rearrangement, at about −40 °C.

^{13}C NMR spectra of complex **I** in CH_2Cl_2 at room temperature and at −50 °C are presented in Fig. 4. Chemical shifts corresponding to particular carbon atoms are presented in Table III. Singular signals of acetylacetonate carbons, CO, CH, CH_3, and singular signals of O-CH_2 and CH_2 carbons in THF are present in the spectrum recorded at room temperature. As expected an intense signal of the *trans* structure appears for the carbon of the CO group at −50 °C. On the higher field side two signals of small intensity, corresponding to the magnetically non-equivalent carbons of the *cis* structure are observed. The CH_3-

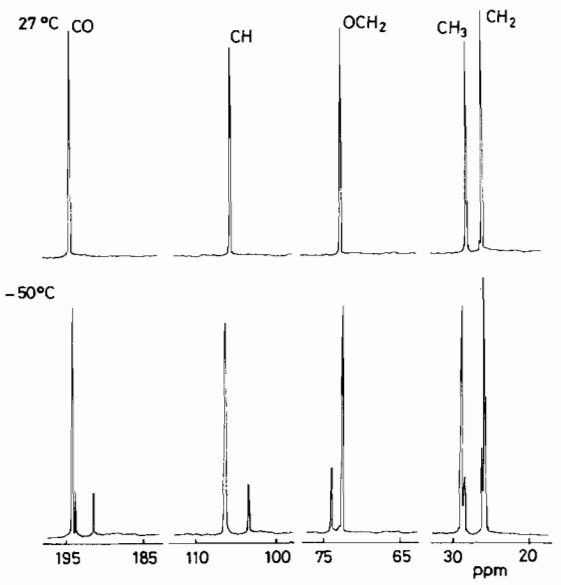


Fig. 4. ^{13}C NMR 62.9 MHz spectra of $[(acac)_2Al \cdot 2THF][AlCl_4]$ in CH_2Cl_2 solution at 27 °C and −50 °C.

TABLE III. ^{13}C NMR Chemical Shifts[a] for $[(acac)_2Al \cdot 2THF][AlCl_4]$ in CH_2Cl_2 Solution

Temperature (°C)	CO	acac		THF	
		CH	CH_3	O-CH_2	CH_2
27	194.7	103.7	26.8	70.8	25.1
−50	194.9				
	194.7	104.1	27.0	71.6	25.2
	192.9	103.1	26.8	70.8	25.0
				68.0[b]	25.6[b]

[a]All values are in ppm relative to internal TMS. [b]Signals of free THF appear in the case of excess THF.

chelate carbons should show an analogous picture in the spectrum. However, only one signal in the higher field is observed corresponding to the CH_3-chelate carbons of the *cis* structure. It can be presumed that the second signals of those carbons overlap with the intense signal of the *trans* isomer (this would be the signal of the CH_3-chelate carbon lying at the *cis* position in relation to THF). The CH-ring carbons are also differentiated for both isomers in the ^{13}C NMR spectrum at −50 °C; two signals lying near each other appear in the spectrum (in the ^1H NMR spectrum only one signal of the CH-ring protons is visible under these conditions). The carbons of the THF complexing molecules are also clearly magnetically non-equivalent in both structures. The carbon signals of O-CH_2 and CH_2 of the *cis* structure appear, however, in the lower field with respect to corresponding signals of the *trans* structure.

The assignment of the signals corresponding to CH_2(THF) and CH_3-chelate presented some difficulties. Only after additional ^{13}C NMR recording of complex I with an excess of THF was it found that the CH_2(THF) signals occur in the higher field with respect to those in free THF and the carbon signals of O-CH_2(THF) occur in the lower field (Table III). However, signals corresponding to the CH_3-chelate carbons appear in a lower field than the CH_2(THF) signal. In the ^1H NMR spectrum both groups of protons signals of complexed THF lie in a lower field with respect to those of free THF.

Discussion

From the experiments carried out it appears that dichloroaluminium acetylacetonate easily forms a stable complex with THF of an ionic structure (eqn. (1))

$$2Cl_2Alacac + 2THF \longrightarrow [(acac)_2Al \cdot 2THF]^+[AlCl_4]^- \quad (1)$$

As was previously described [1], dialkylaluminium acetylacetonate reacts with THF and other Lewis bases yielding disproportionation products (eqn. (2)).

$$3R_2Alacac + 2THF \longrightarrow 2R_3Al \cdot THF + Al(acac)_3 \quad (2)$$

The different course of both reactions can be explained by the stability of the $[AlCl_4]^-$ anion formed in reaction (1) and the relative unstability of the $[R_4Al]^-$ anion, which can be eventually formed in the course of the reaction (2) [4]. Due to this, Cl_2Alacac forms an ionic complex with THF, in which an aluminium diacetylacetonate cation stabilized by two THF molecules occurs besides the stable $[AlCl_4]^-$ anion. The differences in the reaction course of Cl_2Alacac and R_2Alacac with THF can be presented as follows

$$R_2Alacac \overset{THF}{\rightleftharpoons} R_2\overset{+}{A}l \cdot THF + acac^- \xrightarrow{R_2Alacac} R_3Al \cdot THF + RAl(acac)_2 \quad (3)$$

$$Cl_2Alacac \overset{THF}{\rightleftharpoons} Cl_2\overset{+}{A}l \cdot THF + acac^- \xrightarrow{Cl_2Alacac} [AlCl_4]^-[(acac)_2Al \cdot 2THF]^+ \quad (4)$$

In reaction (3) the $R_2\overset{+}{A}l \cdot THF$ cation reacts with the substrate yielding a stable $R_3Al \cdot THF$ complex. In reaction (4) the analogous $Cl_2\overset{+}{A}l \cdot THF$ cation is stabilized by reacting with the substrate forming a stable $[AlCl_4]^-$ anion.

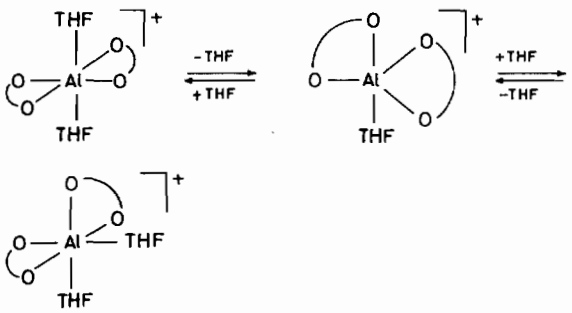
Basic conclusions can be drawn from the ^1H NMR variable temperature spectrum on the mechanism of stereochemical rearrangement processes and donor

exchange in the $[(acac)_2Al \cdot 2THF]^+$ cation complex. The analysis of the variable temperature spectrum of the sole complex **I** and of that complex with an excess of THF indicates that at 0 °C the signals of the THF multiplets join, forming broad bands, which again slowly split at less than −20 °C. A broadening and then splitting of the CH_3-chelate signals is observed simultaneously with those changes. The identical picture of changes in both cases indicates that these two processes, donor exchange and isomerization in the cation, are connected with each other.

The mechanism of rearrangements in the $M\text{-}O_6$ core with bifunctional donors is extensively described in the literature [5]. In most cases the results obtained do not permit a univocal decision on the mechanism of rearrangement. For unsymmetric Al(III) tris-β-diketonates the authors most often suggest a mechanism of stereochemical rearrangements with a cleavage of the Al–O bond and formation of a five-coordinative intermediate. The rearrangements described proceed much slower than those observed by us in the $[(acac)_2Al \cdot 2THF]^+$ cation.

Hence it can be concluded that the rearrangement mechanism in the $[(acac)_2Al \cdot 2THF]^+$ cation is different than for unsymmetric Al(III) tris-β-diketonates and does not proceed with cleavage of one diketonate oxygen aluminium bond.

From the results obtained it appears that the cleavage of the donor–acceptor bond between the aluminium atom and THF with the formation of a five-coordinative intermediate and repeated complexing of the THF molecule (Scheme 1) is responsible for the isomerization and donor exchange in the $[(acac)_2Al \cdot 2THF]^+$ cation. A five-coordinative intermediate is often postulated for the isomerization of octahedral complexes and the stereochemical aspects of such rearrangement mechanisms have been extensively described in the literature [5, 6].



Scheme 1.

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References

1 S. Pasynkiewicz and J. Lewiński, *J. Organomet. Chem., 290,* 15 (1985).
2 W. R. Kroll, I. Kuntz and E. Brinbaum, *J. Organomet. Chem., 26,* 313 (1971).
3 (a) J. W. Akitt, *Annu. Rep. NMR Spectrosc., 5A,* 465 (1972); (b) J. F. Hinton and R. W. Briggs, 'NMR and the Periodic Table', Academic Press, New York, 1978; (c) R. Ben, A. Rufińska, H. Lehmkuhl, E. Janssen and C. Krüger, *Angew. Chem., 10,* 779 (1983).
4 J. Lewiński and S. Pasynkiewicz, to be published.
5 (a) F. Basolo and R. G. Pearson, 'Mechanism of Inorganic Chemistry', Wiley, New York, 1967; (b) L. H. Pignolet, 'Topics in Current Chemistry: Theoretical Inorganic Chemistry', Springer-Verlag, Berlin/Heidelberg/New York, 1975, Chap. 3; (c) R. H. Holm, 'Dynamic Nuclear Magnetic Resonance Spectroscopy', Academic Press, New York, 1975, Chap. 9.
6 C. S. Springer, Jr, *J. Am. Chem. Soc., 95,* 1459 (1973).