Reactions of Dichloroaluminium Acetylacetonate with Lewis Bases. 3. Complexes with Diethyl Ether, 2,6-Dimethylpyridine and Pyridine. Reactions of Ligand Exchange

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(Received May 18, 1987)

Abstract

The reactions of dichloroaluminium acetylacetonate ($Cl_2Alacac$) with diethyl ether (Et_2O), 2,6-dimethylpyridine (DMP) and pyridine (Py) have been studied. Et_2O and $Cl_2Alacac$ form an ionic complex $[(acac)_2Al\cdot 2Et_2O]^+[AlCl_4]^-$ irrespective of the reactant mole ratio. DMP yields a complex $[(acac)_2Al\cdot DMP]^+[AlCl_4]^-$ with a five-coordinative aluminium atom in the cation. Pyridine forms an ionic complex $[(acac)_2Al\cdot 2Py]^+[AlCl_4]^-$ at a reactant equimolar ratio. An excess of pyridine leads to the formation of the $Cl_2Alacac\cdot 2Py$ complex (1:2 mole ratio). It was found that in the studied complexes a coordinated Lewis base easily undergoes exchange by a stronger base. The stabilization of the $[(acac)_2Al]^+$ cation by a base increases in the order: DMP < Et_2O < THF < DME < Py < DMF.

Introduction

Previously we studied the complexes of dichloroaluminium acetylacetonate ($Cl_2Alacac$) with tetrahydrofurane (THF) [1] and with dimethoxyethane (DME) and dimethylformamide (DMF) [2]. THF and DME form ionic complexes of the general formula $[(acac)_2Al\cdot nB]^+[AlCl_4]^-$ irrespective of the reactant mole ratio. Also DMF gives the same complex for a reactant equimolar ratio.

The purpose of this work was to study the reaction of dichloroaluminium acetylacetonate with a weak and strong Lewis base: diethyl ether (Et_2O) and pyridine (Py) and a sterically bulky base: 2,6-dimethylpyridine (DMP). From the literature it appeared that dichloroaluminium acetylacetonate reacts with Et_2O [3] and Py [4] at a 1:1 mole ratio. The authors do not give any information on the structure of the adducts formed.

Moreover, it was our intention to explain whether, and how, the ligand exchange reactions occur in the complexes obtained.

Experimental

All reactions were carried out in an atmosphere of dry, deoxidized nitrogen, using Schlenk tube techniques. Dichloroaluminium acetylacetonate was prepared [1], and THF, DME, DMF and methylene chloride were purified [1, 2] as described previously. Et_2O was distilled from sodium benzophenone ketyl. Pyridine and DMP were predried (molecular sieves 4 Å) and distilled over zinc powder.

^{27}Al NMR spectra were recorded on Bruker WM 250 (Univ. van Amsterdam) and Bruker WM 400 (Max-Planck-Institut f. Kohlenforschung, Mülheim) spectrometers and ^1H NMR spectra on a Tesla 80 MHz spectrometer. IR spectra were recorded on a Perkin-Elmer 225 spectrometer in nujol mulls.

$[(acac)_2Al\cdot 2Et_2O][AlCl_4]$ (I)

Et_2O (0.9 cm^3, *ca.* 8.59 mmol) was dropped into a stirred solution of $Cl_2Alacac$ (1.48 g, 7.51 mmol) in CH_2Cl_2 (8 cm^3) at room temperature; stirring was continued for 15 min. The unreacted Et_2O and solvent were removed by vacuum evaporation at room temperature. Complex **I** obtained in quantitative yields as a white solid is very soluble in CH_2Cl_2, but insoluble in Et_2O. *Anal.* Calc. for $C_{18}H_{34}Al_2Cl_4O_6$: Al, 9.96; C, 39.85; H, 6.27. Found: Al, 9.91; C, 39.80; H, 6.29%.

$[(acac)_2Al\cdot 2Py][AlCl_4]$ (II)

Pyridine (0.50 g, 6.35 mmol) was dropped into a stirred solution of $Cl_2Alacac$ (1.25 g, 6.36 mmol) in CH_2Cl_2 (8 cm^3) at room temperature; stirring was continued for 15 min. The solvent was removed by vacuum evaporation affording a white solid which was washed with Et_2O. Complex **II** is very soluble in CH_2Cl_2 and insoluble in Et_2O. *Anal.* Calc. for $C_{20}H_{24}Al_2Cl_4N_2O_4$: Al, 9.78; C, 43.48; H, 4.35; N, 5.07. Found: Al, 9.69; C, 42.23; H, 4.73; N, 4.97%.

$Cl_2Alacac\cdot 2Py$ (III)

Pyridine (0.92 g, 11.68 mmol) was dropped into a solution of $Cl_2Alacac$ (1.15 g, 5.84 mmol) in

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0020-1693/88/$3.50

CH_2Cl_2 (9 cm^3) while stirring at 0 °C. The mixture was then allowed to warm up to room temperature. A white solid began to precipitate from the solution after *ca.* 3 h of stirring. The reaction was carried out for 3 days. The precipitate was removed and washed with CH_2Cl_2. Complex **III** is insoluble in commonly used solvents. *Anal.* Calc. for $C_{15}H_{17}AlCl_2N_2O_2$: Al, 7.61; C, 5.70; H, 4.79; N, 7.89. Found: Al, 7.58; C, 50.03; H, 4.77; N, 7.74%. The precipitation of the solid was found to occur faster when adding excess amounts of pyridine.

[(acac)$_2$Al·DMP][AlCl$_4$] (IV)

DMP (0.10 cm^3, *ca.* 0.86 mmol) was added dropwise into a solution of Cl_2Alacac (0.17 g, 0.86 mmol) in 1.5 cm^3 CH_2Cl_2 while stirring at 0 °C. The mixture was then allowed to warm up to room temperature. The unreacted DMP and solvent were removed by vacuum evaporation affording a white solid; the residue was dried *in vacuo* for 3 h at room temperature. *Anal.* Calc. for $C_{17}H_{23}Al_2Cl_4NO_4$: Al, 10.78; C, 40.72; H, 4.59; N, 2.79. Found: Al, 10.61; C, 4.96; H, 4.74; N, 2.84%. If the excess of DMP is not removed after heating to room temperature, and the reaction mixture is stirred for *ca.* 3 days $(acac)_3Al$ is formed in a more than 50% yield.

Base Exchange Reactions in [(acac)$_2$Al·nB][AlCl$_4$] Complexes

Pyridine (0.096 g, 1.21 mmol) was added to a solution of complex **I** (0.34 g, 1.21 mmol) in CH_2Cl_2 (4 cm^3) at room temperature and stirred for 15 min. The solvent was removed by vacuum evaporation. The residue was washed with Et_2O and dried *in vacuo* for 2 h at room temperature, and identified by ^1H NMR as complex $[(acac)_2Al\cdot 2Py][AlCl_4]$ (**II**). The other base exchange reactions were carried out analogically. Complex $[(acac)_2Al\cdot DMP][AlCl_4]$ (**IV**) was found to react with Et_2O yielding **I**. Complex $[(acac)_2Al\cdot 2THF][AlCl_4]$ (**V**) was obtained from the reaction of **I** with THF and complex $[(acac)_2Al\cdot DME][AlCl_4]$ (**VI**) from that of **V** with DME. DMF reacts with **VI** yielding $[(acac)_2Al\cdot 2DMF][AlCl_4]$ (**VII**). No base exchange was found in the reaction of **VII** with pyridine. Complexes **V**, **VI** and **VII** were obtained previously [1, 2] from the reaction of dichloroaluminium acetylacetonate with respective Lewis bases.

Reaction of Cl$_2$Alacac·2Py (III) with Cl$_2$Alacac and [(acac)$_2$Al·nB][AlCl$_4$]

Cl_2Alacac (0.31 g, 1.60 mmol) was added to a solution of complex **III** (0.57 g, 1.60 mmol) in CH_2Cl_2 (4 cm^3) at room temperature. After a few minutes of stirring the solution becomes homogeneous; the reaction was carried out for 0.5 h. The solvent was removed by evaporation under reduced pressure and the residue was washed with Et_2O and identified by ^1H NMR and elemental analysis as $[(acac)_2Al\cdot 2Py][AlCl_4]$ (**II**).

The same procedure was followed for the reaction of complex **III** with $[(acac)_2Al\cdot 2Et_2O][AlCl_4]$ (**I**) and $[(acac)_2Al\cdot DME][AlCl_4]$ (**VI**) at the 2:1 reactant mole ratio. Complex **II** was formed in both cases.

Reaction of [(acac)$_2$Al·2Py][AlCl$_4$] (II) with Pyridine

Pyridine (0.6 cm^3, 7.44 mmol) was dropped into a solution of **II** (1.57 g, 2.84 mmol) in CH_2Cl_2 (7 cm^3) while stirring at room temperature. The mixture was allowed to stand for 3 days. Precipitation of a white solid occurred about 2 h after pyridine was added. The product was filtered off, washed with CH_2Cl_2 and identified as Cl_2Alacac·2Py (**III**).

The reaction can be reversed by heating a suspension of complex **III** in CH_2Cl_2 at 40–50 °C in a closed system to a complete decay of **III**. The ^1H NMR spectrum of the homogeneous solution recorded at −40 °C contains the signals of cation $[(acac)_2Al\cdot 2Py]^+$ and free pyridine.

Results

Dichloroaluminium acetylacetonate forms an ionic complex with Et_2O irrespective of the reactant mole ratio (reaction (1)), which is very soluble in CH_2Cl_2 and insoluble in Et_2O.

$$2Cl_2Alacac + 2Et_2O \xrightarrow{CH_2Cl_2} \underset{\textbf{I}}{[(acac)_2Al\cdot 2Et_2O]^+[AlCl_4]^-} \quad (1)$$

The reaction of Cl_2Alacac and pyridine depends on the reactant mole ratio. At an equimolar ratio an ionic complex is formed (reaction (2)), which is soluble in CH_2Cl_2 and insoluble in Et_2O.

$$2Cl_2Alacac + 2Py \xrightarrow{CH_2Cl_2} \underset{\textbf{II}}{[(acac)_2Al\cdot 2Py]^+[AlCl_4]^-} \quad (2)$$

At a 1:2 reactant mole ratio complex **III** precipitates as a white solid from the solution (reaction (3)). It is insoluble in commonly used solvents.

$$Cl_2Alacac + 2Py \xrightarrow{CH_2Cl_2} \underset{\textbf{III}}{Cl_2Alacac\cdot 2Py} \quad (3)$$

Complex **III** is also formed when adding an excess of pyridine to complex **II** (reaction (4)). Reaction (4) can be reversed by heating a suspension of complex **III** in CH_2Cl_2.

$$\underset{\textbf{II}}{[(acac)_2Al\cdot 2Py][AlCl_4]} + 2Py \underset{\Delta t}{\overset{\text{room temp.}}{\rightleftarrows}} 2Cl_2Alacac\cdot 2Py \quad (4)$$

$Cl_2Alacac$ and DMP form an ionic complex irrespective of the mole ratio of substrates reacting at a 2:1 ratio (reaction (5)).

$$2Cl_2Alacac + DMP \xrightarrow{CH_2Cl_2} \underset{\textbf{IV}}{[(acac)_2Al\cdot DMP]^+[AlCl_4]^-} \quad (5)$$

Complex **IV** is unstable in a CH_2Cl_2 solution and disproportionates yielding $(acac)_3Al$ (reaction (6)).

$$3\underset{\textbf{IV}}{[(acac)_2Al\cdot DMP][AlCl_4]} \xrightarrow[DMP]{CH_2Cl_2} 2(acac)_3Al + 4AlCl_3\cdot DMP \quad (6)$$

The disproportionation reaction (6) is accelerated by the presence of free DMP.

The Lewis base (B) coordinated in the cationic part of the complex easily exchanges with the same non-coordinated base (reaction (7)).

$$[(acac)_2Al\cdot 2B]^+ + 2B' \rightleftarrows [(acac)_2Al\cdot 2B']^+ + 2B \quad (7)$$

where B = B′

Such a reaction was described previously [1] for the complex with THF, and now it was found to occur with Et_2O and Py. The exchange reaction (7) was not found between the coordinated and free DME at room temperature [2].

An exchange between the coordinated and free base was found also for different bases. A stronger base is exchanged for a weaker one in the complex (reaction (8)).

$$[(acac)_2Al\cdot 2Et_2O]^+ + 2Py \longrightarrow [(acac)_2Al\cdot 2Py]^+ + 2Et_2O \quad (8)$$

Et_2O is also dislodged by THF from the complex, which results in the formation of $[(acac)_2Al\cdot 2THF]^+$-$[AlCl_4]^-$ (**V**). Complexed THF may be dislogded by DME with the formation of $[(acac)_2Al\cdot DME]^+$-$[AlCl_4]^-$ (**VI**) and DME by DMF with the formation $[(acac)_2Al\cdot 2DMF]^+[AlCl_4]^-$ (**VIII**). Pyridine, however, does not dislodge the coordinated DMF. DMP is most weakly coordinated, and it is completely displaced from the complex by Et_2O. From the above studies it appears that the stability of the bond between the base and aluminium in the $[(acac)_2Al\cdot nB]^+$ ionic complex, when $n = 1$ or 2, increases in the order:

$$DMP < Et_2O < THF < DME < Py < DMF \quad (9)$$

In the complexes obtained not only the exchange of the coordinated base takes place, but also such ligands as the acetylacetonate and chloride anions undergo exchange. The pyridine complex **III** of the 1:2 stoichiometry reacts with $Cl_2Alacac$ yielding the ionic complex **II** of a changed 1:1 stoichiometry (reaction (10)).

$$\underset{\textbf{III}}{Cl_2Alacac\cdot 2Py} + Cl_2Alacac \longrightarrow \underset{\textbf{II}}{[(acac)_2Al\cdot 2Py]^+[AlCl_4]^-} \quad (10)$$

Multi-step exchange reactions take place in reaction (11) between the pyridine complex **III** and the ionic complex with DME (**V**).

$$2Cl_2Alacac\cdot 2Py + \underset{\textbf{V}}{[(acac)_2Al\cdot DME]^+[AlCl_4]^-} \longrightarrow 2[(acac)_2Al\cdot 2Py]^+[AlCl_4]^- + DME \quad (11)$$

The reaction with the ether complex **I** proceeds similarly (reaction (12)).

$$2Cl_2Alacac\cdot 2Py + [(acac)_2Al\cdot 2Et_2O]^+[AlCl_4]^- \longrightarrow 2[(acac)_2Al\cdot 2Py]^+[AlCl_4]^- + 2Et_2O \quad (12)$$

NMR Measurements

The structures of complex **I**, **II** and **IV** were studied on the basis of ^{27}Al and ^1H NMR spectroscopy. The structure of the other complexes, except **III**, was discussed in previous papers [1, 2].

^{27}Al NMR Studies

A sharp signal at 102.6 ppm, characteristic for the $[AlCl_4]^-$ anion appears in the spectra of complexes **I**, **II** and **IV**. Broad signals lying slightly above 0 ppm correspond to the aluminium atom in an octahedral surrounding in the cations of complexes **I** and **II** $[(acac)_2Al\cdot 2B]^+$ (Table I). The signal at 37.1 ppm of aluminium in the complex **IV** cation changes its location and appears in the range typical for four- and six-coordinated aluminium in inorganic compounds [5, 6]. The signals of five-coordinated aluminium in the $ClAlO_4$ surrounding [7] and Cl_3-$Al\cdot 2THF$ complex [8] were also observed in that region. Thus it can be assumed that the aluminium atom in the $[(acac)_2Al\cdot DMP]^+$ cation is five-coordinative.

^1H NMR Studies

Single signals of the CH-ring and CH_3-chelate protons and signals of the complexed Et_2O protons are observed in the ^1H NMR spectrum of complex **I** in a CH_2Cl_2 solution at room temperature. A decrease of temperature to −95 °C does not cause any changes in the spectrum. The introduction of free Et_2O to the solution of complex **I** causes a shift of the Et_2O proton signals at room temperature. The multiplet centre chemical shifts correspond to the weighted average value of the shift for the free and complexed Et_2O. A lowering of temperature

TABLE I. NMR and IR Data for the Complexes of Dichloroaluminium Acetylacetonate with Lewis Bases

Complex		^1H δ (ppm)^a			^{27}Al (ppm)^b cation	IR (cm^{-1})		
		CH-ring 25 °C	CH_3-chelate			C=O	C=C	Al–O(B) Al–N(B)
			25 °C	–50 °C				
$[(acac)_2Al\cdot2Et_2O][AlCl_4]$	**(I)**	5.77	2.09	2.10	3.8	1570	1531	360
$[(acac)_2Al\cdot2Py][AlCl_4]$	**(II)**	5.60	1.95	2.03, 1.93, 1.83	5.7	1573	1532	382
$Cl_2Alacac\cdot2Py$	**(III)**					1578	1530	358
$[(acac)_2Al\cdot DMP][AlCl_4]$	**(IV)**	5.79	2.14	2.11	37.1	1589	1533	405
$[(acac)_2Al\cdot2THF][AlCl_4]$	**(V)**	5.71	2.06	2.07, 2.03, 1.91	4.1	1571	1531	375
$[(acac)_2Al\cdot DME][AlCl_4]$	**(VI)**	5.74	2.03	2.15, 2.04	4.5	1570	1532	395, 380
$[(acac)_2Al\cdot2DMF][AlCl_4]$	**(VII)**	5.60	1.94	2.03, 1.92	5.6	1587	1530	400

^{a}CH_2Cl_2 as an internal standard δ(H) = 5.33. ^{b}$[Al(H_2O)_6]^{3+}$ as an external standard.

to –60 °C causes a clear resolution of the CH_2 proton signals in the free and complexed Et_2O. The CH_3 protons triplet of Et_2O and single signals of acetylacetonate protons do not change their character within the temperature range studied. The presence of only single signals of the CH-ring and CH_3-chelate protons points to a *trans* structure of the $[(acac)_2Al\cdot2Et_2O]^+$ cation, in which both acetylacetonate groups lie in one plane. The changes observed in spectra after the introduction of free Et_2O to the solution of complex **I** indicate a fast exchange of Et_2O molecules at room temperature.

A single signal of CH_3-chelate protons appears in the spectrum of complex **II** recorded at room temperature. It undergoes splitting at –40 °C to three signals. Two other signals of equal relative intensity appear besides the dominating signal in the lower and higher fields. The CH-ring protons signal remains a singlet. These results indicate that the $[(acac)_2Al\cdot2Py]^+$ cation occurs in the form of *cis* and *trans* isomers in the CH_2Cl_2 solution. The most intense signal of the CH_3-chelate protons corresponds to the *trans* structure, and the two other signals correspond to the non-equivalent protons of the *cis* structure. The ratio of the *trans*/*cis* isomers (calculated from the integration of signals) is equal to 5:2 (*ca.* 70% of the *trans* form).

No changes are observed in the spectrum of complex **IV** within the temperature range from room temperature to –60 °C, and only single signals are present corresponding to the CH-ring and CH_3-chelate protons. This may be caused by the magnetic equivalency of particular acetylacetonate protons or that the five-coordinative cation complex $[(acac)_2Al\cdot DMP]^+$ is non-rigid under these conditions.

IR Measurements

IR spectra of complexes **I**–**VII** were recorded within the 1800–350 cm^{-1} range. The most characteristic bands for these complexes are given in Table I.

The band of the free carbonyl group was not observed in the spectra of the complexes studied. Only two very intense bands occur, characteristic for the C=O and C=C stretching vibrations of the chelate system [9] at 1580 and 1530 cm^{-1}, respectively. A very intense band at 495 cm^{-1} is present in the case of all the complexes (except for **III**) in the low frequency. This band has been assigned, according to the literature [10], to the $[AlCl_4]^-$ anion.

An intense band at 488 cm^{-1} appears in the spectrum of complex **III**, which probably corresponds to the asymmetric Al–Cl vibrations [11].

The presence of an intense band within 405–350 cm^{-1} is also a characteristic feature of the complexes studied. This band has been attributed to the stretching vibrations of the donor–acceptor Al–O(B) or Al–N(B) bond. Oxygen or nitrogen are derived from the complexed Lewis base (B). The lack of bands in this region of the $(acac)_3Al$ spectrum [12] points to such an assignment of vibrations. A correlation is also observed between the shift of bands towards higher frequencies with increase in strength of the coordinated base (Table I). This direction is in agreement with the previously described order (9) determined on the basis of the exchange of bases in complexes. Only DMP deviates from this correlation.

Discussion

From the present and previous studies carried out by us [1, 2] it appears that dichloroaluminium acetylacetonate gives ionic complexes of the general formula $[(acac)_2Al\cdot2B]^+[AlCl_4]^-$ with weak bases (B = Et_2O, THF), irrespective of the reactant mole ratio. A bidentate base (DME) gives an ionic complex $[(acac)_2Al\cdot B]^+[AlCl_4]^-$, in which the cation occurs also in an octahedral surrounding [2].

Dichloroaluminium acetylacetonate forms ionic complexes with strong bases like Py and DMF [2] only at equimolar ratios of reactans. An excess of

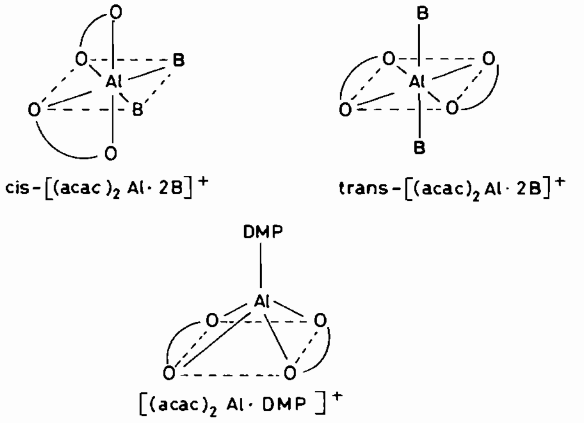

Fig. 1. Structures of octahedral aluminium diacetylacetonate cations and the proposed structure of $[(acac)_2Al{\cdot}DMP]^+$.

a strong base causes the formation of a complex of the $Cl_2Alacac(B)$ mole ratio equal to 1:2. In the case of pyridine the $Cl_2Alacac{\cdot}2Py$ complex precipitates from the reaction medium, which shifts the equilibrium of reaction (3) to the right. It seems that the formation of a complex in which the aluminium atom is bonded with two chlorine atoms, acetylacetonate group and two pyridine molecules is only possible due to the great strength of pyridine as a Lewis base. $AlCl_3$ and Py also form, depending on the reactant mole ratio, an ionic complex, $[Cl_2Al{\cdot}4Py]^+[AlCl_4]^-$ (1:2 mole ratio) and a neutral complex, $AlCl_3{\cdot}3Py$ (1:3 mole ratio) [13]. Complexes of $AlCl_3$ and 2,2-bipyridine with an octahedral cation $[AlCl_2{\cdot}bpy_2]^+$ are also known, in which aluminium coordinates two bpy molecules, besides two chlorine atoms [14].

Dichloroaluminium acetylacetonate reacts with DMP forming a 2/1 (by mole) complex (reaction (5)). Another mole ratio for DMP in comparison with the other complexes results from the steric hindrance of two methyl groups at position 2,6. Aluminium is five-coordinative in the $[(acac)_2Al{\cdot}DMP]^+$ cation and cannot reach the six-coordination state due to steric hindrances. This causes a slow disproportionation of the complex (reaction (6)).

Reactions (6) proceeds much faster in the presence of free DMP, since $AlCl_3$, after formation, is complexed by the base and this hinders the reverse reaction.

There are so far insufficient data to determine the features influencing the structure of octahedral cations. The cations may occur in a *cis* or *trans* configuration (Fig. 1). The cation of the ether complex **I** in a CH_2Cl_2 solution has a *trans* structure (the *cis* signal does not appear in the ^1H NMR spectrum); the cation of the pyridine complex **II**, however, occurs in both forms. It is possible that for the ether complex NMR variable-temperature techniques do not permit a differentiation of the isomers. Serpone and Hersh [15] described a similar case for $(CH_3)_2Sn(acac)_2$. A tetragonal pyramid is the most probable structure of the five-coordinated $[(acac)_2Al{\cdot}DMP]^+$ cation. Both acetylacetonate groups are deflected from the plane due to the repulsion of the DMP methyl groups.

The course of exchange of the coordinated and free base, as well as that of a weaker base by a stronger one, indicate the lability of the base B in the $[(acac)_2Al{\cdot}nB]^+$ cation. Not only is the Lewis base unstably bonded with the aluminium atom, but the acetylacetonate group and chlorine are as well. This indicates the course of reactions (4), (10) and (11), (12). An easy exchange of the coordinated bases B, as well as of the acetylacetonate anions $acac^-$ and chlorine anions Cl^- in the complexes studied should be assumed in order to explain the course of these reactions. Each synthesis or exchange proceeds until a stable octahedral diacetylacetonate cation and stable $[AlCl_4]^-$ anion are formed, or in the case of a strong base also of a neutral octahedral complex. In conclusion it can be stated that the stability of the diacetylacetonate cation, strength of the base and reactant mole ratios play an essential role in the reactions.

From our studies on the structure on dichloroaluminium acetylacetonate it appears that in a diluted CH_2Cl_2 solution the compound occurs as a monomer [16]. Thus, it can be assumed that the formation of an unstable $Cl_2Alacac{\cdot}B$ complex is the first step of the reaction of dichloroaluminium acetylacetonate with a Lewis base

$$Cl_2Alacac + B \longrightarrow \{Cl_2Alacac{\cdot}B\} \qquad (13)$$

This complex decomposes further to ions

$$\{Cl_2Alacac{\cdot}B\} \longrightarrow Cl_2\overset{+}{A}l{\cdot}B + acac^- + Cl\overset{+}{A}lacac{\cdot}B + Cl^- \qquad (14)$$

Six-and four-coordinated aluminium compounds can result from the recombination of ions, which stabilize yielding an ionic $[(acac)_2Al{\cdot}2B]^+[AlCl_4]^-$ complex.

For a strong base the neutral complex **III** may result from consecutive attacks of pyridine on the aluminium atom in $Cl_2Alacac$ (reaction (15)).

$$Cl_2Alacac \xrightarrow{Py} \{Cl_2Alacac{\cdot}Py\} \xrightarrow{Py} \mathbf{III} \qquad (15)$$

or pyridine may attack the previously formed complex **II** (reaction (4)) with the formation and recombination of ions.

Dialkylaluminium acetylacetonate yields disproportionation products under the influence of Lewis bases (reaction (16)) [17].

$$3R_2Alacac + 2B \longrightarrow (acac)_3Al + 2R_3Al{\cdot}B \qquad (16)$$

Dichloroaluminium acetylacetonate reacts differently. These differences can be explained by the relative unstableness of the $[AlR_4]^-$ anion and stability of the $[AlCl_4]^-$ anion and $[(acac)_2Al\cdot 2B]^+$ cation, which form an ionic complex.

The use of a sterically hindered Lewis base in the reaction with dichloroaluminium acetylacetonate, *i.e.* the introduction of a compound destabilizing the diacetylacetonate cation, leads to the formation of products analogous to those resulting from the reactions of dialkylaluminium acetylacetonate (reaction (17)).

$$3Cl_2Alacac + DMP \xrightarrow{DMP} (acac)_3Al + 2Cl_3Al\cdot DMP \tag{17}$$

Acknowledgements

The authors wish to thank the Polish Academy of Sciences for financial support of this work (within the Research Project CPBP 01.12.9.14.5.), the Inorganic Group of Universiteit van Amsterdam, especially to Dr D. J. Stufkens and Mr. J. M. Ernsting; and the Max-Planck-Institut f. Kohlenforschung, Mülheim, especially to Dr. A. Rufińska.

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