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REACTIONS OF DIALKYLALUMINIUM ACETYLACETONATES WITH LEWIS BASES

S. PASYNKIEWICZ* and J. LEWIŃSKI

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

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Summary

The reactions of dialkylaluminium acetylacetonates, $R_2Al(acac)$, (where R = CH_3, C_2H_5 and i-C_4H_9; I–III) with Lewis bases Et_2O, THF, Py, 2,6-dimethylpyridine (DMP), DSMO and HMPT, have been studied. The reaction was found to proceed according to the equation:

$$3R_2Al(acac) + 2B \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 2R_3Al \cdot B + Al(acac)_3$$

With strong bases (B) the reaction is shifted completely to the right, with bases of moderate strength an equilibrium is established and with weak bases the reaction is shifted completely to the left. The reaction rate constant k_1 depends on R and increases in the order i-C_4H_9 < C_2H_5 < CH_3. The reaction starts from the formation of the complex $R_2Al(acac) \cdot B$ (consisting of a five-coordinated aluminium atom) and its further dissociation. The reaction mechanism is discussed.

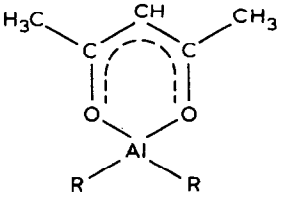
Introduction

During earlier studies [1] it was found that I reacts with pyridine yielding $Al(acac)_3$ and $(CH_3)_3Al \cdot Py$ according to eq. 1

$$3(CH_3)_2Al(acac) + 2Py \rightarrow 2(CH_3)_2Al \cdot Py + Al(acac)_3 \quad (1)$$

In this work the reactions of dialkylaluminium acetonates (I–III) with Lewis bases, (B = Et_2O, THF, Py, 2,6-dimethylpyridine (DMP), DMSO and HMPT) have been studied.

Dialkylaluminium acetylacetonates occur as monomeric, symmetric chelates, in which aluminium is four-coordinated [2].



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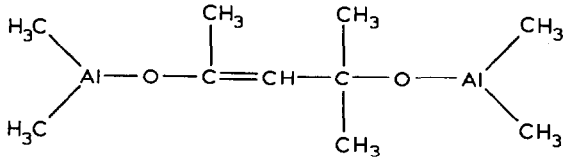
According to Krall [3] the low degree of Lewis acidity of dialkylaluminium acetylacetonates was indicated by their inability to form stable complexes with Lewis bases such as ether, tetrahydrofuran, phosphines or tertiary amines.

We have found that compound I stored at room temperature, slowly decomposes and $Al(acac)_3$ and compound IV were isolated from the reaction products.



(IV)

IV was obtained from the reaction of $(CH_3)_2Al(acac)$ with $(CH_3)_3Al$ [2]. Its presence in the decomposition products indicates the course of reactions (2) and (3) at room temperature.

$$3(CH_3)_2Al(acac) \rightleftharpoons 2(CH_3)_3Al + Al(acac)_3 \quad (2)$$

$$(CH_3)_2Al(acac) + (CH_3)_3Al \rightarrow IV \quad (3)$$

The purpose of this work was to investigate the reaction of dialkylaluminium acetylacetonates with Lewis bases.

Results and discussion

15% solutions of compounds I–III in THF were obtained and studied by ^1H NMR spectroscopy.

The solution of I, in THF gives two signals of the CH_3-chelate protons and two signals of the CH-ring protons. The formation in the spectrum of new signals besides those corresponding to compound I was attributed to the formation of complex $(CH_3)_2Al(acac) \cdot THF$ (V) (Fig. 1, Table 1).

$$I + THF \overset{THF}{\rightleftharpoons} V \quad (4)$$

On the basis of signal integration, the degree of complexation α (calculated as a

TABLE 1

^1H NMR DATA FOR THE REACTION OF $(CH_3)_2Al(acac)$ WITH LEWIS BASES (B) IN CH_3-chelate AND CH_3-Al REGIONS (15% solution in CH_2Cl_2 as internal standard δ(H) 5.33 ppm at 27°C)

Lewis base	δ(ppm) CH_3-chelate			δ(ppm) CH_3-Al	
	$(CH_3)_2Al(acac)$	$(CH_3)_2Al(acac) \cdot B$	$Al(acac)_3$	$(CH_3)_2Al(acac)$	$(CH_3)_3Al \cdot B$ [a]
–	2.09	–	1.94	−0.91	–
THF [b]	2.09	1.98	1.87	−0.83	−0.92
Py (excess)	1.98	1.95	1.88	−1.03	−0.87
DMSO	2.02	1.97	1.94	−0.92	−1.08
DSMO (excess)	1.88	1.83	1.78	−1.12	−1.27
HMPT (excess)	1.91	1.88	1.81	−1.08	−1.25

[a] The CH_3-Al protons in the $(CH_3)_2Al(acac) \cdot B$ complex have almost identical chemical shifts. [b] THF as the solvent, internal standard THF δ(H) 1.79 ppm.

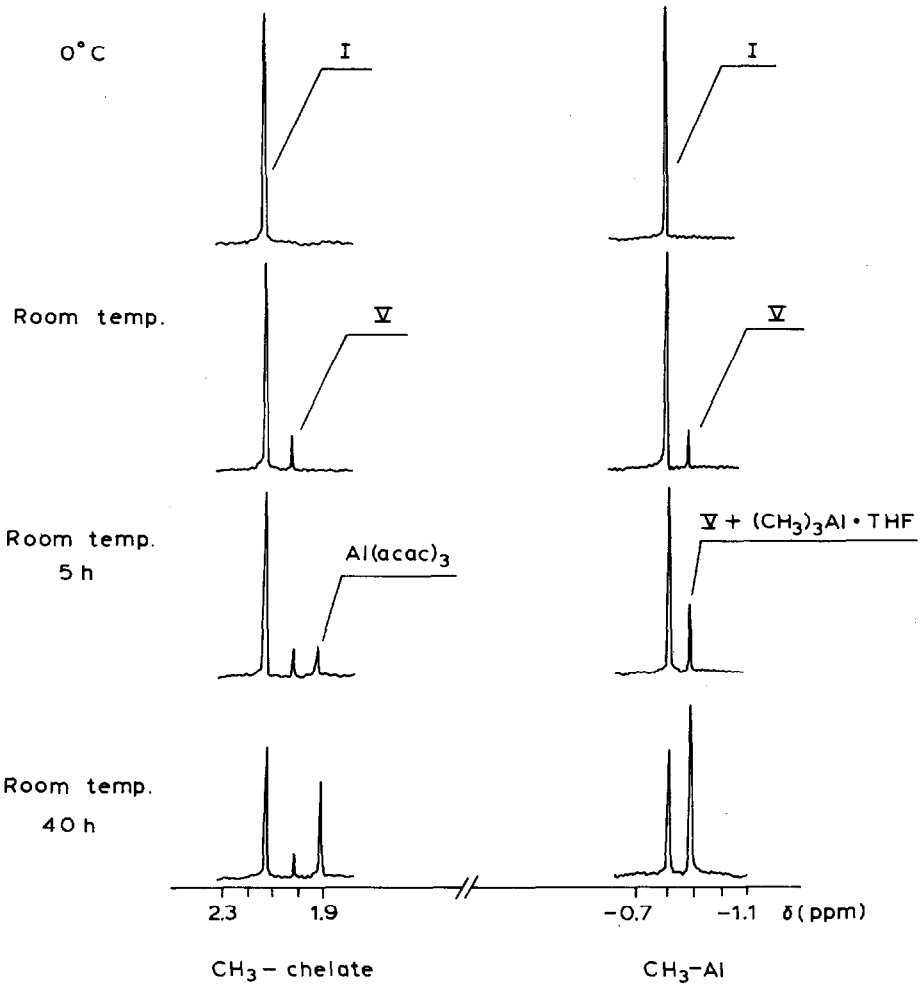


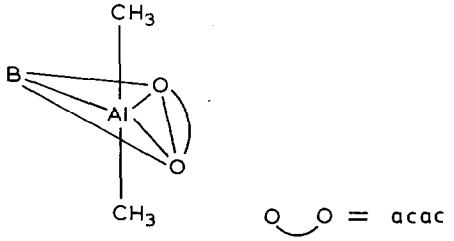
Fig. 1. ^{1}H NMR spectra of the $(CH_3)_2Al(acac)$ solution in THF for the CH_3-chelate and CH_3-Al proton regions.

ratio of the intensity of proton signals in the CH_3-chelate moiety of the complex to the total intensity of those signals in the complex and free $(CH_3)_2Al(acac)$) for reaction 4 was calculated. For a 15% concentration at room temperature $\alpha = 0.15$. Complex V is unstable and decomposes during distillation yielding I and THF. In benzene solution (concentration ca. 15% for I/THF = 1) the equilibrium is shifted towards the left and in the ^{1}H NMR spectrum the complex is not observed. In the ^{1}H NMR spectrum formation of this complex below 0°C is not observed when I was dissolved in THF at −70°C.

II in a THF solution also forms a complex, $(C_2H_5)_2Al(acac) \cdot THF$ (VI). This is confirmed by a shift of the CH_3-chelate and CH-ring proton signals (Table 2). The intensity of the signals corresponding to complex VI is low, which indicates a lower concentration of complex VI compared to complex V.

III in a THF solution does not form a complex with THF of a concentration observable in ^{1}H NMR.

From the above results it can be concluded that steric hindrance is increasing in the order I < II < III and that complex formation with THF is difficult or even impossible. Dialkylaluminium acetylacetonates form unstable complexes, in which aluminium is probably pentacoordinated, while stable compounds of pentacoordina-



tive aluminium surrounded by three oxygen atoms are known [4,5].

The complexes are unstable and decompose slowly yielding $R_3Al \cdot THF$ and $Al(acac)_3$ (eq. 5).

$$3R_2Al(acac) \cdot THF \rightleftharpoons 2R_3Al \cdot THF + Al(acac)_3 + THF \quad (5)$$

^1H NMR signals corresponding to $Al(acac)_3$ and $(CH_3)_3Al \cdot THF$ appear a few hours after mixing the reactants (Fig. 1). This indicates a greater rate of complex formation (eq. 4) than of disproportionation reaction (eq. 5).

Dimethyl- and diethyl-aluminium acetylacetonates react at room temperature with pyridine giving disproportionation products according to eq. 1. The reaction course is well followed by ^1H NMR. For I, after mixing the substrates at $-70°C$ in CH_2Cl_2 no signals indicating that the reaction is proceeding occur. The reaction starts at ca. 5°C and then signals corresponding to the complex $(CH_3)_2Al(acac) \cdot Py$ (VII) appear in the spectrum. With increase of the temperature to room temperature the intensity of the signals corresponding to complex VII increases rapidly. Simultaneously signals of $Al(acac)_3$ and $(CH_3)_3Al \cdot Py$ appear, the intensity of which slowly increases. The degree of complexation (α) and the reaction rate depend on the amount of pyridine added. If the I/Py molar ratio at room temperature equals 1 $\alpha = 0.23$ and reaction 1 is completed in about 40 h. For the reaction of II with pyridine at room temperature the equilibrium 4 is quickly established and the disproportionation of complex $(C_2H_5)_2Al(acac) \cdot Py$ (VIII) formed proceeds much slower. This indicates a greater stability of complex VIII compared to complex V.

TABLE 2

^1H NMR DATA FOR THE REACTION OF $(C_2H_5)_2Al(acac)$ WITH LEWIS BASES (B) IN THE CH_3-CHELATE REGION (15% solution in CH_2Cl_2 as internal standard δ(H) 5.33 ppm at 27°C)

Lewis base B	δ(ppm)		
	$(C_2H_5)_2Al(acac)$	$(C_2H_5)_2Al(acac) \cdot B$	$Al(acac)_3$
–	2.08	–	–
THF [a]	2.10	2.02	1.87
Py	2.09	2.04	1.95
DMSO	2.08	2.03	1.94

[a] Solvent THF, internal standard THF δ(H) 1.79 ppm.

Diisobutylaluminium acetylacetonate also reacts with pyridine giving disproportionation products (eq. 6).

$$3(i\text{-}C_4H_9)_2Al(acac) + 2Py \rightarrow 2(i\text{-}C_4H_9)Al \cdot Py + Al(acac)_3 \quad (6)$$

Reaction 6 which can be observed in ^1H NMR proceeds very slowly in methylene chloride at room temperature. After mixing the reactants the concentration of the III/Py complex (IX) is so low that its signals do not appear in ^1H NMR. In the spectrum of the reaction mixture signals of protons of $Al(acac)_3$ and $(i\text{-}C_4H_9)_3Al \cdot Py$ and those of III appear after 6 days (Table 3). After two and four weeks the intensity of signals of reaction 6 products increases. The signals of III disappear completely after carrying out the reaction with a four-fold excess of pyridine for three months at room temperature. The reaction rate depends on the molar ratio of the reactants and increases with increase of the amount of pyridine introduced. From the above experiments it appears that III reacts with pyridine slowly compared to I and II; this probably results from steric hindrance and difficulties in formation of complex IX.

The reaction of $(CH_3)_2Al(acac)$ with DMP may confirm that the formation of the $R_2Al(acac) \cdot B$ complex is the rate-determining step of the disproportionation of dialkylaluminium acetylacetonate in the presence of Lewis bases. Due to steric hindrance around the basic centre in DMP the formation reaction of the complex is retarded and disproportionation hardly occurs.

Similarly, as with pyridine, I, II, and III react with other strong Lewis bases e.g. HMPT and DMSO. However, then the disproportionation of dialkylaluminium acetylacetonates proceeds much faster, especially with DMSO. For example, in the reaction in an NMR tube at a I/DMSO molar ratio of 1/3 (10% concentration, temperature $-70°C$) and a gradual increase of the temperature, the signals of $(CH_3)_2Al(acac) \cdot DMSO$ (X), $(CH_3)_3Al \cdot DMSO$ and $Al(acac)_3$, which indicate the course of the reaction, appear at 0°C. The reaction of I with DMSO proceeds very fast at room temperature (27°C), which is indicated by the successive changes in the ^1H NMR spectra (Fig. 2). At that temperature the signal intensities of complex X increase rapidly and after a short time (ca. 7 min) an equilibrium between I and X is reached with a degree of complexation of $\alpha = 0.71$. Then the intensity of the signals of $Al(acac)_3$ increases and after about 2 h the signals of I and X disappear completely. This indicates that in this case also complexation proceeds much faster than disproportionation. In the reactions of I with Lewis bases only two signals instead of three from CH_3-Al protons are always observed. This is due to similar chemical shifts of the CH_3-Al protons in $(CH_3)_3Al \cdot B$ and $(CH_3)_2Al(acac) \cdot B$.

In the reaction of II with DMSO, for an identical molar ratio of reactants and comparable conditions as above, a considerable decrease of the complexation degree for $(C_2H_5)_2Al(acac) \cdot DMSO$ XI ($\alpha = 0.25$) is observed. An increase of steric hindrance in comparison to that in complex X is probably the reason for this.

In the presence of pyridine, HMPT or DMSO the disproportionation of dialkylaluminium acetylacetonates is irreversible.

With weak bases such as diethyl ether the disproportionation hardly occurs but the reverse reaction proceeds readily (eq. 7).

$$2R_3Al \cdot Et_2O + Al(acac)_3 \xrightarrow[\text{solvent}]{} 3R_2Al(acac) + 2Et_2O \quad (7)$$

In reaction 7 $R_2Al(acac)$ is obtained with almost a 100% yield. On the basis of ^1H

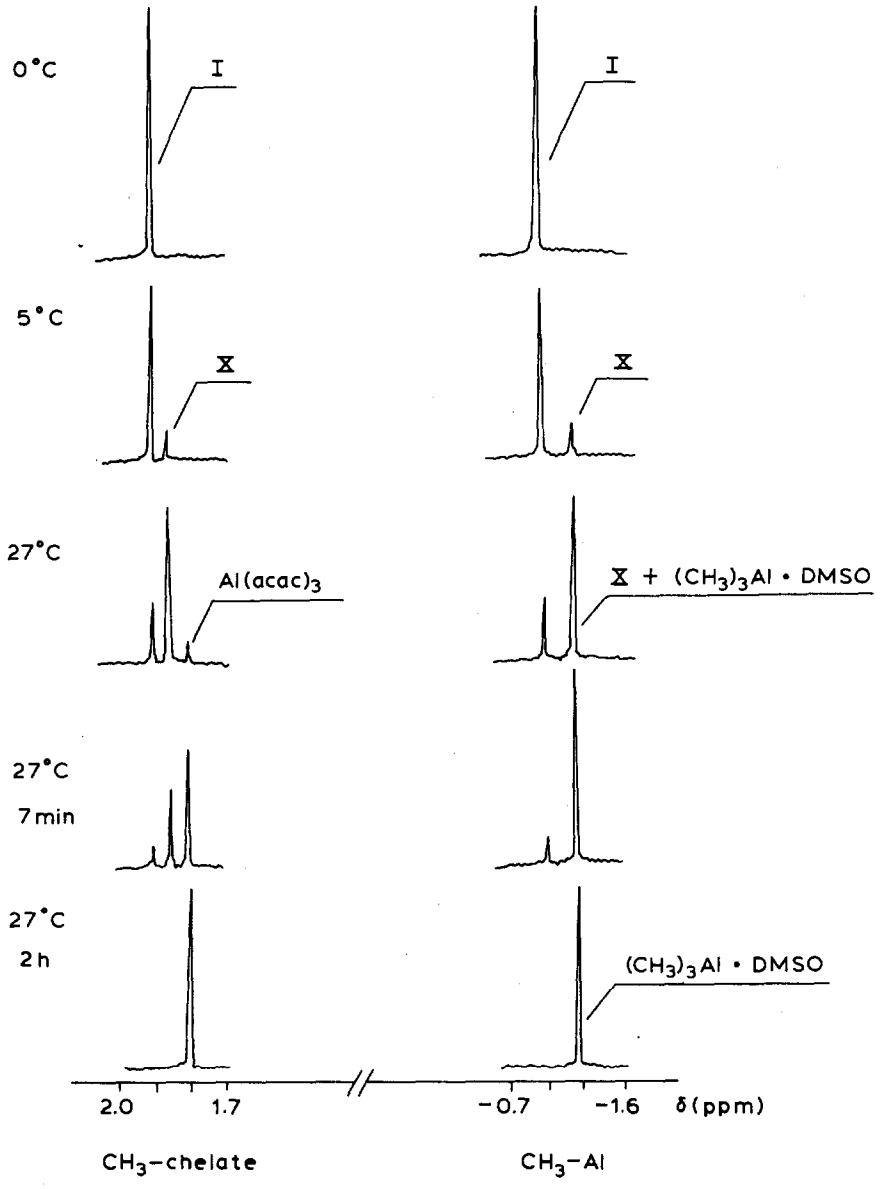


Fig. 2. ^{1}H NMR spectra for the reaction of $(CH_3)_2Al(acac)$ with DMSO in CH_2Cl_2 for the CH_3-chelate and CH_3-Al proton regions.

NMR spectroscopy it was found that $(CH_3)_3Al \cdot Et_2O$ reacts fully after ca. 20 h. When THF is used as the Lewis base, an equilibrium is established after ca. two days and the degree of conversion of $(CH_3)_3Al \cdot THF$ to $(CH_3)_2Al(acac)$ is 0.55.

The reactions described above are of a general character and can be expressed by eq. 8.

$$3R_2Al(acac) + 2B \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 2R_3Al \cdot B + Al(acac)_3 \qquad (8)$$

If B is a strong base reaction 8 is completely shifted to the right, if B is of moderate

strength an equilibrium is established, and with weak bases the reaction is shifted to the left.

For the mechanism of reaction 8 k_1 can be presented as follows. The first step consists of the formation of a complex (eq. 9). This complex dissociates to a

$$R_2Al(acac) + B \rightleftharpoons R_2Al(acac) \cdot B \tag{9}$$

dialkylaluminium cation stabilized by a base and the acetylacetonate anion. The cation is able to react with the complex or free dialkylaluminium acetylacetonate giving a complex of trialkylaluminium and alkylaluminium diacetylacetonate (eq. 10).

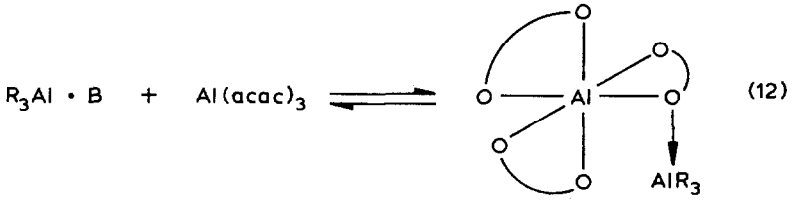
$$R_2Al(acac) \cdot B \rightleftharpoons R_2\overset{+}{A}l \cdot B + (acac)^- \xrightarrow{R_2Al(acac)} R_3Al \cdot B + RAl(acac)_2 \tag{10}$$

Kroll [2] found that this compound is unstable and by an exchange of substituents with $R_2Al(acac) \cdot B$, trialkylaluminium complex and aluminium triacetylacetonate are formed (eq. 11).

$$RAl(acac)_2 + R_2Al(acac) \cdot B \rightarrow R_3Al \cdot B + Al(acac)_3 \tag{11}$$

The strength of the base plays a decissive role in the above mechanism of reaction 8. With an increase in base strength the formation of complex $R_2Al(acac) \cdot B$ is facilitated, the acetylacetonate anion is abstracted and the $R_2Al \cdot B$ cation stabilized.

The strength of the base is also decisive on k_2 in the course of eq. 8. This reaction probably starts from exchange of B in the complex with oxygen of the acetylacetonate group.



(12)

With strong bases reaction 12 is completely hindered or proceeds with a very low yield, which precludes a further exchange of ligands bonded to aluminium.

TABLE 3

^{1}H NMR DATA FOR THE REACTION OF $(i\text{-}C_4H_9)_2Al(acac)$ WITH PYRIDINE IN THE CH_3-chelate, $-CH_2-$ AND $-CH_3$ REGIONS. (15% solution in CH_2Cl_2 as internal standard δ(H) 5.33 ppm at 27°C)

Compound	δ(ppm)		
	CH_3-chelate	$(CH_3)_2CHCH_2$-Al	$(CH_3)_2CHCH_2$-Al
$(i\text{-}C_4H_9)_2Al(acac)$	2.10	0.85	−0.14
$(i\text{-}C_4H_9)_3Al \cdot Py$	–	1.00	0.10
$Al(acac)_3$	1.94	–	–

Experimental

Commercial trialkylaluminiums, aluminium triacetylacetonate, acetylacetone, diethyl ether, THF, pyridine, DMSO and HMPT were used. Dialkylaluminium acetylacetonates were obtained from R_3Al and $Al(acac)_3$ or from R_3Al and acetylacetonate by methods described in the literature [2]. All the reactions were carried out under dry, deoxidized nitrogen. The alkylaluminium compounds were distilled immediately before use; the remaining reactants were dried, deoxidized and distilled under nitrogen.

Reactions of $R_2Al(acac)$ with Et_2O and THF. The dialkylaluminium acetylacetonates I, II and III were directly added to a Lewis base in an NMR tube at room temperature. Concentrations of ca. 15% were used and changes in the ^1H NMR spectrum were then observed. In the reaction with Et_2O no new signals were observed immediately after preparing the solution, nor after one day, in the NMR spectrum besides those of $R_2Al(acac)$. In the reaction with THF the ^1H NMR spectrum recorded after 0.5 h showed the presence of signals corresponding to $(CH_3)_2Al(acac)\cdot THF$ and $(C_2H_5)_2Al(acac)\cdot THF$ complexes, and their intensity compared to that of the signals of the uncomplexed compounds did not change with time. No complex formation between THF and $(i\text{-}C_4H_9)_2Al(acac)$ was observed. For I new signals of the disproportionation products $Al(acac)_3$ and $(CH_3)_3Al\cdot THF$ appear in the spectrum after a few hours and their intensity gradually increases. An equilibrium was established after about 40 h. After that time the mutual ratio of the intensity of signals did not change.

Reactions of $R_2Al(acac)$ with Py, DMSO and HMPT. The reactions were carried out either in an NMR tube, directly recording the spectrum, or in a Schlenk vessel taking samples at required time intervals for NMR recordings. To the solution of $R_2Al(acac)$ in CH_2Cl_2 (10–15% concentration) the Lewis base was added dropwise at room temperature and changes in the ^1H NMR spectrum were observed. When preparing the solutions at low temperature, Py and DMSO precipitated on the walls of the NMR tube which was refrigerated by a cool mixture of acetone and dry ice, and then the mixture of $R_2Al(acac)_3Py$ and DMSO easily redissolved.

Reaction of $(CH_3)_2Al(acac)$ with DMP. To an NMR tube a 15% solution of $(CH_3)_2Al(acac)$ in CH_2Cl_2 was introduced and DMP added at room temperature at a molar ratio of $(CH_3)_2Al(acac)$/DMP 1/3. In the ^1H NMR no signals indicating the formation of the $(CH_3)_2Al(acac)\cdot DMP$ complex and of its decomposition products (i.e. $(CH_3)_2Al\cdot DMP$ and $Al(acac)_3$) were observed even after three weeks.

Reaction of $(CH_3)_3Al\cdot Et_2O$ with $Al(acac)_3$. To 2.36 g (16.2 mmol) of $(CH_3)_3Al\cdot Et_2O$ in 10 cm^3 of Et_2O, $Al(acac)_3$ (2.62 g, 8.1 mmol) was added at room temperature under nitrogen in a Schlenk vessel. The suspension of $Al(acac)_3$ in the solution disappears 1.5 h after mixing the reactants. On the basis of ^1H NMR studies it was found that the reaction proceeds completely after about 20 h. After that time only $(CH_3)_2Al(acac)$ signals were observed in the spectrum. After 20 h 3.74 g (24 mmol) of $(CH_3)_2Al(acac)$ (b.p. 45°C, 3 Torr, yield 99%) was distilled off from the reaction mixture.

Reaction of $(CH_3)_3Al\cdot THF$ with $Al(acac)_3$. To 1.43 g (9.8 mmol) of $(CH_3)_3Al\cdot THF$ in 10 cm^3 of THF, Al(acac) (1.59 g, 4.9 mmol) was added at room temperature under nitrogen in a Schlenk vessel. When taking several samples at hourly intervals and recording their ^1H NMR spectra it was observed that the equilibrium, identical

to that in the reaction of $(CH_3)_2Al(acac)$ with THF, is reached also after 40 h. No reaction was observed when $(CH_3)_3Al \cdot Py$ or $(CH_3)_3Al \cdot DMSO$ were mixed with $Al(acac)_3$ in a CH_2Cl_2 solution at room temperature. The ^1H NMR spectrum of these mixtures recorded after a few days contained only the signals of the initial reactants.

Measurements. ^1H NMR spectra were recorded at 100 MHz using a JEOL-JNM-100 MHz spectrometer. The spectrometer was equipped with variable temperature probes.

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