Reactivity of 1-Aza-4-oxa-1,3-butadienes (α-Imino Ketones) toward Triorganoaluminum Reagents. 2. Syntheses of Triorganoaluminum α-Imino Ketone Coordination Complexes, Diorganoaluminum (α-Imino)alkoxides, and Diorganoaluminum (α-Imino)enolates and Study of Their Dynamic Behavior in Solution (^{1}H and ^{13}C NMR)

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The reactions of triorganoaluminum reagents with α-imino ketones [$R^1N{=}C(R^2)C(R^3){=}O$] and 2-oxopyridyl derivatives [NC_5H_4-2-$C(R^3){=}O$] follow a distinct course in which product formation is almost quantitative. The first stage of these reactions involves formation of 1:1 and 2:1 coordination products of type 1, [$(AlR_3)\{\sigma$-N- or σ-O-($R^1N{=}C(R^2)C(R^3){=}O$)}] and [$(AlR_3)_2\{\sigma,\sigma$-N,O-($R^1N{=}C(R^2)C(R^3){=}O$)}], respectively. Intermolecular exchange processes between the compounds 1 and either free ligand or free $(AlR_3)_2$ occur and have been studied by NMR spectrometry. Addition products [$Me_2Al(R^1)N{=}C(R^2)$-$C(R^3,R^4)OAlMe_3$] (2) with an oxygen-coordinated trimethylaluminum unit were formed from the 2:1 coordination complexes. At higher temperatures the methyl groups of the Me_2Al and the Me_3Al units undergo exchange involving dissociation of the dimethylaluminum–nitrogen bond followed by methyl exchange as in $(AlMe_3)_2$. The 1:1 AlR_3:α-imino ketone coordination complexes react further to dimeric addition complexes [$R_2Al(R^1)N{=}C(R^2)C(R^3,R^4)O]_2$ (3). If $R^3 \neq R^4$, two diastereoisomers are formed. In one case optically pure (*R*)-1-(2-pyridyl)ethanol was used to synthesize the dimeric aluminum complex **3d** in order to identify (assign) the enantiomeric pairs of these diastereoisomers. For one isomer, the *RR*/*SS* one, equilibria between a five- and a four-coordinate species could be established involving an Al–N bond dissociation–association process with retention of the dinuclear structure via the Al_2O_2 bridge. Finally, oxygen-coordinated diorganoaluminum (α-imino)enolates, [$R_2Al(R^1)N{=}C(R^2)C(=CH_2)O]_n$ (4), have been synthesized, isolated, and characterized. An equilibrium between mononuclear and higher nuclearity species was established.

Introduction

There has been considerable interest in the coordination properties of 1,4-dihetero-1,3-butadienes toward metal centers.[1] From these studies information has emerged concerning the extent of activation for further reaction of the various heteroolefinic groups in the heterobutadiene molecule as a result of their interplay with metal center(s). Application of this knowledge has recently led to the development of novel routes for the chemo- and regioselective conversion of heterobutadienes; i.e. 1,4-diaza- and 1-aza-4-oxa-1,3-butadienes, by organozinc and -aluminum reagents.[2]

In general organoaluminum compounds are important reagents for the conversion of organic substrates containing C=N or C=O functional groups.[3] Although already much is known about the overall course of these reactions,[4] only a restricted amount of information is available concerning the organoaluminum compounds formed as intermediates or as transient species. In order to obtain more insight into the factors that are responsible for the observed high chemo- and regioselectivity in the reactions with heterobutadienes, we have studied the reactions of organoaluminum compounds with 1-aza-4-oxa-1,3-butadienes in greater detail.

In principle the formation of two types of organoaluminum intermediates in these reactions can be anticipated: (i) coordination complexes in which both substrate and triorganoaluminum monomer are unchanged (i.e. the substrate is coordinated to the aluminum center via either one (N or O) or both donor atoms) and (ii) complexes in which the substrate skeleton is reduced by transfer of one of the organo groups from the aluminum reagent to the substrate. In particular the coordination complexes are of interest because these represent the first stages of the reaction and may explain the observed regioselectivity because of preferential coordination with either the N or the O donor atoms. However, the study of the formation as well as the isolation of these complexes is often made difficult by the occurrence of fast, subsequent reactions leading to the second type of complex.

Recently, we found that for a distinct substitution pattern of the 1-aza-4-oxa-1,3-butadiene skeleton the stability of the coordination complexes could be increased to such an extent that both their isolation and characterization by an X-ray structure determination became possible. In the preceding paper we reported the structure

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Table I. The ^1H and ^{13}C NMR Data[a] for $[(AlMe_3)_m(R^1N{=}C(Ph)C(Ph){=}O)_n]$ (1a-c)

^1H NMR

compd	m:n	T, °C	$AlMe_3$	R^1		Ph
ligand	0	25		R^1 = Me	3.23 s	6.93–7.93 m
ligand	0	25		R^1 = *i*-Pr	1.39 d, 3.75 sept	7.15–8.20 m
1a	1:1	25	−0.40 s	R^1 = Me	3.30 s	7.04–8.05 m
"1a"[b]	1:4	−90	−0.01 s	R^1 = Me	3.10, 3.41 s	6.7–9.0 m
		−70	−0.06s		3.34 br	7.04–8.25 m
		−50	−0.10 s		3.34 s	7.1–8.1 m
		25	−0.32 s		3.40 s	7.15–7.28 m, 7.93–8.03 m
"1b"[c]	2:1	−90	−1.14 s, −1.28 s	R^1 = Me	3.23 br	7–8 m
		−72	−1.02 br		3.37 br	7–8 m
		−60	−1.10 s		3.45 s	7–8 m
	2:1	−80	0.08 s	R^1 = Me	2.95 s	6.70–7.79 m
1b		25	−0.24 s		3.27 s	7.10–7.98 m
		50[d]	−0.28 s		3.31 s	7.04–8.00 m
		90[d]	−0.34 s		3.36 s	7.02–8.01 m
"1b"[e]	4:1	−100	−0.57 s, −0.54 s, −0.50 s, 0.18 s	R^1 = Me	3.0 br	6.5–7.3 m
		−40	−0.50 s, −0.40 br		3.20 s	7.1–8.0 m
		25	−0.25 s		3.30 s	7.15–8.05 m
1c	2:1	25	−0.14 s	R^1 = *i*-Pr	1.40 d, 3.72 sept	7–8 m

^{13}C NMR

compd	m:n	T, °C	$AlMe_3$	R^1		N=C	C=O	Ph
ligand[f]	0	RT[h]		R^1 = Me	40.7	168.0	198.8	126.8, 128.3, 128.8, 128.8, 130.5, 134.3, 134.9
ligand[f]	0	RT		R^1 = *i*-Pr	23.5, 53.7	163.7	198.6	127.1, 128.4, 128.9, 130.4, 134.3, 134.8, 135.3, 136.0
1a[g]	1:1	RT	−4.4	R^1 = Me	41.7	179.8	194.8	126–135 m
1b[g]	2:1	RT	−4.9	R^1 = Me	42.9	176.4	199.4	126–135 m

[a] In toluene-d_8; all values are in ppm relative to external Me_4Si: s = singlet, d = doublet, sept = septet, m = multiplet, br = broad. Assignments are based on the multiplicity (for ^{13}C NMR) of the resonances in the off-resonance spectra. [b] Ligand (R^1 = Me) in excess [c] In CD_2Cl_2. [d] At these temperatures conversion to compound **2c** already occurs. [e] In a 1:1 C_7D_8:methylcyclopropane mixture; excess of Al_2Me_6. [f] In $CDCl_3$. [g] In C_6D_6. [h] RT = room temperature.

in the solid state of the first example of such a coordination complex, i.e. $[(AlMe_3)_2\{\sigma,\sigma\text{-N,O-}(MeN{=}C(Ph)C(Ph){=}O)\}]$ (see Figure 1A), as well as the structure in the solid state of a rearranged coordination product, i.e. $[Me_2Al(t\text{-Bu})\text{-}N{=}CHC(Me)_2OAlMe_3]$ (see Figure 1B), in which one methyl group has been transferred from Al to the substrate.[5] In this paper we report the results of a study of the structures and the dynamic behavior of these well-defined complexes in solution. Moreover, the results will be compared with the dynamic behavior in solution of dinuclear diorgano[(2-pyridyl)methoxy]aluminum compounds, e.g., $[i\text{-}Bu_2AlOCH_2\text{-}2\text{-}C_5H_4N]_2$ (see Figure 1C for the structure in the solid), which likewise contain the NCCO skeleton.[6] In the latter case the dynamic process (established by ^1H and ^{13}C NMR experiments at various temperatures)[6b] involved an equilibrium between a five- (at the slow exchange limit) and a four-coordinate species via an Al–N dissociation–association process.

These results are very useful for the interpretation of the formation and structural features of the much less stable organoaluminum intermediates that are formed in the reactions of triorganoaluminum compounds with the substrates containing a highly reactive N=C—C=O skeleton.

Experimental Section

Physical Measurements. The ^1H NMR spectra were recorded on a Bruker WM 250, Varian T60, Varian A60, or Varian XL100 NMR spectrometer, ^{13}C NMR spectra on Bruker WM 250, Bruker WP80, and Varian CFT20 NMR spectrometers (off-resonance ^{13}C spectra were recorded for all compounds to aid assignment), and ^{27}Al NMR spectra on a Bruker WM 250 spectrometer. The ^1H and ^{13}C NMR spectroscopic data are summarized in Tables I–IV. Cryoscopic molecular weight determinations of various organoaluminum compounds were carried out in benzene under dry oxygen-free nitrogen in a homemade apparatus (accuracy for a molecular weight of about 500 is ±5%) (cf. Table VI). Elemental analyses were carried out by the Analytical Section of the Institute for Applied Chemistry TNO, Zeist, The Netherlands. For all isolated compounds correct elemental analytical data were obtained (Table VII).

Syntheses. All reactions were carried out under dry, oxygen-free nitrogen. Solvents were carefully dried and distilled before use. ***Caution***! *Most of the new aluminum compounds decompose with violence when dissolved in halogenated solvents.*

Hexane solutions of the $(AlR_3)_2$ compounds with R as Me, Et, or *i*-Bu are commercially available (Alfa Products); solid $(AlPh_3)_2$ was synthesized and purified according to published methods.[8] The α-imino ketones $[R^1N{=}C(R^2)C(R^3){=}O]$ with R^1 = *t*-Bu, R^2 = H, R^3 = Me as well as with R^1 = Me, *i*-Pr, R^2 = R^3 = Ph were prepared as described in the literature.[9] The new α-imino ketone *t*-BuN=CHC(Ph)=O was synthesized starting from phenylglyoxal monohydrate and *tert*-butylamine, following the described procedure for (*N*-*tert*-butylimino)propanone:[9b] yield 50%; bp 120 °C (0.01 mmHg). IR (Nujol, NaCl, cm^{-1}): 1708 (vs, ν(C=O)), 1658 (m, ν(C=N)). ^1H NMR (in $CDCl_3$, room temperature, Me_4Si internal, δ): 1.26 (s, 9 H, *t*-Bu), 7.60 (m, 5 H, Ph), 7.90 (s, 1 H, N=C*H*). ^{13}C NMR (in $CDCl_3$, room temperature, Me_4Si internal, δ): 28.4 (q) and 58.9 (s) (*t*-Bu); 127.9, 130.2, 133.2, and 134.4 (Ph); 153.5 (d, N=*C*H); 191.4 (s, *C*=O).

The 2-substituted pyridine derivatives (2-aldehyde, 2-acetyl, and 2-benzoyl) are commercially available (Janssen Chimica). The

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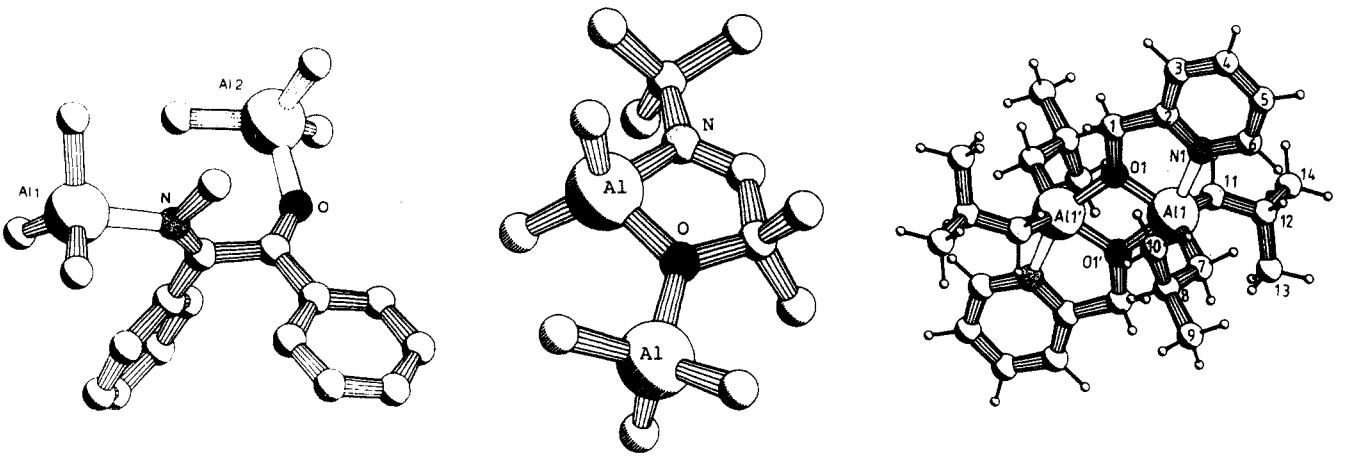

1A 1B 1C

Figure 1. PLUTO drawings of $[(AlMe_3)_2\{\sigma,\sigma\text{-N,O-}(MeN{=}C(Ph)C(Ph){=}O)\}]$ (1A), $[Me_2\overline{Al(t\text{-}Bu)N{=}CHC(Me)_2O}AlMe_3]$ (1B), and $[i\text{-}Bu_2\overline{AlOCH_2\text{-}2\text{-}C_5H_4N}]_2$ (1C). Oxygen atoms are represented with a black sphere and nitrogen atoms with dotted spheres.

Table II. The ^1H and ^{13}C NMR Data[a] for $[Me_2\overline{Al(R^1)N{=}C(R^2)C(R^3,R^4)O}AlMe_3]$ (2a–d) and $[Me_2\overline{AlNC_5H_4\text{-}2\text{-}C(R^3,R^4)O}AlMe_3]$ (2e–g)

^1H NMR

compd	T, °C	$AlMe_3$	$AlMe_2$	R^1		R^2		R^3		R^4	
2a	25	−0.11 s	−0.14 s	R^1 = *t*-Bu	1.06 s	R^2 = H	7.20 s	R^3 = Me	1.50 s	R^4 = Me	1.50 s
	90	−0.20 s	−0.20 s		1.13 s		7.34 s		1.53 s		1.53 s
2b	40	−0.31 s	−0.01s, 0.05 s	R^1 = *t*-Bu	0.99 s	R^2 = H	7.23 s	R^3 = Ph	7–8 m	R^4 = Me	1.95 s
	60	−0.35 s	−0.05 br		1.04 s		7.25 s		7–8 m		1.96 s
	90	−0.40 s	−0.08 s		1.09 s		7.29 s		7–8 m		1.96 s
2c	25	−0.33 s	0.03 s, 0.08 s	R^1 = Me	2.58 s	R^2 = Ph	6.2–7.4 m	R^3 = Ph	6.2–7.4 m	R^4 = Me	1.99 s
2d	25	−0.31 s	0.09 s, 0.21 s	R^1 = *i*-Pr	1.10 d/d 3.40 m	R^2 = Ph	7.2–8.2 m	R^3 = Ph	7.2–8.2 m	R^4 = Me	2.03 s
				NC_5H_4							
2e	25	−0.04 s	−0.12 s, −0.10 s	6.34 d, 6.53m, 6.97 m, 7.43 d				R^3 = H	5.36 q	R^4 = Me	1.53 d
	80	−0.18 s	−0.18 s	6.56 d, 6.64 m, 7.12 m, 7.67 d					5.41 q		1.55 d
2f[b]	25	−0.15 s	0.02 s, 0.14 s	6.8–8.2 m				R^3 = H	6.10 m	R^4 = Et	1.35 t, 2.2–3.2 m
2g	25	−0.18 s	−0.14 s	6.8–8.1 m				R^3 = Me	1.21 s	R^4 = Me	1.21 s

^{13}C NMR

compd	T, °C	$AlMe_3$	$AlMe_2$	R^1		R^2		R^3		R^4		N=*C*	*C*=O
2a[c]	25	−4.3 br	−4.3 br	R^1 = *t*-Bu	29.4, 59.0	R^2 = H		R^3 = Me	25.7	R^4 = Me	25.7	177.2	80.0
2c[c]	25	−6.15	−3.50	R^1 = Me	35.39	R^2 = Ph	127–139 m	R^3 = Ph	127–139 m	R^4 = Me	24.8	188.1	86.5
				NC_5H_4									
2e[c]	25	−7.6	−6.4	121.4, 124.7, 141.9, 143.3, 162.1				R^3 = H		R^4 = Me	25.0		73.2

[a] In toluene-d_8; all values are in ppm relative to external Me_4Si: s = singlet, d = doublet, sept = septet, m = multiplet, br = broad. Assignments are based on the multiplicity (for ^{13}C NMR) of the resonances in the off-resonance spectra. [b] In $CDCl_3$. [c] In C_6D_6.

α-substituted (2-pyridyl)methanol derivatives (i.e. α-methyl-, α-ethyl-, α-isopropyl-, and α-*tert*-butyl(2-pyridyl)methanol) were synthesized via reactions of 2-pyridinecarboxaldehyde with an excess of the corresponding Grignard reagent in diethyl ether.

The products were isolated from the reaction mixtures as follows. The reaction mixtures were acidified with dilute aqueous acetic acid, and the ether was evaporated under reduced pressure. The residual aqueous solutions were made alkaline with 20% aqueous sodium hydroxide and then carefully extracted with diethyl ether. The combined ether extracts were dried on sodium sulfate, and the ether was evaporated under vacuum. The oily residues were distilled under reduced pressure: NC_5H_4-2-C-H(CH_3)OH, bp 75 °C (0.1 mmHg); NC_5H_4-2-CH(C_2H_5)OH, bp 90 °C (0.1 mmHg); NC_5H_4-2-CH(*i*-C_3H_7)OH, bp 98 °C (0.1 mmHg), and NC_5H_4-2-CH(*t*-C_4H_9)OH, bp 120 °C (0.1 mmHg).

Synthesis of Optically Pure (*R*)-1-(2-Pyridyl)ethanol. Solutions of 3.45 g of racemic 1-(2-pyridyl)ethanol (28.1 mmol) and of 10.58 g of dibenzoyl-L-(+)-tartaric acid monohydrate (Merck) in ethanol (150 mL total) were thoroughly mixed and stirred for 2 h at room temperature. Slow crystallization (60 h at −20 °C) afforded light yellow crystals of the corresponding salt (mp 145 °C; yield 5.84 g, 39%). The salt was hydrolyzed in a mixture of 100 mL of a 25% v/v solution of NH_3 in water and 10 g of KOH. The mixture was stirred for 1 h and then extracted with diethyl ether (3 × 50 mL) and subsequently with dichloromethane (3 × 50 mL). The combined organic layers were dried on sodium sulfate and the solvents evaporated in vacuo: yield, after distillation (bp 73 °C, 0.1 mmHg), 0.8 g of (*R*)-1-(2-pyridyl)ethanol; $[\alpha]_D$ −56° (*c* 0.8, EtOH) (lit. $[\alpha]_D$ −56.6°).[10]

Synthesis of 1: The Coordination Complexes with $AlMe_3$. The 1:1 complex $[(Me_3Al)(MeN{=}C(Ph)C(Ph){=}O)]$ (**1a**) was synthesized by slow addition of a hexane solution of $(AlMe_3)_2$ (5

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Table III. The ^1H and ^{13}C NMR Data[a] for $[R_2\overline{Al(t\text{-}Bu)N{=}CHC(R^3,R^4)O}]_2$ (3a–c) and $[R_2\overline{AlNC_5H_4\text{-}2\text{-}C(R^3,R^4)O}]_2$ (3d–p)

^1H NMR

compd	T, °C	isomer (rel intens)	AlR_2		t-Bu	N=CH	R^3		R^4	
3a	25	*RS,SR* (1)	R = Me	−0.20 s, −0.57 s	1.25 s	8.29 s	R^3 = Ph	7.3–8.0 m	R^4 = Me	1.98 s
		RR,SS (5)		−0.37 s	1.53 s	8.25 s		7.3–8.0 m		1.87 s
3b	25	1 isomer	R = *i*-Bu	0.44 d, 1.43 d, 2.30 m	1.33 s	7.48 s	R^3 = Me	1.47 d	R^4 = H	4.80 q
3c	25	1 isomer	R = Ph	6.8–8.0 m	1.47 s	7.95 s	R^3 = Me	1.78 s	R^4 = Ph	6.8–8.0 m
					NC_5H_4					
3d[b]	30	*RR*	R = Me	−0.11 s	6.60–8.50 m		R^3 = Me	1.79 d	R^4 = H	5.50 q
3d	−20	*RR,SR* (1)	R = Me	−0.17 s, 0.11 s	6.48 m, 6.60 m, 6.95 m, 8.40 d/d		R^3 = Me	1.76 d	R^4 = H	5.41 q
		RR,SS (4)		−0.10 s, 0.07 s				1.74 d		5.45 q
	30	*RS,SR* (1)		−0.28 s, 0.00 s	6.64 m, 6.77 m, 7.12 m, 8.52 d/d			1.82 d		5.43 q
		RR,SS (4)		−0.11 br				1.79 d		5.50 q
	45	*RS,SR* (1)		−0.31 s, −0.03 s	6.70 m, 6.75 m, 7.20 m, 8.47 d/d			1.80 d		5.45 q
		RR,SS (4)		−0.15 s				1.77 d		5.49 d
3e	40	*RS,SR* (1)	R = Me	−0.40 s, −0.07 s	6.8–8.2 m		R^3 = Et	1.34 t, 2.1–3.1 m	R^4 = H	5.80 m
		RR,SS (5)		−0.17 br				1.33 t, 2.1–3.1 m		5.80 m
3f	25	*RS,SR* (1)	R = Me	−0.42 s, 0.10 s	7.8 m, 8.80 d		R^3 = *i*-Pr	1.07 d/d, 3.01 m	R^4 = H	5.53 d
		RR,SS (7)		−0.30 s, 0.08 s	6.76 m, 6.83 m, 7.08 m, 8.47 d			1.13 d/d, 3.01 m		5.44 d
	60	*RS,SR* (1)		−0.47 s, 0.03 s	6.8–8.3 m			1.11 d/d, 3.03 m		5.57 d
		RR,SS (7)		−0.20 br				1.13 d/d, 3.03 m		5.46 d
3g	25	*RS,SR* (1)	R = Me	−0.63 s, 0.18 s	6.8–8.2 m		R^3 = *t*-Bu	1.21 s	R^4 = H	5.06 s
		RR,SS (20)		−0.59 s, 0.13 s	6.70 m, 6.91 d, 7.01 m, 8.39 d			1.19 s		5.06 s
	100	*RS,SR* (1)	not observed		not observed			1.22 s		5.08 s
		RR,SS (20)		−0.3 br	6.7–8.4 m			1.18 s		5.08 s
3h	25	1 isomer	R = Me	−0.86 s	7.36 m, 7.40 m, 7.84 m, 8.38 d		R^3 = Me	1.65 s	R^4 = Me	1.65 s
3i	25	*RS,SR* (1)	R = Me	−0.02 s, −0.65 s	6.7–8.2 m		R^3 = Ph	6.7–8.2 m	R^4 = Me	2.38 s
		RR,SS (5)		−0.04 s, −0.75 s						2.38 s
3j	25	*RS,SR* (1)	R = *i*-Bu	0.5 m, 1.3 m, 2.1 m	6.71 m, 6.77 m, 7.13 m, 8.62 m		R^3 = Me	1.87 d	R^4 = H	5.54 q
		RR,SS (3)						1.88 d		5.55 q
3k–p[c]										

^{13}C NMR

compd	T, °C	isomer (rel intens)	AlR_2		t-Bu	N=C	R^3 = Me	C=O
3b	25	1 isomer	R = *i*-Bu	24.8, 27.7, 31.3	29.8, 58.5	173.2	21.4	71.5
3k–p[c]								

[a] In toluene-d_8; all values are in ppm relative to external Me_4Si: s = singlet, d = doublet, m = multiplet, br = broad. Assignments are based on the multiplicity (for ^{13}C NMR) of the resonances in the off-resonance spectra. [b] Starting from enantiomerically pure NC_5H_4-2-C*(H,Me)OH (R configuration). [c] See ref 6.

mmol, 1 M solution) to a stirred solution of MeN=C(Ph)C(Ph)=O (10 mmol) in 100 mL of diethyl ether at room temperature. After 10 min of additional stirring, the clear solution was concentrated to 30 mL. The new complex crystallized as small white crystals at −30 °C; yield 1.77 g, 60%. The 2:1 complexes $[(Me_3Al)_2\{\sigma,\sigma\text{-}N,O\text{-}(R^1N{=}C(Ph)C(Ph){=}O)\}]$ with R^1 = Me (**1b**) and with R^1 = *i*-Pr (**1c**) were synthesized as described previously.[5]

Synthesis of 2: The Addition Products with Trimethylaluminum Coordination. $[Me_2\overline{Al(R^1)N{=}C(R^2)C(R^3,Me)O}\text{-}AlMe_3]$ (R^1 = *t*-Bu, R^2 = H, R^3 = Me (2a); R^1 = *t*-Bu, R^2 = H, R^3 = Ph (2b); R^1 = Me, R^2 = R^3 = Ph (2c); R^1 = *i*-Pr, R^2 = R^3 = Ph (2d)). Compounds **2a** and **2b** were synthesized by adding a hexane solution of $(AlMe_3)_2$ (10 mmol) to a stirred solution of 5 mmol of the corresponding α-imino ketone (*t*-BuN=CHC(Me)=O and *t*-BuN=CHC(Ph)=O, respectively) in 100 mL of pentane at −96 °C. Immediately a white precipitate

Table IV. The ^1H and ^{13}C NMR Data[a] for $[R_2Al(t\text{-}Bu)N{=}CHC(=CH_2)O]_n$ (4a-c) and $[Me_2AlNC_5H_4\text{-}2\text{-}C(=CH_2)O]_n$ (4d)

^1H NMR

compd, solvent	assocn (molar fractn)	R		*t*-Bu	N=CH	CH_2
4a, Tol-d_8	n = 1 (2)	R = Me	−0.13 s	1.50 s	7.72 s	4.46, 5.13, J = 0.3 Hz
	n = 2 (1)		−0.22 s	1.29 s	7.50 s	4.58 d, 5.40 d, J = 0.8 Hz
4b, Tol-d_8	n = 1 (1)	R = Et	0.50 m, 1.37 t, J = 6.9 Hz	1.53 s	7.75 s	4.44, 5.11, J = 0.3 Hz
	n = 2 (2)		0.50 m, 1.50 t, J = 8.1 Hz	1.28 s	7.59 s	4.56 d, 5.34 d, J = 0.8 Hz
CD_2Cl_2	n = 1[b] (...)		0.10 br, 0.90 m	1.50 s	7.96 s	4.38, 4.76, J = 0.3 Hz
CD_2Cl_2	n = 1[c] (1)		−0.03 m, 0.94 m	1.49 s	7.94 s	4.30, 4.78, J = 0.3 Hz
	n = 2[c] (1)			1.45 s	8.07 s	4.66 d, 5.00 d, J = 0.6 Hz
CD_2Cl_2	n = 1[d] (1)		−0.03 m, 0.89 t	1.49 s	7.94 s	4.35, 4.74, J = 0.3 Hz
	n = 2[d] (2)		−0.03 m, 0.97 t	1.45 s	8.04 s	4.64 d, 4.98 d, J = 0.7 Hz
4c, Tol-d_8	n = 1 (...)	R = Ph	7.36 m	1.30 s	7.83 s	4.56, 5.25, J = 0.3 Hz
				NC_5H_4		
4d,[e] CD_2Cl_2	n = 1 (2)	R = Me	−0.84 s	7.4–8.1 m	8.59 d	4.52 d, 4.86 d, J = 1.0 Hz
	n = 2 (1)		−0.95 s	7.4–8.1 m	8.40 d	5.02 d, 5.20 d, J = 2.3 Hz

^{13}C NMR

		R		*t*-Bu		N=CH	CH_2	C=O
4a[f], $CDCl_3$	n = 1	R = Me	−6.6	30.2	57.4	161.3	96.7	153.3
	n = 2		−6.9	30.3	57.5	163.0	100.8	153.4
4b[f], $CDCl_3$	n = 1	R = Et	2.1, 10.5	30.6	58.2	164.6	97.7	157.7
	n = 2			30.9	58.3	165.8	102.2	159.3
4c[f], $CDCl_3$	n = 1	R = Ph	126–137 m	30.2	57.8	163.4	97.3	157.7

[a] Probe temperature, concentration 10^{-2}; all values are ppm relative to external Me_4Si: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad. Assignments are based on the multiplicity (or ^{13}C NMR) of the resonances in the off resonance spectra. [b] Concentration 10^{-3}. [c] Concentration 5×10^{-3}. [d] Concentration 10^{-1}. [e] Concentration 10^{-2}. [f] Concentration 10^{-2}.

Table V. ^{27}Al NMR Data[a] of $[Me_2Al(t\text{-}Bu)N{=}CHC(Me)_2OAlMe_3]$ (2a), $[Me_2AlOCH(Me)\text{-}2\text{-}C_5H_4N]_2$ (3d), and $[i\text{-}Bu_2AlOCH_2\text{-}2\text{-}C_5H_4N]_2$

compd	*T*, K	$\delta(^{27}Al)$	$\omega_{1/2}$
$[Me_2Al(t\text{-}Bu)N{=}CHC(Me)_2OAlMe_3]$ (**2a**)	353	168	3380
	293	157	8800
$[Me_2AlOCH(Me)\text{-}2\text{-}C_5H_4N]_2$ (**3d**)	353	112	3560
	293	107	5630
$[i\text{-}Bu_2AlOCH_2\text{-}2\text{-}C_5H_4N]_2$	353	108	4700

[a] Frequency of measurements 65.14 MHz; all values in ppm (±10 ppm) relative to $Al(H_2O)_6^{3+}$ external; line width at half peak height in Hz; 10% solution in C_7D_8.

was formed, which dissolved when the reaction mixture was slowly (in 1 h) warmed up to room temperature. The resulting clear solution was concentrated to 30 mL in vacuo. The new complexes crystallized as long yellow needles at −20 °C; yield 0.98 and 1.1 g, 78% and 66%, respectively.

Compounds **2c** and **2d** have been prepared by heating the 2:1 Me_3Al:α-imino ketone complexes **1b** and **1c** in toluene at 80 °C (see the preceding paper)[5] and have also been obtained via a one-pot reaction in toluene at 80 °C.

$[Me_2AlNC_5H_4\text{-}2\text{-}C(R^3,R^4)OAlMe_3]$ (R^3 = H, R^4 = Me (2e); R^3 = H, R^4 = Et (2f); R^3 = R^4 = Me (2g)). A hexane solution of $(AlMe_3)_2$ (20 mmol) was added to a stirred suspension of 2-pyridinecarboxaldehyde (for **2e**) and 2-acetylpyridine (for **2g**) (15 mmol) in 100 mL of hexane. During the addition of the $(AlMe_3)_2$ solution a transient blue coloration of the reaction solution was observed. Additional stirring of the solution for 30 min resulted in the precipitation of a white solid, which was filtered off and subsequently washed with cold (−20 °C) hexane. Recrystallization from dichloromethane/hexane (1:5) afforded pure crystalline **2e** (3.31 g, 88%) and **2g** (3.12 g, 79%).

Compound **2f** was synthesized by slow addition of a hexane solution of $(AlMe_3)_2$ (6 mmol) to a stirred solution of 1-(2-pyridyl)propanol (15 mmol) in 100 mL of diethyl ether at −60 °C. After the methane evolution had ceased, the solution was warmed up to room temperature in 1 h and then stirred for an additional 3 h. The solvents were evaporated in vacuo at ambient temperature. The resulting white residue was washed three times with 50 mL of cold hexane (−20 °C) and then recrystallized from a dichloromethane/hexane mixture (1:4) at −30 °C; yield of pure **2f**, 2.41 g, 61%.

Synthesis of 3: Dinuclear Addition or Reduction Complexes. $[R_2Al(t\text{-}Bu)N{=}CHC(R^3,R^4)O]_2$ (R = Me, R^3 = Ph, R^4 = Me (3a); R = *i*-Bu, R^3 = Me, R^4 = H (3b); R = Ph, R^3 = Me, R^4 = Ph (3c)). A hexane solution of $(AlR_3)_2$ (5 mmol) was slowly added to a stirred solution of *t*-BuN=CHC(R^3)=O (11 mmol) in 100 mL of hexane. For R^3 = Me and Ph a transient red coloration of the solution was observed upon the addition of $(AlR_3)_2$. For R = *i*-Bu a reduction complex, **3b**, was formed and

Table VI. Cryoscopic Molecular Weight Determinations[a] of Various Organoaluminum Compounds in Benzene

compd	formula	[concn]	*m* = 1 found	*m* = 1 calcd	apparent assocn *m*
$Me_2Al(t\text{-}Bu)N{=}CHC(Me_2)OAlMe_3$ (**2a**)	$C_{13}H_{31}Al_2N_1O_1$	*a*	230	271	0.85
$Me_2AlNC_5H_4\text{-}2\text{-}C(H,Me)OAlMe_3$ (**2e**)	$C_{12}H_{23}Al_2N_1O_1$	*a*	225	251	0.90
$[i\text{-}Bu_2Al(t\text{-}Bu)N{=}CHC(H,Me)O]_2$ (**3b**)	$(C_{15}H_{32}Al_1N_1O_1)_2$	*a*	501	269	1.86
$[Me_2AlNC_5H_4\text{-}2\text{-}C(H,Me)O]_2$ (**3d**)	$(C_9H_{14}Al_1N_1O_1)_2$	*a*	342	179	1.91
$[Et_2Al(t\text{-}Bu)N{=}CHC(-CH_2)O]_m$ (**4b**)	$C_{11}H_{22}Al_1N_1O_1$	2.7×10^{-3}	180	211	0.85
		8×10^{-3}	315	211	1.50
		1.4×10^{-2}	460	211	2.18
		4×10^{-2}	496	211	2.35

[a] In the concentration range 10^{-3} to 10^{-1} M.

Table VII. Elemental Analysis

			C		H		N	
compd	formula	mol wt	found	calcd	found	calcd	found	calcd
1a	$C_{18}H_{22}Al_1N_1O_1$	295	72.81	73.22	7.29	7.46		4.75
1b	$C_{21}H_{31}Al_2N_1O_1$	367	67.70	68.66	8.38	8.45	3.85	3.81
1c	$C_{23}H_{35}Al_2N_1O_1$	395	69.78	69.87	9.11	8.86	3.49	3.54
2a	$C_{13}H_{31}Al_2N_1O_1$	271	56.82	57.56	11.68	11.44	5.09	5.17
2b	$C_{18}H_{33}Al_2N_1O_1$	333	65.12	64.86	10.07	9.91		4.20
2c	$C_{21}H_{31}Al_2N_1O_1$	367	69.07	68.66	8.01	8.45	3.27	3.81
2d	$C_{23}H_{35}Al_2N_1O_1$	395	68.30	69.87	8.63	8.86	3.34	3.54
2e	$C_{12}H_{23}Al_2N_1O_1$	251	57.65	57.37	9.09	9.16		5.58
2f	$C_{13}H_{25}Al_2N_1O_1$	265	59.01	58.87	9.77	9.43		5.28
3a	$(C_{15}H_{24}Al_1N_1O_1)_2$	261	69.00	68.97	9.21	9.20		5.36
3b	$(C_{15}H_{32}Al_1N_1O_1)_2$	269	65.88	66.91	12.03	11.90	4.90	5.20
3c	$(C_{25}H_{28}Al_1N_1O_1)_2$	385	77.38	77.92	7.45	7.27		3.64
3d	$(C_9H_{14}Al_1N_1O_1)_2$	179	60.72	60.34	7.88	7.82		7.82
3e	$(C_{10}H_{16}Al_1N_1O_1)_2$	193	62.21	62.18	8.58	8.29		7.25
3f	$(C_{11}H_{18}Al_1N_1O_1)_2$	207	64.21	63.77	9.25	8.70		6.76
3g	$(C_{12}H_{20}Al_1N_1O_1)_2$	221	64.93	65.16	9.33	9.05		6.33
3h	$(C_{10}H_{16}Al_1N_1O_1)_2$	193	62.25	62.18	8.36	8.29		7.25
3i	$(C_{15}H_{18}Al_1N_1O_1)_2$	255	70.37	70.59	6.93	7.06		5.49
3j	$(C_{15}H_{26}Al_1N_1O_1)_2$	263	68.45	68.44	10.06	9.89		5.32
3k	$(C_8H_{12}Al_1N_1O_1)_2$	165	57.72	58.18	7.58	7.27	8.41	8.48
3l	$(C_{10}H_{16}Al_1N_1O_1)_2$	193	61.91	62.18	8.56	8.29	7.17	7.25
3m	$(C_{12}H_{20}Al_1N_1O_1)_2$	221	65.03	65.16	8.97	9.05	6.25	6.33
3n	$(C_{14}H_{24}Al_1N_1O_1)_2$	249	67.78	67.47	9.91	9.64	5.54	5.62
3o	$(C_{20}H_{20}Al_1N_1O_1)_2$	317	75.94	75.71	6.54	6.31	4.20	4.42
3p	$C_8H_{11}Al_1N_1O_1Cl$	199.5	48.61	48.12	5.75	5.51		7.02
4a	$(C_9H_{18}Al_1N_1O_1)_2$	183	57.76	59.02	9.89	9.84	7.38	7.65
4b	$(C_{11}H_{22}Al_1N_1O_1)_2$	211	62.49	62.56	11.07	10.43	6.35	6.64
4c	$(C_{19}H_{22}Al_1N_1O_1)_2$	307	74.62	74.27	7.55	7.17	4.19	4.56
4d	$(C_9H_{12}Al_1N_1O_1)_2$	177	60.84	61.02	6.44	7.78	7.95	7.61

the formation of isobutylene was established by ^1H NMR spectroscopy.[11] After additional stirring for 10 min the solutions were filtered and then concentrated to 30 mL. The new complexes crystallized from the reaction mixture as white crystals at −30 °C. Yields: **3a**, 1.78 g, 62%; **3b**, 1.62 g, 60%; **3c**, 2.03 g, 52%.

$[Me_2\overline{AlNC_5H_4\text{-}2\text{-}C(H,R^4)O}]_2$ (R^4 = Me (3d), Et (3e), *i*-Pr (3f), and *t*-Bu (3g)). A hexane solution of $(AlMe_3)_2$ (5 mmol) was slowly added to a stirred solution of the corresponding α-alkyl(2-pyridyl)methanol derivatives (12 mmol) in 100 mL of diethyl ether at room temperature. After methane evolution had ceased, the reaction solutions were stirred for 3 h. The solutions were concentrated to 20 mL in vacuo and then filtered. The new complexes crystallized from the filtrate as white crystal, at −30 °C. Yield: **3d**, 1.31 g, 73%; **3d*** (*R,R* diastereomer), 0.96 g, 54%; **3e**, 1.22 g, 63%; **3f**, 1.67 g, 81%; **3g**, 1.72 g, 78%. Compound **3d** was also synthesized by addition of 10 mmol of 2-pyridinecarboxaldehyde to a stirred solution of **2e** (10 mmol) in 100 mL of diethyl ether. A similar workup procedure as described above afforded a compound which was identical with an authentic sample of compound **3d**; yield 1.68 g, 94%.

$[Me_2\overline{AlNC_5H_4\text{-}2\text{-}C(Me)_2O}]_2$ (3h). A hexane solution of $(AlMe_3)_2$ (2.5 mmol) was slowly (in 10 min) added to a solution of 2-acetylpyridine in refluxing hexane. The solution was refluxed for 1 h and then stirred for 16 h at room temperature. The white precipitate formed was filtered off, washed three times with 50 mL of hexane, and then recrystallized from boiling toluene; yield 0.73 g, 76%. Compound **3h** could also be obtained by the addition of 2-acetylpyridine to a stirred solution of compound **2g**. However, in this case the formation of compound **3h** was accompanied by formation of the corresponding enolization product **4d**.

$[Me_2\overline{AlNC_5H_4\text{-}2\text{-}C(Me,Ph)O}]_2$ (3i). A hexane solution of $(AlMe_3)_2$ (5 mmol) was added to a solution of 2-benzoylpyridine (10 mmol) in 100 mL of diethyl ether at room temperature. The solution was stirred for 1 h and then concentrated to 50 mL. The new complex crystallized as white crystals at −80 °C; yield 1.22 g, 47.8%.

$[i\text{-}Bu_2\overline{AlNC_5H_4\text{-}2\text{-}C(H,Me)O}]_2$ (3j). A hexane solution of $Al(i\text{-}Bu)_3$ (10 mmol) was slowly added to a stirred solution of 2-acetylpyridine (10 mmol) in 100 mL of pentane at −80 °C. There was a transient yellow coloration of the solution during the addition of $Al(i\text{-}Bu)_3$, and isobutylene was formed. The solution was warmed up to room temperature in 30 min and then concentrated to 20 mL. A white solid precipitated, which was filtered off and subsequently recrystallized from toluene; yield 2.11 g, 80%.

The syntheses of $[R_2\overline{AlNC_5H_4\text{-}2\text{-}CH_2O}]_2$ (**3k–p**) have been described in a previous publication.[6a] Compound **3n** was also obtained by the addition of a hexane solution of either $Al(i\text{-}Bu)_3$ or $(i\text{-}Bu)_2AlH$ to 2-pyridinecarboxaldehyde.

Synthesis of 4: The Enolization Products. $[R_2\overline{Al(t\text{-}Bu)N{=}CHC(=CH_2)O}]_n$ (R = Me (4a), Et (4b), Ph (4c)). A hexane solution of $(AlR_3)_2$ (5 mmol) was added to a stirred solution of *t*-BuN=CHC(Me)=O (10 mmol) in diethyl ether at −80 °C. The solution was warmed up to room temperature and, after the gas evolution had ceased, stirred for 1 h. Then 20 mL of dichloromethane was added and the resulting solution filtered. White crystals crystallized from the clear filtrate at −30 °C; these were filtered off and washed with 50 mL of cold hexane (−80 °C). Yield: **4a**, 1.16 g, 63%; **4b**, 0.99 g, 47%; **4c**, 1.33 g, 43%.

$[Me_2\overline{AlNC_5H_4\text{-}2\text{-}C(=CH_2)O}]$ (4d). 2-Acetylpyridine (10 mmol) was slowly added over a period of 1 h to a boiling solution of 5 mmol of $(AlMe_3)_2$ in 100 mL of diethyl ether. After the reaction mixture cooled to room temperature the solvent was evaporated in vacuo. The resulting white product was washed three times with 50 mL of hexane and then recrystallized from dichloromethane; yield 0.76 g, 43%.

Results

The reactions of triorganoaluminum compounds with α-imino ketones $[R^1N{=}C(R^2)C(R^3){=}O]$ and 2-oxopyridyl derivatives $[NC_5H_4\text{-}2\text{-}C(R^3){=}O]$ follow a very distinct reaction course in which product formation is usually quantitative. The high reactivity of these N=C—C=O containing substrates prevented in most cases the study of the intermediate organometallic complexes formed during these reactions. However, in all cases the ultimate organoaluminum products as well as the organic products obtained after hydrolyses could be isolated and charac-

(11) Bothner-By, A.; Naar-Colin, C. *J. Am. Chem. Soc.* **1961**, *83*, 231.
(12) van Vliet, M. R. P.; van Koten, G.; van Beek, J. A. M.; Vrieze, K.; Muller, F.; Stam, C. H. *Inorg. Chim. Acta* **1986**, *112*, 77.

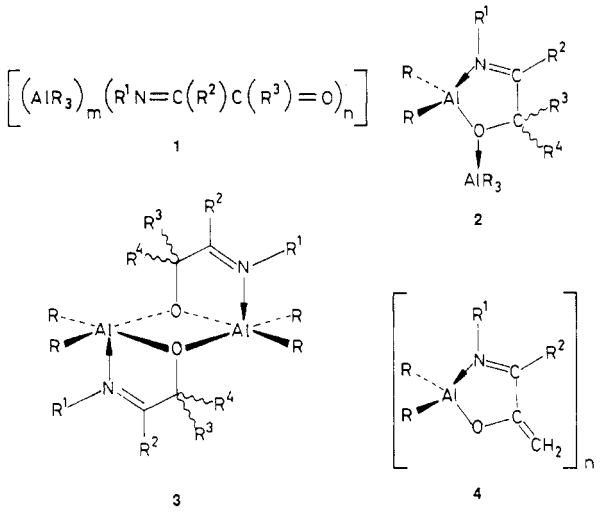
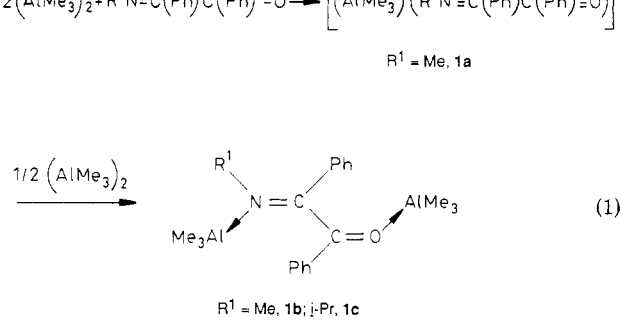


Figure 2. The four different types (1–4) of the novel organoaluminum complexes.

terized. Depending on the substitution pattern of the α-imino ketone and 2-oxopyridyl skeletons three types of new organoaluminum complexes have been characterized; see Figure 2. For special substitution patterns of the N=C—C=O skeleton the formation of the 2:1 coordination complexes of type 1 (see Figure 1A for a structure of a stable example) as well as of 1:1 complexes could be detected. (A detailed discussion of the structural features of some of these compounds has been presented in ref 5 and 6.)

Compounds 1a–c: The 1:1 and 2:1 $AlMe_3$:α-Imino Ketone Coordination Complexes. According to eq 1 both 1:1 and 2:1 $AlMe_3$:L complexes (**1a–c**) could be isolated for the specific α-imino ketones shown.



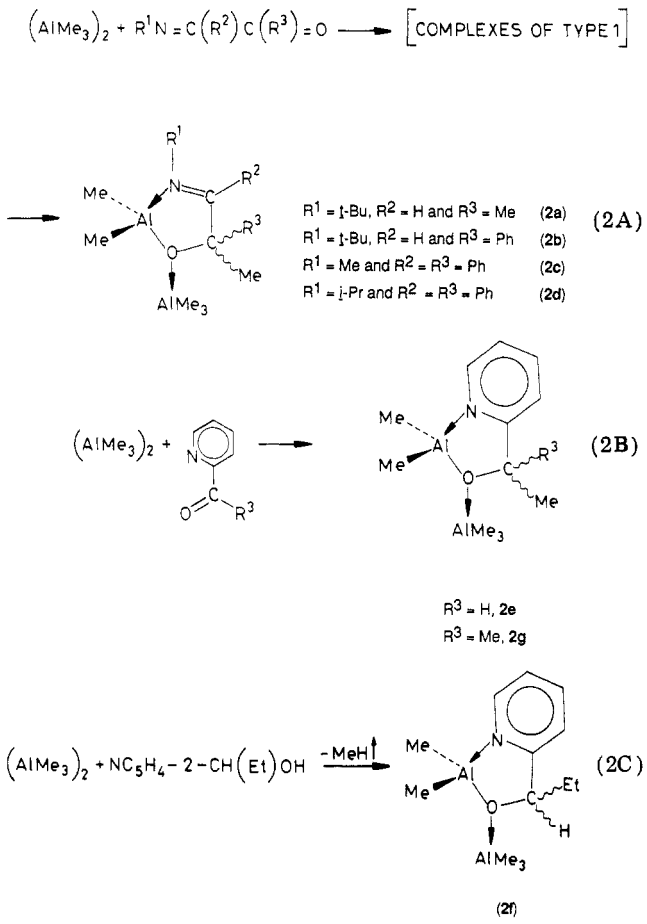
Elemental analytical data of the complexes confirmed the respective 1:1 and 2:1 stoichiometries shown.[7] Compounds **1a–c** are soluble in the common aprotic organic solvents. They decompose with violence when dissolved in halogenated solvents at room temperature and are extremely sensitive toward H_2O and O_2.

The exact structure of the white 1:1 $AlMe_3$:L coordination complex [$(Me_3Al)(MeN{=}C(Ph)C(Ph){=}O)$] (**1a**) is uncertain. It is clear from the observation of the N=*C* and *C*=O ^{13}C resonances at 179.8 and 194.8 ppm, respectively (see Table I), that the ligand N=C—C=O skeleton is still present. However, it is not possible to distinguish from the available data whether the α-imino ketone coordinates via its N or O donor site (see Discussion).

The low-temperature (<−70 °C) ^1H NMR spectra (see Table I) of the organoaluminum compound **1b** is in agreement with the structure found in the solid state (see Figure 1A). Two trimethylaluminum hydrogen resonances are observed at −1.28 and −1.14 ppm, respectively. The ^{13}C NMR spectrum at room temperature shows two high-field ^{13}C resonances at ca. 177 (N=*C*) and ca. 199 (*C*=O) ppm, which is in agreement with the presence of the unchanged N=C—C=O skeleton in this complex. The NMR experiments at different temperatures and concentrations of Al_2Me_6 and α-imino ketones (see Discussion) show that in solution the 2:1 $AlMe_3$–α-imino ketone complexes are in equilibrium with the uncoordinated ligand and hexamethyldialuminum.

It must be recalled that only in the above cases (**1a–c**) could complexes be successfully isolated. In all other cases it was not possible to isolate coordination complexes because of their high reactivity and fast subsequent conversions to the carbonyl-alkylated products.

Compounds 2a–g: Carbonyl-Alkylated Products with One Trimethylaluminum Molecule Coordinated to the Oxygen Atom. According to eq 2A–C these complexes can be formed via *two* different routes, i.e. starting either from the ketones and reacting these with $(AlMe_3)_2$ (eq 2A and 2B) or from the alcohol via an acid–base reaction (eq 2C). The latter route only was applied for the synthesis of the pyridylmethanolate complex **2f**.



Elemental analytical data of the complexes **2** confirmed the stoichiometries as shown in the eq 2A–C (Table VII). Cryoscopic molecular weight determinations confirmed that the organoaluminum compounds of type **2** are monomeric in benzene (Table VI). The compounds **2a–g**, which are extremely sensitive toward H_2O and O_2, are soluble in aprotic organic solvents. Slow decomposition occurs in halogenated solvents.

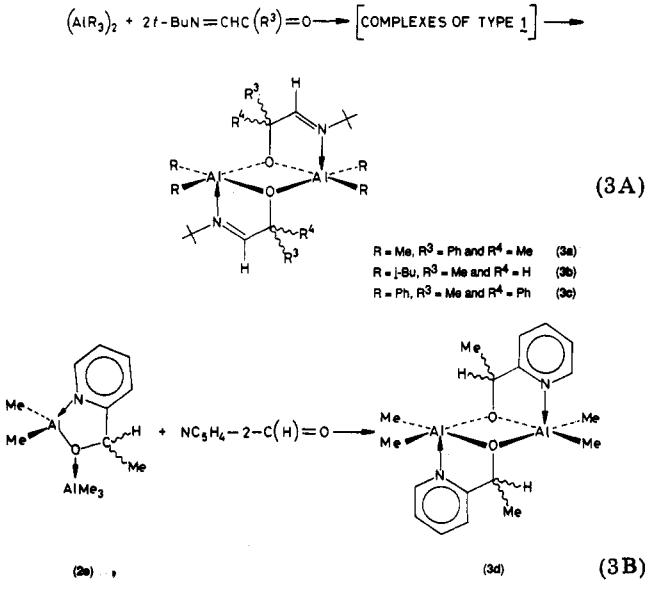
The structure in the solid of [$Me_2Al(t\text{-Bu})N{=}CHC(Me)_2OAlMe_3$] (**2a**) as revealed by an X-ray structure determination is shown in Figure 1B.[5] The molecule contains a monomeric $Me_2Al(t\text{-Bu})N{=}CHC(Me)_2O$ unit resulting

from the addition of one of the Me–Al bonds of the first equivalent of $AlMe_3$ over the carbonyl group. The oxygen donor site of this monomeric unit then coordinates with a second molecule of trimethylaluminum.

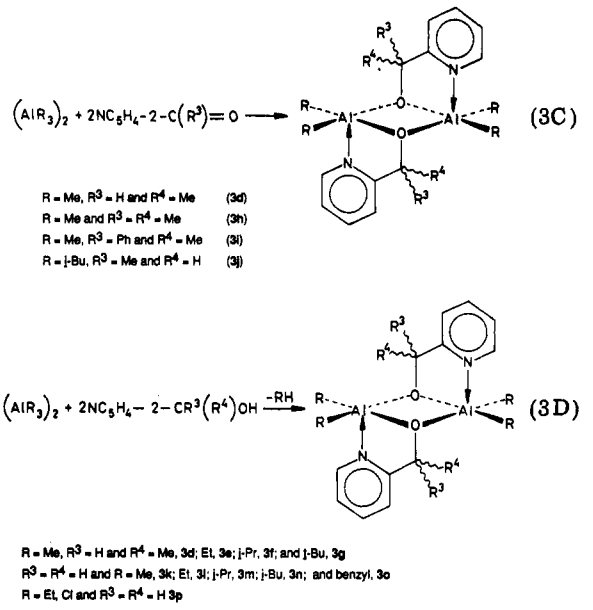
The ^1H and ^{13}C NMR spectra of the compounds **2a–g** point to a structure in solution similar to that found for **2a** in the solid state. The ^1H NMR spectra (see Table II) are in agreement with structures consisting of a dimethylaluminum entity to which either an (*E*)-imine $[R^1N{=}C(R^2)C(R^3,R^4)O]^-$ (**2a–d**) or a 2-pyridylalkylmethanolate, $[NC_5H_4\text{-}2\text{-}C(R^3,R^4)O]^-$, anion (**2e–g**) is bidentate bonded. One hydrogen resonance (**2a** and **2b**) is found at low field, ca. 7 ppm, which is indicative of a *HC*=N bonded proton. At room temperature, two different Me–Al resonances are observed with a 2:3 intensity ratio: one for the Me_2Al unit and a second for the neutral Me_3Al entity, which is coordinated to the oxygen donor site. The ^{13}C NMR spectra of **2a** and **2c** (Table II) showed two different resonances for the N=C—C—O skeleton ^{13}C nuclei: the N=*C* at ca. 180 ppm belongs to an unchanged imine carbon atom whereas the $-C(R^3,R^4)O^-$ resonance found at ca. 80 ppm is in the characteristic region for alkanoate carbon atoms.[6,13]

The methanolate carbon atoms in the compounds **2b–f** are stable chiral centers. The chirality of this carbon center renders the prochiral Me_2Al grouping diastereotopic, which results in two different Me–Al resonances in the ^1H NMR spectra of these compounds (see Table II). Also the *i*-Pr methyl groupings in **2d** are diastereotopic, resulting in two doublets for the $(CH_3)_2CH$ protons. The observation of this diastereotopicity establishes not only the presence of the five-membered chelate ring in these compounds but also indicates that processes involving aluminum–nitrogen bond association–dissociation are slow or even blocked on the NMR time scale at room temperature. At higher temperatures the molecules showed a dynamic behavior that will be discussed below (see Discussion).

Compounds 3a–p: Dinuclear Alkylated or Reduced Products. The 1:1 reactions of triorganoaluminum derivatives with both α-imino ketones and 2-oxopyridyl derivatives resulted in quantitative formation of the corresponding dinuclear alkoxyaluminum compounds (**3a–d,h–j**) containing a covalent aluminum–oxygen bond according to eq 3A and 3B. In these reactions, except for R = *i*-Bu,



(13) Johnson, L. F.; Jankowski, W. C. *Carbon-13 NMR Spectra*; Wiley-Interscience, New York, 1972.



the organo group R was transferred from aluminum to the keto-carbon atom. In the case of R = *i*-Bu the reduction products **3b** and **3j** were formed together with 1 equiv of isobutylene. Interestingly, in two cases (**3a** and **3d**) it was found that similar aluminum compounds are also accessible via the route shown in eq 3C for the synthesis of **3d**; i.e. by the 1:1 reaction of the isolated compounds **2a** and **2e**, respectively, with either *t*-BuN=CHC(Me)=O or 2-pyridinecarboxaldehyde. Most probably this is a general route for the preparation of compounds of type **3**, but this has not been checked for all compounds mentioned here.

Finally, the acid–base reaction already shown for the syntheses of compounds of type **2** is also applicable for the synthesis of the dinuclear aluminum compounds **3**. The 1:1 reaction of the organoaluminum compounds R_nAlX_{3-n} (n = 3, R = Me, Et, *i*-Pr, *i*-Bu, benzyl; n = 2, R = Et, X = Cl) with $C_5H_4N\text{-}2\text{-}C(R^3,R^4)OH$ afforded in quantitative yield the corresponding alkane or arene and the alkoxyaluminum compounds **3e–g** and **3k–p**, according to eq 3D.

Elemental analytical data of **3a–p** confirmed the stoichiometry of the compounds. According to cryoscopic molecular weight determinations, the compounds **3** exist as dimers in benzene (concentration range of 3×10^{-3} to 10^{-1} M). The organoaluminum compounds **3**, which are sensitive toward H_2O and O_2, are insoluble in alkanes but are soluble in diethyl ether as well as in aromatic and halogenated solvents.

For this type of compound the structure in the solid of a representative example, i.e. $[i\text{-}Bu_2AlOCH_2\text{-}2\text{-}C_5H_4N]_2$ (**3n**), has also been established by an X-ray structure determination; see Figure 1C.[6] The dimeric structure of **3n** consists of two five-coordinate aluminum atoms. Each aluminum center is bonded to two isobutyl groups and to a N,O chelate bonded 2-pyridylmethanolato ligand. The O atom of the latter monoanionic group is also coordinating to the second aluminum center, which leads to the formation of a planar four-membered Al_2O_2 ring.

The low-temperature (<0 °C) ^1H and ^{13}C NMR spectra in noncoordinating solvents of the organoaluminum compounds **3a–p** are in agreement with the structural features found for **3n** in the solid state: i.e. five-coordinate Al centers and a central Al_2O_2 ring. A recent NMR study of **3n** already revealed that this central Al_2O_2 ring is rigid on the NMR time scale and, furthermore, that the fluxional behavior of this compound involves an on–off movement of the pyridine N donor atom as is shown in Figure 3.[6,7]

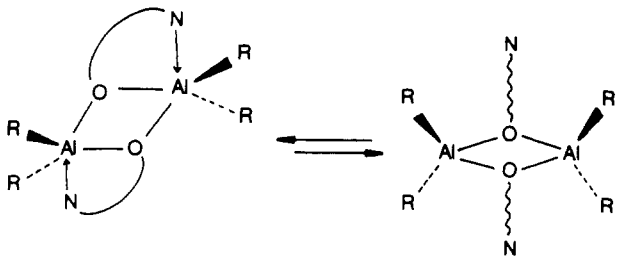
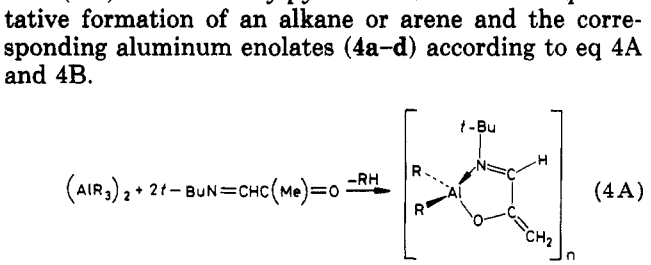


Figure 3. Equilibrium between a five-coordinate species, $[R_2AlOCH_2\text{-}2\text{-}C_5H_4N]_2$, and a four-coordinate species, $[R_2AlOCH_2\text{-}2\text{-}C_5H_4N]_2$.

It must be noted that besides the dynamic behavior described above the spectra of compounds **3a–g,i,j** show another interesting feature: for these compounds two different NMR patterns were observed. This can be explained on the basis of the fact that in these compounds the formerly ketonic C atom became a stable chiral center through the addition reaction with the organoaluminum reagent. Subsequent dimerization then produced two enantiomeric pairs of diastereomeric dimers, which have different NMR spectra. This diastereotopism is reflected by the prochiral groupings present in the various compounds (see Table III), which show anisochronous resonances. For example, the ^1H NMR spectra of the latter compounds show two pairs of doublets for the prochiral Me_2Al unit. It is also obvious from Table III that the diastereomers are present in different molar ratios of which the value seems to depend on the bulkiness of the groups R^3 and R^4 (see Discussion). Furthermore, the isomer ratio appeared to be constant over the whole temperature range investigated (−30 to +47 °C). This behavior indicates that the isomers are kinetically stable; i.e., these isomers are formed in a distinct molar ratio and do not interconvert subsequently. The dynamic behavior of these compounds is discussed later (see Discussion).

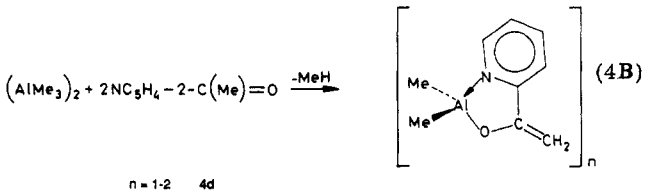
In order to further substantiate the above conclusions the reaction shown in eq 3D was also carried out by using optically pure (*R*)-(2-pyridyl)ethanol from which, by reaction with Al_2Me_6, optically pure (*R,R*)-$[Me_2AlNC_5H_4\text{-}2\text{-}C^*(H,Me)O]_2$ (**3d***) was obtained. The ^1H NMR spectrum of the latter compound showed only one pattern, indicating that only one diastereoisomer was present in solution (see Table III, **3d***).

Compounds 4a–d: Enolate Complexes. The reactions of triorganoaluminum compounds with either *t*-BuN=CHC(Me)=O or 2-acetylpyridine resulted in the quantitative formation of an alkane or arene and the corresponding aluminum enolates (**4a–d**) according to eq 4A and 4B.



(4A)

R = Me, 4a; Et, 4b and Ph, 4c n = 1-2



(4B)

n = 1-2 4d

Elemental analytical data of **4a–d** confirmed the 1:1 Al:monoanionic ligand stoichiometry of the compounds; see Table VII. According to cryoscopic molecular weight determinations (Table VI) these compounds possess an association degree in benzene that varies from 0.85, i.e. monomeric species, at low concentrations (10^{-3} M) to 2.35, i.e. dimeric and higher nuclearity species, at higher concentrations (10^{-1} M). The organoaluminum compounds, which are sensitive to H_2O and O_2, are soluble in hexane (**4b**) and diethyl ether as well as in aromatic and halogenated solvents (**4a–d**).

Evidence for the enolate structure comes from hydrolysis experiments. Hydrolysis with D_2O afforded in quantitative yield the starting ligand with deuterium incorporated in the methyl group, i.e. *t*-BuN=CHC(CH_2D)=O and NC_5H_4-2-C(CH_2D)=O, respectively.

Two different ^1H and ^{13}C NMR patterns are observed for solutions of the compounds **4b** in dichloromethane (see Table IV). The imine proton resonance for **4a–c** is found at ca. 7–8 ppm, indicating the presence of an unchanged HC=N grouping. The resonance of the CH_3 groups in the starting α-imino ketones is now found with a reduced intensity (equivalent to two H atoms) in the aluminum enolates at ca. 4.5 ppm, which is the olefinic region. The ^{13}C NMR spectra (see Table IV) show one imine N=*C* resonance at ca. 163 ppm and two resonances for the ^{13}C nuclei in the *C*(=*C*H_2)O^- grouping. The olefinic methylene atom resonates at ca. 100 ppm while the $C(O)^-$ atom is found at ca. 155 ppm. These observations establish that the Al center is not bound to this carbon atom but that the enolate anion is coordinated via the nitrogen and oxygen atoms as shown in eq 4A and 4B.

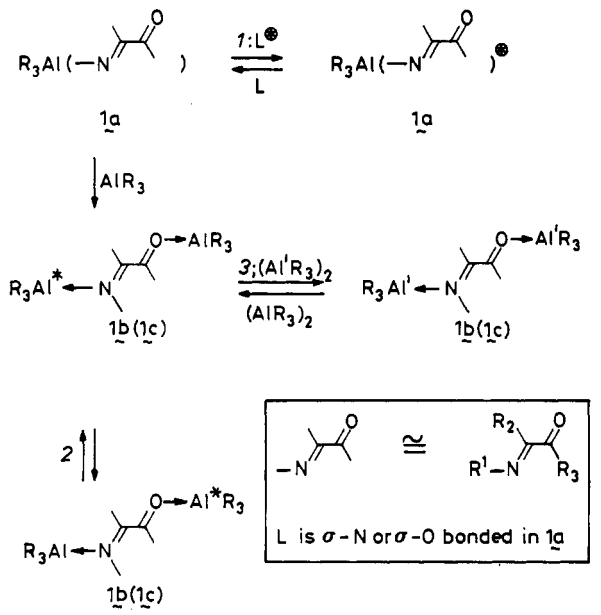
Discussion

Since dimers Al_2R_6 differ from monomers AlR_3 in both structure and reactivity, the interconversion of these two forms is important in understanding reaction mechanisms. The dimer–monomer interconversion of trimethylaluminum lends itself readily to NMR spectra analysis, since the room-temperature exchange of methyl groups between the bridge and terminal positions can be slowed down by cooling to −40 °C,[14] and much controversy has arisen concerning various interpretations of such data.[15] Consensus, however, seems to exist on the conclusion that the activation energy of exchange is more consistent with the rupture of both methyl bridges to form monomers (perhaps trapped in a solvent cage) than with the rupture of one bridge only.[16] The tendency for association of organoaluminum compounds is often so great that the product of a reaction between Al_2R_6 and an organic substrate may capture the reactive AlR_3 monomer in the form of an hetero-associated complex,[17] a situation which for example has also been met in the present work with the isolation of compounds of type **2**.

With unsaturated organic substrates bearing unshared electron pairs such as ketones and imines, preliminary complexation of the very reactive monomeric organoaluminum reagent at the most active Lewis base site of the substrate will occur. The lifetime of most of these intermediates is very short. In 1968 Ashby et al. examined a yellow coordination complex of trimethylaluminum with benzophenone,[18] and evidence for the existence of a tran-

(14) Oliver, J. P. *Adv. Organomet. Chem.* **1970**, *8*, 167; **1977**, *16*, 111.
(15) (a) Jeffery, E. A.; Mole, T. *Aust. J. Chem.* **1973**, *26*, 739. (b) Brown, T. L.; Murell, L. L. *J. Am. Chem. Soc.* **1972**, *94*, 378.
(16) Eisch, J. J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., ed.; Pergamon: New York, 1982; Vol. 1, Chapter 6, p 602.
(17) Eisch, J. J.; Rhee, S. G. *J. Organomet. Chem.* **1974**, *96*, 7276.
(18) Ashby, E. C.; Laemmle, J.; Neumann, H. M. *J. Am. Chem. Soc.* **1968**, *90*, 5179.

Scheme I



sition state of the type [$(AlMe_3)_n$ benzophenone] was obtained.[19]

The α-imino ketones used in our study have at least two anchoring sites for the AlR_3 monomers, i.e. the ketone and the imine grouping. In a previous study we showed already that in the case of α-diimines monodentate imine–AlR_3 coordination via one imino N atom occurs in solution.[2c,d] These 1:1 complexes (e.g. *t*-BuN=CHC(H)=Nt—Bu·AlR_3) are very reactive and convert at temperatures above 0 °C into the [alkylated α-diimine]AlR_2 complexes so that the dynamic behavior of the initially formed coordination complexes could not be studied. In our present study of the reactivity of α-imino ketones toward organoaluminum reagents we observed the formation of the corresponding 1:1 and 2:1 donor:acceptor complexes, which in several cases, e.g. compounds **1a**, **1b**, and **1c** appeared to be stable even at higher temperatures. Accordingly, the dynamic behavior in solution of the stable complexes could be studied, thus providing important information concerning the subsequent reactions that take place between the more reactive α-imino ketones and the organoaluminum reagents.

Dynamic Behavior of the Coordination Complexes 1. Because of the absence of suitable NMR probes in the molecules **1** their solution structures and dynamic behavior could only be studied in a qualitative way. The available data for the $AlMe_3$/MeN=C(Ph)C(Ph)=O system for which the $AlMe_3$:MeN=C(Ph)C(Ph)=O molar ratio has been varied between 4:1 and 1:4 strongly indicate that in solution the system is prone to intermolecular exchange processes. A summary of some possible equilibria that can be used to explain the observed data are shown in Scheme I.

The ^1H and ^{13}C NMR patterns as well as the small coordination chemical shifts of the alkyl substituents in the stable 1:1 complexes do not provide direct evidence for the presence of the monodentate coordination mode (σ-N or σ-O) of the α-imino ketone as has been possible for the σ-N monodentate bonded *t*-BuDAB ligand in related [$AlMe_3$(*t*-BuDAB)].[2d]

Addition of a fourfold excess of the free α-imino ketone ligand MeN=C(Ph)C(Ph)=O to a solution of the 1:1 complex [$(AlMe_3)$(MeN=C(Ph)C(Ph)=O)] (**1a**) in toluene-d_8 illustrates nicely that intermolecular exchange between **1a** and the free α-imino ketone occurs (equilibrium 1, Scheme I). At room temperature the Me–N groups of complex **1a** and the free ligand appear in the ^1H NMR spectra as one single resonance at 3.40 ppm. At −80 °C the slow-exchange limit is reached with two different Me–N resonances at 3.07 and 3.44 ppm (see Table I). This behavior demonstrates that the intermolecular exchange between complex **1a** and the free α-imino ketone is fast on the NMR time scale at room temperature. In the presence of excess free ligand the occurrence of a dissociative mechanism for this intermolecular exchange process seems unlikely. An associative mechanism could proceed via a five-coordinate [$(AlMe_3)$(MeN=C(Ph)C(Ph)=O)$_2$] intermediate formed by attack of a second ligand molecule in a S_N2-type of mechanism.[20–22]

Equation 1 shows that addition of an equivalent amount of $AlMe_3$ (or $Al(i\text{-}Pr)_3$) to the monodentate imino ketone complex **1a** yields the 2:1 coordination compounds [$(AlMe_3)_2$(R^1N=C(Ph)C(Ph)=O)] (R^1 = Me (**1b**) and R^1 = *i*-Pr (**1c**)). The ^1H NMR spectra (see Table I) of these 2:1 coordination compounds demonstrate that the structure found for **1b** in the solid state, i.e. a σ,σ-N,O-bonded α-imino ketone bridging between two $AlMe_3$ units (cf. Figure 1A), is observable at −90 °C in CD_2Cl_2 solution. At this temperature the slow-exchange limit is just reached as shown by the two singlets for the $AlMe_3$ hydrogen resonances (both with an intensity of 9 H) belonging to a σ-N and a σ-O coordinated $AlMe_3$ group. At already slightly higher temperatures these two $AlMe_3$ hydrogen resonances coalesce and appear as one single resonance (intensity 18 H). This behavior points to the occurrence of an exchange process for these molecules that involves both $AlMe_3$ entities (equilibrium 2, Scheme I).

Addition of a fourfold excess of free $(AlMe_3)_2$ to a solution of complex **1b** leads to one single resonance at −0.25 ppm for all $AlMe_3$ groups. Accordingly, at room temperature fast intermolecular exchange between complex **1b** and $(AlMe_3)_2$ takes place (equilibrium 3, Scheme I) while concomitantly Al_2Me_6 also undergoes exchange (not shown). With the use of a solvent mixture of CD_2Cl_2 and methylcyclopentane (1:1) the slow-exchange limit of both processes could be reached. At −100 °C four different Al–Me hydrogen resonances were observed; i.e. two resonances for the σ-N and σ-O coordinated $AlMe_3$ groupings and two for $(AlMe_3)_2$, being the bridge and terminal methyl groupings.[23]

The observed intermolecular exchange processes for the complexes **1** both with an excess of either $(AlMe_3)_2$ or free ligand contrast with the high stability of the monodentate N coordination of the imino ketone ligand in *trans*-[$PtCl_2(PR_3)$\{σ-N-(R^1N=C(R^2)C(R^3)=O)\}] complexes.[12] Clearly Al–O and Al–N bonds in the 1:1 and 1:2 complexes **1a** and **1b** are not stable on the NMR time scale, and it is only for **1b** that the slow-exchange-limit structure was observed.

Dynamic Behavior of 2: Addition Products with Coordinated Trimethylaluminum. Although at room temperature the $AlMe_2$ and the oxygen coordinated $AlMe_3$ groups possess different Al–Me hydrogen resonances (with

(19) (a) Leammle, J.; Ashby, E. C.; Roling, P. V. *J. Org. Chem.* **1973**, *38*, 2526. (b) Neumann, H. M.; Leammle, J.; Ashby, E. C. *J. Am. Chem. Soc.* **1973**, *95*, 2597.

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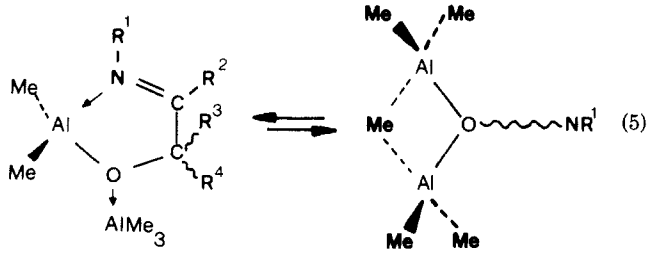
(22) (a) Mole, T. *Aust. J. Chem.* **1963**, *16*, 801. (b) Lub, J. Thesis, University of Amsterdam, 1985; Chapter 4, pp 70–76.

(23) Muller, N.; Pritchard, D. E. *J. Am. Chem. Soc.* **1960**, *82*, 284.

an intensity of 6:9; see eq 2 for a structure), at higher temperatures only one Al–Me resonance (intensity 15 H) is observed, e.g. for compound **2a** at temperatures higher than 90 °C (see Table II). A mechanism for a dynamic process through which all Al–Me groups can become equivalent is proposed in eq 5.



(5)

(S)

In view of the considerable stability of the covalent Al–O bond in $R_2AlOCCN$ fragments rupture of an Al–N(imine) donative bond seems to be a plausible first step.[6] This dissociation is followed by (or occurs concomitantly with) a switch of the methyl groups from terminal 2-center, 2-electron Me–Al bonding into 3-center, 2-electron (electron-deficient) $MeAl_2$ bridging position resulting in the formation of the intermediate S. The latter dinuclear intermediate also contains one 4-electron, 3-center Al–O–Al bridge. Such combinations of electron-precise and -deficient bonding have been encountered frequently in organoaluminum chemistry, e.g. by Stucky et al. in $[Al_2Me_5NPh_2]$.[24,25] Reattack of the free imine function leads to the cleavage of the Me bridge, which then reproduces the ground-state structure with the bridging Me_2Al and the terminal Me_3Al groupings.[14,26]

Dynamic Behavior of the Stereoisomers of the Dinuclear Addition Complexes 3. Optically pure (*R*,*R*)-$[Me_2AlNC_5H_4$-2-C*(H,Me)O$]_2$ (**3d***) was synthesized (see Results) in order to substantiate the presence of two enantiomeric pairs of diastereomeric dimers, the *RR,SS* and the *RS,SR* ones, formed during the synthesis of compounds of type **3** (vide supra). These diastereomers are formed in a characteristic *RR,SS*:*RS,SR* molar ratio, which seems to depend on the bulkiness of the substituents R^3 and R^4 as well as on the kinetic stability of the Al_2O_2 central unit. For R^4 = H and R^3 = Me, Et, *i*-Pr, and *t*-Bu (respectively, **3d**, **3e**, **3f**, and **3g**) this ratio enhances from 4:1 for R^3 = Me (**3d**) to 20:1 for R^3 = *t*-Bu (**3g**). That steric interactions between the two halves of the dimer are most likely the determining factor for the observed behavior is indicated by the different dynamic behavior of the two diastereomeric pairs.

Figure 4 shows the ^1H NMR resonances of the Al–Me region of the diastereomeric mixture (4:1 ratio) of $[Me_2AlNC_5H_4$-2-C(H,Me)O$]_2$ (**3d**).

At low temperatures (T < −20 °C, see Table III) the Al*Me*$_2$ groups are diastereotopic for both stereoisomers resulting in spectra with two pairs of doublets for the prochiral $AlMe_2$ units. Interestingly, at higher temperatures (T > 45 °C) only one isomer (the *RR,SS* pair) shows fluxional behavior, while the resonances arising from the other isomer (the *RS,SR* pair) remained sharp over the whole temperature range measured. The fluxional behavior for the *RR,SS*, pair is similar to that studied in detail for the dinuclear compounds $[R_2AlOCH_2$-2-$C_5H_4N]_2$; see ref 6. The diastereotopic groups become enantiotopic as a result of the Al–N bond dissociation–association process, which takes place in the dinuclear species with retention of the flat AlO_2Al bridge structure; see Figure 3. An isochronous signal is found for the $AlMe_2$ methyl groups. Accordingly this process proceeds via a dinuclear intermediate containing four-coordinate Al centers and nonbonded pyridyl N atoms. Study of molecular models show that for the diastereomers with the greatest steric repulsion between the substituents R^3 and R^4 of the two halves of the dimer, i.e. the *RS,SR* pair, the five-coordinate situation at the aluminum centers is stabilized because in this configuration this repulsion is much less than in the conformer having the four-coordinate aluminum centers. The increased coalescence temperature for the $AlMe_2$ methyl resonances in the *RR,SS* isomers (and in the *RR* isomer **3d** also) going from R^3 = Me ($T^{coal.}$ = 30 °C) to R^3 = *t*-Bu ($T^{coal.}$ = 100 °C) supports this line of reasoning. Interestingly these dimers **3**, which are stable to bases like pyridine, are cleaved easily into monomeric structures by adding the Lewis acids $(AlR_3)_2$ forming compounds of type **2**. From this behavior it is clear that the alkoxide O in the monoanionic α-iminoalkoxides is a stronger base than pyridine.

Equilibria of the Enolization Products 4. In contrast to the previously discussed diorganoaluminum alkoxides **3**, molecular weight determinations at different concentrations of compounds of type **4** show an apparent molecular weight corresponding to a monomer at low concentration and to higher nuclearity species ($n \geq 2$) at higher concentrations (see Table VI). The NMR experiments (see Table IV) point to the existence of at least two species, of which the molar ratio is concentration dependent. In accordance with the molecular weight data at very low concentrations (e.g. **4b**, concentration < 10^{-3} M) only one resonance pattern belonging to one species (monomer) is present while two resonance patterns are present at higher concentrations. This behavior is consistent with an equilibrium that is slow on the NMR time scale. By comparison with the highly stable Al_2O_2 bridges in compounds **3** such bridges that would be present in, for example, dimeric **4** can be anticipated to be easily cleaved. This can be attributed to the decreased electron density on the bridging oxygen atom in **4**, which is an enolate O and not an alkoxide O as in **3**.[27] Accordingly, for a possible monomer–dimer equilibrium of **4** one can propose the process shown in Figure 5, which involves cleavage and re-formation of the Al_2O_2 frame.

Formation of 2–4. When the reactions of the α-imino ketones with AlR_3 are compared with those reported previously for ketones and imines, some interesting differences become apparent.[28,29] In the latter reactions complex formation is also considered to be the first step in the addition process. However, in these organoaluminum ketone or imine complexes the substrate is anchored to the aluminum center via a monodentate interaction of the hetero atom of the grouping that will be

(24) Magnuson, V. R.; Stucky, G. D. *J. Am. Chem. Soc.* **1969**, *91*, 2544.
(25) (a) Boleslawski, M.; Serwatowski, J. *J. Organomet. Chem.* **1983**, *254*, 159. (b) Ashby, E. C.; Laemmle, J.; Paris, G. E. *J. Organomet. Chem.* **1969**, *19*, 24.
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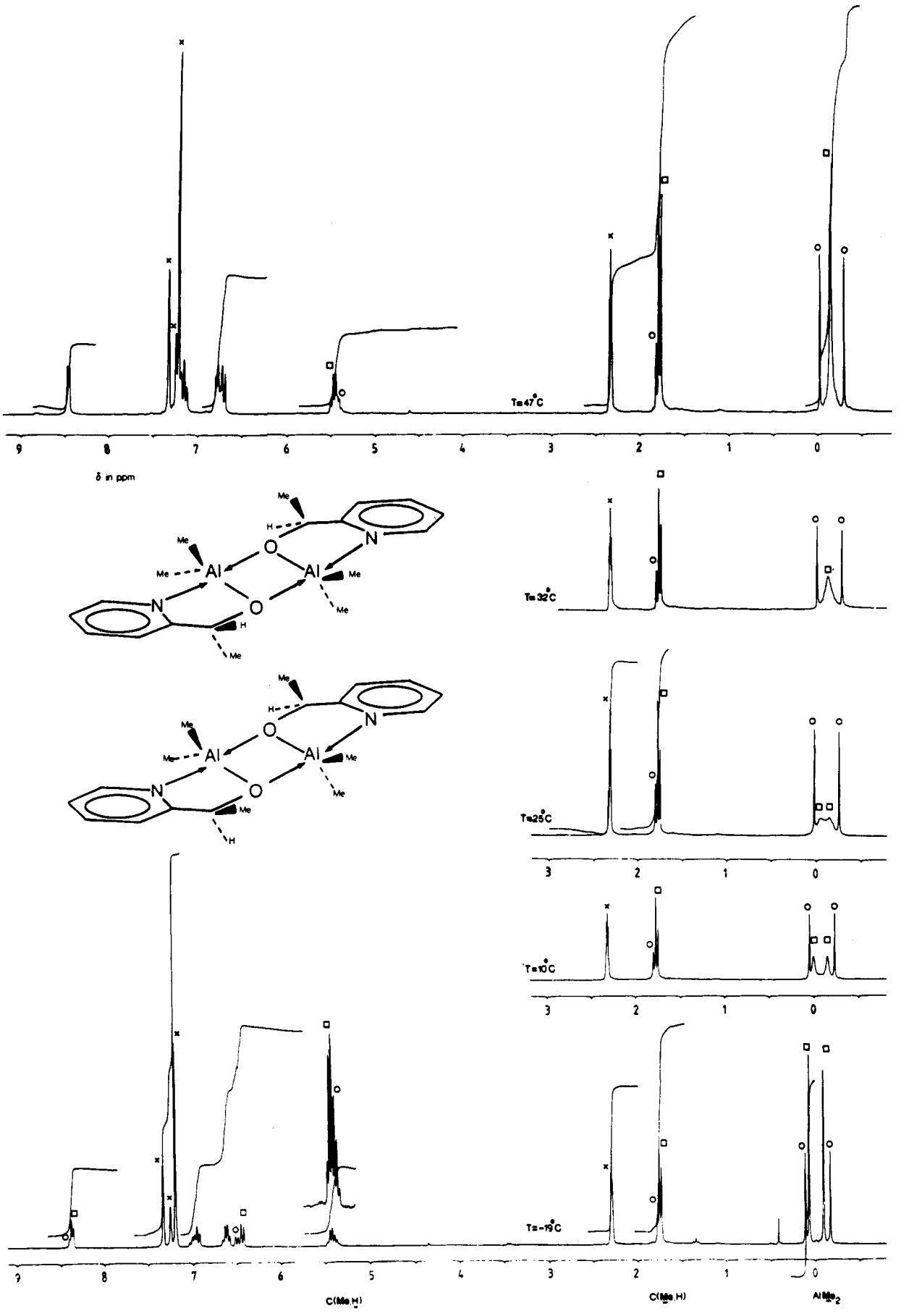

Figure 4. Variable-temperature ^{1}H NMR spectra of $[Me_2AlNC_5H_4\text{-}2\text{-}C(H,Me)O]_2$ (**3d**): ×, peaks due to toluene; □, peaks due to the *RR,SS* isomer; ○, peaks due to the *RS,SR* isomer.

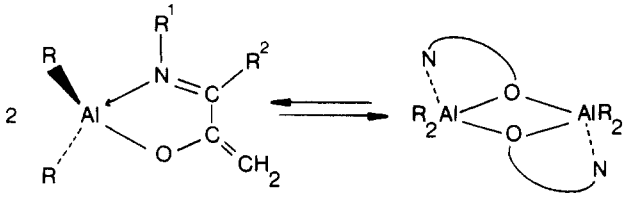

Figure 5. A possible monomer–dimer equilibrium of diorganoaluminum (α-imino)enolates, involving cleavage of the Al_2O_2 frame.

converted in the subsequent steps. Ashby et al. have shown that these reactions may be either of a radical nature involving primary electron transfer or occur via concerted pathways. Irrespective of the actual route followed, dissociation of the substrate from the aluminum center during this process can occur leading to the formation of various products instead of a selective conversion.[19]

The present work shows that in the case of the conversion of α-imino ketones with organoaluminum reagents not only does the substrate act as a monodentate through either one of its heteroatoms but also that bidentate interactions may become very important during the transfer of the R group from the Al center to the substrate and can make these conversions selective.

Although one can only speculate about the precise nature of the precursor complexes for the rearranged products **2**, **3**, and **4**, it seems reasonable to assume that the compounds of type **2** are formed via starting compounds like **1b** and **1c** while the compounds of type **3** and **4** are formed via starting compounds like **1a**.

The organic implications of our results are obvious and have led to the development of one-pot synthetic procedures for the selective and often quantitative syntheses of new organic products. Furthermore, the reactive aluminum intermediates, such as the aluminum enolates **4**, have been found to be sufficiently reactive to attack carbonyl compounds under mild conditions.

Addendum: Variable-Temperature 65.14 MHz ^{27}Al NMR. An interesting, direct way to study the dynamics of the aluminum complexes **1–4** would be ^{27}Al NMR spectroscopy, because it has been established that ^{27}Al chemical shift values for compounds with a high coordination number at aluminum appear at higher field than those for compounds with a lower coordination number.[31-33] However, ^{27}Al is a quadrupolar nucleus and accordingly line widths are sensitive both to the symmetry at Al and to the temperature, with line widths increasing when both the symmetry decreases and the temperature is lowered. Under unfavorable conditions (low symmetry and low temperature) background signals (e.g. arising from the probe) often become dominant so that the observation of the very broad ^{27}Al resonances from the compounds is made difficult or even impossible.[32]

As an extension of the above described ^{1}H and ^{13}C NMR studies we have measured the 65.14-MHz ^{27}Al NMR spectra of three representative compounds with a well-defined structure; see Table V.

The ^{27}Al NMR spectra of [$Me_2Al(t\text{-}Bu)N{=}CHC(Me)_2OAlMe_3$] (**2a**), which has a high solubility, showed one broad resonance with a chemical shift that is independent of the temperature and showed the expected broadening with decreasing temperature. The background signal measured at both 253 and 293 K was in this case negligible compared to the signal from **2a** itself. However, for less soluble [$Me_2AlOCH(Me)\text{-}2\text{-}C_5H_4N]_2$ (**3d**) and [$i\text{-}Bu_2AlOCH_2\text{-}2\text{-}C_5H_4N]_2$ the $\delta(^{27}Al)$ could only be determined with reasonable precision at 353 K. At 253 K the background signal overwhelmed the ^{27}Al resonances from the organoaluminum compounds to such an extent that reliable $\delta(^{27}Al)$ values could not be obtained; see the deposited ^{27}Al NMR spectra of these compounds.

The observed chemical shifts for all three compounds are in line with the geometries about the aluminum centers as established by ^{1}H and ^{13}C NMR spectroscopy: i.e., the $\delta(^{27}Al)$ of about 160 for **2a** is in the region for four-coordinate Al centers[31,32] while for **3d** and [$i\text{-}Bu_2AlOCH_2\text{-}2\text{-}C_5H_4N]_2$ the $\delta(^{27}Al)$ of about 110 is in the range for five-coordinate aluminum.

However, it must be noted that as a consequence of the broad signals these 65.14-MHz ^{27}Al NMR spectra do not provide information concerning the facts that (i) in compound **2a** both Al centers are different and (ii) **3d** exists in solution as a mixture of enantiomeric pairs of two diastereomers. Furthermore, whereas ^{1}H and ^{13}C NMR spectra of **3d** and of [$i\text{-}Bu_2AlOCH_2\text{-}2\text{-}C_5H_4N]_2$ have revealed that an equilibrium between a five- and a four-coordinate dimeric diorganoaluminum species exists, involving an on–off movement of the pyridyl nitrogen atoms,[5] 65.14-MHz ^{27}Al NMR spectra do not show evidence for such dynamics. The study of [$i\text{-}Bu_2AlOCH_2\text{-}2\text{-}C_5H_4N]_2$ was a reinvestigation of earlier 65.14-MHz ^{27}Al NMR work on this compound (cf. also ref 32 for a 104.2-MHz ^{27}Al NMR spectrum of related [$Et_2AlOCH_2\text{-}2\text{-}C_5H_4N]_2$, which is even less soluble). The problems and limitations outlined above clearly hamper the study of the dynamic behavior of these types of diorganoaluminum compound in solution by 65.14-MHz ^{27}Al NMR spectroscopy.

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Registry No. **1b**, 101859-60-3; **1c**, 101859-61-4; **2a**, 101859-64-7; **2b**, 108120-14-5; **2c**, 101859-62-5; **2d**, 101859-63-6; **2e**, 108120-15-6; **2f**, 108120-16-7; **2g**, 108120-17-8; **3a**, 108120-18-9; **3b**, 108120-30-5; **3c**, 108120-19-0; **3d**, 108120-20-3; **3e**, 108120-21-4; **3f**, 108120-22-5; **3g**, 108120-23-6; **3h**, 108120-24-7; **3i**, 108120-26-9; **3j**, 108148-09-0; **4a**, 108120-27-0; **4b**, 108148-10-3; **4c**, 108120-28-1; **4d**, 108120-25-8; *t*-BuN=CHC(Ph)=O, 91850-96-3; (±)-NC_5H_4-2-$CH(CH_3)OH$, 20988-55-0; NC_5H_4-2-$CH(C_2H_5)OH$, 3616-83-9; NC_5H_4-2-$CH(i\text{-}C_3H_7)OH$, 102439-95-2; NC_5H_4-2-$CH(t\text{-}C_4H_9)OH$, 20609-11-4; (*R*)-NC_5H_4-2-$CH(CH_3)OH$, 27911-63-3; $(AlMe_3)_2$, 75-24-1; MeN=C(Ph)C(Ph)=O, 53601-37-9; *t*-BuN=CHC(Me)=O, 67122-50-3; $AlBu\text{-}i_3$, 100-99-2; $AlPh_3$, 841-76-9; $(i\text{-}Bu)_2AlH$, 1191-15-7; $AlEt_3$, 97-93-8; ^{27}Al, 7429-90-5; phenylglyoxal, 1074-12-0; *tert*-butylamine, 75-64-9; 2-pyridinecarboxaldehyde, 1121-60-4; (*R*)-1-(2-pyridyl)ethanol dibenzoyl-L-(+)-tartrate, 108120-29-2; 2-acetylpyridine, 1122-62-9; 2-benzoylpyridine, 91-02-1.

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