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Dinuclear Five-Coordinate Diorgano[(2-pyridyl)methoxy]aluminum Compounds. Dynamic Behavior in Solution (^{1}H, ^{13}C, and ^{27}Al NMR) and Molecular Geometry of $[i\text{-}Bu_2AlOCH_2\text{-}2\text{-}C_5H_4N]_2$ (X-ray)

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The reaction of organoaluminum compounds $R_{3-n}AlX_n$ (n = 0, 1; R = Me, Et, i-Pr, i-Bu, benzyl; X = Cl) with 2-pyridylmethanol yields quantitatively RH and dimeric $[R_{2-n}X_nAlOCH_2\text{-}2\text{-}C_5H_4N]_2$. An X-ray structure determination for R = i-Bu and n = 0 (IV) has established the dimeric structure which contains two five-coordinate Al atoms. Each metal center has two R groups and a N,O chelate bonded 2-pyridylmethanolate monoanionic ligand whose O atom also coordinates to the second metal center leading to formation of a planar four-membered Al_2O_2 ring. Crystals of $[i\text{-}Bu_2AlOCH_2\text{-}2\text{-}C_5H_4N]_2$ are triclinic of space group $P\bar{1}$ and cell constants a = 9.942 (1) Å, b = 10.0987 (7) Å, c = 10.150 (1) Å, α = 57.28 (1)°, β = 71.77 (1)°, γ = 67.75 (1)°, and Z = 1. The structure was refined to a final R = 0.0583 with 1104 observed reflections. The structure of the complexes in solution at low temperatures, as determined by ^{1}H and ^{13}C NMR spectroscopy, is compatible with the structural features found for IV in the solid. Furthermore, an equilibrium between a five- (at low temperature) and a four-coordinate species (above 25 °C) could be established involving an Al–N bond dissociation–association process with retention of the dinuclear Al structure via the Al_2O_2 bridge. Interestingly the existence of this equilibrium could also be established with ^{27}Al NMR; e.g., $\delta(^{27}Al)$ for IV 33 (−60 °C, five-coordinate) and 100 ppm (+80 °C, four-coordinate); see Conclusions.

Introduction

In recent years we have had considerable interest in organometallic and inorganic complexes containing the 1,4-diaza-1,3-butadiene ligand R-DAB.[1] The main theme is the study of the influence of the nature of the R-DAB ligand used on the bonding as well as the reactivity properties of the R-DAB–metal complexes. From these studies information concerning the extent of activation of the heterobutadiene molecule itself as a result of the interplay with the metal center(s) is also emerging. Application of this knowledge for the selective conversion of the R-DAB skeleton to 1,2-diaminoethane or 1-amino-2-iminoethane molecules has been successful.[2] Recently this aspect has also been studied for related heterobutadienes containing a N and a O atom in the α-position.[3] For example the 1/1 reaction of Et_2Zn with ($tert$-butylimino)propanone ($t\text{-}BuN{=}C(H)C(Me){=}O$) leads to quantitative formation of dinuclear $[EtZn(Et)(t\text{-}Bu)NC(H){=}C(Me)O]_2$ (which upon hydrolysis gives ($tert$-butylethylamino)propanone) while the reaction with $(Me_3Al)_2$ produces $MeAl(t\text{-}Bu)N{=}C(H)C(Me_2)O{\rightarrow}AlMe_3$. As part of this study it appeared necessary to get more information about the bonding present in the organoaluminum complexes $[R_1R_2AlOCH_2\text{-}2\text{-}C_5H_4N]_2$ formed before hydrolysis.

Dimeric compounds of this general type, having various monoanionic bidentate ligands, have been the subject of several investigations. As early as 1967 the structure and chemistry of $[R_2AlOC_2H_4NMe_2]_2$ had been investigated.[4] Hurley et al. proposed structures having four-coordinate aluminum centers in a four-membered aluminum–oxygen ring and uncoordinated dimethylamino groups. However, no suitable low-temperature NMR spectra were recorded and no crystal structure determinations were reported. Mononuclear diorganoaluminum nitrogen derivatives with a chelated four-coordinate Al center have only been investigated in recent years with $Me_2Al(Ph)N{=}C(Me)C(Me_2)NPh$ being the first reported example.[5] Then Beachley et al. published studies concerning the chemistry and structural aspects of various compounds of this type.[6] It appeared that several factors such as chelate ring size and base strengths of the potential donor sites as well as steric effects have a distinct influence on the coordination about Al and the degree of association of aluminum oxygen and nitrogen derivatives.[7-9] Equilibria (see eq 1) between

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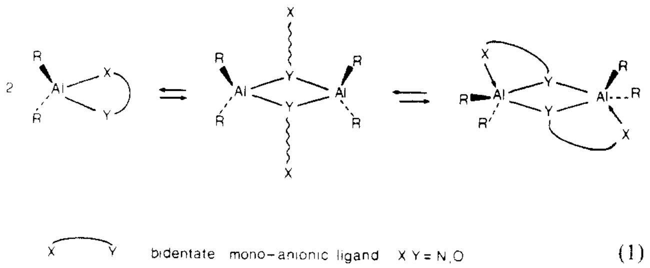

(1)

monomeric chelates and dimeric species have been proposed. There is also some evidence that in such dimeric species the nonbridging heteroatoms might be interacting weakly with the central aluminum atoms to form five-coordinate aluminum centers (vide infra and ref 19b).

In this paper we report the results of a study designed to elucidate relationships and differences between the solid-state and solution structures of $[R_1R_2\overline{AlOCH_2\text{-}2\text{-}C_5H_4N}]_2$ compounds. Special attention has been paid to detection of dynamics of the aluminum compounds not only with ^1H and ^{13}C NMR but also with ^{27}Al NMR spectroscopy.

Experimental Section

All reactions were carried out under dry oxygen-free nitrogen. Solvents were carefully dried and distilled before use. The R_3Al compounds with R is Me, Et, or *i*-Bu as well as Et_2AlCl are commercially available (Alfa Products) while the R_3Al compounds with *R* = *i*-Pr and benzyl were synthesized and purified according to published methods.[10] 2-Pyridylmethanol is commercially available (Merck) and was distilled before use ("Kugelrohr" distillation, 150 °C (1 mmHg)).

Hydrogen-1 NMR spectra were recorded on a Bruker WM 250, Varian T 60, Varian A 60, or Varian XL 100 NMR spectrometer, ^{13}C NMR spectra on Bruker WP 80 and Varian CFT 20 NMR spectrometers (off-resonance ^{13}C spectra were recorded for all compounds to aid assignments), and ^{27}Al NMR spectra on a Bruker WM 250 spectrometer. Mass spectra were obtained with a Varian Mat 711 mass spectrometer, applying field desorption technique. Cryoscopic molecular weight determinations in benzene of various organoaluminum compounds were carried out under dry oxygen-free nitrogen in a homemade apparatus (accuracy for molecular weight of about 500 is ±5%). Elemental analyses were carried out by the Analytical Section of the Institute for Applied Chemistry, TNO Utrecht, The Netherlands.

The course of the reactions leading to the organoaluminum compounds I–VI appeared to be independent of the solvent used; i.e., the same products were obtained irrespective of whether toluene, THF, pyridine, or diethyl ether was used. Correct elemental analytical and molecular weight data were obtained (see supplementary material, Tables SII and SIII) while the ^1H, ^{13}C, and ^{27}Al NMR spectroscopic data are summarized in Tables IV–VI.

Preparation of $[R_{2-n}X_n\overline{AlOCH_2\text{-}2\text{-}C_5H_4N}]_2$ (I–VI). As a typical example the synthesis of $[Et_2AlL]_2$ (II) [L = bidentate bonded 2-pyridylmethanolate] is described. A hexane solution of Et_3Al (12 mmol, 2 M solution) was slowly added to 2-pyridylmethanol (15 mmol) in 100 mL of diethyl ether at −60 °C. After the ethane evolution had ceased, the solution was warmed up to room temperature in 1 h and then stirred for a further 3 h. The solvent was evaporated in vacuo at ambient temperature to dryness. The resulting white product was washed three times with 50 mL of hexane and then recrystallized from a dichloromethane/hexane mixture (1/4) at −80 °C; yield 2.0 g, 92%. All reactions proceeded readily at ambient temperature except those involving $(benzyl)_3Al$ and Et_2AlCl. In the latter two cases, it was necessary to reflux the ether solutions for 3 h in order to obtain complete reaction.

Table I. Crystal Data and Details of the Structure Analysis of $[i\text{-}Bu_2\overline{AlOCH_2\text{-}2\text{-}C_5H_4N}]_2$

(a) Crystal Data	
formula	$(C_{14}H_{24}AlNO)_2$
M_r	498.7
crystal system	triclinic
space group	No. 2, $P\bar{1}$
a, Å	9.942 (1)
b, Å	10.0987 (7)
c, Å	10.150 (1)
α, deg	57.28 (1)
β, deg	71.77 (1)
γ, deg	67.75 (1)
V, Å^3	785.8 (2)
Z	1
D(calcd), g cm^{-3}	1.054
F(000), electrons	272
μ(Mo Kα), cm^{-1}	0.83

(b) Data Collection (294 K)	
radiation, Å	Mo Kα (Zr filtered), 0.71069
θ_{min}, θ_{max}, deg	2.2, 20.0
ω scan, deg	$\Delta\omega = 1.00 + 0.35 \tan \theta$
horizontal and vertical apert, mm	$1.30 + 0.70 \tan \theta$, 3.0
ref reflctns (std dev)	010 (0.5%), 112 (0.9%)
data set	$\pm h, \pm k, +l$ ($l = 0$; $h \geq 0$)
total scanned reflctns (including ref reflctns and ψ scan)	1629
total unique reflections	1462
obsd data ($I > 2.5\sigma(I)$)	1107
crystal size, mm	0.125 × 0.125 × 0.750

(c) Refinement	
No. of reflctns	1101
no. of parameters	168
final $R_F = \sum\lvert\Delta F\rvert/\sum\lvert F_o\rvert$	0.0583
final $R_{wF} = (\sum w\lvert\Delta F\rvert^2/\sum w\lvert F_o\rvert^2)^{1/2}$	0.0575
weight	1
maximum shift/error	0.3 [*z* of C(13)]
S	0.65

Data Collection, Structure Determination, and Refinement. Crystal data and other numerical details of the structure determination are listed in Table I. A preliminary examination with a Weissenberg photograph indicated that only limited resolution data were obtainable at room temperature. Data were collected on an Enraf-Nonius CAD4F diffractometer for an opaque, white crystal that was mounted in a Lindemann glass capillary. Unit cell parameters were derived by least-squares procedures from the angular settings of 36 reflections. The intensities of two reference reflections showed a small decay of 1% over the 26 h of X-ray exposure time and fluctuations less than 2%. The data were corrected for Lorentz and polarization effects as well as for the small decay, but not for absorption. The latter was judged to be unnecessary in view of the constancy of the psi scan for $0\bar{1}0$.

The structure was solved by Patterson and Fourier methods and refined with full-matrix least-squares techniques minimizing $\sum w|\Delta F|^2$. A scale factor and the atomic coordinates of the nonhydrogen atoms with their anisotropic thermal parameters were refined. The hydrogen atoms were introduced at calculated positions and refined in the riding mode on their carrier atoms. The four methyl groups of the two independent *iso*-butyl moieties were treated as rigid groups. In addition, two isotropic temperature parameters were refined: one for the hydrogen atoms of the 2-pyridylmethanolate ligand and one for the *iso*-butyl groups. Six low order reflections, suspected from extinction, were excluded from the final cycles of the refinement. Scattering factors from Cromer and Mann corrected for anomalous dispersion were used.[11,12] The values for hydrogen were taken from Stewart et

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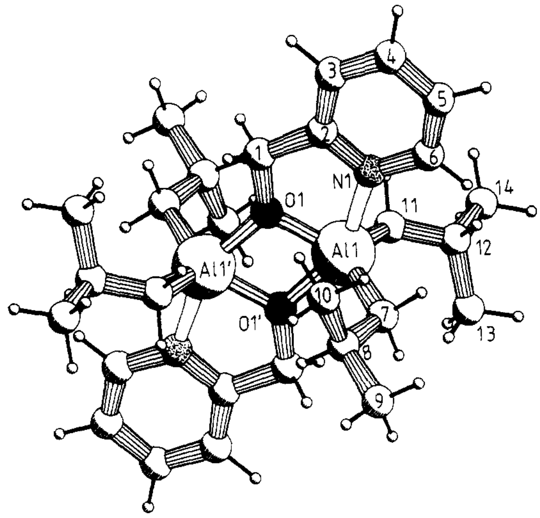
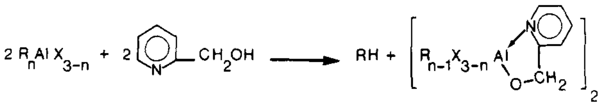


Figure 1. PLUTO drawing of the dimer $[i\text{-Bu}_2\overline{\text{AlOCH}_2\text{-2-C}_5\text{H}_4\text{N}}]_2$. The adopted numbering scheme is indicated. Oxygen atoms are represented with a black sphere and nitrogen atoms with dotted spheres.

al.[13] The calculations were carried out on either an in-house DG-Eclipse S/230 minicomputer using the programs of the ILIAS package [an adaptation and extention by A. L. Spek of the SHELX 76 package][14] or the CDC-CYBER 175 of the University of Utrecht with programs of the EUCLID package (calculation of geometrical data and preparation of illustrations including an extended version of the program PLUTO).[15]

Results and Discussion

Syntheses. The 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 the bidentate Lewis base $C_5H_4N\text{-2-}CH_2OH$ (2-pyridylmethanol), containing an "acidic" hydrogen, results in the quantitative formation of an alkane or arene and an alkoxyaluminum compound containing an aluminum–heteroatom bond according to eq 2.



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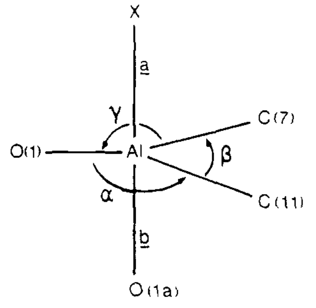
I–VI

I, R = Me, n = 3; II, R = Et, n = 3; III, R = i-Pr, n = 3; IV, R = i-Bu, n = 3; V, R = benzyl, n = 3; VI, R = Et, X = Cl, n = 2

Elemental analyses (see supplementary material) of I–VI confirmed the stoichiometry of the compounds which according to cryoscopic molecular weight determinations are dimeric in benzene solution. Both the apparent molecular weights (see supplementary material) and the NMR spectra were concentration independent in the range 3 × 10^{-3}–10^{-1} M. The different NMR patterns at various temperatures point to a dynamic behavior of these dimers in solution (vide infra). Unambiguous proof for the dimeric structure and the five-coordination of the aluminum atoms in the diorganoaluminum 2-pyridylmethanolate compounds in the solid state comes from the X-ray structure determination of $[i\text{-Bu}_2\overline{\text{AlOCH}_2\text{-2-C}_5\text{H}_4\text{N}}]_2$ (IV).

Table II. Positional Parameters for Non-Hydrogen Atoms and Their Estimated Standard Deviations for $[i\text{-Bu}_2\overline{\text{AlOCH}_2\text{-2-C}_5\text{H}_4\text{N}}]_2$

atom	x/a	y/b	z/c
Al(1)	0.9759 (2)	0.0145 (2)	0.8524 (2)
O(1)	1.0596 (4)	0.1003 (4)	0.9190 (4)
N(1)	1.0708 (5)	0.1842 (5)	0.6347 (5)
C(1)	1.1328 (7)	0.2230 (7)	0.8181 (7)
C(2)	1.1377 (6)	0.2672 (7)	0.6502 (7)
C(3)	1.2031 (6)	0.3826 (7)	0.5231 (8)
C(4)	1.2043 (7)	0.4141 (8)	0.3730 (8)
C(5)	1.1354 (8)	0.3295 (8)	0.3563 (8)
C(6)	1.0704 (7)	0.2177 (8)	0.4870 (8)
C(7)	1.0736 (7)	−0.1761 (7)	0.8166 (7)
C(8)	1.2174 (8)	−0.2865 (8)	0.8769 (9)
C(9)	1.264 (1)	−0.4431 (9)	0.864 (1)
C(10)	1.3387 (8)	−0.206 (1)	0.798 (1)
C(11)	0.7682 (7)	0.1374 (8)	0.8068 (8)
C(12)	0.6973 (8)	0.118 (1)	0.719 (1)
C(13)	0.661 (1)	−0.042 (1)	0.805 (1)
C(14)	0.558 (1)	0.248 (1)	0.668 (1)



$[\text{Me}_2\overline{\text{AlOC(Ph)N(Ph)CH(Me)O}}]_2$ (19a)

X=O

a	Al-X	2.045(7)	∠X-Al-O(1A)	158.3(3)
b	Al-O(1A)	1.985(6)	Σα,β,γ	359.9
	Al-O(1)	1.858(6)		
	Al-C(7)	1.965(13)		
	Al-C(11)	1.962(12)		
	Σ a,b	4.030		

$[\text{Me}_2\overline{\text{AlOC}_2\text{H}_4\text{O}}\text{Me}]_2$ (19b)

X=O

a	Al-X	2.269(3)	∠X-Al-O(1A)	151.9
b	Al-O(1A)	1.892(3)	Σα,β,γ	358.4
	Al-O(1)	1.827(3)		
	Al-C(7)	1.940(5)		
	Al-C(11)	1.962(5)		
	Σ a,b	4.161		

$[i\text{-Bu}_2\overline{\text{AlOCH}_2\text{-2-C}_5\text{H}_4\text{N}}]_2$ (Present work, IV)

X=N

a	Al-X	2.130(5)	∠X-Al-O(1A)	151.7(2)
b	Al-O(1A)	1.935(5)	Σα,β,γ	360.0
	Al-O(1)	1.853(5)		
	Al-C(7)	1.974(6)		
	Al-C(11)	2.014(6)		
	Σ a,b	4.065		

Figure 2. The coordination geometry around the aluminum atoms, bond distances (Å), and bond angles (deg) in the known five-coordinate diorganoaluminum compounds.

Molecular Geometry of Dimeric $[i\text{-Bu}_2\overline{\text{AlOCH}_2\text{-2-C}_5\text{H}_4\text{N}}]_2$ (IV).

Figure 1 gives a PLUTO view of the dimer. Positional parameters and bond lengths and angles with their esd's are listed in Tables II and III.

The basic structural unit of this complex is the $[i\text{-Bu}_2\overline{\text{AlOCH}_2\text{-2-C}_5\text{H}_4\text{N}}]_2$ dimer. Each molecule of the complex contains a central four-membered Al_2O_2 ring linking via donative O interactions two monomeric units in such a way that the dimer possesses a center of symmetry. Thus, each Al center is bonded covalently to two i-Bu

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Table III. Bond Distances and Bond Angles for the Non-Hydrogen Atoms[a]

(a) Bond Distances (Å)

Al(1)-Al(1′)	3.024 (4)	N(1)-C(6)	1.35 (1)	C(7)-C(8)	1.50 (1)
Al(1)-N(1)	2.130 (5)	N(1)-C(2)	1.341 (8)	C(8)-C(10)	1.48 (1)
Al(1)-O(1)	1.853 (5)	C(1)-C(2)	1.50 (1)	C(8)-C(9)	1.54 (1)
Al(1)-O(1′)	1.935 (5)	C(2)-C(3)	1.367 (9)	C(11)-C(12)	1.42 (2)
Al(1)-C(7)	1.974 (7)	C(3)-C(4)	1.38 (1)	C(12)-C(13)	1.49 (1)
Al(1)-C(11)	2.014 (7)	C(4)-C(5)	1.38 (1)	C(12)-C(14)	1.50 (1)
O(1)-C(1)	1.400 (7)	C(5)-C(6)	1.36 (1)		

(b) Bond Angles (deg)

O(1)-Al(1)-N(1)	77.7 (2)	Al(1)-O(1)-C(1)	124.7 (4)	C(4)-C(5)-C(6)	119.7 (9)
O(1′)-Al(1)-N(1)	151.7 (2)	Al(1′)-O(1)-C(1)	129.4 (4)	N(1)-C(6)-C(5)	122.6 (7)
N(1)-Al(1)-C(7)	96.2 (3)	Al(1)-N(1)-C(2)	114.4 (5)	Al(1)-C(7)-C(8)	119.6 (6)
N(1)-Al(1)-C(11)	94.2 (3)	Al(1)-N(1)-C(6)	128.1 (4)	C(7)-C(8)-C(10)	113.3 (6)
O(1)-Al(1)-O(1′)	74.1 (2)	C(2)-N(1)-C(6)	117.5 (5)	C(9)-C(8)-C(10)	109.3 (7)
O(1)-Al(1)-C(7)	126.1 (2)	O(1)-C(1)-C(2)	109.1 (5)	C(7)-C(8)-C(9)	112.2 (8)
O(1)-Al(1)-C(11)	114.8 (3)	C(1)-C(2)-C(3)	123.4 (7)	Al(1)-C(11)-C(12)	123.4 (6)
O(1′)-Al(1)-C(7)	98.5 (3)	N(1)-C(2)-C(1)	114.0 (5)	C(13)-C(12)-C(14)	107.4 (8)
O(1′)-Al(1)-C(11)	99.5 (3)	N(1)-C(2)-C(3)	122.5 (8)	C(11)-C(12)-C(13)	113 (1)
C(7)-Al(1)-C(11)	119.1 (3)	C(2)-C(3)-C(4)	119.6 (7)	C(11)-C(12)-C(14)	113.3 (9)
Al(1)-O(1)-Al(1′)	105.9 (2)	C(3)-C(4)-C(5)	118.1 (7)		

[a] The prime indicates the symmetry operation $2 - x, -y, 2 - z$.

groups and two O atoms (the second interaction being donative) and by a donative bond involving the pyridine N atoms, resulting in formation of two five-membered Al-NCCO rings.

An important structural feature is the observation that both aluminum atoms are five-coordinate and have a distorted trigonal-bipyramidal geometry; see Figure 2.

Both *i*-Bu C atoms and the covalently bonded O(1) atom of the chelate ligand lie in the equatorial plane with bond distances to Al of 1.974 (6), 2.014 (6), and 1.853 (5) Å, respectively. All the bond angles involving Al in this plane are close to 120° [114.8 (3)–126.1 (2)°], and the sum [360.0 (4)°] is that to be expected for this geometry. The apical positions of this array are occupied by an oxygen and a nitrogen atom [Al(1)–O(1′) = 1.935 (5) Å; Al(1)–N(1) = 2.130 (5) Å] of two different chelating ligands with a bond angle of N(1)–Al(1)–O(1′) = 151.7 (2)°. The angles these N(1)–Al(1) and O(1′)–Al(1) bonds make with the least-squares plane through the equatorial atoms amount to 78.4 (2) and 73.2 (2)°, respectively. The large deviations from the ideal 90° for the apical ligands arise from the constrains brought about by both the specific angles in the chelating bidentate monoanionic ligand as well as in the acute O(1)–Al(1)–O(1′) angle of 74.1 (2)° in the $(\mu\text{-oxo})_2Al_2$ ring.

The Al–O distance of the apical location is significantly longer [1.935 (5) Å] than the equatorial one [1.853 (3) Å][16] though it is still considerably shorter than the value of 2.017 (2) Å found in the trigonal-bipyramidal complex of the *catena*-trichloro(μ-1,4-dioxane-*O*,*O*′)aluminum(III) 1,4-dioxolane solvate. In this latter species the lengthening of the Al–O bond appears to be a consequence of the oxygen-bridged polymeric structure.[17] Although five-coordination in diorganoaluminum complexes has been proposed frequently to explain their reactivity and dynamic behavior in solution,[4–7] only two other crystal structure determinations showing the occurrence of this coordination in the solid state have been reported.[19] The geometries about Al in these known, five-coordinate diorganoaluminum compounds are fairly similar and are summarized in Figure 2. In all three structures two carbon atoms and one oxygen atom lie in the equatorial plane at comparable distances. In the two previously reported complexes the heteroatoms in the apical positions are both oxygen ligands. The complex of the present study, however, is the first one in which one oxygen and one nitrogen atom occupy the apical positions.

Here, the apical Al–N dative bond length (2.130 (5) Å) is significantly larger than those reported for other Al–N bonds (1.90–2.02 Å).[21] This is in line with the fact that the second apical ligand is an oxygen group which has a somewhat higher apicophilicity than nitrogen.[24] Furthermore it appears that a shorter Al–O bond length (cf. *a* and *b* in the two other derivatives at a nearly constant O–Al–X bond angle; see Figure 2) causes a larger Al–N bond length. This observation is in line with the results of several studies of structural distorsions of five-coordination of main-group and transition elements[25a–c] and with the elegant analysis by Dunitz and Britton of the relation between the sum of the bond lengths to apical ligands and their individual values in trigonal-bipyramidal arrays of triorganotin X complexes R_3SnXL.[25d] Five-coordination in the latter compounds is viewed as the intermediate stage in a S_N2-like process in which a fifth, neutral, ligand attacks the Sn center and X is the leaving group (cf. extensive studies of five-coordinate triorganotin compounds by van Koten et al.).[18] Most interestingly this view seems

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Table IV. ^{1}H NMR Data[a] for $[R_1R_2AlOCH_2\text{-}2\text{-}C_5H_4N]_2$

compd	*T*, °C	R_1R_2	CH_2O	H_3 (d)	H_4 (m), H_5 (m)	H_6 (d)
I[b]	25	$R_1 = R_2$ = Me: 0.09 (s)	5.15 (s)	7.10	7.50, 7.70	8.65
II[c]	-53	$R_1 = R_2$ = Et: 0.76 (m), 1.74 (t, *J* = 8 Hz)	5.05 (s)	6.14	6.53, 6.81	8.40
	0	0.60 (q/d, *J* = 3 Hz), 1.61 (t, *J* = 8 Hz)	5.07 (s)	6.30	6.62, 6.98	8.43
	+30	0.52 (q/d, *J* = 1 Hz), 1.53 (t, *J* = 8 Hz)	5.08 (s)	6.48	6.71, 7.05	8.45
	+60	0.42 (q), 1.43 t, *J* = 8 Hz)	5.09 (s)	6.67	6.82, 7.17	8.49
III[c]	-60	$R_1 = R_2$ = *i*-Pr: 1.12 (m), 1.73 (d)/1.80 (d)	5.19 (a)	6.15	6.48, 6.82	8.38
	-30	1.04 (m), 1.64 (d)/1.72 (d)	5.18 (s)	6.29	6.57, 6.92	8.42
	0	0.91 (m), 1.57 (d)/1.65 (d)	5.20 (s)	6.42	6.65, 7.01	8.46
	+30	0.93 (m), 1.56 (d/d)	5.21 (s)	6.51	6.71, 7.09	8.49
	+60	0.91 (sept), 1.53 (d, *J* = 7.5 Hz)	5.19 (s)	6.59	6.72, 7.10	8.48
IV[c]	-80	$R_1 = R_2$ = *i*-Bu: 0.77 (d/d/d), 1.54 (d)/1.75 (d), 2.48 (m)	5.21 (s)	6.07	6.49, 6.73	8.47
	-10	0.60 (d/d/d), 1.38 (d)/1.52 (d), 2.29 (m)	5.21 (s)	6.40	6.68, 6.98	8.51
	+25	0.58 (d/d), 1.25 (d)/1.35 (d), 2.28 (m)	5.20 (s)	6.50	6.70, 7.00	8.56
	+40	0.54 (d/d), 1.36 (d/d br), 2.25 (m)	5.20 (s)	6.54	6.76, 7.08	8.57
	+70	0.40 (d), 1.28 (d), 2.18 (sept/d)	5.21 (s)	6.80	7.00, 7.30	8.70
IV[b]	-20	0.31 (d/d/d), 1.13 (d)/1.27 (d), 2.10 (m)	5.20 (s)	7.27	7.55, 7.70	8.60
	+25	0.28 (d), 1.04 (d), 2.02 (m)	5.18 (s)	7.36	7.56, 7.75	8.68
V[e]	-30	$R_1 = R_2$ = benzyl: 1.50 (d/d), 7.3 (m)	5.40 (s)	7.3 (m)	7.8 (m)	8.53
	+25	1.59 (s), 7.3 (m)	5.38 (s)	7.3 (m)	7.8 (m)	8.59
VI[e] A	-30	R_1 = Cl,R_2 = Et: cis, -0.08 (m), 0.76 (t)	5.16 (dd, AX)	7.41	7.51, 7.97	8.63
B		trans, -0.08 (m), 0.86 (t)	5.06 (dd, AB)	7.41	7.51, 7.97	8.63
A	+40	cis, 0.05 (m), 0.87 (t)	5.11 (dd, AX)	7.49	7.54, 8.00	8.72
B		trans, 0.05 (m), 0.95 (t)	5.14 (dd, AB)	7.49	7.54, 8.00	8.72

[a] All values are in ppm relative to internal Me_4Si: s = singlet, d = doublet, t = triplet, q = quartet, sept = septet, m = multiplet. [b] In C_5D_5N. [c] In C_7D_8. [d] In CD_2Cl_2.

Table V. ^{13}C NMR Data[a] for $[R_1R_2AlOCH_2\text{-}2\text{-}C_5H_4N]_2$

compd	*T*, °C	R_1R_2	CH_2O	C_2	C_3	C_4	C_5	C_6
II[b]	30	$R_1 = R_2$ = Et: 2.07 (br), 10.08	62.82	159.37	119.87	138.13	122.66	145.29
IV[b]	-30	$R_1 = R_2$ = *i*-Bu: 24.83 (br), 26.83, 28.17/29.08	62.64	158.77	120.23	138.25	122.84	145.29
	0	24.71 (br), 26.77, 28.11/28.90	62.64	158.95	120.11	138.13	122.66	145.41
	+20	24.65 (br), 26.71, 28.11/28.78	62.64	159.13	120.05	138.07	122.60	145.48
	+27	24.59 (br), 26.65, 28.41 (br)	62.64	159.13	119.99	138.01	122.54	145.48
	+35	24.59 (br), 26.65, 28.41	62.64	159.07	119.99	138.01	122.54	145.48
IV[c]	+20	25.47 (br), 27.35, 29.05	63.16	159.28	120.87	139.01	123.36	145.75

[a] All values are in ppm relative to internal Me_4Si. Multiplicity, obtained from off-resonance spectra, is in agreement with the proposed assignments. [b] In $CDCl_3$. [c] In C_5D_5N.

also to apply to the five-coordinate Al compounds shown in Figure 2. Whereas in $[Me_2AlOC_2H_4OMe]_2$ the Al–X distance is longer than that in IV, the trend in the opposite Al–apical distances is reversed resulting in an almost constant sum *a* + *b*. Therefore it can be anticipated that dissociation of the Al–N bond, resulting in four-coordinate Al centers, will cause strengthening of the Al–O(1′) bonding, i.e., on dissociation the dinuclear structure becomes stabilized.

In the present complex the Al_2O_2 ring, which forms the double bridge, is planar, with an Al···Al interatomic distance of 3.024 (4) Å and two different Al–O distances (1.853 (5) and 1.935 (5) Å). The dialuminooxane ring is also found in $[Me_2AlO{\cdot}AlMe_3]_2^{2-}$ but here with almost equal Al–O distances (1.78–1.80 Å).[20] An interesting feature of the structure is the coplanarity of this Al_2O_2 ring with the plane of the chelating 2-pyridylmethoxy ligands and as a consequence the pyridyl ring also. Since the two halves of the dimer are related by an inversion operation, the basic molecular frame is completely flat (vide infra).

Dynamic Behavior in Solution. The ^{1}H, ^{13}C, and ^{27}Al NMR spectra (in CD_2Cl_2, $CDCl_3$, benzene-d_6, toluene-d_8, or pyridine-d_5) of most of the $[R_{2-n}X_nAlOCH_2\text{-}2\text{-}C_5H_4N]_2$ compounds are temperature dependent in the range −70 to +90 °C. At the lower temperatures the spectra point to a molecular geometry similar to that found for $[i\text{-}Bu_2AlL]_2$ (IV), i.e., five-coordination at Al through Al–N coordination. All R groups in $[R_2AlL]_2$ are isochronous, and this is consistent with the presence of a plane of symmetry through the 18 atoms of the main molecular frame [Al(1), O(1), N(1), C(1)–C(6), Al(1′), etc]. The five-coordination around the aluminum is apparent in both the ^{1}H and the ^{13}C NMR spectra of the compounds II–V containing prochiral centers in the organo groups R bound to Al. For example the methylene protons next to aluminum in $[\{(CH_3)_2CHCH_2\}_2AlL]_2$ (IV) (see Table IV) are diastereotopic (−80 to −10 °C) giving rise to one eight-line ABX ^{1}H NMR spectrum, while the CH_3 protons, in the same compound, are likewise diastereotopic and appear as two doublets. The presence of the aluminum atom in the molecular symmetry plane renders the *i*-Bu groups enantiotopic (and they are isochronous). The ^{13}C NMR spectrum (see Table V) of IV at −30 °C also reflects the diastereotopicity of the CH_3 groups in $[\{(CH_3)_2CHCH_2\}_2AlL]_2$ and shows carbon resonances at 28.17 and 29.08 ppm.

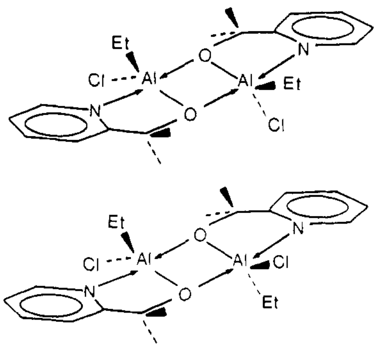

Figure 3. Cis (top) and trans (bottom) isomers of $[EtClAlOCH_2\text{-}2\text{-}C_5H_4N]_2$.

Further evidence both for five-coordination in solution of the dimeric species and, more importantly, for the

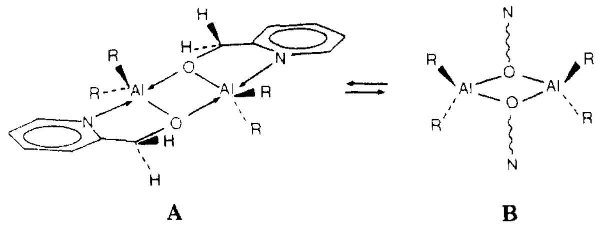

Figure 4. (A) Five-coordination in $[R_2\overline{\text{AlOCH}_2\text{-2-C}_5\text{H}_4\text{N}}]_2$: one apparent molecular symmetry plane (through the molecular frame). (B) Four-coordination in $[R_2\text{AlOCH}_2\text{-2-C}_5\text{H}_4\text{N}]_2$: two apparent molecular symmetry planes (one through the Al_2O_2 ring and one perpendicular to the Al_2O_2 ring through the Al atoms).

stability of the Al_2O_2 bridge on the NMR time scale comes from the compounds $[\text{EtClAlL}]_2$ (VIA and VIB). The dimer exists as a mixture of the cis and trans isomers (shown in Figure 3) in a 3:1 ratio. Accordingly whereas the methoxy C atoms of the 2-pyridyl-CH_2O monoanionic bidentate ligand are still residing in the Al_2O_2 plane, the Al atoms are now chiral centers and consequently the protons connected to these C atoms become diastereotopic giving rise to a four-line AB pattern for each isomer.

The isomer ratio in solution is constant over the whole temperature range investigated (−90 to +100 °C), thus indicating that the isomers are kinetically stable; i.e., these isomers are formed in a 3:1 molar ratio and subsequently do not interconvert on the NMR time scale, proving the stability of the Al_2O_2 frame. Such cis/trans isomerism has been observed for $[\text{Me}_2\text{Al}(\text{NRR}^1)]_2$[22] pointing to a lower stability for the Al_2N_2 frame as compared with the Al_2O_2 frame in VI.

All the available ^1H and ^{13}C NMR data of I–V at *lower* temperatures point to the fact that the dimeric structure as found for IV in the solid with a five-coordinate aluminum atom remains unchanged in solution. In the case of $[\text{EtClAlL}]_2$ (VIA and VIB), at +40 °C, the presence of both the cis and trans isomers and the diastereotopicity of the OCH_2 protons proves that the dimeric structure is likewise maintained. Compared with the Al centers in the other diorganoaluminum compounds (I–V) the Al center of $[\text{EtClAlL}]_2$ should be a stronger Lewis acid and therefore five-coordination should also be strongly favoured.

The diorganoaluminum compounds II–V (vide infra) show at *higher* temperatures a reversible dynamic behavior which is reflected in both the ^1H and ^{13}C NMR spectra (see Tables IV and V). In the temperature range of 25 °C [for R = CH_2Ph (V)] to 40 °C [for R = Et (II)] the diastereotopic groups become enantiotopic as a result of an Al–N bond dissociation–association process. For example isochronous signals are found in ^1H NMR spectra for the methylene protons of $[(\text{CH}_3\text{C}H_2)_2\text{AlL}]_2$ (II), $[\{(\text{CH}_3)_2\text{CH}\text{C}H_2\}_2\text{AlL}]_2$ (IV), $[(\text{PhC}H_2)_2\text{AlL}]_2$ (V) and in the ^{13}C NMR spectra for the $[\{(\text{CH}_3)_2\text{CHCH}_2\}_2\text{AlL}]_2$ (IV) C atoms. As the molecules are dimeric (see supplementary material, Table SII; FD mass for $[i\text{-Bu}_2\text{AlL}]_2$ calcd 498, found 442, parent ion minus isobutene fragment), this behavior, which renders the attached C atoms enantiotopic, indicates a second molecular plane of symmetry that is perpendicular to the Al_2O_2 plane and which passes through the Al atoms and both attached C atoms. Because of the strength of the Al–O–Al bridges (see also $[\text{EtClAlL}]_2$ (VIA and VIB)), these data have to be interpreted as four-coordinate Al dimers with nonbonded pyridyl N atoms and sp^3-hybridized Al atoms (vide supra).

Since on lowering the temperature the original five-coordinate species are reformed, the NMR data at ambient temperatures would appear to be consistent with a situation where there is an equilibrium (fast on the NMR time scale) between a five- and a four-coordinate dimeric diorganoaluminum species with an on–off movement of the pyridyl nitrogen atoms (see Figure 4).

Table VI. ^{27}**Al NMR Data**[a] **for** $[R_1R_2\text{AlOCH}_2\text{-2-C}_5\text{H}_4\text{N}]_2$

compd	T °C	δ (^{27}Al)	$w_{1/2}$
I, V, VI[e]			
II[b]	−60	44	3950
	+22	105	4880
	+80	109	2700
III[b]	−60	45	3030
	+22	90	3900
	+80	99	3380
IV[b]	−60	33	2440
	+22	90	3350
	+80	100	2800
IV[c]	−30	37	8000
	0	63	10000
	+20	91	11000
IV[d]	−35	48	2890
	+22	44	2700
	+80	43	2685

[a] Frequency of measurements 65.177 MHz; all values in ppm relative to $Al(H_2O)_6^{3+}$ external; line width at half peak height in Hz. [b] 10% solution in C_7D_8; 5-mm tubes. [c] 30% solution in CH_2Cl_2/CD_2Cl_2 (4:1); 10-mm tubes. [d] 20% solution in C_5D_5N; 5-mm tubes. [e] Insufficiently soluble to provide reliable data.

Variable-Temperature ^{27}**Al NMR.** The most direct way to look at the coordination around the metal centers is ^{27}Al NMR spectroscopy. It has been established that the observed metal chemical shift values for organometallic compounds with a high coordination number appear at higher field than those for compounds with a lower coordination number[23] and so it should be possible to distinguish four-coordination from the much discussed five-coordination. Recently Lehmkuhl et al. showed for a series of organoaluminum compounds the existence of a correlation between the coordination number and the ^{27}Al NMR chemical shift (measured at room temperature).[19b] Until now no ^{27}Al-NMR measurements have been reported for dynamic processes of organoaluminum compounds involving species with different coordination numbers for the aluminum center(s).

Our measurements on the well-defined $[R_1R_2\overline{\text{AlOCH}_2\text{-2-C}_5\text{H}_4\text{N}}]_2$ compounds (see Table VI) show a large temperature dependency[26] of the ^{27}Al chemical shifts. At low temperature, the observed values for $[R_2\text{AlL}]_2$ (−60 °C in toluene, II, 44 ppm, III, 45 ppm, and IV, 33 ppm; −30 °C in dichloromethane, IV, 37 ppm) are at considerably higher field than those found at higher temperatures (+22 °C in toluene, respectively 105, 90, 90, and 91 ppm). The shift of the resonances from 30–50 ppm to 90–110 ppm would be in accordance with the change from an average five- to a four-coordinate aluminum species and runs parallel with the ^1H and ^{13}C NMR experiments. Accordingly the results by Lehmkuhl et al. need complementation as far as the range indicated for five-coordination (110–130 ppm) is concerned. In their compounds (measured at room temperature[19c] to +100 °C) a similar dynamic process is most probably operative and the reported range is that which one should now consider typical for four-coordinate diorganoaluminum compounds and not for five-coordinate ones.

In pyridine-d_5 as the solvent the ^{27}Al chemical shift of these compounds becomes temperature independent (IV, −35 °C; 48 ppm, and +80 °C, 43 ppm), and it would appear

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[26] Because of the small value of $\Delta\delta(^{27}\text{Al})$/°C (10 ppm/100 °C), the observed large chemical shifts are caused by chemical reasons.

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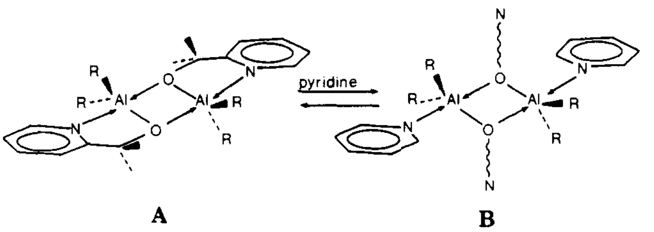

Figure 5. Five-coordination either through *intramolecular* (A) or *intermolecular* (B) pyridine *N*-to-Al coordination.

that the Al center is on the NMR time scale five-coordinate. A plausible explanation is the presence of the equilibrium shown in Figure 5.

Since in pyridine, the ^{1}H NMR spectra (see Table IV, compound IV) prove that this species is still subject to the on–off movement of the pyridyl N atom, the Al centers remain predominantly five-coordinate as a result of the Al–pyridine solvent interaction. While the (intramolecular) pyridyl N atom is leaving, a pyridine solvent molecule occupies the fifth coordination position.

Conclusions

The present results shows that care should be taken in extrapolating crystallographic information about the structure of five-coordinate diorganoaluminum compounds, both to their structure in solution and to the interpretation of the observed reactivity. Although, in the solid state, the dimeric diorganoaluminum 2-pyridylmethanolate compounds possess five-coordinate aluminum centers, in solution there is an equilibrium between the five-coordinate and a four-coordinate dimeric species via an on–off movement of the neutral pyridyl N donor site. In addition to ^{1}H and ^{13}C NMR spectroscopy, ^{27}Al NMR is shown to be extremely useful for the study of the changing coordination number at the metal center. The chemical shift values for the present series of five-coordinate (in the slow exchange limit) diorganoaluminum compounds in solution are in the range of 35–45 ppm (cf. ref 19b).

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Registry No. I, 96999-31-4; II, 96999-32-5; III, 97011-46-6; IV, 97011-47-7; V, 96999-33-6; VIA, 96999-34-7; VIB, 97059-10-4; Me_3Al, 75-24-1; Et_3Al, 97-93-8; *i*-Pr_3Al, 2397-67-3; *i*-Bu_3Al, 100-99-2; (benzyl)$_3$Al, 14994-03-7; Et_2AlCl, 96-10-6; 2-pyridylmethanol, 586-98-1.

Supplementary Material Available: Tables of positional and thermal parameters for all atoms, a list of observed and calculated structure factors, a complete list of bond lengths and bond angles (Table SI), and an ORTEP plot of [*i*-Bu_2AlOCH_2-2-$C_5H_4N]_2$, cryoscopic molecular weight determinations in benzene (Table SII), and elemental analyses (Table SIII) (13 pages). Ordering information is given on any current masthead page.

Synergistic Behavior of Homogeneous Ruthenium–Rhodium Catalysts for Hydrogenation of Carbon Monoxide

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Homogeneous solutions containing complexes of both ruthenium and rhodium are shown to exhibit good selectivity for the catalytic hydrogenation of carbon monoxide to ethylene glycol. Reactions were studied at pressures from 400 to 850 atm and temperatures from 190 to 240 °C. Iodide ion is an effective promoter for this reaction. The total activity of the bimetallic system does not depend on the amount of rhodium present, but addition of this metal affects product selectivity. Metal complexes observed in catalytic solutions are $[HRu_3(CO)_{11}]^-$, $[Ru(CO)_3I_3]^-$, and $[Rh(CO)_2I_2]^-$. A mechanism consistent with these results is presented, which involves hydride transfer from $[HRu(CO)_4]^-$ to an electrophilic carbonyl ligand on a rhodium complex. A correlation of CO stretching force constants of metal carbonyls with their reactivities toward $[HRu(CO)_4]^-$ suggests that the rhodium complex involved in this reaction is likely to contain Rh(III) and may be $[Rh(CO)_2I_4]^-$.

Introduction

The hydrogenation of carbon monoxide to oxygenates by homogeneous catalysts has been most extensively studied for complexes of cobalt, rhodium, and ruthenium.[1] These catalytic systems produce varying amounts of methanol, ethylene glycol, ethanol, and other minor products. Several recent reports have indicated that mixtures of ruthenium and rhodium complexes provide an effective bimetallic catalytic system with enhanced selectivity for ethylene glycol,[2-6] the most valuable product. We now wish to report our independent discovery[7] and studies of a ruthenium–rhodium–halide catalytic system for homogeneous CO hydrogenation. A mechanistic scheme is also presented which is consistent with the catalytic observations.

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