Synthesis and Spectroscopic Investigations of Alkylaluminum Derivatives of 2-Allyl-6-methylphenoxide and 2-Naphthoxide: Crystal Structure of $[Me_2Al(\mu\text{-2-allyl-6-methylphenoxide})]_2$

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The reaction of trialkylaluminum, R_3Al (R = Me, Et, or *i*-Bu), with phenols such as 2-allyl-6-methylphenol and 2-naphthol yields quantitatively dialkylaluminum phenoxide, R_2AlOR' (R = Me, **1a**: Et, **1b**; *i*-Bu, **1c**; OR′ = 2-allyl-6-methylphenoxide; and R = Et, **2b**; *i*-Bu, **2c**; OR′ = 2-naphthoxide) and the corresponding alkane RH. The resulting phenoxides have been characterized by ^1H and ^{13}C NMR spectroscopy. The single-crystal X-ray study of **1a** established that it crystallizes in the monoclinic cell system, space group $P2_1/n$, with cell constants $a = 9.862$ (2) Å, $b = 9.682$ (1) Å, $c = 13.417$ (2) Å, $\beta = 97.98$ (1)°, and $Z = 2$ (dimers); final $R = 5.62\%$, $R_w = 4.87\%$, based on 1021 observed reflections; $F_o \geq 2.5\sigma(F)$. The molecular unit is a dimer, bridged by two 2-allyl-6-methylphenoxide ligands, leading to the formation of a planar four-membered Al_2O_2 ring. Attempts to disrupt the Al–O bridge bonds and form stable adducts with the bases diethyl ether, tetrahydrofuran, and methyl benzoate failed, but 4-picoline gives a 1:1 complex. In solution, at low temperature, **1a** exists as two conformers that undergo rapid exchange on the NMR time scale at room temperature. The observed behavior is consistent with the rotational process in which the syn and anti conformers interconvert by rotation of the bridging phenoxide group with an activation energy of 9.7 ± 2 kcal mol^{-1}.

Introduction

Phenols react readily with alkylaluminum derivatives to give organoaluminum phenoxides.[1] The resulting aluminum alkoxides are strongly associated in solution through the bridging alkoxide oxygen and typically exist as dimers or trimers with the position of the equilibrium dependent on the substituents on both the aluminum and oxygen atoms. If the phenoxide ligand is sufficiently sterically demanding (such as 2,6-di-*tert*-butylphenoxide), then the equilibrium is shifted to monomers as in diisobutylaluminum 2,6-di-*tert*-butylphenoxide.[2,3] The monomeric species, usually prepared from 2,6-di-*tert*-butylphenol, are highly regio- and stereoselective in organic synthesis and find application in the preparation of Ziegler–Natta catalysts that display an unusual combination of high selectivity and stereospecificity in the polymerization of propene.[4,5] To further investigate the steric and electronic factors influencing the structure and reactivities of organoaluminum complexes,[6] we have studied the reaction of 2-allyl-6-methylphenol and 2-naphthol with simple aluminum alkyls. The results of these investigations are reported in this paper.

Experimental Section

General Experimental Procedures. All solvents were purified and dried by standard techniques.[7] Argon gas was purified by passing it through a series of columns containing Deox catalyst (Alfa), phosphorus pentoxide, and calcium sulfate. Aluminum alkyls (Aldrich: $AlMe_3$, 2 M solution in toluene; $AlEt_3$, 1.9 M solution in toluene; and $Al(i\text{-}Bu)_3$, 1 M solution in hexane), 2-allyl-6-methylphenol (Aldrich), and 2-naphthol (MCB) were used as received. All glassware used in the synthetic work was oven-dried. The compounds are both oxygen and water sensitive, so standard Schlenk line techinques were employed. ^1H and ^{13}C NMR spectra were recorded either on a General Electric QE-300 NMR or on a GN-300 NMR spectrometer. The chemical shifts were referenced to the residual proton line from benzene-d_6 (δ 7.15). The variable-temperature NMR spectra were obtained on toluene-d_8 solutions and were referenced to the methyl resonance of toluene (δ 2.09). Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

Reaction of $AlMe_3$ with 2-Allyl-6-methylphenol To Yield 1a. 2-Allyl-6-methylphenol (1 mL, 6.69 mmol) was dissolved in pentane (60 mL), and $AlMe_3$ (3.35 mL, 6.69 mmol) was added over 5 min. The resulting reaction was exothermic, bringing the pentane to reflux. The reaction appeared to be instantaneous, but to ensure complete reaction the solution was stirred for 2 h. the volume of the solution was reduced to half under vacuum, and then the white solid that precipitated was isolated. The product was collected, washed with 10–15 mL of very cold pentane, and dried in vacuo. The product was purified by dissolving it in the minimum amount of pentane and then recrystallizing it from this solution by cooling it to −20 °C overnight. This solid was identified from its NMR spectra as Me_2Al(2-allyl-6-methylphenoxide), yield 80%, mp 136–138 °C. Anal. Calcd for $C_{12}H_{17}AlO$: C, 70.59; H, 8.33. Found: C, 70.52; H, 7.96. NMR spectral results are presented in Tables I and II.

Reaction of $AlEt_3$ with 2-Allyl-6-methylphenol To Yield 1b. The reaction of 2-allyl-6-methylphenol (1 mL, 6.69 mmol) was dissolved in pentane (60 mL) and reacted with $AlEt_3$ (3.52 mL, 6.69 mmol) following the procedure given for **1a**. This solid was identified as Et_2Al(2-allyl-6-methylphenoxide) from its ^1H and ^{13}C NMR spectra. NMR spectral results are presented in Tables I and II; yield >90%, mp 138–141 °C.

Reaction of $Al(i\text{-}Bu)_3$ with 2-Allyl-6-methylphenol To Yield 1c. The reaction of 2-allyl-6-methylphenol (1 mL, 6.70 mmol) with $Al(i\text{-}Bu)_3$ (6.70 mL, 6.70 mmol) was carried out by using the procedure described for **1a**. This solid was identified as $(i\text{-}Bu)_2Al$(2-allyl-6-methylphenoxide). NMR spectral results are presented in Tables I and II; yield 96%, mp 120–123 °C.

Attempted Synthesis of 1:1 Addition Compounds. The synthesis of $R_2(R'O)Al{\cdot}base$ complexes was attempted by the same general procedure as described for the synthesis of **1a** up to the final workup, then 10 mL of diethyl ether was added, and the mixture was allowed to stir for 2 h. The solvent was removed

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Table I. ^1H NMR Chemical Shifts (δ) in C_6D_6

	^1H NMR chemical shifts						
	alkyl			phenoxide			
compound	α-CH	β-CH	γ-CH	Ar–H	–OH	$CH_2^a—CH^b═CH_2^c$	Ar–Me
2-allyl-6-methylphenol				6.99 (m, 3 H)	5.06 (s, 1 H)	6.10 (m, 1 H)^b, 5.27 (m, 2 H)^c, 3.49 (m, 2 H)^a	2.33 (s, 3 H)
2-naphthol				7.05 (m, 7 H)	4.25 (s, 1 H)		
Me_3Al	–0.32 (s, 9 H)						
Et_3Al	0.32 (q, 6 H)	1.10 (t, 9 H)					
$(i\text{-}Bu)_3Al$	0.24 (d, 6 H)	1.91 (m, 3 H)	0.97 (d, 18 H)				
1a	–0.40 (s, 6 H)			6.97 (m, 3 H)		5.91 (m, 1 H)^b, 5.07 (m, 2 H)^c, 3.70 (d, 2 H)^a	2.40 (s, 3 H)
1b	0.34 (q, 4 H)	1.02 (t, 6 H)		6.96 (m, 3 H)		5.95 (m, 1 H)^b, 5.13 (m, 2 H)^c, 3.74 (d, 2 H)^a	2.41 (s, 3 H)
1c	0.52 (d, 4 H)	1.90 (m, 2 H)	0.87 (br s, 12 H)	6.97 (m, 3 H)		6.01 (m, 1 H)^b, 5.16 (m, 2 H)^c, 3.80 (d, 2 H)^a	2.47 (s, 3 H)
2b	0.52 (q, 4 H)	1.35 (t, 6 H)		7.37 (m, 7 H)			
2c	0.66 (d, 4 H)	2.14 (m, 2 H)	1.06 (d, 12 H)	7.41 (m, 7 H)			

Table II. ^{13}C NMR Chemical Shifts (δ) in C_6D_6

	^{13}C NMR chemical shifts					
	alkyl			phenoxide		
compound	α-C	β-C	γ-C	Ar	$C^a—C^b═C^c$	Ar–C
2-allyl-6-methylphenol				152.9, 136.9, 129.6, 128.3, 125.2, 124.4	120.8^b, 116.2^c, 35.4^a	15.8
2-naphthol				153.9, 135.2, 130.0, 129.4, 128.1, 126.7, 123.7, 118.0, 109.9		
Me_3Al	–7.3					
Et_3Al	0.4	8.8				
$(i\text{-}Bu)_3Al$	21.4	26.3	28.3			
1a	–7.6			147.3, 136.8, 131.9, 130.3, 130.0, 129.0	124.8^b, 117.0^c, 34.30^a	18.0
1b	1.7	8.2		148.0, 136.6, 131.6, 130.2, 129.7, 128.7	124.8^b, 117.3^c, 34.0^a	17.6
1c	24.8	25.9	28.2	148.0, 136.6, 131.7, 130.4, 129.8, 128.8	124.7^b, 117.6^c, 34.8^a	18.9
2b	0.2	8.9		149.9, 134.9, 131.2, 130.7, 128.1, 127.4, 127.3, 125.3, 119.1, 114.5		
2c	23.2	26.1	28.5	149.7, 134.8, 130.8, 128.1, 127.4, 127.3, 125.4, 120.1, 115.9		

under vacuo to leave a white solid, which was purified by recrystallization from pentane as previously described. The ^1H NMR spectrum of this product was identical with that of Me_2Al(2-allyl-6-methylphenoxide). By using an analogous procedure, attempts were made to prepare the Et_2Al(2-allyl-6-methylphenoxide) adducts of Et_2O, THF, methyl benzoate, and 4-picoline. In the latter case, a white solid was obtained from the –20 °C recrystallization from pentane, which transformed into a colorless oil at room temperature. The product was identified as Et_2Al(2-allyl-6-methylphenoxide)·4-picoline by ^1H NMR spectral data: 0.35 (q, 4 H) $CH_2(AlCH_2CH_3)$; 1.26 (t, 6 H) $CH_3(AlCH_2CH_3)$; 8.19 (m, 2 H) CH (4-picoline); 6.94 (m, 3 H) ArH; 6.44 (d, 2 H) CH (4-picoline); 6.05 (m, 1 H) CH (2-allyl); 5.00 (m, 2 H) CH_2 (2-allyl); 3.48 (d, 2 H) CH_2 (2-allyl); 2.28 (s, 3 H) 6-CH_3; 1.70 (s, 3 H) 4-CH_3 (4-picoline). The ^1H NMR spectrum of authentic 4-picoline showed resonances at 8.36 (d, 2 H), 6.98 (d, 2 H), 2.23 (s, 3 H) CH_3.

Reaction of $AlMe_3$ with 2-Naphthol To Yield 2a. The reaction of 2-naphthol (1.00 g, 6.94 mmol) dissolved in toluene (60 mL) with $AlMe_3$ (3.47 mL, 6.94 mmol) was carried out using the same procedure described for **1a**. The ^1H NMR spectrum of this product showed two sets of resonances for both alkyl and naphthoxide groups, implying that there are two compounds present. The ^1H NMR spectrum of the Al–Me region indicated that these compounds were present in a 2:1 ratio. Attempts to separate them by recrystallization were unsuccessful.

Reaction of $AlEt_3$ with 2-Naphthol To Yield 2b. 2-Naphthol (4.23 g, 29.3 mmol) was suspended in pentane (50 mL), and $AlEt_3$ (15.4 mL, 29.3 mmol) added over ca. 10 min. The resulting reaction was exothermic, bringing the pentane to reflux. The reaction was allowed to stir for an additional 2 h after gas evolution stopped. The solvent was completely removed under vacuum to give a white solid. The product was recrystallized from pentane at –20 °C. The solid was identified as Et_2Al(2-naphthoxide). The ^1H and ^{13}C NMR spectral results are presented in Tables I and II; yield >90%, mp 75–77 °C. Anal. Calcd for $C_{14}H_{17}AlO$: C, 73.66; H, 7.51. Found: C, 71.03; H, 7.75.

Reaction of $Al(i\text{-}Bu)_3$ with 2-Naphthol To Yield 2c. The procedure for this reaction is the same as described above for $AlEt_3$, using 2-naphthol (4.14 g, 28.7 mmol) and $Al(i\text{-}Bu)_3$ (28.7 mL, 28.7 mmol). Recrystallization from pentane at –20 °C afforded $(i\text{-}Bu)_2Al$(2-naphthoxide). The ^1H and ^{13}C NMR spectral results are presented in Tables I and II; yield >95%, mp 66–67 °C.

X-ray Structure Determination of $[Me_2Al(2\text{-allyl-6-methylphenoxide})]_2$, 1a. Crystals of $[Me_2Al(2\text{-allyl-6-methylphenoxide})]_2$ were grown from a mixture of pentane and diethyl ether in a 3:1 ratio at –20 °C. A crystal suitable for X-ray diffraction studies was mounted in a thin-walled capillary tube in a drybox, plugged with grease, removed from the drybox, flame sealed, mounted on a goniometer head, and placed on a Nicolet R3 diffractometer for data collection. Crystal structure parameters are presented in Table III.

The dimer was found to be monoclinic. Lattice constants were verified by axial photographs. It was assigned to the space group $P2_1/n$ on the basis of the systematic absences $0k0$, k = odd and $h0l$, $h + l$ = odd. Data reduction and calculations were carried out using the SHELXTL program.[8] The direct method routines produced an acceptable solution for the structure, yielding positions for all of the non-hydrogen atoms. Full-matrix least-squares refinement was carried out using SHELX-76.[9] The data were corrected for Lorentz and polarization effects, and scattering factors for neutral carbon and aluminum atoms were used.[10] Each hydrogen atom was placed in a calculated position with a C–H

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(8) Sheldrick, G. M. SHELXTL, University of Gottingen, Federal Republic of Germany, 1978.

(9) Sheldrick, G. M. SHELX-76, University Chemical Laboratory, Cambridge, England, 1976.

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Table III. Experimental Parameters for the X-ray Diffraction Study of [Me$_2$Al(2-allyl-6-methylphenoxide)]$_2$

compound: bis[dimethylaluminum(2-allyl-6-methylphenoxide)]	
formula: $C_{24}H_{34}Al_2O_2$	
mol wt: 408.4 amu	
crystal preparation: recrystallized from pentane/diethyl ether at −20 °C	
crystal color: colorless crystals	
crystal dimensions: 0.22 × 0.3 × 0.37 mm^3	
crystal system: monoclinic	
space group: $P2_1/n$	
cell constants constrained from 25 high-angle reflections	
a, Å	9.862 (2)
b, Å	9.682 (1)
c, Å	13.417 (2)
β, deg	97.98 (1)
Z	2 (dimers)
volume, Å^3	1268.7 (4)
density (calcd), g cm^{-3}	1.08
radiation type	Mo K$\bar{\alpha}$ = 0.71073 Å with a graphite monochromator
temp	room temp (27 °C)
type of data collection	$\theta/2\theta$ scan
2θ scan range, deg	4–45
octants used	$+h,+k,\pm l$
scan rate, deg/min	variable 2–5
std reflections	3 measd per every 100 reflections, no significant dev from the standard was observed (max dev was 3%).
no. of data collected	1983
obsd reflections	1025 with $F_o \geq 2.5\sigma(F)$
data used in final refinement	1021 (4 reflections were omitted due to secondary extinction)
scan width	1–1.3
background/scan ratio	0.50
linear abs coeff (μ), cm^{-1}	1.03 cm^{-1}
$F(000)$	440 electrons
abs correction	none applied
no. of parameters refined	132
obsd/parameter ratio	7.7:1
$R = \sum(\lvert F_o\rvert - \lvert F_c\rvert)/\sum\lvert F_o\rvert$, %	5.62
$R_w = [\sum(\lvert F_o\rvert - \lvert F_c\rvert)^2/\sum w\lvert F_o\rvert^2]^{1/2}$ ($w = 1/\sigma^2(F)$), %	4.87
overall shift/esd	0.000
maximum shift/esd	0.001
residual electron density	0.33 e/Å^3, 1.40 Å from C11

bond distance of 0.95 Å and assigned isotropic thermal parameters on the basis of the thermal parameters of the carbon atom to which it was bound. The C–H vector is held constant in magnitude and direction but not position, during subsequent refinement. A few additional cycles of refinement of the data led to a convergence with R = 5.62% (R_w = 4.87%). The final difference Fourier map showed a maximum electron density of 0.33 e/Å^3, 1.40 Å from C(11) with an overall shift/error of 0.000.

Results and Discussion

Synthesis. The hydroxy functionality of 2-allyl-6-methylphenol and 2-naphthol reacts rapidly at room temperature with aluminum alkyls in a 1:1 stoichiometry, liberating the alkane and affording the corresponding organoaluminum phenoxides, R$_2$AlOR′, in high yield according to the general reaction scheme (eq 1). These

$$R_3Al + R'OH \xrightarrow[\text{room temp}]{\text{pentane}} \underset{\substack{\textbf{1a–c}\\\textbf{2a–c}}}{R_2AlOR'} + RH \qquad (1)$$

1a, R = Me, R′ = 2-allyl-6-methylphenol
1b, R = Et, R ′ = 2-allyl-6-methylphenol
1c, R = *i*-Bu, R′ = 2-allyl-6-methylphenol
2a, R = Me, R′ = 2-naphthol
2b, R = Et, R′ = 2-naphthol
2c, R = *i*-Bu, R′ = 2-naphthol

results are in contrast to the one obtained from the reaction of 2,6-butylated hydroxytoluene (H-BHT) with alkylaluminum, in which the initial phenoxide species, R$_2$AlBHT, disproportionates to alkylaluminum bis(phenoxide) and trialkylaluminum species upon crystallization according to eq 2,[11] but are in full accord with the known

$$2R_2AlBHT \rightleftharpoons RAl(BHT)_2 + R_3Al \qquad (2)$$

chemistry of organoaluminum alkoxides, which typically form stable oxygen bridged dimers or, with small alkyl groups such as methyl, may form higher aggregates.

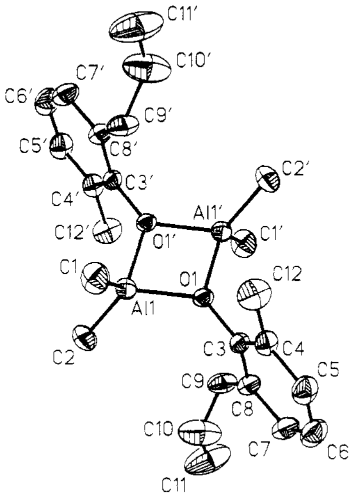
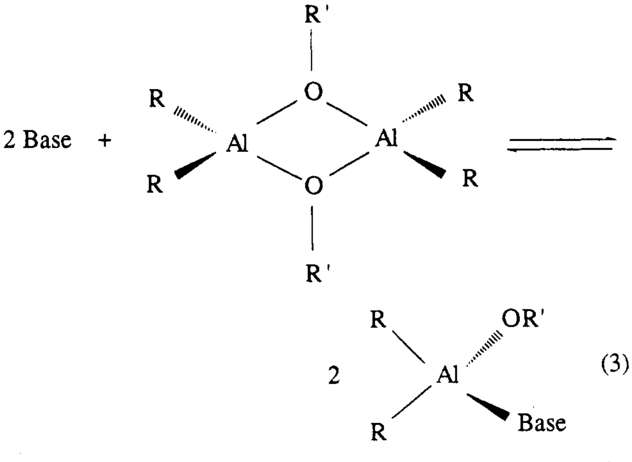


Figure 1. ORTEP diagram (30% thermal ellipsoids) of [Me$_2$Al(2-allyl-6-methylphenoxide)]$_2$, **1a**, showing the atom labeling scheme. Hydrogen atoms have been omitted for clarity.

It is of interest to determine the stability of the Al–O–Al bridge toward dissociation. One measure of this is the ability of the monomeric species R$_2$AlOR′ to form stable adducts of the form R$_2$(R′O)Al·base via the reaction shown in eq 3. Attempts to obtain adducts of this type with



(3)

Et$_2$O, THF, methyl benzoate, and 4-picoline were made. Only 4-picoline yielded an isolable addition product, indicating that the energy released on formation of the adduct Al–O bond in the other cases was less than that produced with formation of the Al–O–Al bridge bond.

Structure. The molecular structure of [Me$_2$Al(2-allyl-6-methylphenoxide)]$_2$ is shown in Figure 1. The gross features of the molecular structure are similar to known organoaluminum alkoxides. Atomic positional parameters are given in Table IV. The bond distances and bond angles are presented in Table V. The pertinent values from **1a** and a number of other organoaluminum compounds are given in Table VI.[12-17] A comparison of these

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[11] Shreve, A. P.; Mulhaupt, R.; Fultz, W.; Calabrese, J.; Robbins, W.; Ittel, S. D. *Organometallics* **1988**, *7*, 409.

Table IV. Atomic Positional Parameters for $[Me_2Al(2\text{-allyl-6-methylphenoxide})]_2$

atom	x/a	y/b	z/c	U_{eq}[a]
Al1	0.0885 (2)	0.4426 (2)	0.0835 (1)	0.0454 (6)
O1	0.0879 (3)	0.5778 (3)	−0.0149 (2)	0.038 (1)
C1	0.0938 (5)	0.5136 (6)	0.2199 (4)	0.077 (3)
C2	0.2090 (6)	0.2871 (5)	0.0696 (4)	0.078 (3)
C3	0.1897 (5)	0.6715 (5)	−0.0339 (4)	0.041 (2)
C4	0.1936 (5)	0.8002 (5)	0.0133 (4)	0.048 (2)
C5	0.2923 (6)	0.8924 (6)	−0.0080 (4)	0.066 (3)
C6	0.3835 (6)	0.8595 (7)	−0.0728 (5)	0.076 (3)
C7	0.3768 (6)	0.7321 (7)	−0.1182 (4)	0.066 (3)
C8	0.2804 (5)	0.6344 (6)	−0.0997 (4)	0.049 (2)
C9	0.2754 (5)	0.4944 (6)	−0.1512 (4)	0.065 (2)
C10	0.4060 (8)	0.4281 (9)	−0.1473 (7)	0.129 (4)
C11	0.4708 (8)	0.3830 (8)	−0.2133 (7)	0.149 (5)
C12	0.0986 (6)	0.8398 (6)	0.0869 (5)	0.077 (3)

[a] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i^*\cdot a_j^*\bar{a}_i\cdot\bar{a}_j$.

Table V. Bond Distances (Å) and Angles (deg) for $[Me_2Al(2\text{-allyl-6-methylphenoxide})]_2$[a]

atoms	dist, Å	atoms	dist, Å
Al–O	1.859 (3)	C4–C5	1.380 (8)
Al–O′	1.862 (3)	C4–C12	1.503 (8)
Al–C1	1.950 (5)	C5–C6	1.371 (8)
Al–C2	1.943 (6)	C6–C7	1.374 (9)
Al′–O	1.862 (3)	C7–C8	1.387 (8)
Al′–O′	1.859 (3)	C8–C9	1.519 (8)
O–C3	1.403 (6)	C9–C10	1.433 (9)
C3–C4	1.395 (7)	C10–C11	1.24 (1)
C3–C8	1.388 (7)	Al–Al′	2.866 (3)

atoms	angle, deg	atoms	angle, deg
Al–O–Al′	100.8 (1)	C3–C4–C5	117.3 (5)
Al–O–C3	130.7 (3)	C3–C4–C12	123.1 (5)
Al–O′–Al′	100.8 (1)	C3–C8–C7	117.1 (5)
Al′–O–C3	128.5 (3)	C3–C8–C9	122.5 (5)
O–Al–O′	79.2 (1)	C4–C3–C8	122.7 (5)
O–Al–C1	114.6 (2)	C4–C5–C6	121.6 (5)
O–Al–C2	114.8 (2)	C5–C4–C12	119.5 (5)
O–Al′–O′	79.2 (1)	C5–C6–C7	119.6 (6)
O–C3–C4	118.0 (4)	C6–C7–C8	121.6 (5)
O–C3–C8	119.3 (4)	C7–C8–C9	120.4 (5)
O′–Al–C1	113.7 (2)	C8–C9–C10	114.3 (5)
O′–Al–C2	114.4 (2)	C9–C10–C11	132.9 (8)
C1–Al–C2	115.3 (2)		

[a] The prime indicates the symmetry operation $-x$, $1 - y$, $-z$.

values confirms the fact that the Al–O distances are similar to other alkoxides and less than Al–O distances observed in the ether adducts. The Al–C distances are clearly within the range expected for Al–C terminal bond distances.

The aromatic rings are normal. Thermal motion in the allyl group leads to less precise bond distances and angles, but this feature has no effect on the overall structural features of the molecule. The Al–Al distance of 2.866 Å also is in the range typically found for dimeric aluminum derivatives and certainly substantially longer than the Al–Al single-bond distance of 2.66 Å recently reported in $((Me_3Si)_2CH)_2Al\text{–}Al(CH(SiMe_3)_2)_2$.[18]

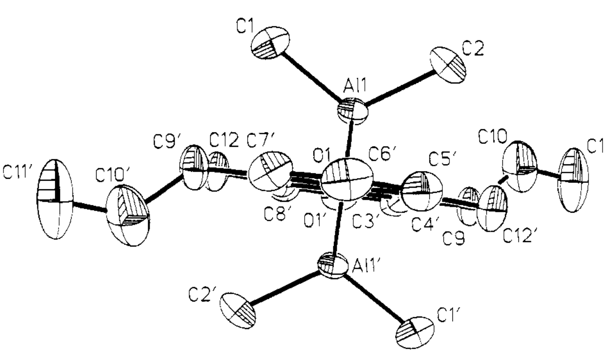

Figure 2. ORTEP diagram (50% thermal ellipsoids) of $[Me_2Al(2\text{-allyl-6-methylphenoxide})]_2$, **1a**, showing the orientation of the 2-allyl-6-methylphenoxide moieties relative to the Al_2O_2 ring. Hydrogen atoms have been omitted for clarity.

The molecule has a center of inversion requiring the Al_2O_2 unit to be rigorously planar and also requiring that the aromatic groups be equivalent. Further, the plane of the aromatic moiety is virtually perpendicular to the Al–Al axis, and the O–C3–C6 axis is almost perpendicular to the plane described by the two aluminum atoms and the four methyl carbon atoms. This can be seen clearly in Figure 2.

NMR Studies and Dynamic Behavior in $[Me_2Al(2\text{-allyl-6-methylphenoxide})]_2$. In the ^1H NMR spectrum of R_2AlOR' (Tables I and II), the absence of the –OH resonance of either 2-allyl-6-methylphenol or 2-naphthol and the presence of a sharp upfield resonance for the alkyl group attached to aluminum in the $-AlR_2$ moiety of R_2AlOR' provides good evidence for the $-AlR_2$ coordination at the phenoxy oxygen. The position of ^1H resonances associated with the alkyl groups attached to aluminum are virtually the same as for the corresponding protons in the parent trialkylaluminum. Similar observations in chemical shifts have been reported in Et_2AlBHT.[11] The ^{13}C spectra of the R_2AlOR' (R' =2-allyl-6-methylphenyl) compounds show that the resonances due to C(2), C(3), C(4), C(5), and C(6) are shifted downfield, while the resonance due to C(1) is shifted upfield from the corresponding resonances in the phenoxy ring of 2-allyl-6-methylphenol, with the most pronounced change in chemical shift ($\Delta\delta$) occurring at C(1), C(2), and C(6). These shift effects probably are associated with the overall electron-withdrawing ability of the $-OAlR_2$ group, which is a strong Lewis acid center. Again, these observations reflect the dimeric nature of the complex R_2AlOR'. The ^{13}C resonances of the alkyl group in the $-AlR_2$ moiety on complexation are shifted slightly downfield from the corresponding resonance in the parent AlR_3. We can also rule out the possibility of interaction of aluminum with the allylic group of 2-allyl-6-methylphenol in solution on the following basis. In the ^1H NMR and ^{13}C NMR spectra, the chemical shifts of the allylic group exhibit only small displacement on complex formation, which is contrary to what one would expect if there was an allylic interaction with the aluminum center.

The NMR spectra of the alkylmethyl systems show interesting behavior as a function of temperature. The solid-state structure shows that there are two sets of equivalent Al–Me groups, with each set distinguished by the relative positions to the allylic groups on the ring (see Figure 2). In solution, the low barrier to rotation about the C–C single bond should lead to equivalence of the allyl groups on the NMR time scale. In the room-temperature spectrum, all methyl groups are equivalent, and the bridging aromatic groups show equivalence. As the temperature is decreased, a variety of changes occur. These include the broadening and ultimate formation of two sets

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Table VI. Bond Distances and Angles in Selected Organoaluminum Derivatives

	dist, Å			angle, deg		
compound	Al–O	Al–C	Al–Al	C–Al–C	O–Al–O	Al–O–Al
[Me_2Al-2-allyl-6-methylphenoxide]$_2$[a]	1.861	1.946	2.866	115.3	79.1	100.8
[Me_2Al(*l*-mentholate)]$_2$[b]	1.837	1.949	2.807	122.3	82.0	99.4
[Me_2Al(*l*-bornolate)]$_2$[b]	1.841	1.963	2.779	118.7	80.6	98.0
[Me_6Al_2OPh]K·dibenzo-18-crown-6[c]	1.89	2.01		122.7		
[$Me_2Al(OPh)_2$]K[c]	1.800	1.968		119.4	96.8	
[$Me_2AlO(MeO)(CH_2)_2$]$_2$[d]	1.827	1.951	2.924	120.8	76.3	103.1
[$Me_2AlO(O)MeCHPhNPhC$]$_2$[e]	1.922 (br) 2.045 (adduct)	1.964		119.4	73.3	105.3
[Me_2AlOCH_2-2-C_5H_4N]$_2$[f]	1.894	1.994	3.024	119.1	74.1	105.9
[$(Me_3Si)_2CHAl$]$_2$[g]		1.982	2.66			
$(Me_3Al)_2$·*p*-dioxane[h]	2.02	1.97		116.8		
(*o*-Tol)$_3$Al·OEt_2[i]	1.928	1.990		114.4		
$Me_3Al·OMe_2$(gas)[j]	2.014	1.973		117.8		
$(Me_3Al)_2$·dibenzo-18-crown-6[k]	1.960			115.5		
Me_3Al[l] (gas)		1.957				
[Me_2Al(O-*t*-Bu)]$_2$[m] (gas)	1.864	1.962	2.82	121.7	81.9	98.1
$Me_2AlBHT·PMe_3$[n]	1.736	1.970		111.7		

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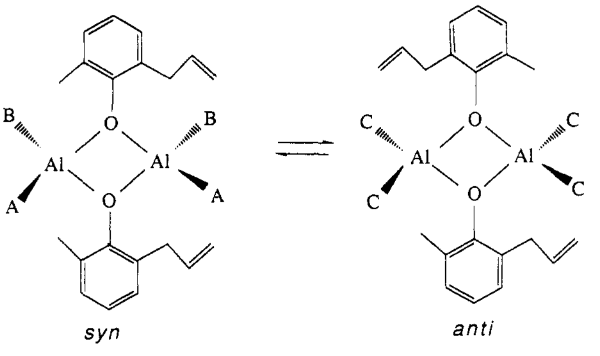
of resonances for all of the spectral regions. The two most readily monitored regions of the spectrum are those associated with the 6-methyl group and the Al-Me groups. At −80 °C, the 6-Me group is clearly resolved into two signals while the Al–Me region of the spectrum shows three lines (see Figure 3). These changes can be accounted for if one assumes that in solution there is rapid rotation about the Al–O bridge bond and the C–O bond, at room temperature, while at low temperature the rotational processes become slow on the NMR time scale. To account for the observed patterns, it appears that in solution there are two different conformers of the molecule present, one with 2-allyl-6-methylphenoxide groups in the anti configuration, as observed in the structure, and one with the 2-allyl-6-methylphenoxide group in the syn configuration. In each of these configurations the 6-Me groups are magnetically equivalent but are different between the two conformers. In the anti conformer the aluminum methyl groups are all equivalent, but in the syn form the Al–Me groups are in different magnetic environments, giving rise to two separate resonance lines for these moieties, or a total of three lines in the equilibrium mixture. A limited, variable-temperature NMR study has been carried out on this system with variable-temperature spectra of the 6-Me and Al–Me groups shown in Figure 3. A line-shape analysis gave a barrier of activation for this process of 9.7 ± 2 kcal mol^{-1} and showed that the rate of exchange is independent of the concentration. This is consistent with interconversion of the syn and anti conformations shown in eq 4.



(4)

A minor complication encountered in this analysis is that the syn and anti conformations may not be of equal energy, leading to different concentrations for each conformer, which may also be a function of temperature. This appears to be the case for **1a** with an isomer ratio of 1:1.2 at −80 °C.

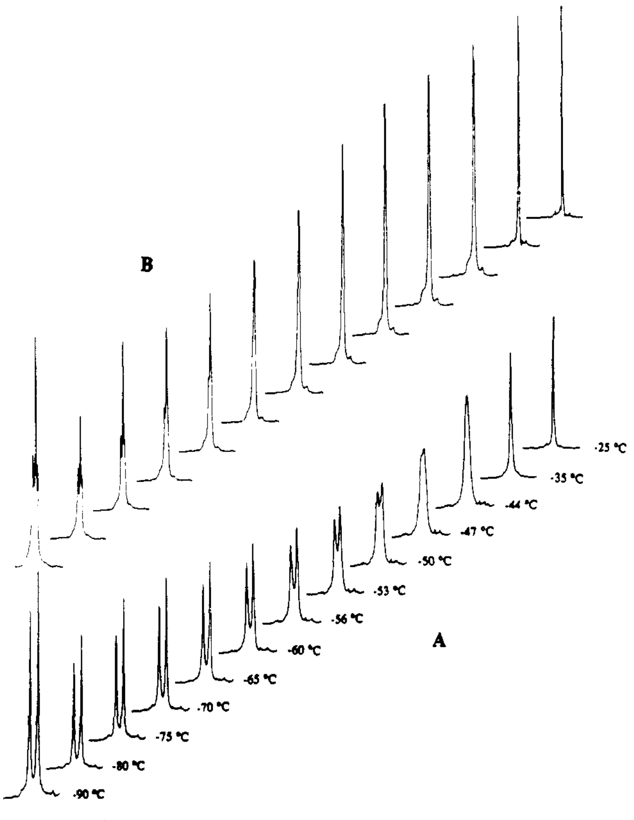


Figure 3. ^1H NMR spectrum of the 6-Me region (A) and of the Al–Me region (B) of [Me_2Al(2-allyl-6-methylphenoxide)]$_2$, as a function of temperature.

A full investigation of the influence of the substituents both on the bridging alkoxide and on the aluminum center is planned to determine the influence of substituents on both the rate of rotation and on the position of the equilibrium for these and related systems.

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Supplementary Material Available: Listings of anisotropic thermal parameters for the heavy atoms, hydrogen atom positional parameters, torsion angles, and least-squares planes and deviations (7 pages); a complete listing of the observed and calculated structure factors (7 pages). Ordering information is given on any current masthead page.

Organorhenium Imido Complexes: Syntheses, Structure, and Reactivity[1]

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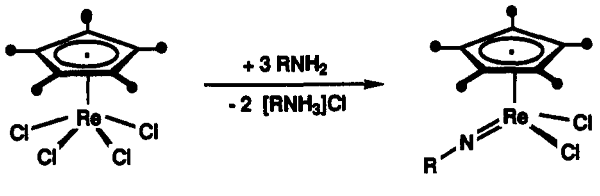
Imido complexes of heptavalent rhenium have been synthesized by three different routes: (i) aminolysis of the half-sandwich complex (η^5-C_5Me_5)$ReCl_4$ (**1**) (Me = CH_3) with primary amines gives the imido derivatives (η^5-C_5Me_5)Re(N^tBu)Cl_2 (**2a**, ^{t}Bu = *tert*-butyl) and (η^5-C_5Me_5)Re(NCH_3)Cl_2 (**2b**). The rhenium–nitrogen distance in compound **2a** (1.709 (3) Å) corresponds to a triple bond (single-crystal X-ray diffraction), while the analogous oxo congener (η^5-C_5Me_5)$ReOCl_2$ has relatively little rhenium–oxygen triple-bond character. (ii) Sequential deoxygenation of methyltrioxorhenium(VII) (**6**) via decarboxylation upon treatment with 2,6-diisopropylphenyl isocyanate yields mono- and dinuclear methylrhenium(VII) imido complexes **7–9** in good yields; imido bridging occurs when the mononuclear compounds of types $CH_3ReO(NR)_2$ (**8a**) and $CH_3Re(NR)_3$ (**9a**) are dissolved in polar solvents such as typically 1,2-dimethoxyethane. (iii) Nucleophilic substitution of Me_3SiO–Re(N^tBu)$_3$ (**10**) by organolithium or Grignard reagents was used to synthesize the new methyl-, allyl-, ethyl-, and phenylalkynyl derivatives R′–Re(N^tBu)$_3$ (R′ = CH_3, **11a**; C_3H_5, **11b**; C_2H_5, **11c**; $C_6H_5C{\equiv}C$, **11d**). These compounds are thermally very robust even though **11b,c** exhibit alkyl groups with β-hydrogen atoms. σ- instead of π-coordination of the allyl ligand of **11b** underlies the strong electron-releasing character of the three imido ligands; this suggests that even π-ligands R′ in compounds of type R′–$Re(NR)_3$ will be only σ-coordinated, in contrast to the oxo congeners R′–ReO_3. [2 + 2] Cycloaddition intermediates can be trapped in the reaction of the oxorhenium(III) alkyne complexes of type (η^5-C_5Me_5)ReO(η^2-RC≡CR) (**3a**, R = CH_3; **3b**, C_6H_5) with phenyl isocyanate to give phenyl carbamidato-*N,O* complexes **4a,b** that undergo consecutive decarboxylations and isocyanate addition to yield finally ureato-*N,N′* compounds **5a,b**.

Introduction

We have previously reported on the synthesis, reactivity, and catalytic properties of high-valent rhenium oxo complexes of types R–ReO_3 (R = CH_3,[3] mesityl[4]), Cp^*ReO_3,[5-7] and Cp^*ReOX_2 (X = alkyl, halide).[6,7] To better understand the behavior of multiply bonded ligands in these systems, we have examined synthetic pathways to analogous imido complexes, R–Re(NR′)$_3$, $Cp^*Re(NR)_3$, and $Cp^*Re(NR)X_2$. In this context, the synthesis of the half-sandwich complex $Cp^*Re(N^tBu)Cl_2$ (**2a**) via aminolysis of the tetrachloro precursor compound **1** (Scheme I) has recently been communicated in a review article.[7a] Imido complexes of rhenium in high oxidation states are important models and possible catalysts of oxyamination reactions known for osmium(VIII) imido systems.[8] Since related rhenium oxo complexes are effective catalysts in

Scheme I



1

2a,b

• = CH_3

a: R = $^tC_4H_9$
b: R = CH_3

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