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Synthesis and Characterization of Alkylaluminum and -gallium Derivatives of 2-(Methylthio)- and 2-Methoxyphenol. Crystal Structures of the Dimeric Complexes $[R_2M(\mu\text{-}OC_6H_4\text{-}2\text{-}ECH_3)]_2$ (M = Al, E = S, R = Me, *i*-Bu; M = Al, E = O, R = Et, *i*-Bu; M = Ga, E = O, R = Me) Featuring Five-Coordinate Metal Centers

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2-(Methylthio)- and 2-methoxyphenol react in a 1:1 ratio with trialkylaluminum derivative R_3Al (R = Me, Et, *i*-Bu) or trimethylgallium to yield $[R_2M(\mu\text{-}OC_6H_4\text{-}2\text{-}ECH_3)]_2$ species (M = Al, E = S, R = Me (**1a**), Et (**1b**), *i*-Bu (**1c**); M = Al, E = O, R = Me (**2a**), Et (**2b**), *i*-Bu (**2c**); M = Ga, E = O, R = Me (**3**)) and the corresponding alkane, RH, in high yield. The resulting phenoxides have been characterized by ^1H and ^{13}C NMR spectroscopy, and the structures of **1a**, **1c**, **2b**, **2c**, and **3** were determined by single-crystal X-ray diffraction techniques. **1a** was assigned to the triclinic cell system, space group $P\bar{1}$ (No. 2), with cell constants $a = 9.828$ (2) Å, $b = 13.547$ (2) Å, $c = 14.164$ (2) Å, $\alpha = 62.15$ (1)°, $\beta = 87.26$ (1)°, $\gamma = 75.05$ (2)°, and $Z = 3$ (dimers). The structure was refined to a final $R = 6.20\%$ ($R_w = 6.33\%$) based on 2735 ($F_o \geq 3.0\sigma(F)$) observed reflections. **1c** was assigned to the triclinic cell system, space group $P\bar{1}$ (No. 2), with cell constants $a = 9.408$ (2) Å, $b = 9.796$ (4) Å, $c = 10.509$ (5) Å, $\alpha = 83.66$ (4)°, $\beta = 68.69(3)$°, $\gamma = 66.07$ (3)°, and $Z = 1$ (dimer). The structure was refined to a final $R = 3.5\%$ ($R_w = 3.8\%$) based on 1563 ($F_o \geq 3.0\sigma(F)$) observed reflections. **2b** was assigned to the monoclinic cell system, space group $P2_1/n$ (No. 14), with cell constants $a = 7.9733$ (9) Å, $b = 9.3984$ (8) Å, $c = 15.935$ (1) Å, $\beta = 101.06$ (1)°, and $Z = 2$ (dimers). The structure was refined on 1232 ($F_o \geq 3.0\sigma(F)$) observed reflections to a final $R = 3.83\%$ ($R_w = 4.15\%$). **2c** was assigned to the monoclinic cell system, space group $P2_1/c$ (No. 14), with cell constants $a = 9.037$ (2) Å, $b = 19.427$ (3) Å, $c = 9.332$ (2) Å, $\beta = 100.71$ (1)°, and $Z = 2$ (dimers). The structure was refined to a final $R = 3.52\%$ ($R_w = 3.47\%$) based on 1808 ($F_o \geq 3.0\sigma(F)$) observed reflections. **3** crystallizes in the orthorhombic cell system, space group P_{cab} (nonstandard setting of space group No. 61), with cell constants $a = 6.845$ (2) Å, $b = 15.994$ (6) Å, $c = 18.722$ (6) Å, and $Z = 4$ (dimers). The structure was refined to a final $R = 4.32\%$ ($R_w = 4.62\%$) based on 1022 ($F_o \geq 3.0\sigma(F)$) observed reflections. The 2-(methylthio)- and 2-methoxyphenyl groups in the dimer are in the same plane as the Al_2O_2 ring and are oriented in an anti fashion with respect to one another. The Al–S distances in **1a** and **1c** are long with an average value of 2.76 Å, comparable to those found in simple addition compounds. The molecular units of **2b**, **2c**, and **3** are similar. In the case of the aluminum complexes, **2b** and **2c**, the average Al–O coordinate bond distance is 2.25 Å. For the gallium complex, **3**, the Ga–O coordinate bond distance is 2.52 Å. Examination of the variable-temperature NMR spectra of **1a**, **2b**, and **3** shows no dramatic changes occur as a result of change in temperature. However, the chemical shifts of both the metal alkyl groups and of the ER units change in a linear fashion. This is interpreted in terms of rapid rotation on the NMR time scale of the $-C_6H_4\text{-}2\text{-}EMe$ group around the O–C bond. The observed chemical shift is a weighted average of the "free" and "bound" species.

Introduction

The chemistry of organoaluminum compounds bound either to a group 15 or 16 element has been under investigation for many years. The group 15 elements containing derivatives of aluminum and the heavier elements of group 13 have been studied extensively in recent years because of their semiconducting properties.[1] On the other hand, 13–16 compounds have received only limited attention. The recent recognition that 13–16 compounds may serve as precursors for ceramic materials, as models for aluminum oxides catalysts, and in regio- and stereoselective organic synthesis has led to a renewed interest in the synthesis and characterization of these derivatives.[2] Specifically, the reaction of alcohols or phenols with group 13 alkyl reagents has been studied. Early work on these derivatives was concentrated on the study of physical properties and the aggregate size.[2] X-ray crystallographic and electron diffraction studies established that the alkoxy derivatives typically are bridged dimers or trimers or monomers when very bulky groups are present. When bidentate ligands are used, more complex species may be obtained. The structures of these depend on the nature of the ligand and include monomeric species, dimeric derivatives containing five-coordinate metal centers, and more complex molecules containing metals in different coordination environments in the same molecule. Alternatively, species containing extended ring structures or monomeric four-coordinate metal centers have been found. We have reviewed much of this information recently and note that the type of complex or aggergate formed is dependent on several variables, including the size and structure of the bidentate or polydentate ligand.[3] We have now embarked on a series of studies to elucidate the structure and bonding of simple monodentate 13–16 compounds and of more complex derivatives containing bidentate and polydentate ligands. In this paper we report

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(1) (a) Cowley, A. H.; Jones, R. A. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1208. (b) Steigerwald, M. L.; Sprinkle, C. R. *J. Am. Chem. Soc.* **1987**, *109*, 7200. (c) Steigerwald, M. L.; Sprinkle, C. R. *Organometallics* **1988**, *7*, 245. (d) Interrante, L. V.; Carpenter, L. E.; Whitmarsh, C.; Lee, W.; Slack, G. A. *Mater. Res. Soc. Symp. Proc.* **1986**, *73*, 986. (e) Steigerwald, M. L; Sprinkle, C. R. *Organometallics* **1988**, *7*, 245.

(2) (a) Mole, T.; Jeffery, E. A. *Organoaluminum Compounds*; Elsevier: Amsterdam, 1972. (b) Maruoka, K.; Banno, H.; Yamamoto, H. *J. Am. Chem. Soc.* **1990**, *112*, 7791. (c) Noyori, R.; Tomino, I.; Tanimoto, Y.; Nishizawa, M. *J. Am. Chem. Soc.* **1984**, *106*, 6709. (d) Power, M. B.; Bott, S. G.; Atwood, J. L.; Barron, A. R. *J. Am. Chem. Soc.* **1990**, *112*, 3446. (e) Maruoka, K.; Nagahara, S.; Yamamoto, H. *J. Am. Chem. Soc.* **1990**, *112*, 6115. (f) Maruoka, K.; Concepcion, A. B.; Hirayama, N.; Yamamoto, H. *J. Am. Chem. Soc.* **1990**, *112*, 7422.

(3) Oliver, J. P.; Kumar, R. *Polyhedron* **1990**, *9*, 409.

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on the synthesis, the structures, and NMR studies on a series of dialkylaluminum and dialkylgallium derivatives bound to the rigid difunctional ligands 2-(methylthio)- and 2-methoxyphenoxide. The structures of these derivatives are compared with other organoaluminum derivatives containing more flexible bidentate ligands, and the temperature dependence of their NMR spectra is interpreted in terms of a rapid rotational process about the O–C bond.

Experimental Section

General Data. All solvents were purified and dried by standard techniques.[4] Argon gas was purified by passing it through a series of columns containing Deox catalyst (Alfa), phosphorus pentoxide, and calcium sulfate. The trialkylaluminum derivatives (Me_3Al, 2 M solution in toluene; Et_3Al, 1.9 M solution in toluene; $(i\text{-}Bu)_3Al$, 1 M solution in toluene (Aldrich), Me_3Ga (Strem)), 2-methoxyphenol (Aldrich), and 2-(methylthio)phenol (Aldrich) were used as received. All glassware used in the synthetic work was oven dried. The aluminum and gallium derivatives are both oxygen and water sensitive so standard Schlenk line techniques were employed. ^1H and ^{13}C NMR spectra were recorded on either a General Electric QE-300 or GN-300 NMR spectrometer. The ^1H and ^{13}C chemical shifts (ppm) were referenced to benzene peaks ($\delta = 7.15$ ppm for ^1H and $\delta = 128.00$ ppm for ^{13}C), while ^{27}Al chemical shifts (ppm) were referenced to an external 1 M solution of $Al(NO_3)_3$ in D_2O. Variable-temperature ^1H NMR spectra were recorded on a GN-300 NMR spectrometer in toluene-d_8 solutions of the respective compounds and were referenced to the residual CH_3 peak of toluene (^1H, $\delta = 2.09$ ppm). Elemental analysis on selected compounds was performed by Galbraith Laboratories, Knoxville, TN.

Preparation of $[Me_2Al(\mu\text{-}OC_6H_4\text{-}2\text{-}SCH_3)]_2$ (1a). 2-(Methylthio)phenol (1 mL, 8.33 mmol) was dissolved in pentane (50 mL), and Me_3Al (4.2-mL solution, 8.33 mmol) was added over a period of 5 min. The resulting reaction was exothermic, bringing the pentane to reflux. After the addition was complete, the reaction was stirred for an additional 2 h, during which a white solid was deposited. The liquid was separated from the solid by cannula. The solid was then crystallized from hot toluene (ca. 10 mL). The product was collected, washed with 10–15 mL of cold pentane, and dried in vacuo. This solid was identified as $[Me_2Al(\mu\text{-}OC_6H_4\text{-}2\text{-}SCH_3)]_2$. The pentane filtrate also deposited white solid when left standing at −20 °C overnight. It was isolated as described above. Total yield: 90%. Anal. Calcd for $C_9H_{13}OSAl$: C 55.10; H 6.63. Found: C, 54.59; H 6.62. ^1H NMR: 7.42–7.45 (m, 1 H), 7.15–7.18 (m, 1 H), 6.90–6.96 (m, 1 H), 6.62–6.68 (m, 1 H), 1.79 (s, 3 H, SMe), −0.12 (s, 6 H, Al–Me). $^{13}C\{^1H\}$ NMR: 155.0, 135.0, 130.7, 123.1, 122.7, 119.2 (aromatics), 21.5 (SMe), −7.1 (Al–Me). ^{27}Al (benzene-d_6, 2% THF) NMR: 133 (shoulder), 177.

Preparation of $[Et_2Al(\mu\text{-}OC_6H_4\text{-}2\text{-}SCH_3)]_2$ (1b). The preparation was the same as described for **1a**, using 2-(methylthio)phenol (1 mL, 8.33 mmol) and Et_3Al (4.40-mL solution, 8.33 mmol). The solid was isolated and purified as described for **1a**. This solid was identified as $[Et_2Al(\mu\text{-}OC_6H_4\text{-}2\text{-}SCH_3)]_2$. Yield: 80%. ^1H NMR: 7.36–7.39 (m, 1 H), 6.18–7.21 (m, 1 H), 6.94–7.0 (m, 1 H), 6.63–6.68 (m, 1 H), 1.90 (s, 3 H, SMe), 1.30 (t, $^3J_{H-H}$ = 8.1 Hz, 6 H, Al–$CH_2\mathit{Me}$), 0.48 (q, $^3J_{H-H}$ = 8.1 Hz, 4 H, Al–CH_2Me). $^{13}C\{^1H\}$ NMR: 155.5, 135.2, 130.9, 122.6, 122.4, 118.7 (aromatics), 21.6 (SMe), 9.8 (Al–$CH_2\mathit{Me}$), 2.2 (Al–CH_2Me). ^{27}Al (benzene-d_6, 2% THF) NMR: 146.

Preparation of $[(i\text{-}Bu)_2Al(\mu\text{-}OC_6H_4\text{-}2\text{-}SCH_3)]_2$ (1c). The reaction was carried out by using the same procedure as described for **1a**, using 2-(methylthio)phenol (1 mL, 8.33 mmol) and $(i\text{-}Bu)_3Al$ (8.33-mL solution, 8.33 mmol). The solvent was removed by vacuum evaporation, leaving a white solid that was crystallized from hot pentane (ca. 30 mL). This solid was identified as $[(i\text{-}Bu)_2Al(\mu\text{-}OC_6H_4\text{-}2\text{-}SCH_3)]_2$. Yield: 96%. ^1H NMR: 7.55–7.58 (m, 1 H), 7.16–7.19 (m, H), 6.98–7.03 (m, 1 H), 6.66–6.71 (m, 1 H), 1.96 (s, 3 H, SMe), 2.03 (m, $^3J_{HH}$ = 6.3 Hz, 2 H, $AlCH_2\mathit{CH}Me_2$), 1.09 (d, $^3J_{H-H}$ = 6.3 Hz, 12 H, $AlCH_2CH\mathit{Me}_2$), 0.56 (d, $^3J_{H-H}$ = 6.9 Hz, 4 H, $Al\mathit{CH}_2CHMe_2$). $^{13}C\{^1H\}$ NMR: 154.7, 134.3, 130.1, 123.6, 123.1, 119.7 (aromatics), 21.3 (SMe), 24.5 ($Al\mathit{CH}_2CHMe_2$), 26.5 ($AlCH_2\mathit{CH}Me_2$), 28.6 ($AlCH_2CH\mathit{Me}_2$). ^{27}Al (benzene-d_6, 2% THF) NMR: 144.

Preparation of $[Me_2Al(\mu\text{-}OC_6H_4\text{-}2\text{-}OCH_3)]_2$ (2a). Excess Me_3Al (8.0-mL solution, 16.0 mmol) was added dropwise to 1.0 g (0.89 mL, 8.06 mmol) of 2-methoxyphenol in 20 mL of pentane with stirring. During the addition of Me_3Al, a vigorous evolution of gas was observed. The resulting solution was then stirred for 2 h, followed by removal of all volatile material by vacuum evaparation to give a white powder, $[Me_2Al(\mu\text{-}OC_6H_4\text{-}2\text{-}OCH)_3]_2$, in quantitative yield. ^1H NMR: 7.29–7.32 (m, 1 H), 6.60–6.80 (m, 2 H), 6.23–6.26 (m, 1 H), 3.16 (s, 3 H, OMe), −0.28 (s, 6 H, Al–Me). $^{13}C\{^1H\}$ NMR: 146.4, 144.2, 122.9, 120.7, 116.4, 110.1 (aromatics), 54.0 (OMe), −9.5 (Al–Me).

Preparation of $[Et_2Al(\mu\text{-}OC_6H_4\text{-}2\text{-}OCH_3)]_2$ (2b). **2b** was prepared by the same method as **2a** by addition of 1 equiv of Et_3Al (4.3-mL solution, 8.17 mmol) to 1.0 g of 2-methoxyphenol in 20 mL of pentane. The product was dissolved in hot benzene (ca. 10 mL). The benzene solution was allowed to cool to ambient temperature, affording a transparent crystalline product, $[Et_2Al(\mu\text{-}OC_6H_4\text{-}2\text{-}OCH_3)]_2$. Yield: 90%. Anal. Calcd for $C_{11}H_{17}O_2Al$: C, 63.45; H, 8.23. Found: C, 63.16; H, 8.18. ^1H NMR: 7.26–7.29 (m, 1 H), 6.62–6.80 (m, 2 H), 6.30–6.33 (m, 1 H), 3.30 (s, 3 H, OMe), 1.28 (t, $^3J_{H-H}$ = 8.4 Hz, 6 H, $AlCH_2\mathit{Me}$), 0.38 (q, $^3J_{H-H}$ = 8.1 Hz, 4 H, $Al\mathit{CH}_2Me$). $^{13}C\{^1H\}$ NMR: 146.8, 144.4, 122.8, 120.8, 116.6, 109.9 (aromatics, 54.8 (OMe), 9.8 ($AlCH_2\mathit{Me}$), 1.0 ($Al\mathit{CH}_2Me$).

Preparation of $[(i\text{-}Bu)_2Al(\mu\text{-}OC_6H_4\text{-}2\text{-}OCH_3)]_2$ (2c). **2c** was prepared by the same method as **2a** by addition of 1 equiv of $i\text{-}Bu_3Al$ (8.1-mL solution, 8.1 mmol) to 1.0 g of 2-methoxyphenol in 20 mL of pentane. The product was dissolved in hot benzene (ca. 10 mL). The benzene solution was allowed to cool to ambient temperature, affording a transparent crystalline product identified as $[(i\text{-}Bu)_2Al(\mu\text{-}OC_6H_4\text{-}2\text{-}OCH_3)]_2$. Yield: 85%. Anal. Calcd for $C_{15}H_{25}O_2Al$: C, 68.16; H, 9.53. Found: C, 67.66; H, 9.64. ^1H NMR: 7.44–7.47 (m, 1 H), 6.62–6.84 (m, 2 H), 6.33–6.36 (m, 1 H), 3.36 (s, 3 H, OMe) 2.02 (septet, $^3J_{H-H}$ = 6.6 Hz, 2 H, $Al\mathit{CH}_2CHMe_2$), 1.09 (d, $^3J_{H-H}$ = 6.3 Hz, 12 H, $AlCH_2CH\mathit{Me}_2$), 0.43 (d, $^3J_{H-H}$ = 7.2 Hz, 4 H, $Al\mathit{CH}_2CHMe_2$). $^{13}C\{^1H\}$ NMR: 146.5, 144.0, 122.7, 121.1, 117.0, 110.1 (aromatics), 55.2 (OMe), 28.8 ($AlCH_2CH\mathit{Me}_2$), 26.3 ($AlCH_2\mathit{CH}Me_2$), 23.8 ($Al\mathit{CH}_2CHMe_2$).

Preparation of $[Me_2Ga(\mu\text{-}OC_6H_4\text{-}2\text{-}OCH_3)]_2$ (3). Compound **3** was prepared by the same method used for preparation of **2a** by addition of excess Me_3Ga (1.6-mL solution, 16.0 mmol) to 1.0 g (0.89 mL, 8.06 mmol) of 2-methoxyphenol in 20 mL of pentane. Removal of volatiles in vacuo resulted in a white powder identified as $[Me_2Ga(\mu\text{-}OC_6H_4\text{-}2\text{-}OCH_3)]_2$ in quantitative yield. Anal. Calcd for $C_9H_{13}O_2Ga$: C, 48.49; H, 5.88. Found: C, 48.32; H, 5.88. ^1H NMR: 6.33–6.36 (m, 1 H), 6.60–6.85 (m, 2 H), 7.38 (broad, 1 H) 3.13 (s, 3 H, OMe), 0.17 (s, 6 H, Ga–Me). $^{13}C\{^1H\}$ NMR: 111.2, 116.6, 119.2, 122.3, 147.6, 147.7 (aromatics), 54.0 (OMe), −4.6 (Ga–Me).

X-ray Structure Determinations of $[Me_2Al(\mu\text{-}OC_6H_4\text{-}2\text{-}SCH_3)]_2$ (1a), $[(i\text{-}Bu)_2Al(\mu\text{-}OC_6H_4\text{-}2\text{-}SCH_3)]_2$ (1c), $[Et_2Al(\mu\text{-}OC_6H_4\text{-}2\text{-}OCH_3)]_2$ (2b), $[(i\text{-}Bu)_2Al(\mu\text{-}OC_6H_4\text{-}2\text{-}OCH_3)]_2$ (2c), and $[Me_2Ga(\mu\text{-}OC_6H_4\text{-}2\text{-}OCH_3)]_2$ (3). Crystals of **1a** were grown from a toluene solution at −20 °C, while crystals of **1c** were obtained from hot pentane. Crystals of both **2b** and **2c** were obtained from a hot benzene solution. Crystals of **3** were grown from a benzene solution at 10 °C. In each case a crystal suitable for X-ray diffraction studies was mounted in a Lindamen glass capillary tube in a drybox, plugged with grease, removed from the drybox, flame sealed, mounted on a goniometer head, and placed for data collection on a Nicolet R3 diffractometer for **1c** and **2c**, on a P3/V diffractometer for **1a** and **2b**, and on a $P2_1$ diffractometer for **3**. Parameters for the data collections and for the crystal structure determinations are presented in Table I.

Crystals of **1a** and **1c** were found to be in the triclinic cell system; crystals of **2b** and **2c** were monoclinic, and the crystal of **3** was orthorhombic. Lattice constants were verified by axial photographs, and the crystal was assigned to the space groups $P\bar{1}$ (**1a**, **2c**), $P2_1/c$ (**1c**), $P2_1/n$ (**2b**), and *Pcab* (**3**), which were later confirmed by successful refinement of the structures. Unit cell parameters were obtained from the least-squares fit of the angular settings of the 25 high-angle reflections with 40° < 2θ < 60° for

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[4] Shriver, D. F. *The Manipulation of Air-Sensitive Compounds*; McGraw-Hill: New York, 1969.

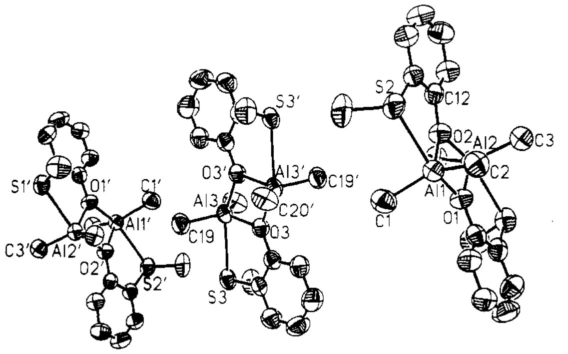

Figure 1. ORTEP diagram of the $[Me_2Al(\mu\text{-}OC_6H_4\text{-}2\text{-}SCH_3)]_2$ dimer, **1a** showing the atom-labeling scheme. Hydrogen atoms are omitted for clarity.

1a, **2b**, and **3** and 20° < 2θ < 30° for **1c** and **2c**. Data reduction was carried out by using the SHELXTL program.[5] The structure of **1a** was solved by the Patterson heavy-atom method, while the direct-methods routine produced acceptable solutions for the structures of **1c**, **2b**, **2c**, and **3**. Full-matrix least-squares refinement was carried out by using SHELX-76.[6] The data were corrected for Lorentz and polarization effects, and scattering factors for neutral carbon, oxygen, sulfur, aluminum, and gallium atoms were used.[7] The hydrogen atoms for **1c**, **2c**, and **3** were found from the difference Fourier map, while each hydrogen atom in **1a** and **2b** was placed in a calculated position with a C–H bond distance of 0.96 Å. The C–H vector held constant in magnitude and direction, but not position, during subsequent refinement. The atomic coordinates and isotropic thermal parameters for the non-hydrogen atoms of **1a**, **1c**, **2b**, **2c**, and **3** are listed in Table II–VI. Selected bond distances and angles for each of the compounds are listed in Table VII. Other structural data are available in the supplementary material.

Results and Discussion

Synthesis. The hydroxyl proton of 2-(methylthio)- and 2-methoxyphenol reacts rapidly at room temperature with trialkylaluminum derivatives and trimethylgallium in a 1:1 stoichiometry, liberating the alkane and affording the corresponding phenoxides, $[R_2M(\mu\text{-}OC_6H_4\text{-}2\text{-}ECH_3)]_2$ (E = O, S), in high yield according to the general reaction scheme (eq 1). Compounds **1a–c**, **2a–c**, and **3** have been

$$2\ R_3M\ +\ 2\ R'OH \longrightarrow [R_2Al(\mu\text{-}OR')]_2\ +\ 2\ RH \qquad (1)$$

M = Al, OR′ = 2-methylmercaptophenoxide
R = Me, **1a**; Et, **1b**; *i*-Bu, **1c**
M = Al, OR′ = 2-methoxyphenoxide
R = Me, **2a**; Et, **2b**; *i*-Bu, **2c**
M = Ga, OR′ = 2-methoxyphenoxide
R = Me, **3**

isolated as colorless, transparent crystals. The complexes are both air and moisture sensitive, decomposing over a period of seconds in the solid state on exposure to air. They are very soluble both in hydrocarbons such a pentane, benzene, and toluene and in the donor solvents such as diethyl ether and tetrahydrofuran. Attempts to react these phenols with 2 equiv of trialkylaluminum reagents in an effort to use each of the coordination sites to bind different metal atoms gave rise to the same products obtained by using 1:1 stoichiometry. This indicates that the second coordination site, the methoxy or methylthio group, is unavailable to coordinate additional metal atoms or at least the secondary site is unable to retain the second metal atoms in the complex.

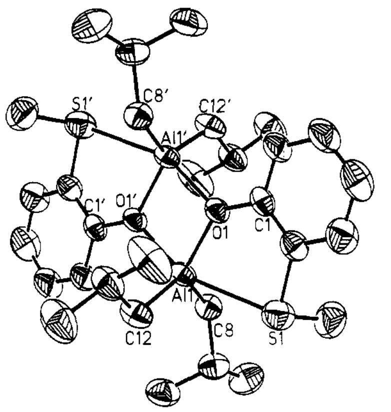

Figure 2. ORTEP diagram of the $[(i\text{-}Bu)_2Al(\mu\text{-}OC_6H_4\text{-}2\text{-}SCH_3)]_2$ dimer, **1c**, showing the atom-labeling scheme. Hydrogen atoms are omitted for clarity.

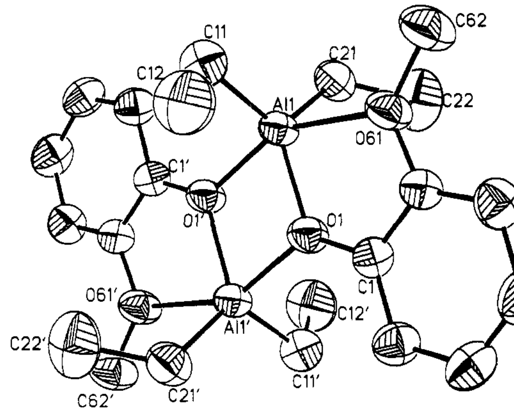

Figure 3. ORTEP diagram of the $[Et_2Al(\mu\text{-}OC_6H_4\text{-}2\text{-}OCH_3)]_2$ dimer, **2b**, showing the atom-labeling scheme. Hydrogen atoms are omitted for clarity.

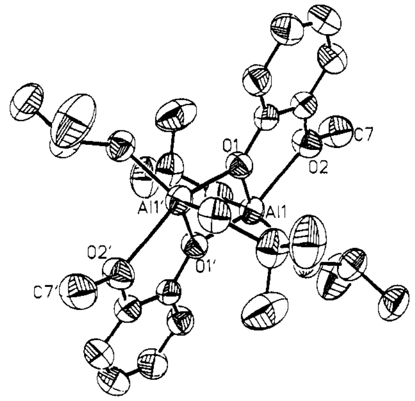

Figure 4. ORTEP diagram of the $[(i\text{-}Bu)_2Al(\mu\text{-}OC_6H_4\text{-}2\text{-}OCH_3)]_2$ dimer, **2c**, showing the atom-labeling scheme. Hydrogen atoms are omitted for clarity.

Molecular Geometry of the Dimeric $[R_2(\mu\text{-}OC_6H_4\text{-}2\text{-}ECH_3)]_2$ Derivatives. The ORTEP diagrams for **1a**, **1c**, **2b**, **2c**, and **3** are shown in Figures 1–5. The central structural unit of all five molecules is substantially determined by the rigid geometry of the ligands and the tendency of group 13 metal alkoxides to form oxygen-bridged dimers. The central unit consists of a four-membered ring composed of the two aluminum or gallium

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[5] Sheldrick, G. M. SHELXTL. University of Gottingen, Federal Republic of Germany, 1978.

[6] Sheldrick, G. M. SHELX-76. University Chemical Laboratory, Cambridge, England, 1976.

[7] *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV (present distributor D. Reidel, Dordrecht, The Netherlands).

Table I. Experimental Parameters for X-ray Diffraction Studies of [$Me_2Al(\mu$-OC_6H_4-2-$SCH_3)]_2$ (1a), [*i*-$Bu_2Al(\mu$-OC_6H_4-2-$SCH_3)]_2$ (1c), [$Et_2Al(\mu$-OC_6H_4-2-$OCH_3)]_2$ (2b), [*i*-$Bu_2Al(\mu$-OC_6H_4-2-$OCH_3)]_2$ (2c), and [$Me_2Ga(\mu$-OC_6H_4-2-$OCH_3]_2$ (3)

compd	[$Me_2Al(\mu$-OC_6H_4-2-$SCH_3)]_2$	[*i*-$Bu_2Al(\mu$-OC_6H_4-2-$SCH_3)]_2$	[$Et_2Al(\mu$-OC_6H_4-2-$OCH_3)]_2$	[*i*-$Bu_2Al(\mu$-OC_6H_4-2-$OCH_3)]_2$	[$Me_2Ga(\mu$-OC_6H_4-2-$OCH_3]_2$
formula	$C_{18}H_{26}Al_2O_2S_2$	$C_{30}H_{50}Al_2O_2S_2$	$C_{22}H_{34}O_4Al_2$	$C_{30}H_{50}O_4Al_2$	$C_{18}H_{26}O_4Ga_2$
mol wt	392.498	560.81	416.47	528.69	445.84
cryst prep	crystallized from toluene, −20 °C	crystallized from pentane, 25 °C	recrystallized from benzene, ambient temp	recrystallized from benzene, ambient temp	recrystallized from benzene, 10 °C
cryst color	colorless	colorless	colorless	colorless	colorless
cryst system	triclinic	triclinic	monoclinic	monoclinic	orthorhombic
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	*Pcab* (nonstandard setting of No. 61)
cell consts constrained from 25 high-angle reflcns					
a, Å	9.828 (2)	9.408 (2)	7.9733 (9)	9.037 (2)	6.845 (2)
b, Å	13.547 (2)	9.796 (4)	9.3984 (8)	19.427 (3)	15.994 (6)
c, Å	14.164 (2)	10.509 (5)	15.935 (1)	9.332 (2)	18.722 (6)
α, deg	62.15 (1)	83.66 (4)	90.000	90.000	90.000
β, deg	87.26 (1)	68.69 (3)	101.06 (1)	100.71 (1)	90.000
γ, deg	75.05 (2)	66.07 (3)	90.000	90.000	90.000
V, $Å^3$	1605.1 (5)	823.9 (6)	1171.95 (2)	1609.9 (4)	2050 (1)
d(calcd), g cm^{-3}	1.22	1.13	1.18	1.09	1.45
Z	3 (dimers)	1 (dimer)	2 (dimers)	2 (dimers)	4 (dimers)
radiation type (λ, Å)	Cu Kα (1.54178) with Ni filter	Mo K$\bar{\alpha}$ (0.71073) with graphite monochromator	Cu Kα (1.54178) with Ni filter	Mo Kα (0.71069) with graphite monochromator	Cu Kα (1.54178) with Ni filter
temp, K	293	293	293	293	293
type of data collcn	$\theta/2\theta$ scan	$\theta/2\theta$ scan	$\theta/2\theta$ scan	$\theta/2\theta$ scan	$\theta/2\theta$ scan
2θ scan range, deg	8–110	3–45	8–100	3–45	6–110
octants used	$+h,\pm k,\pm l$	$+h,\pm k,\pm l$	$+h,+k,\pm l$	$+h,+k,\pm l$	$+h,+k,\pm l$
scan rate, deg/min	variable 2–5	variable 4–29.3	variable 2.0–5.0	variable 4.0–29.3	variable 4.0–29.3
scan width	1.0° below Kα1 to 1.2° above Kα2	1.0° below Kα1 to 1.1° above Kα2	1.0° below Kα1 to 1.0° above Kα2	1.2° below Kα1 to 1.2° above Kα2	1.0° below Kα1 to 1.1° above Kα2
bckgd/scan ratio	1.0	1.0	1.0	1.0	1.0
std reflcns	3 measd per every 100 reflcns; decay less than 5%	3 measd per every 100 reflcns; decay less than 3%	3 measd per every 100 reflcns; decay less than 1%	3 measd per every 100 reflcns; decay less than 1%	3 measd per every 100 reflcns; decay less than 3%
no. of data collcd	4467	2236	1478	2442	1584
no. of unique data	3726	2165	1429	2334	1523
no. of obsd reflcns	2735 with $F_o \geq 3.0\sigma(F)$	1563 with $F_o \geq 3.0\sigma(F)$	1232 with $F_o \geq 3.0\sigma(F)$	1808 with $F_o \geq 3.0\sigma(F)$	1022 with $F_o \geq 3.0\sigma(F)$
linear abs coeff (μ), cm^{-1}	22.60	15.81	5.62	0.92	36.3
F(000), electrons	624	304	448	576	912
abs corr	none applied	none applied	none applied	none applied	empirical ψ scans
no. of params refined	385	239	144	263	137
$R = \sum(\|F_o\| - \|F_c\|)/\sum\|F_o\|$, %	6.2	3.5	3.83	3.52	4.32
$R_w = [\sum(\|F_o\| - \|F_c\|)^2/\sum w\|F_o\|^2]^{1/2}$, %	6.33	3.8	4.15	3.47	4.62
overall shift/esd	0.000	0.000	0.000	0.000	0.000
max shift/esd	0.001	0.001	0.001	0.002	0.007
resid electron density, e/$Å^3$	0.58, 1.3 Å from 53	0.18, 1.67 Å from C12	0.18, 1.31 Å from C2	0.2, 1.20 Å from C12	0.5, 1.27 Å from Gal
obsd/param ratio	7.10:1	6.54:1	6.17:1	6.87:1	7.46:1

atoms and the two bridging phenoxide oxygen atoms. This is depicted clearly in Figure 6A for **2b**. The second dominant structural feature is that the aromatic ring lies in the same plane as the M_2O_2 ring with the 2-methoxy or 2-(methylthio) moieties oriented so that they are "anti" to each other with the methoxy or methylthio group interacting with the aluminum or gallium atom in each case, giving rise to five-coordinate metal centers. The M_2O_2 ring is virtually planar in all cases, which is shown graphically in Figure 6B,C. The interatomic M···M distances range from 2.977 to 3.163 Å and are typical for molecules of this type. The M1–O1 and M1–O2 bridge-bond distances differ substantially in length. These distances are listed in Table VII and can be compared with the dialuminaoxane ring found in the diorganoaluminum compounds [$R_2Al(\mu$-$OR')]_2$ (R = Me, Et; OR′ = $-OC_6H_3$-2-allyl-6-CH_3, *l*-mentholate, *l*-borneolate).[3,8] The distances in these simple oxygen-bridged dimers are equal within experimental error and close to the short Al–O1 distance observed in these phenoxides. The axial Al–O2 bond distances shown in Table VII are greater than the sum of the covalent radii of the atoms[9] and are significantly longer than those found in simple ether adducts of trialkylaluminum[3] but comparable to those reported in the related complexes listed in Table VII for the axial distances.[10] The gallium–oxygen ring

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(8) Kumar, R.; Sierra, M. L.; de Mel, V. S. J.; Oliver, J. P. *Organometallics* **1990**, *9*, 484.

(9) Pauling, L. *The Nature of Chemical Bonds*; University Press: Ithaca, New York, 1960.

Table II. Atomic Coordinates and Isotropic Thermal Parameters for Non-Hydrogen Atoms in $[Me_2Al(\mu\text{-}OC_6H_4\text{-}2\text{-}SCH_3)]_2$ (1a)

atom	x	y	z	U_{eq},[a] Å^2
Al1	−0.0345 (3)	0.2327 (2)	0.3518 (2)	0.058 (1)
C1	0.1622 (9)	0.2148 (7)	0.3811 (6)	0.083 (6)
C2	−0.1479 (9)	0.1194 (6)	0.4085 (6)	0.079 (6)
O1	−0.1237 (5)	0.3377 (4)	0.4101 (4)	0.063 (3)
C5	−0.1228 (9)	0.3102 (7)	0.5152 (7)	0.057 (5)
C6	−0.0441 (9)	0.2041 (7)	0.5949 (7)	0.070 (6)
C7	−0.043 (1)	0.1772 (8)	0.7016 (7)	0.078 (6)
C8	−0.122 (1)	0.258 (1)	0.7297 (8)	0.092 (7)
C9	−0.202 (1)	0.3622 (9)	0.6554 (8)	0.087 (7)
C10	−0.2000 (9)	0.3899 (7)	0.5479 (7)	0.065 (5)
S1	−0.3057 (3)	0.5267 (2)	0.4480 (2)	0.074 (1)
C11	−0.198 (1)	0.6179 (7)	0.4450 (7)	0.108 (7)
Al2	−0.2356 (3)	0.4636 (2)	0.2925 (2)	0.056 (1)
C3	−0.4253 (8)	0.4480 (6)	0.2882 (6)	0.076 (5)
C4	−0.1552 (9)	0.5951 (6)	0.2109 (6)	0.082 (6)
O2	−0.1347 (5)	0.3637 (4)	0.2306 (4)	0.063 (3)
C12	−0.1597 (9)	0.3792 (7)	0.1311 (7)	0.057 (5)
C13	−0.260 (1)	0.4748 (7)	0.0580 (7)	0.074 (6)
C14	−0.287 (1)	0.4886 (8)	−0.0429 (7)	0.085 (6)
C15	−0.215 (1)	0.4067 (9)	−0.0717 (7)	0.094 (7)
C16	−0.114 (1)	0.3109 (8)	−0.0003 (8)	0.082 (7)
C17	−0.0907 (9)	0.2940 (7)	0.1016 (7)	0.062 (5)
S2	0.0368 (2)	0.1702 (2)	0.1946 (2)	0.070 (1)
C18	0.1990 (9)	0.2070 (8)	0.1489 (8)	0.101 (7)
A13	0.6064 (3)	1.0650 (2)	−0.0120 (2)	0.056 (1)
C19	0.7996 (8)	0.9773 (7)	−0.0016 (6)	0.077 (6)
C20	0.529 (1)	1.2345 (6)	−0.0887 (7)	0.099 (6)
O3	0.4955 (5)	0.9835 (4)	0.0902 (4)	0.061 (3)
C21	0.4980 (9)	0.9514 (7)	0.1990 (7)	0.059 (5)
C22	0.411 (1)	0.8824 (8)	0.2614 (8)	0.081 (6)
C23	0.413 (1)	0.8509 (9)	0.3699 (8)	0.100 (7)
C24	0.499 (1)	0.8842 (9)	0.4153 (8)	0.103 (8)
C25	0.583 (1)	0.9528 (8)	0.3538 (8)	0.081 (6)
C26	0.5796 (8)	0.9883 (6)	0.2446 (7)	0.057 (5)
S3	0.6834 (2)	1.0819 (2)	0.1642 (2)	0.066 (1)
C27	0.578 (1)	1.2168 (7)	0.1577 (7)	0.096 (6)

[a] B values for anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2U_{11} + b^2U_{22} + c^2U_{33} + ab(\cos\gamma)U_{12} + ac(\cos\beta)U_{13} + bc(\cos\alpha)U_{23}]$.

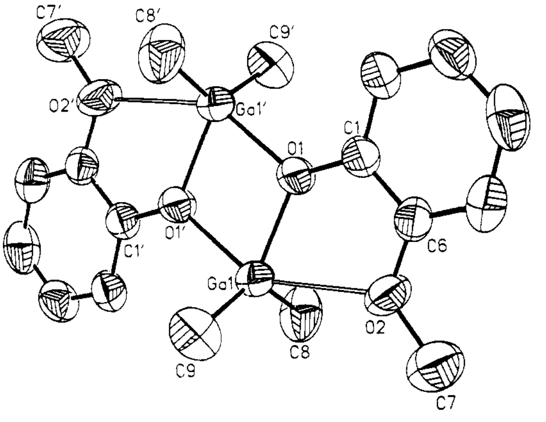


Figure 5. ORTEP diagram of the $[Me_2Ga(\mu\text{-}OC_6H_4\text{-}2\text{-}OCH_3)]_2$ dimer, **3**, showing the atom-labeling scheme. Hydrogen atoms are omitted for clarity.

system is very similar with the Ga–O distances only slightly greater than those observed for the aluminum derivatives.

Table III. Atomic Coordinates and Isotropic Thermal Parameters for Non-Hydrogen Atoms in $[i\text{-}Bu_2Al(\mu\text{-}OC_6H_4\text{-}2\text{-}SCH_3)]_2$ (1c)

atom	x	y	z	U_{eq},[a] Å^2
S1	−0.1560 (1)	0.2323 (1)	0.4322 (1)	0.0582 (4)
Al1	0.0022 (1)	0.3476 (1)	0.5418 (1)	0.0371 (9)
O1	−0.0773 (2)	0.5010 (2)	0.4314 (2)	0.039 (1)
C1	−0.1436 (3)	0.5000 (3)	0.3342 (3)	0.041 (2)
C2	−0.1729 (4)	0.6195 (4)	0.2492 (3)	0.053 (2)
C3	−0.2302 (5)	0.6149 (5)	0.1463 (4)	0.065 (1)
C4	−0.2591 (5)	0.4944 (5)	0.1274 (4)	0.071 (1)
C5	−0.2357 (5)	0.3773 (4)	0.2126 (4)	0.062 (2)
C6	−0.1783 (4)	0.3796 (3)	0.3178 (3)	0.046 (2)
C7	−0.3717 (6)	0.2827 (6)	0.5370 (5)	0.080 (2)
C8	−0.1575 (4)	0.3396 (4)	0.7242 (3)	0.044 (2)
C9	−0.1565 (4)	0.1877 (4)	0.7786 (3)	0.050 (2)
C10	−0.0084 (6)	0.0988 (5)	0.8219 (4)	0.068 (2)
C11	−0.3162 (6)	0.2032 (5)	0.8961 (4)	0.076 (1)
C12	0.2152 (4)	0.1820 (4)	0.4520 (3)	0.050 (1)
C13	0.3418 (4)	0.2000 (4)	0.3208 (3)	0.057 (1)
C14	0.5106 (5)	0.0708 (5)	0.2873 (5)	0.082 (1)
C15	0.3858 (6)	0.2286 (6)	0.2005 (4)	0.090 (1)

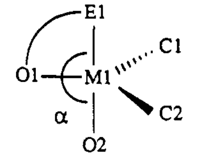
[a] B values for anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2U(1,1) + b^2U(2,2) + c^2U(3,3) + ab(\cos\gamma)U(1,2) + ac(\cos\beta)U(1,3) + bc(\cos\alpha)U(2,3)]$.

Table IV. Atomic Coordinates and Isotropic Thermal Parameters for Non-Hydrogen Atoms in $[Et_2Al(\mu\text{-}OC_6H_4\text{-}2\text{-}OCH_3)]_2$ (2b)

atom	x	y	z	U_{eq},[a] Å^2
Al1	0.0704 (2)	0.8513 (1)	0.01584 (8)	0.0402 (5)
O1	−0.0257 (4)	0.9975 (3)	0.0695 (2)	0.045 (1)
C1	−0.0486 (5)	0.9921 (5)	0.1524 (2)	0.039 (2)
C2	−0.1172 (5)	1.1012 (5)	0.1919 (3)	0.051 (2)
C3	−0.1361 (6)	1.0859 (6)	0.2765 (3)	0.057 (2)
C4	−0.0863 (6)	0.9621 (6)	0.3197 (3)	0.062 (2)
C5	−0.0165 (5)	0.8513 (5)	0.2810 (3)	0.053 (2)
C6	0.0022 (5)	0.8680 (5)	0.1973 (3)	0.042 (2)
O61	0.0689 (4)	0.7694 (3)	0.1483 (2)	0.051 (2)
C62	0.1366 (7)	0.6389 (5)	0.1867 (3)	0.067 (2)
C11	0.3198 (5)	0.8357 (5)	0.0372 (3)	0.058 (2)
C12	0.4155 (7)	0.9280 (7)	0.1097 (4)	0.087 (2)
C21	−0.0819 (6)	0.7011 (5)	−0.0382 (3)	0.055 (2)
C22	−0.2332 (7)	0.6585 (8)	0.0023 (4)	0.085 (3)

[a] B values for anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2U(1,1) + b^2U(2,2) + c^2U(3,3) + ab(\cos\gamma)U(1,2) + ac(\cos\beta)U(1,3) + bc(\cos\alpha)U(2,3)]$.

The coordination sphere around the aluminum or gallium atoms can be described in terms of a distorted trigonal bipyramid. This is shown in I. The alkyl carbon atoms and the more tightly bound bridging phenoxide oxygen atom, O1, lie in the equatorial plane. The bite angle, O1–M1–E1, for this chelate ring varies from 73 to 76° for the methoxy derivatives and is 77° for the methylthio complexes (Table VII). The methoxy or methylthio group from this phenoxide ligand and the phenoxide oxygen from the second ligand are the axial positions. The sum of the bond angles in the equatorial plane ranges from 358 to 360°, which is a measure of the planarity of the equatorial groups. The axial E1–M1–O2 angles, α, for each of the compounds is given in Table VII and range from 145 to 156°. The large deviation from the ideal 180° arises from the constraints placed on it by the rigid geometry of



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(10) (a) van Vliet, M. R. P.; Buysingh, P.; van Koten, G.; Vrieze, K.; Kojić-Prodić, B.; Spek, A. L. *Organometallics* **1985**, *4*, 1701. (b) Kai, Y.; Yasuoka, N.; Kasai, N.; Kakudo, M. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 3397. (c) Benn, R.; Rufińska, A.; Lehmkuhl, H.; Janssen, E.; Kruger, C. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 779. (d) Sierra, M. L.; de Mel, V. S. J.; Oliver, J. P. *Organometallics* **1989**, *8*, 2486. (e) Dzugan, S. T.; Goedken, V. L. *Inorg. Chim. Acta* **1988**, *154*, 169.

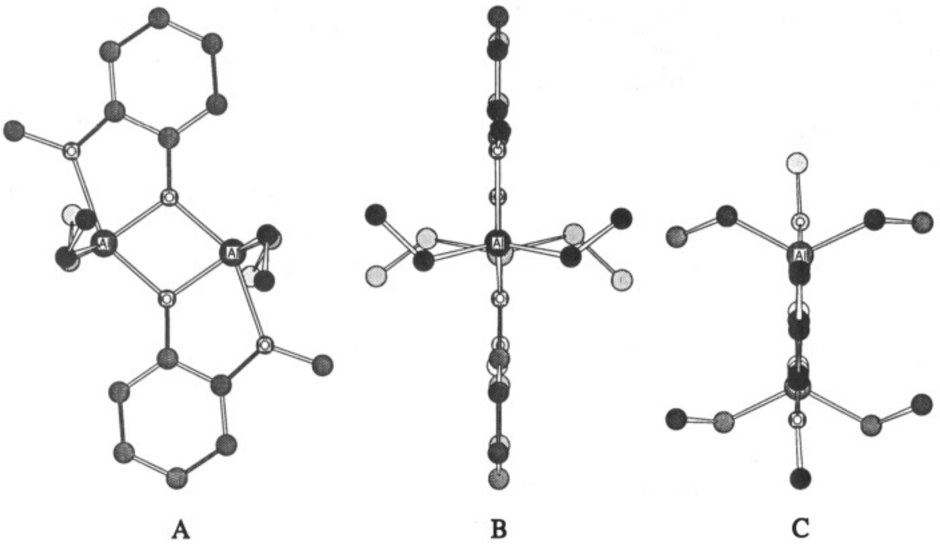

Figure 6. Molecular structure of $[Et_2Al(\mu\text{-}OC_6H_4\text{-}2\text{-}OCH_3)]_2$ (**2b**): **A**, viewed perpendicular to the Al_2O_2 plane; **B**, rotated 90° about the *y* axis; **C**, rotated 90° about the *x* and *y* axes.

Table V. Atomic Coordinates and Isotropic Thermal Parameters for Non-Hydrogen Atoms in $[i\text{-}Bu_2Al(\mu\text{-}OC_6H_4\text{-}2\text{-}OCH_3)]_2$ (2c)

atom	x	y	z	U_{eq},^{a} Å^2
Al1	0.52391 (7)	0.57451 (3)	0.04507 (7)	0.0467 (2)
O1	0.4474 (1)	0.49231 (6)	0.1032 (1)	0.0468 (5)
O2	0.4383 (2)	0.60085 (7)	0.2519 (2)	0.0603 (6)
C1	0.3829 (2)	0.4854 (1)	0.2246 (2)	0.0464 (7)
C2	0.3760 (2)	0.5442 (1)	0.3068 (2)	0.0501 (8)
C3	0.3124 (3)	0.5429 (2)	0.4292 (3)	0.066 (1)
C4	0.2544 (3)	0.4821 (2)	0.4694 (3)	0.075 (1)
C5	0.2605 (3)	0.4236 (2)	0.3901 (3)	0.071 (1)
C6	0.3258 (3)	0.4250 (1)	0.2667 (2)	0.0584 (9)
C7	0.4184 (4)	0.6665 (2)	0.3161 (4)	0.077 (1)
C11	0.7347 (3)	0.5937 (1)	0.1335 (3)	0.0564 (1)
C12	0.7872 (3)	0.6572 (1)	0.2221 (3)	0.071 (1)
C13	0.9523 (4)	0.6530 (2)	0.2955 (4)	0.092 (1)
C14	0.7605 (5)	0.7219 (2)	0.1340 (5)	0.116 (2)
C21	0.3893 (3)	0.6415 (1)	−0.0731 (3)	0.0591 (9)
C22	0.2452 (3)	0.6155 (1)	−0.1694 (3)	0.066 (1)
C23	0.1787 (5)	0.6678 (2)	−0.2862 (4)	0.096 (1)
C24	0.1305 (4)	0.5941 (3)	−0.0803 (5)	0.107 (2)

^{a} *B* values for anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3]a^2U(1,1) + b^2U(2,2) + c^2U(3,3) + ab(\cos\gamma)U(1,2) + ac(\cos\beta)U(1,3) + bc\ (\cos\alpha)U(2,3)]$.

Table VI. Atomic Coordinates and Isotropic Thermal Parameters for Non-Hydrogen Atoms in $[Me_2Ga(\mu\text{-}OC_6H_4\text{-}2\text{-}OCH_3)]_2$ (3)

atom	x	y	z	U_eq,^{a} Å^2
Ga1	0.1003 (1)	0.08487 (5)	0.52311 (4)	0.0492 (3)
O1	0.0671 (7)	−0.0309 (3)	0.5548 (2)	0.056 (2)
C1	0.161 (1)	−0.0688 (4)	0.6096 (3)	0.048 (2)
C2	0.146 (1)	−0.1555 (5)	0.6211 (4)	0.060 (3)
C3	0.248 (1)	−0.1916 (5)	0.6763 (4)	0.068 (3)
C4	0.362 (1)	−0.1443 (6)	0.7214 (4)	0.076 (4)
C5	0.376 (1)	−0.0581 (5)	0.7113 (4)	0.065 (3)
C6	0.277 (1)	−0.0220 (4)	0.6560 (3)	0.050 (2)
O2	0.2743 (8)	0.0630 (3)	0.6403 (3)	0.070 (2)
C7	0.394 (2)	0.1164 (5)	0.6823 (5)	0.095 (4)
C8	−0.082 (2)	0.1596 (8)	0.5717 (6)	0.084 (4)
C9	0.343 (1)	0.1046 (5)	0.4723 (4)	0.079 (3)

^{a} *B* values for anisotropically refined atoms are given in the form of teh isotropic equivalent thermal parameter defined as $^4/_3[a^2U(1,1) + b^2U(2,2) + c^2U(3,3) + ab(\cos\gamma)U(1,2) + ac(\cos\beta)U(1,3) + bc(\cos\alpha)U(2,3)]$.

the ligand and from the internal O1–M1–O2 angle in the M_2O_2 ring. It should be noted that there is some distortion of the ligand angles. The O1–C5–C6 angles observed in the 2-methoxyaluminum derivatives are 116.5–116.7°, less than the idealized angle of 120°. The E1–C6–C5 angle in the three 2-methoxy derivatives is 112°, substantially less than the expected 120° angle. These facts provide additional evidence for the coordination of the EMe group to the metal center. Distortion of these angles is not observed in the 2-methylthio derivatives but may be accounted for by the greater Al–S and C–S bond distances.

The Al–S distances in these compounds are listed in Table VIII along with those for a number of other compounds reported in the literature. The 2.724-Å distance is considerably longer than that observed in dimeric organoaluminum thiolato complexes[11] but is in the range observed in the sulfur addition compounds.[12] The geometry around the sulfur atom in the methylthio derivatives may be described as pyramidal with the sum of the angles around the sulfur atom just under 300° in both cases. The C7–S–C6 angles are approximately 100°, the Al–S–C7 angles, 90°, and the Al–S–C6 angles, 108°. The geometry around the methoxy oxygen atom shows this atom to be in a three-coordinate planar environment in all cases.

NMR Studies. The ^{1}H NMR spectra of all of the derivatives taken at room temperature are essentially as expected. There is no OH or SH resonance, indicating loss of hydroxyl or thiol protons. The alkyl groups attached to the metal center and the EMe groups are in the expected chemical shift ranges with both the ^{13}C and ^{1}H signals shifted only slightly from the starting materials (Table IX). Examination of the ^{1}H NMR spectra of all five compounds shows that the alkyl groups bound to the metal atoms in a given complex are equivalent. This is also true for the bridging ligands. These simple NMR spectra are in contrast to the results obtained from earlier studies where two sets of Al–R resonances due to different magnetic environments are found in complexes containing

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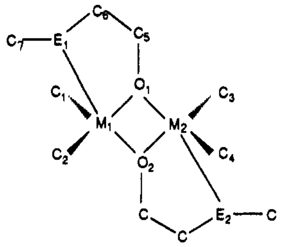
(11) (a) Kumar, R.; de Mel, V. S. J.; Oliver, J. P. *Organometallics* **1989**, *8*, 2488. (b) de Mel, V. S. J.; Kumar, R.; Oliver, J. P. *Organometallics* **1990**, *9*, 1303. (c) Brauer, D. J.; Stucky, G. D. *J. Am. Chem. Soc.* **1969**, *91*, 5462. (d) Robinson, G. H.; Self, M. F.; Pennington, W. T.; Sangokoya, S. A. *Organometallics* **1988**, *7*, 2424. (e) Boardman, A.; Small, R. W. H.; Worrall, I. J. *Inorg. Chim. Acta* **1986**, *120*, L23. (f) Nöth, H.; Konrad, P. *Chem. Ber.* **1983**, *116*, 3552.

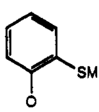
(12) (a) Robinson, G. H.; Sangokoya, S. A. *J. Am. Chem. Soc.* **1988**, *110*, 1494. (b) Robinson, G. H.; Zhang, H.; Atwood, J. L. *Organometallics* **1987**, *6*, 887. (c) Sangokoya, S. A.; Lee, B.; Pennington, W. T.; Robinson, G. H. *J. Coord. Chem.* **1989**, *19*, 331. (d) Fernholt, L.; Haaland, A.; Hargittai, M.; Seip, R.; Weidlein, J. *Acta Chem. Scand., Ser. A* **1981**, *A35*, 529.

Table VII. Selected Bond Distances (Å) and Bond Angles (deg) for $[R_2M(\mu\text{-}OC_6H_4\text{-}2\text{-}EMe)]_2$[a]

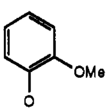
	1a[b]	1c	2b	2c	3	4[c]	5[d]	6[e]	7[f]	8[g]
M1–M2	2.985 (3) 2.977 (3)	3.005 (1)	3.018 (2)	3.023 (8)	3.163 (3)	3.115		3.055	3.024	3.000
M1–O1	1.865 (6) 1.856 (6) 1.865 (6)	1.870 (2)	1.859 (3)	1.861 (1)	1.957 (4)	1.868	1.827	1.858	1.853	1.864
M1–O2	1.963 (6) 1.980 (6) 1.946 (6)	1.966 (2)	1.952 (3)	1.950 (1)	2.046 (4)	2.002	1.892	1.985	1.935	1.946
M1–E1	2.734 (6) 2.714 (4) 2.767 (4)	2.778 (1)	2.249 (3)	2.267 (1)	2.521 (5)	2.136	2.269	2.045	2.130	2.193
M1–C1	1.973 (8) 1.962 (8) 1.970 (8)	1.976 (4)	1.957 (4)	1.972 (2)	1.95 (1)	1.05	1.962	1.96	2.014	1.999
M1–C2	1.926 (9) 1.937 (8) 1.934 (8)	1.966 (2)	1.952 (5)	1.966 (2)	1.942 (8)	1.95	1.940	1.96	1.974	1.989
O1–M1–O2	77.7 (3) 77.5 (3) 77.3 (3)	76.86 (9)	73.3 (1)	75.00 (6)	75.6 (2)	72.6	76.3	73.3	74.1	74.8
M1–O1–M2	102.8 (3) 101.8 (3) 102.7 (3)	103.1 (1)	104.7 (1)	105.00 (6)	104.4 (2)	107.5	103.7	105.3	105.5	104.0
E1–M1–O2	155.8 (2) 156.3 (2) 155.6 (2)	154.8 (1)	150.4 (1)	150.1 (1)	145.8 (2)	152.7		158.3	151.7	151.6
C1–M1–C2	130.8 (4) 131.5 (4) 127.5 (4)	124.3 (1)	123.2 (2)	123.97 (11)	132.5 (4)	122.7	120.8	119.4	126.1	118.5
E1–C6–C5	118 (1) 119 (1) 121 (1)	120.1 (4)	112.2 (3)	112.9 (2)	112.7 (6)					
O1–C5–C6	121 (1) 120.6 (9) 121.7 (9)	120.9 (4)	116.7 (3)	116.5 (2)	120.2 (6)					
E1–M1–O1	77.7 (3) 77.5 (3) 77.3 (3)	77.95 (7)	75.2 (1)	75.01 (6)	70.1 (2)	79.2	75.9	85.1	77.2	78.5

[a] The numbering system used, along with the structures of each of the ligands used in complex formation, is shown as follows:

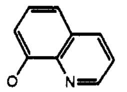




1a, 1c



2b, 2c, 3



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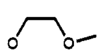

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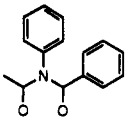

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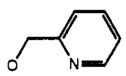

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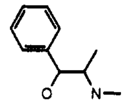

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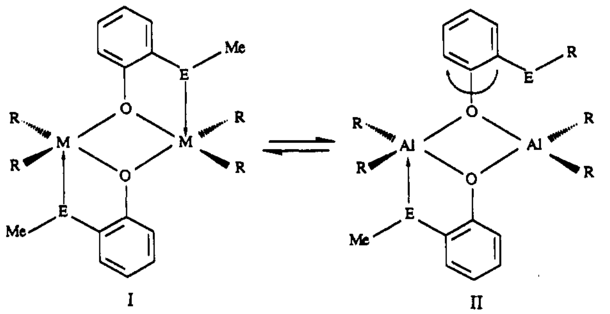
The values taken from the literature have been renumbered according to this scheme, and average values have been used when more than one independent distance occurs in the molecule. [b] The solid-state structure contains $1^1/_2$ dimers in the asymmetric unit, giving rise to the independent distances and angles listed for **1a**. [c] Reference 9e. [d] Reference 9c. [e] Reference 9b. [f] Reference 9a. [g] Reference 9d.

Table VIII. Al–S Bond Distances in Organoaluminum Thioether Derivatives

compd	Al–S, Å	ref
$[Me_2Al(\mu\text{-}OC_6H_4\text{-}2\text{-}SCH_3)]_2$ (molecule 1)	2.734 2.714	this work this work
$[Me_2Al(\mu\text{-}OC_6H_4\text{-}2\text{-}SCH_3)]_2$ (molecule 2)	2.767	this work
$[i\text{-}Bu_2Al(\mu\text{-}OC_6H_4\text{-}2\text{-}SCH_3)]_2$	2.778	this work
$[(Me_3Al)(12)aneS_4$	2.718	11a
$(Me_3Al)_4(14)aneS_4$	2.522	11b
$(Me_3Al)_4(12)aneS_4$	2.515	11c
$Me_3Al{\cdot}SMe_2$ (gas phase)	2.55	11d

five-coordinate aluminum centers.[3,10a,d,e] In the $[Et_2Al(8\text{-}quinolinolato)]_2$ dimer nonequivalence of the methylene groups only appears at low temperature where exchange is slowed.[10e] In the present system there are two possible explanations for the observed equivalence of the groups. They may be equivalent by symmetry, giving rise to the observed spectra, or alternatively, the weak M–E dative bond may undergo dissociation in solution, giving rise to the equilibrium with the four-coordinate species shown in eq 2 with rapid interchange occurring among the syn, anti,



(2)

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and five-coordinate species. The possibility of this exchange and the observed temperature-dependent NMR spectra of the $[Et_2Al(8\text{-}quinolinolato)]_2$ dimer by Dzugan and Goedken[10e] led us to examine the NMR spectra of several of these complexes as a function of temperature.

Table IX. ^1H and ^{13}C Chemical Shifts for $[R_2Al(\mu\text{-}OC_6H_4\text{-}2\text{-}EMe)]_2$ Derivatives[a]

	^1H				^{13}C			
	Al-R				Al-R			
	α	β	γ	E–Me	α	β	γ	E–Me
1a	–0.11 (s)			1.79	-7.1			21.5
1b	–0.47 (q)	1.30 (4)		1.90	2.2	9.8		21.7
1c	0.56 (d)	2.03 (m)	1.09 (d)	1.96	24.5	26.5	28.6	21.3
2a	–0.28 (s)			3.16	-9.5			54.0
2b	0.38 (q)	1.28 (t)		3.30	1.0	9.8		54.8
2c	0.43 (d)	2.02 (m)	1.09 (d)	3.36	23.8	26.3	28.8	55.2
3	0.17 (s)			3.13	-4.6			54.0
9[b]				3.16				55.2
10[c]				1.80				19.2
$AlMe_3$[d]	–0.32 (s)				-7.3			
$AlEt_3$[d]	0.32 (q)	1.10 (t)			0.4	8.8		
A(*i*-Bu)$_3$[d]	0.24 (d)	1.19 (m)	0.97 (d)		21.4	26.3	28.3	

[a] All values are for benzene solutions taken at room temperature. [b] 2-methoxyphenol. [c] 2-(methylthio)phenol. [d] The alkylaluminum spectra were obtained at room temperature and represent average chemical shifts for the bridge and terminal groups and monomers under fast-exchange conditions.

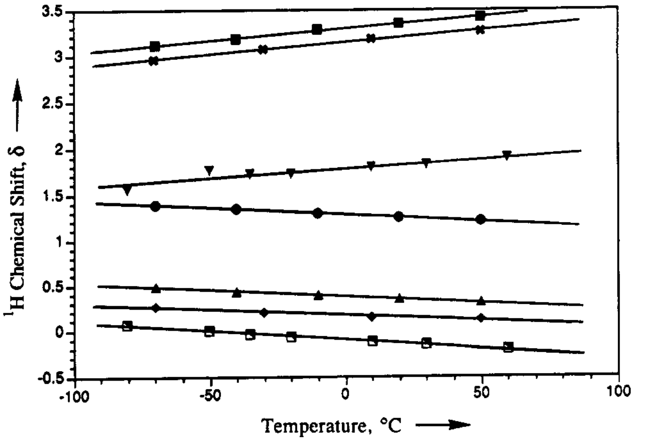

Figure 7. Plot of the ^1H chemical shift (δ) versus the temperature (*T*, °C) for the alkyl group, R, and the EMe group in **1a** (Me, ◪; SMe, ▼), **2b** ($\mathit{CH_2}CH_3$, ▲; $CH_2\mathit{CH_3}$, ●; OMe, ■), and **3** (Me, ◆; OMe, ×).

There are no dramatic changes in the spectra as a function of temperature, indicating a single environment for the alkyl groups under all conditions studied. There are, however, substantial changes in the chemical shifts of these groups. The changes in the ^1H chemical shifts for the alkyl group attached to the metal, R, and for the EMe group for compounds **1a**, **2b**, and **3** are shown in Figure 7. In each case the ^1H chemical shifts of the metal–alkyl group move to higher field with increasing temperature while the EMe group moves in the opposite direction. The ^{13}C chemical shifts also show a temperature dependence with the OMe group moving downfield and the metal–alkyl groups moving upfield with increasing temperature. These observed changes in chemical shift are consistent with a shift in the equilibrium shown in eq 2 to the right with rapid rotation about the O–C bond. At low temperature, species I predominates; as the temperature is increased, increasing proportions of the ER groups are rotated away from the fifth coordination site, giving rise to four-coordinate aluminum species such as the bridged dimeric conformation depicted in II. The rapid exchange among the possible conformations gives rise to a single magnetic environment on the NMR time scale.

^{27}Al NMR spectra could not be observed on benzene-d_6 solutions of the $[R_2Al(\mu\text{-}OC_6H_4\text{-}2\text{-}SCH_3)]_2$ compounds, but addition of one drop of THF to these solutions led us to observe a broad resonance with δ = 133 ppm and a shoulder at 177 ppm for **1a**, 146 ppm for **1b**, and 144 ppm for **1c**. The initial failure to observe the ^{27}Al signal likely results from the quadrupolar relaxation in the very asymmetric field in the five-coordinate species. The observation of the ^{27}Al resonance in the presence of added THF indicates the electric field gradient around the Al atom has become more symmetric. This is consistent with the disruption of the bridge bond and the formation of a four-coordinate addition compound. The observed chemical shifts are also consistent with this proposal, since they are typical of four-coordinate aluminum complexes.[13]

The conclusions that can be drawn from these studies are that the 2-methoxy- and 2-(methylthio)phenols form stable bridged dimers with aluminum and gallium alkyls that contain five-coordinate metal centers. The structures are dominated by the geometry and rigid nature of the ligands. The NMR studies indicate that the equilibrium shown in eq 2 occurs with rapid rotation of the bridging groups. The change in chemical shift, especially of the OMe, SMe, and alkyl groups as a function of temperature, is consistent with a rotation/dissociation process with the OMe or SMe spending an increasing amount of time twisted away from the metal center as the temperature increases. Finally, the ^{27}Al studies can be interpreted in terms of the disruption of the bridge bond by THF with formation of a monomeric four-coordinate species in solution.

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Supplementary Material Available: For **1a**,**c**, **2b**,**c**, and **3**, tables of anisotropic thermal parameters for the non-hydrogen atoms, atomic coordinates and isotropic thermal parameters for the hydrogen atoms, complete bond angles and distances, and least-squares planes (71 pages); listings of observed and calculated structure factors (61 pages). Ordering information is given on any current masthead page.

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(13) (a) Benn, R.; Janssen, E.; Lehmkuhl, H.; Rufińska, A. *J. Organomet. Chem.* **1987**, *333*, 155. (b) Benn, R.; Janssen, E.; Lehmkuhl, H.; Rufińska, A. *J. Organomet. Chem.* **1987**, *333*, 169. (c) Benn, R.; Janssen, E.; Lehmkuhl, H.; Rufińska, A. *J. Organomet. Chem.* **1987**, *333*, 181.