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Phenoxides and Thiophenoxides of Aluminum and Gallium. Evidence of a $^1H-^{19}F$ Coupling in $(R_2MOC_6F_5)_2$ in Solution. Crystal and Molecular Structures of $(Me_2AlOC_6F_5)_2$ and $(Me_2GaSC_6F_5)_2$

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The reaction of trialkylaluminum and -gallium derivatives with pentafluorophenol and pentafluorothiophenol yields the corresponding phenoxides and thiophenoxides, $(R_2MEC_6F_5)_2$ (M = Al, E = O, R = Me (**1a**), Et (**1b**), and *i*-Bu (**1c**); M = Ga, E = O, R = Me (**2a**); M = Ga, E = S, R = Me (**2b**)) quantitatively. These compounds have been characterized by ^1H, ^{13}C, and ^{19}F NMR spectroscopy, and the structures of **1a** and **2b** were determined by single-crystal X-ray diffraction techniques. **1a** was assigned to the orthorhombic cell system, space group *Cmcm* (No. 63), with cell constants $a = 11.058$ (2) Å; $b = 16.908$ (2) Å, $c = 10.764$ (2) Å, and $Z = 4$ (dimers). The refinement converged with $R = 6.99\%$ ($R_w = 7.87\%$) based on 541 ($I \geq 2.5\sigma(I)$) observed reflections. The molecule exists as an oxygen-bridged dimer with a central planar four-membered Al_2O_2 ring. The average Al–O bridge bond distance is 1.895 (5) Å. **2b** was assigned to the triclinic cell system, space group $P\bar{1}$ (No. 2) with cell constants $a = 9.790$ (3) Å, $b = 10.122$ (1) Å, $c = 11.284$ (1) Å, $\alpha = 76.08$ (1)°, $\beta = 89.67$ (2)°, $\gamma = 86.99$ (2)°, and $Z = 2$ (dimers). The refinement converged with $R = 4.65\%$ ($R_w = 4.89\%$) based on 1920 ($I \geq 3.0\sigma(I)$) observed reflections. The molecule exists as a sulfur-bridged dimer with a puckered four-membered Ga_2S_2 ring. The average Ga–S bridge bond distance is 2.450 (3) Å. **1a** does not react with diethyl ether or tetrahydrofuran but is cleaved by 4-picoline to give a 1:1 addition complex. ^1H and ^{19}F NMR spectra of $(R_2MOC_6F_5)_2$ in toluene-d_8 or benzene-d_6 solutions show $^1H-^{19}F$ coupling with a $^6J_{FH} = 2.0$ Hz. In contrast, long-range H–F coupling is not observed in the sulfur derivatives of either gallium or aluminum. Variable-temperature ^1H NMR studies established that the Al_2S_2 and Ga_2S_2 ring systems undergo rapid inversion/exchange, which leads to equivalence of the alkyl groups attached to the metal atoms.

Introduction

We have had a long-standing interest in the structure and spectral properties of organoaluminum and -gallium compounds containing a group 15 or 16 bridging atom[1] and have recently reported the structure of the pentafluorothiophenoxide $(Me_2AlSC_6F_5)_2$.[2] These studies now have been extended to the preparation and characterization of the pentafluorophenoxides of aluminum and gallium $(R_2AlOC_6F_5)_2$ (R = Me (**1a**), Et (**1b**), *i*-Bu (**1c**)) and $(Me_2GaOC_6F_5)_2$ (**2a**). We also have prepared and characterized the pentafluorothiophenoxide of gallium $(Me_2GaSC_6F_5)_2$ (**2b**). This work includes the crystal and molecular structures of **1a** and of **2b** and a multinuclear NMR study of these systems. It has been established that long-range $^1H-^{19}F$ coupling between the ortho-fluorine atoms and the protons on the α-carbon attached to the metal occurs in the pentafluorophenoxide derivatives but does not occur in the pentafluorothiophenoxides. It also has been shown that the alkyl groups attached to the metal in the sulfur derivatives are equivalent on the NMR time scale, which has been interpreted in terms of rapid intramolecular motion. These studies and others provide some insight into the stability of the Al–O–Al and Ga–O–Ga bridge bonds.

Experimental Section

General Data. All solvents were purified and dried by standard techniques.[3] Argon gas was purified by passing it through a series of columns containing Deox catalyst (Alfa), phosphorous 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), pentafluorothiophenol (Aldrich), and pentafluorophenol (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, ^{13}C, and ^{19}F NMR spectra were recorded on either a General Electric QE-300 or GN-300 NMR spectrometer. The ^1H and ^{13}C chemical shifts were referenced to toluene-d_8 peaks ($\delta = 2.09$ ppm for ^1H and $\delta = 20.4$ ppm for ^{13}C) or benzene-d_6 peaks ($\delta = 7.15$ ppm for ^1H and $\delta = 128.0$ ppm for ^{13}C). The ^{19}F chemical shifts were referenced to an external standard of 10% $CFCl_3$ in acetone-d_6 ($\delta = 0.00$ ppm).

Preparation of $(Me_2AlOC_6F_5)_2$ (1a). Pentafluorophenol (1.78 g, 9.7 mmol) was dissolved in pentane (50 mL), and Me_3Al (4.83 mL, 9.7 mmol) was added over a period of 5 min. The resulting reaction was exothermic, bringing the pentane to reflux. Although the reaction appeared to be instantaneous, the reaction mixture was left stirring for an additional 2 h to ensure completion. The resulting solution deposited colorless needles on standing overnight at −20 °C. The product was collected, washed with 10–15 mL of cold pentane, and dried in vacuo. This solid was identified as $Me_2AlOC_6F_5$. Yield: >90%. Anal. Calcd for $C_8H_6AlF_5O$: C, 40.0; H, 2.5. Found: C, 39.6; H, 2.5. NMR parameters (ppm): ^1H, −0.31 (quintet, Al–Me, $^6J_{H-F} = 2$ Hz); $^{13}C\{^1H\}$, −10.6 (Al–Me); ^{19}F, −154.9 (2,6-F, m, $^3J_{F-F} = 21$ Hz), −160.8 (3,5-F, m, $J_{F-F} = 23$ Hz), −161.8 (4-F, m, $^3J_{F-F} = 23$ Hz). ^1H NMR (ppm): (C_6F_5OH): 4.2 (s, br, C_6F_5OH). ^{19}F NMR (ppm): −163.1 (2,6-F, m), −164.1 (3,5-F, m), −168.7 (4-F, m).

Preparation of $(Et_2AlOC_6F_5)_2$ (1b). The procedure for this reaction is the same as described for **1a**, using pentafluorophenol (1.763 g, 9.6 mmol) and Et_3Al (5.04 mL, 9.6 mmol). The solvent was removed in vacuo to leave a white solid. The product was recrystallized by dissolving it in 15 mL of pentane and cooling the solution to −20 °C overnight. This solid was identified as $Et_2AlOC_6F_5$. Yield: 80%. NMR parameters (ppm): ^1H, 0.28 (m, $^6J_{H-F} = 2$ Hz, Al–$CH_2$$CH_3$), 1.19 (t, Al–$CH_2$*$CH_3$*); $^{13}C\{^1H\}$, −0.3 (s, Al–*CH_2*CH_3), 8.4 (s, Al–CH_2*CH_3*); ^{19}F, −156.7 (2,6-F, m), −160.5 (3,5-F, m), −161.8 (4-F, m).

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[2] Kumar, R.; de Mel, V. S. J.; Oliver, J. P. *Organometallics* **1990**, *9*, 1303.

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Table I. Experimental Parameters for the X-ray Diffraction Study of $(Me_2AlOC_6F_5)_2$ and $(Me_2GaSC_6F_5)_2$

compound	bis[dimethylaluminum pentafluorophenoxide] (**1a**)	bis[dimethylgallium pentafluorothiophenoxide] (**2b**)
formula	$C_{16}H_{12}Al_2F_{10}O_2$	$C_{16}H_{12}Ga_2F_{10}S_2$
mol wt	506.29	597.83
cryst preparation	recrystallized from toluene/pentane (25 °C)	recrystallized from toluene/pentane (−20 °C)
cryst color	colorless crystals	colorless crystals
cryst system	orthorhombic	triclinic
space group:	*Cmcm* (No. 63)	$P\bar{1}$ (No. 2)
cell consts obtained from 25 high-angle reflcns	20–30°	40–80°
a, Å	11.058 (2)	9.790 (3)
b, Å	16.908 (2)	10.122 (1)
c, Å	10.764 (2)	11.284 (1)
α, deg	90	76.08 (1)
β, deg	90	89.67 (2)
γ, deg	90	86.99 (2)
V, Å^3	2012.5 (4)	1083.8 (4)
density(calcd), g cm^{-3}	1.67	1.83
Z	4 (dimers)	2 (dimers)
radiation type (λ, Å)	Mo K$\bar{\alpha}$ (0.71073) with a graphite monochromator	Cu K$\bar{\alpha}$ (1.54178) with a Ni filter
temp, °C	20	20
type of data collcn	$\theta/2\theta$ scan	$\theta/2\theta$ scan
2θ scan range, deg	3–45	8–100 deg
octants used	$+h,+k,+l$	$+h,\pm k,\pm l$
scan rate, deg/min	variable 3–5	variable 1.5–15.0
scan width	1:1	0.7:0.7
bckgd/scan ratio	1.0	0.5
std reflcns	3 measd per every 100 reflections; max deviation from the stds obs was 1%	3 measd per every 97 reflections; max deviation from the std obsd was 17%
no. of data collcd	762	2394
no. of obsd reflcns	541 with $F_o \geq 2.5\sigma(F)$	1920 with $F_o \geq 3.0\sigma(F)$
linear abs coeff (μ), cm^{-1}	2.02	57.71
F(000)	960 electrons	584 electrons
abs cor	none applied	none applied
no. of params refined	97 in two blocks (56 on block 1 and 41 on block 2)	271
$R = \sum(\lvert F_o\rvert - \lvert F_c\rvert)/\sum\lvert F_o\rvert$, %	6.99	4.65
$R_w = [\sum(\lvert F_o\rvert - \lvert F_c\rvert)^2/\sum w\lvert F_o\rvert^2]^{1/2}$,[a] %	7.87	4.89
overall shift/esd	0.001	0.000
resid electron dens, e/Å^3	0.43, 0.58 Å from F2	0.53, 0.58 Å from Ga1

[a] $w = 1/\sigma^2(F)$.

Preparation of $(i\text{-}Bu_2AlOC_6F_5)_2$ (1c). The reaction was carried out by using the same procedure as described for **1a**, using pentafluorophenol (1.436 g, 7.8 mmol) and $(i\text{-}Bu)_3Al$ (7.8 mL, 7.8 mmol). The solvent was removed in vacuo to leave a white solid. The product was recrystallized from 10 mL of pentane at −20 °C. This solid was identified as $(i\text{-}Bu)_2AlOC_6F_5$. Yield: 96%. NMR parameters (ppm): ^{1}H, 0.46 [m, $^6J_{H-F}$ = 2 Hz, Al-CH_2CH(CH$_3$)$_2$], 2.05 [m, Al-CH$_2$$CH$(CH$_3$)$_2$], 1.04 [d, Al-CH$_2$CH($CH_3$)$_2$]; ^{13}C{^{1}H}, 22.1 [s, Al-CH_2CH(CH$_3$)$_2$], 25.4 [s, Al-CH$_2$$CH$(CH$_3$)$_2$], 28.1 [s, Al-CH$_2$CH($CH_3$)$_2$]; ^{19}F, −153.0 (2,6-F, m, $^3J_{F-F}$ = 22 Hz), −160.2 (3,5-F, m, $^3J_{F-F}$ = 22 Hz), −159.8 (4-F, m, $^3J_{F-F}$ = 23 Hz).

Adduct Formation. $(Me_2AlOC_6F_5)_2$ was prepared in situ via the procedure used for **1a**, and then either 10 mL of diethyl ether or tetrahydrofuran was added to the reaction mixture. The reaction was allowed to stir for 2 h, and the solvent was removed in vacuo to leave a white solid. The ^{1}H NMR spectral results of the products from each of these reactions showed that no ether was retained. When 4-picoline (0.92 mL) was used and the solvent was removed under vacuum, a new product was obtained. This was recrystallized from 10 mL of pentane at −20 °C and identified as the 1:1 adduct, $Me_2AlOC_6F_5$·pic (pic = 4-picoline). NMR parameters (ppm): ^{1}H, −0.27 (s, 6 H) (AlCH_3), 8.06 (d, 2 H), *CH* (4-picoline)), 6.13 (2 H, *CH* (4-picoline)), 1.41 (s, 3 H, 4-CH_3 (4-picoline)). The ^{1}H NMR spectrum of 4-picoline showed resonances at 8.36 (d, 2 H), 6.98 (d, 2 H), 2.23 (s, 3 H, CH_3). No ^{1}H–^{19}F coupling was observed in the ^{1}H NMR spectrum of the adduct.

Preparation of $(Me_2GaOC_6F_5)_2$ (2a). To 0.5 g (2.7 mmol) of pentafluorophenol in 15 mL of pentane and 5 mL of toluene was added 0.30 mL (0.34 g, 3.0 mmol) of Me_3Ga at 0 °C. The resulting solution was then stirred overnight. Following removal of volatiles in vacuo, a white solid was obtained and identified from its NMR spectra. Yield: 85%. NMR parameters (ppm): ^{1}H, 0.11 (quintet, $^6J_{H-F}$ = 2.0 Hz, Ga–Me); ^{13}C{^{1}H}, −4.4 (Ga–Me); ^{19}F, −158.6 (2,6-F, d, $^3J_{F-F}$ = 23 Hz), −162.5 (3,5-F, t, $^3J_{F-F}$ = 23 Hz), −168.1 (4-F, tt, $^3J_{F-F}$ = 23 Hz, $^4J_{F-F}$ = 6.5 Hz).

Preparation of $(Me_2GaSC_6F_5)_2$ (2b). To 1.0 g (0.67 mL, 5.0 mmol) of pentafluorothiophenol in 20 mL of toluene was added 0.50 mL (0.57 g, 5.00 mmol) of Me_3Ga at 0 °C. The resulting solution was then allowed to stir overnight. Following removal of volatiles in vacuo, a white solid was obtained, which was then dissolved in 15 mL of pentane and 5 mL of toluene. After sitting 48 h at −20 °C, this solution afforded a crystalline product. Yield: 80%. NMR parameters (ppm): ^{1}H, 0.10 (singlet, Ga–Me); ^{13}C{1H}, −2.3 (Ga–Me); ^{19}F, −131.3 (2,6-F, dd, $^3J_{F-F}$ = 24.6 Hz, $^4J_{F-F}$ = 6.8 Hz), −153.3 (3,5-F, t, $^3J_{F-F}$ = 21.6 Hz), −159.8 (4-F, t, $^3J_{F-F}$ = 20.0 Hz).

X-ray Structure Determination of $(Me_2AlOC_6F_5)_2$ (1a) and $(Me_2GaSC_6F_5)_2$ (2b). Crystals of **1a** were grown from a toluene/pentane (1:10) solution at 25 °C whereas crystals of **2b** were obtained from a toluene/pentane (1:3) solution at −20 °C. In each case 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 gonimeter head, and placed on an R3 (for **1a**) or P3 (for **2b**) Nicolet diffractometer for data collection. Parameters from the crystal structure determinations of **1a** and **2b** are presented in Table I.

1a was found to be in the orthorhombic cell system, and **2b** was in the triclinic cell system. Lattice constants were verified by axial photographs. **1a** was assigned to the space group *Cmcm* (No. 63) on the basis of the systematic absences and solved in this space group. All attempts to find a structural solution for **1a** in acentric space groups such as $Cmc2_1$ (No. 36) and *Ama*2 (No. 40) were unsuccessful. **2b** was assigned to the space group $P\bar{1}$. Attempts to refine the structure in *P*1 were unsuccessful. Data reduction was carried out by using the SHELXTL program.[4] The

Table II. Atomic Parameters for $(Me_2AlOC_6F_5)_2$ (1a)

atom	*x*	*y*	*z*	U_{eq},[a] Å^2
Al	0.3665 (2)	0.3922 (1)	0.2500	0.0588 (8)
F1	0.7116 (5)	0.5474 (3)	0.25000	0.084 (1)
F2	0.7123 (5)	0.7068 (3)	0.2500	0.095 (1)
F3	0.50000	0.7884 (4)	0.25000	0.084 (2)
F4	0.50000	0.2396 (3)	0.4678 (5)	0.092 (1)
F5	0.50000	0.0809 (3)	0.4686 (6)	0.117 (2)
F6	0.50000	0.0013 (4)	0.25000	0.123 (2)
O1	0.50000	0.4640 (4)	0.25000	0.058 (2)
O2	0.50000	0.3233 (4)	0.25000	0.053 (2)
C9	0.2901 (7)	0.3873 (3)	0.0901 (6)	0.091 (2)
C1	0.50000	0.5451 (6)	0.25000	0.053 (2)
C2	0.6063 (7)	0.5873 (4)	0.25000	0.059 (2)
C3	0.6051 (7)	0.6682 (4)	0.25000	0.060 (2)
C4	0.50000	0.7092 (6)	0.25000	0.063 (2)
C5	0.50000	0.2432 (6)	0.25000	0.050 (2)
C6	0.50000	0.2009 (4)	0.3617 (8)	0.063 (2)
C7	0.50000	0.1189 (5)	0.3555 (9)	0.075 (2)
C8	0.50000	0.0798 (7)	0.25000	0.078 (2)

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

Table III. Selected Bond Lengths (Å) and Angles (deg) for $(Me_2AlOC_6F_5)_2$ (1a)

	Distances		
Al-O1	1.911 (5)	Al-C9	1.920 (7)
Al-O2	1.880 (5)	Al···Al′	2.951 (5)
	Angles		
Al-O1-Al′	101.1 (3)	C9-Al-C9″	127.5 (3)
O1-Al-O2	77.7 (2)	Al-O1-C1	129.4 (2)
O1-Al-C9	111.6 (2)	Al-O2-C5	128.3 (2)
Al-O2-Al′	103.4 (3)		

direct methods routine produced initial positions for all of the non-hydrogen atoms in both **1a** and **2b**. Full-matrix least-squares refinement was carried out by using SHELTX-76.[5] The data were corrected for Lorentz and polarization effects, and scattering factors for neutral carbon, oxygen, sulfur, fluorine, aluminum, and gallium atoms were used.[6] Each hydrogen atom was placed in an idealized position for an sp^3 carbon atom 0.96 Å away from the carbon atom and not refined. Atomic coordinates and isotropic thermal parameters for the non-hydrogen atoms for **1a** are listed in Table II; bond lengths and bond angles are in Table III. Atomic coordinates and isotropic thermal parameters for the non-hydrogen atoms for **2b** are listed in Table IV; bond lengths and bond angles are in Table V. Additional data for the crystal structures are provided in the supplementary material.

Results and Discussion

Table IV. Atomic Parameters for $(Me_2GaSC_6F_5)_2$ (2b)

atom	*x*	*y*	*z*	U_{eq},[a] Å^2
Ga1	0.3169 (1)	0.7843 (1)	0.8532 (1)	0.0670 (5)
Ga2	0.0119 (1)	0.8404 (1)	0.70223 (9)	0.0647 (4)
S1	0.1078 (2)	0.6571 (2)	0.8677 (2)	0.0575 (8)
S2	0.2421 (3)	0.9129 (2)	0.6484 (2)	0.0691 (9)
F1	0.2444 (5)	0.6094 (5)	0.6460 (4)	0.084 (2)
F2	0.3762 (5)	1.0364 (6)	0.4177 (4)	0.088 (2)
F3	0.4752 (6)	0.9188 (7)	0.2447 (5)	0.121 (3)
F4	0.3440 (6)	0.4930 (6)	0.4723 (5)	0.099 (3)
F5	0.4615 (6)	0.6448 (7)	0.2721 (5)	0.123 (3)
C1	0.3681 (9)	0.900 (1)	0.4348 (8)	0.070 (4)
C2	0.3008 (9)	0.6886 (9)	0.5484 (8)	0.066 (4)
C3	0.3065 (8)	0.8255 (9)	0.5381 (7)	0.062 (4)
C4	0.3517 (9)	0.627 (1)	0.4595 (9)	0.074 (4)
C5	0.420 (1)	0.839 (1)	0.3443 (8)	0.083 (5)
C6	0.412 (1)	0.704 (1)	0.3598 (9)	0.084 (5)
F6	0.2157 (6)	0.6226 (6)	1.1226 (4)	0.093 (3)
F7	−0.1918 (5)	0.7126 (5)	0.8917 (5)	0.083 (2)
F8	−0.3319 (6)	0.7302 (6)	1.0912 (6)	0.107 (3)
F9	−0.2005 (7)	0.6954 (6)	1.3089 (5)	0.126 (3)
F10	0.0723 (7)	0.6397 (6)	1.3232 (5)	0.119 (3)
C7	−0.121 (1)	0.6993 (8)	0.9979 (8)	0.064 (4)
C8	0.0165 (9)	0.6744 (8)	0.9996 (7)	0.056 (4)
C9	−0.129 (1)	0.688 (1)	1.2087 (9)	0.086 (5)
C10	−0.198 (1)	0.7062 (9)	1.0972 (9)	0.077 (5)
C11	0.006 (1)	0.659 (1)	1.2153 (8)	0.083 (5)
C12	0.080 (1)	0.6539 (9)	1.1135 (8)	0.069 (4)
C13	0.470 (1)	0.660 (1)	0.840 (1)	0.093 (5)
C14	−0.058 (1)	0.9918 (9)	0.7670 (9)	0.086 (4)
C15	0.295 (1)	0.918 (1)	0.9496 (9)	0.092 (5)
C16	−0.064 (1)	0.758 (1)	0.5821 (9)	0.093 (5)

[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. Selected Bond Lengths (Å) and Angles (deg) for $(Me_2GaSC_6F_5)_2$ (2b)

	Distances		
Ga1-S1	2.460 (2)	Ga1-C15	1.94 (1)
Ga1-S2	2.458 (3)	Ga2-C14	1.94 (1)
Ga2-S1	2.445 (3)	Ga2-C16	1.93 (1)
Ga2-S2	2.436 (3)	Ga1···Ga2	3.397
Ga1-C13	1.94 (1)		
	Angles		
Ga1-S1-Ga2	87.75 (8)	Ga2-S1-C8	105.0 (3)
Ga1-S2-Ga2	87.99 (9)	S1-Ga2-S2	89.45 (9)
C13-Ga1-C15	130.5 (5)	S1-Ga1-S2	88.59 (9)
C14-Ga2-C16	130.6 (5)	Ga1-S2-C3	109.1 (3)
Ga1-S1-C8	109.0 (3)	Ga2-S2-C3	107.9 (3)

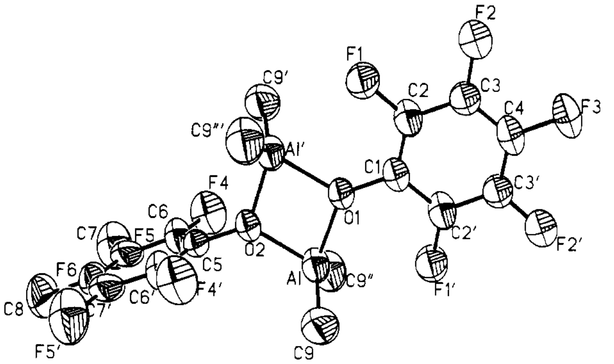
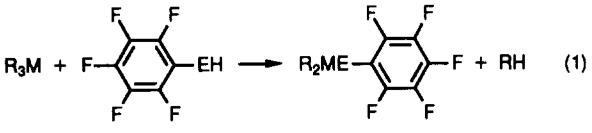


Figure 1. ORTEP diagram (50% thermal ellipsoids) of the $(Me_2AlOC_6F_5)_2$ dimer (**1a**), showing the atom-labeling scheme. Hydrogen atoms are omitted for clarity. The molecule is on a special position and posseses *mm* symmetry, as required by the space group *Cmcm*.

Synthesis. The E–H proton in pentafluorophenol and pentafluorothiophenol reacts rapidly at room temperature with trialkylaluminum or -gallium derivatives in a 1:1 stoichiometry, liberating the alkane and affording the corresponding organoaluminum phenoxides and thiophenoxides, $R_2MEC_6F_5$, in high yield according to the general reaction scheme of eq 1. Compounds **1a–c** and **2a,b** have been isolated as colorless, transparent crystals that are both air and moisture sensitive, decomposing over a period of seconds in the solid state on exposure to air. They are soluble in hydrocarbons such as pentane, benzene, and toluene and in the donor solvents such as diethyl ether and tetrahydrofuran. The latter solvents do not appear to form stable isolable addition compounds with disruption of the Al–O–Al bridge bond (see Experimental



M = Al, E = O, R = Me, Et, *i*-Bu; M = Al, E = S, R = Me
M = Ga, E = O, S, R = Me

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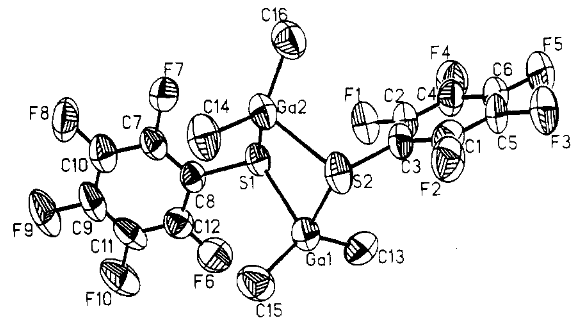

Figure 2. ORTEP diagram (50% thermal ellipsoids) of the $(Me_2GaSC_6F_5)_2$ dimer (**2b**), showing the atom-labeling scheme. Hydrogen atoms are omitted for clarity.

Section), but 4-picoline disrupts the bridge bond with formation of the addition compound $Me_2(C_6F_5O)Al{\cdot}pic$.

Molecular Geometry. The molecular structures of **1a** and **2b** have been determined, and the molecular structure of $(Me_2AlSC_6F_5)_2$ was previously reported.[2] All three compounds have similarities with each forming a dimeric molecule. The central core of the dimer is composed of an M_2E_2 four-membered ring. An ORTEP diagram of the molecular unit for **1a** is shown in Figure 1. The Al_2O_2 ring is strictly planar as required by the symmetry of the space group *Cmcm*. The two pentafluorophenyl groups in $(Me_2AlOC_6F_5)_2$ are oriented so that the plane of ring A (defined by carbon atoms C1–C4) is parallel to the Al–Al axis and ring B (defined by carbon atoms C5–C8) is perpendicular to the Al–Al axis. This brings the ortho-fluorine atoms of ring A within 2.762 Å of the aluminum center, while those of ring B are 3.878 Å away. This close approach (note the sum of the van der Walls radii is 3.91 Å)[7] may indicate some interaction in the solid state, but no supporting evidence is available; the *o*-F–C bond distance is within experimental error of the other F–C bond distances, and the F–C–C bond angle is only slightly less (118.7°) than the expected 120°. The ortho-fluorine atoms in ring A are within 3.33–4.50 Å of the hydrogen atoms on the methyl groups. The geometry around the aluminum atom is normal for this type of compound and can be described as a distorted tetrahedron. The Al–O and Al–C bond distances in $(Me_2AlOC_6F_5)_2$ are typical of related organoaluminum alkoxides.[1]

An ORTEP diagram of the molecular unit of **2b** is shown in Figure 2. The central structural unit of $(Me_2GaSC_6F_5)_2$ is a four-membered ring composed of two gallium and two sulfur atoms. The Ga_2S_2 ring is butterfly shaped with the angle between the two planes described by Ga1–S1–Ga2 and Ga1–S2–Ga2 equal to 152.3°. The aluminum derivative, $(Me_2AlSC_6F_5)_2$, is isostructural, showing the similarity between the aluminum and gallium compounds.[2] This geometry for the Ga_2E_2 ring also has been found in $[I_2GaS(i\text{-}Pr)]_2$[8] and $[(Me_3CCH_2)_2GaTePh]_2$.[9] However, the Ga_2S_2 ring in other gallium complexes, $(I_2GaSMe)_2$[10] and $(Ph_2GaSEt)_2$,[11] is planar. The two pentafluorophenyl groups in $(Me_2GaSC_6F_5)_2$ are in the anti conformation relative to the Ga_2S_2 ring. The pentafluorophenyl groups in $(Me_2AlSC_6F_5)_2$ are also in the anti conformation as are the ethyl groups in $(Ph_2GaSEt)_2$ and the methyl groups in $(I_2GaSMe)_2$. In $[I_2GaS(i\text{-}Pr)]_2$, which has the butterfly Ga_2S_2 ring, the isopropyl groups are in the syn conformation.

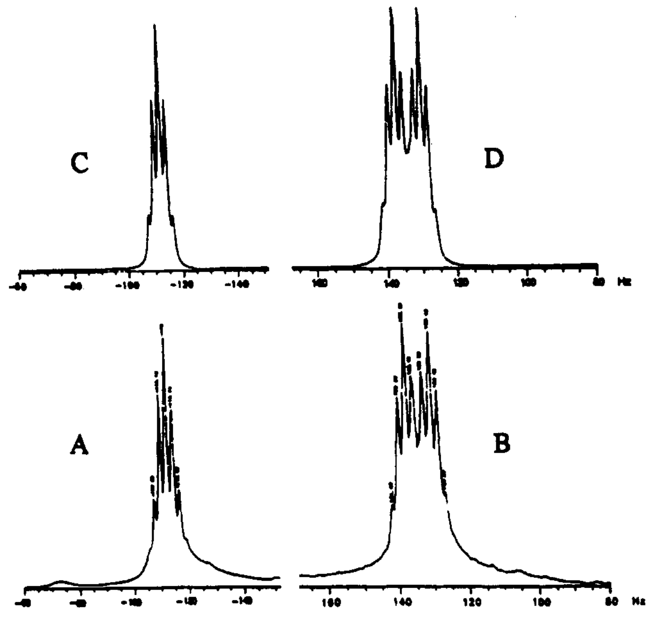

Figure 3. ^1H NMR spectra for the $[Me_2AlOC_6F_5]_2$ dimers (**1a**,**c**), showing the observed (A, B) and calculated (C, D) spectra.

The geometry around the sulfur atom is pyramidal with angles of 106.7° (C8–S1–Ga1), 126.2° (C8–S1–Ga2), and 87.8° (Ga1–S1–Ga2). This geometry is consistent with other three-coordinate sulfur derivatives and, along with the butterfly conformation, gives rise to nonequivalence of the alkyl groups attached to the metal in the solid state similar to the cyclopropylaluminum system.[12] The geometry around the gallium atom is normal for this type of compound and can be described as a distorted tetrahedron. The important angles and distances are summarized in Table V. The average value of the Ga–S distance in this compound is 2.45 Å, which is slightly longer than that observed in the related complexes $(Ph_2GaSEt)_2$, $(I_2GaSMe)_2$, and $[I_2GaS(i\text{-}Pr)]_2$. The separation between the gallium atoms and the fluorine atoms ranges from 3.02 to 3.35 Å; in the Al–S derivatives these distances range from 3.108 to 3.903 Å.

NMR Studies. ^1H, ^{13}C, and ^{19}F NMR data for the individual compounds are listed in the Experimental Section. The parameters are observed to be in the normal range for all of the compounds, but there are several interesting features observed in the ^1H and ^{19}F spectra of the pentafluorophenoxide derivatives. The first of these is clearly illustrated in Figure 3A,B, which shows the proton spectra of the methyl- and isobutylaluminum derivatives. The protons on the α-carbon atom attached to the metal are clearly split into a quintet and into a complex multiline pattern. Studies on the diethylaluminum and the dimethylgallium species show similar splitting patterns. These have been attributed in all cases to the interaction of the four ortho-fluorine atoms with the protons on the α-carbon atom bound to the metal. The coupling is also readily observed in the ^{19}F spectra for these compounds. Simulation of the proton spectra allows the determination of the magnitude of these long-range coupling constants to be made with reasonable accuracy at 2.0 Hz in each of

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the cases studied. This is illustrated in Figure 3C,D. A further observation is that the coupling remains up to about 75 °C in all cases and, in fact, show sharper lines at the elevated temperatures. These observations suggest two things. First, the M–O–M bridge bonds remain intact or at least do not undergo rapid exchange throughout this temperature range, and second, the equivalence of coupling between the ortho-fluorine atoms and the protons indicates that the pentafluorophenyl rings are rotating rapidly about the C–O bond. If the latter were not the case, one might expect different magnitudes for the coupling between the fluorine atoms on the rings parallel and perpendicular to the M–M axis.

The mechanism for transmission of spin–spin coupling information involves electronic interactions through bonds and/or through space components. "Through-bond" coupling information in these systems requires interaction across six bonds, F-C-C-O-M-C-H. "Through-space" coupling requires the spin information to be transferred directly between the nuclei and depends on their proximity. In the present system these nuclei are separated by 3–5 Å and are rapidly fluctuating. Other workers have examined pentafluorophenyl derivatives and pentafluorophenoxides and have suggested that the long-range F–H coupling observed in their systems occurs via a through-space mechanism.[13,14]

When one drop of picoline was added to the ethyl derivative, the methylene region (Al–CH_2CH$_3$) showed a simple quartet with no ^{1}H–^{19}F coupling observed. For picoline (4-methylpyridine), the equilibrium between the phenoxide-bridged dimer and the monomeric adduct favors the adduct. Since the distance between F and H will not differ dramatically between the adduct and the dimer, the loss of ^{1}H–^{19}F coupling, which results when the dimeric system is disrupted, is inconsistent with the through-space mechanism.

Comparison of the pentafluorophenoxide derivatives with the analogous pentafluorothiophenoxide derivatives aids in the discussion of coupling mechanisms. In no case is ^{1}H–^{19}F coupling observed in pentafluorothiophenoxide derivatives. The solid-state structures of the methyl derivatives are similar, however. For bis(dimethylaluminum μ-pentafluorothiophenoxide), the central Al_2S_2 ring is not planar, but bent, with the geometry around S bridge pyramidal. For bis(dimethylaluminum μ-pentafluorophenoxide), the geometry around O bridge is trigonal planar, indicating the oxygen participates in an extended π system. This has also been suggested by Graham,[14] who carried out an extensive study of pentafluorophenoxide derivatives and proposed extensive interaction between the π-electron system of the ring and the oxygen. In our system the oxygen interacts strongly with the Al atoms, providing a path for the transfer of spin information.

The geometry around the bridging oxygen and sulfur atoms differs substantially. Typically, in oxygen-bridged species, the oxygen atom is trigonal planar; in the sulfur-bridged system, the sulfur atom is in a trigonal-pyramidal environment. This is illustrated for the three compounds of interest by considering the sum of the angles around the bridging atom. In the oxygen derivative this is 360°, as required in a planar system. This implies that the oxygen uses sp^2 hybrid orbitals to bind with the metal atoms. For the sulfur derivatives the sums of the angles around sulfur are in the range 300–310°; for a tetrahedral system the sum would be 329°. This is consistent with metal–sulfur bonds made up primarily of p orbitals from the sulfur atom. Since the through-bond coupling is dominated by the Fermi contact interaction, which is determined by the s character of the orbitals used in bond formation, the substantial change in s character of the bridge bonds going from O to S leads to the observed decrease in the coupling constant. Similarly, on formation of the four-coordinate adduct $R_2(C_6F_5O)Al\cdot pic$, the s character of the bonds to oxygen is reduced, leading to diminished coupling.

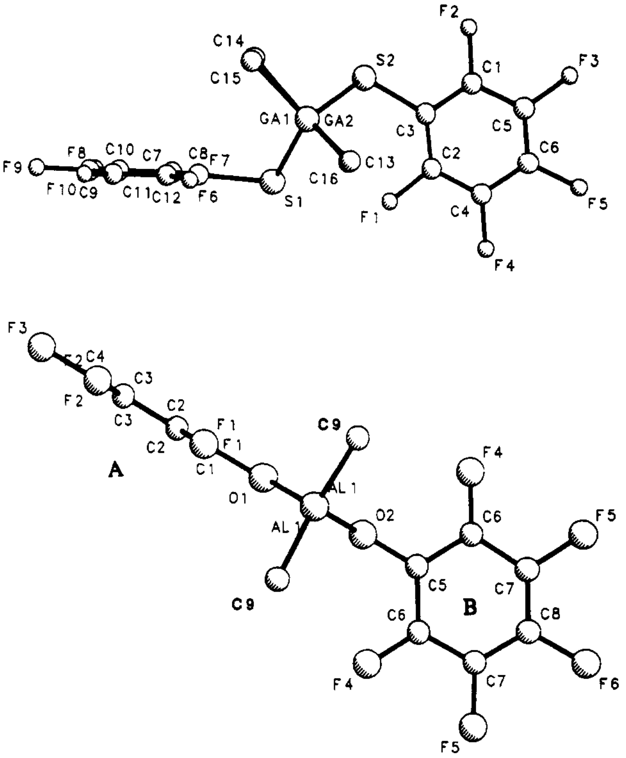

Figure 4. PLUTO diagrams, showing the $(Me_2AlOC_6F_5)_2$ (bottom) and $(Me_2GaSC_6F_5)_2$ (top) molecules viewed along the metal–metal axes.

Therefore, although the through-space mechanism may contribute to the coupling mechanism, it is reasonable to conclude the primary mechanism for transmission of spin information in the dialkylaluminum μ-pentafluorophenoxide derivatives is electronic.

The principal differences between the structures of the oxygen- and the sulfur-bridged compounds are illustrated in Figure 4. The oxygen ring system is planar, while the sulfur-containing ring is puckered. Further, the geometry around the sulfur is pyramidal, which gives rise to further asymmetry in the molecule. These differences have significant implications for the behavior of these compounds in solution. The environment surrounding the alkyl groups on the metal atoms on the planar systems should be equivalent for the anti conformation and in different environments for the syn conformation; those on the puckered systems should be in nonequivalent magnetic environments for both conformations and, therefore, should give two signals for the ^{1}H NMR spectrum. This is further complicated by the fact that inversion at sulfur can occur but typically has a substantial (15–30 kcal/mol) barrier to inversion.

These properties make the sulfur-containing system similar to that of tricyclopropylaluminum and its methyl derivatives.[12] The possible pathways for interchange are shown in eq 2. If the puckered ring remains rigid in solution, then the alkyl groups bound to the metal must

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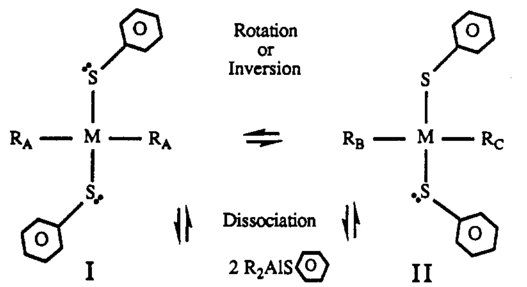

(2)

remain nonequivalent. Previous studies, on the cyclopropylaluminum system and on sulfur-bridged systems which have been found to be planar indicate that the conversion from the puckered configuration to planar should be a low-energy, rapid process. The rotation/inversion to convert I to II (eq 2) also must be rapid on the NMR time scale to lead to equivalence of the alkyl groups. The inversion barrier for sulfur bound to three centers is typically in the range 15–30 kcal/mol, and in the more complex system $[Me_2M(\mu\text{-}S\text{-}2,6Me_2C_6H_3)]_4$, the interconversion of ring conformations is slow on the NMR time scale with a barrier in excess of 25 kcal/mol.[15] These facts are inconsistent with inversion at sulfur. In contrast, we have established that the barrier to rotation of the cyclopropyl group in $[Me_2Al(\mu\text{-}C_3H_5)]_2$ is 11 kcal/mol[12] and that the barrier to rotation when oxygen is in the bridge varies widely depending on the substituent.[16] With C_6F_5 it is low, as noted earlier, giving rise to rapid rotation of the C_6F_5 group in **1a** and **2a**. We therefore conclude that the equivalence of the alkyl groups bound to the metal in $(R_2MSC_6F_5)_2$ results from two processes, flattening or rapid bending of the ring and rapid rotation of the $S\text{–}C_6F_5$ group about the C–S bond.

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Supplementary Material Available: For **1a** and **2b** 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 and deviations and figures showing packing diagrams (23 pages); listings of observed and calculated structure factors (16 pages). Ordering information is given on any current masthead page.

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Structures of Organo-f-Element Compounds Differing in the Oxidation State of the Central Metal: Crystal Structures of Bis([8]annulene) Complexes of Cerium(IV), Ytterbium(III), and Uranium(III)

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Crystal structures of bis(methyl[8]annulene)cerium(IV) (**5**), [(diethylene glycol dimethyl ether)potassium] [bis([8]annulene)ytterbate(III)] (**14**), and [(diethylene glycol dimethyl ether)potassium] [bis(methyl[8]annulene)uranate(III)] (**12**) are reported. These include the first structures of an organocerium(IV) compound and of a reduced uranocene. Crystals of **5** are orthorhombic, $P2_12_12_1$, with $a = 11.690$ (3) Å, $b = 14.315$ (3) Å, $c = 8.977$ (2) Å, $Z = 4$, and $R_F = 2.9\%$. Crystals of **14** are also orthorhombic, *Pbca*, with $a = 16.611$ (4) Å, $b = 14.219$ (5), Å, $c = 9.257$ (4) Å, $Z = 4$, and $R_F = 3.6\%$. Crystals of **12** are monoclinic, $P2_1/c$, with a = 13.833 (4) Å, $b = 9.989$ (3) Å, $c = 17.581$ (3) Å, $\beta = 95.87$ (3)°, $Z = 4$, and $R_F = 3.8\%$. These structures are compared to the previously reported structures of [(diethylene glycol dimethyl ether)potassium] [bis([8]annulene)cerate(III)] (**13**), bis[(dimethoxyethane)potassium] [bis([8]annulene)ytterbate(II)] (**15**), and uranocene (**1**). A comparison of the structural parameters of several additional [8]annulene metal complexes is also presented. The effect of coordination number on metal ligand distances in ionic complexes is discussed in terms of electrostatic interactions among the ligands.

Introduction

One of the most important factors affecting the structure and properties of an organometallic compound is the oxidation state of the central metal. In order to assess the effect of a change in oxidation state on the structural characteristics of a compound it is necessary to compare compounds in which there is little or no change in the coordinating ligands. However, the number of systems of this type for which structural information is available is quite limited, the principal examples thus far being the metallocenes. For example, in ferrocene[1] the metal–carbon distance is shorter than in the ferrocenium cation[2] despite the fact that the ionic radius of six-coordinate Fe(III) is generally smaller than that of six-coordinate Fe(II). A rationalization based on a covalent model suggests that

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