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Notes

Synthesis and Characterization of Alkylaluminum Compounds of Pentafluorothiophenol. Crystal and Molecular Structure of $[Me_2Al(\mu\text{-}SC_6F_5)]_2$

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Summary: The reaction of trialkylaluminum derivatives, R_3Al (R = Me, Et, *i*-Bu), with pentafluorothiophenol yields $[R_2Al(\mu\text{-}SC_6F_5)]_2$ (R = Me (**1a**), Et (**1b**), *i*-Bu (**1c**) and the corresponding alkane, RH, quantitatively. The resulting thiolates have been characterized by ^1H, ^{13}C, and ^{19}F NMR spectroscopy. The structure of **1a** was determined by single-crystal X-ray diffraction techniques and found to be in the monoclinic cell system, space group $P2_1/a$, with cell constants a = 14.133 (2) Å, b = 11.146 (2) Å, c = 15.287 (2) Å, β = 116.72 (1)°, and Z = 4. The structure was refined to a final R = 4.2% (R_w = 5.8%) based on 1335 observed reflections. The molecule exists as a sulfur-bridged dimer with a central puckered four-membered Al_2S_2 ring. The average Al-S bridge bond distance is 2.408 Å. The dimer $[Me_2Al(\mu\text{-}SC_6F_5)]_2$ reacts with ether and tetrahydrofuran to give 1:1 addition complexes, while both $[Me_2Al(\mu\text{-}SC_6F_5)]_2$ (**1a**) and *i*-$Bu_2AlSC_6F_5$ (**1c**) reacted with methyl benzoate to give the corresponding thioester $PhC(O)SC_6F_5$ in excellent yield.

The interaction of alkylaluminum compounds with protic substrates such as alcohols, phenols, and amines has been extensively investigated.[1,2] In contrast, the reaction of thiols with group 13 organometallic derivatives has received little attention.[3] Species of the type Me_2AlSR (R = Et, Ph) have been proposed as intermediates in thioester syntheses,[4] with the only well-characterized example reported being a binary thiolate derivative of the formula Me_2AlSMe. An X-ray diffraction investigation has shown crystalline Me_2AlSMe to be a one-dimensional polymer with MeS groups bridging dimethylaluminum groups to form zigzag infinite chains,[5] while gas-phase electron diffraction studies have established it to be a dimer.[6] As a part of our investigations on organoaluminum thiolate chemistry,[7] we now report the synthesis, characterization, and reactions of dialkylaluminum pentafluorobenzenethiolato complexes. The structure of the dimeric $[Me_2Al(\mu\text{-}SC_6F_5)]_2$, as determined by single-crystal X-ray diffraction techniques, is also reported.

Experimental Section

General Data. All solvents were purified and dried by standard techniques.[8] Argon gas was purified by passing it through a series of columns containing Deox catalyst (Alfa), phosphorous pentoxide, and calcium sulfate. The trialkylaluminum derivatives ($AlMe_3$, 2 M solution in toluene; $AlEt_3$, 1.9 M solution in toluene; $Al(i\text{-}Bu)_3$, 1 M solution in toluene (Aldrich)) and pentafluorothiophenol (Aldrich) were used as received. All glassware used in the synthetic work was oven-dried. The aluminum derivatives are both oxygen and water sensitive, so standard Schlenk line techniques were employed. ^1H, ^{13}C, ^{19}F NMR spectra were recorded on either a General Electric QE-300 NMR or a GN-300 NMR spectrometer. The ^1H and ^{13}C chemical shifts were referenced to benzene-d_6 peaks (δ = 7.15 ppm for ^1H and δ = 128.00 ppm for ^{13}C). The ^{19}F chemical shifts were referenced to an external standard of 10% $CFCl_3$ in acetone-d_6. Elemental analysis on selected compounds was performed by Galbraith Laboratories, Knoxville, TN.

Reaction of $AlMe_3$ with Pentafluorothiophenol To Give 1a. Pentafluorothiophenol (1 mL, 7.49 mmol) was dissolved in pentane (50 mL), and $AlMe_3$ (3.75 mL, 7.49 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 solution was stirred for 2 h to ensure completion. The resulting solution deposited a colorless crystalline solid when left standing for 48 h at -20 °C. The product was collected, washed with 10-15 mL of very cold pentane, and dried in vacuo. This solid was identified as $Me_2AlSC_6F_5$: yield >90%; mp 123-125 °C. Anal. Calcd for $C_8H_6AlF_5S$: C, 37.50; H, 2.34. Found: C, 37.09; H, 2.32. ^1H, ^{13}C, and ^{19}F NMR spectral results are presented in Table I.

Reaction of $AlEt_3$ with Pentafluorothiophenol To Give 1b. The procedure for this reaction is the same as described for **1a**, with use of pentafluorothiophenol (1 mL, 7.49 mmol) and $AlEt_3$ (3.94 mL, 7.49 mmol). The solvent was removed in vacuo to leave

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Table I. ^1H, Partial ^{13}C, and ^{19}F NMR Spectral Results (δ in ppm) of Organoaluminum Compounds[a]

	^1H NMR alkyl			^1H NMR	^{13}C NMR alkyl			^{19}F NMR		
compd	α-CH	β-CH	γ-CH	-SH	α-CH	β-CH	γ-CH	2,6-F	3,5-F	4-F
C_6F_5SH				2.93 (s)				-137.3	-161.9	-158.9
$AlMe_3$	-0.32 (s)				-7.3					
$Me_2AlSC_6F_5$	-0.32 (s)				-8.3			-130.7	-159.1	-151.8
$AlEt_3$	0.31 (q)	1.10 (t)			0.4	8.8				
$Et_2AlSC_6F_5$	0.26 (q)	1.91 (t)			1.58	8.3		-131.4	-158.9	-151.9
Al(*i*-Bu)$_3$	0.22 (d)	1.89 (m)	0.96 (d)		21.4	26.3	28.3			
(*i*-Bu)$_2$AlSC$_6$F$_5$	0.47 (d)	2.10 (m)	1.06 (d)		23.2	26.0	27.8	-129.9	-159.8	-153.0
$Me_2AlSC_6F_5$·THF[b]	-0.57 (s)				-10.2			-133.0	-160.5	-163.6

[a] Abbreviations: s = singlet; d = doublet; t = triplet; q = quartet. [b] ^1H and ^{13}C NMR data for the THF molecule in adduct: 1.008 (α-CH_2; m, 4 H), 3.362 (β-CH_2; m, 4 H); 24.793 (β-C), 71.604 (α-C).

a white solid. The product was purified by dissolving it in 15 mL of pentane, from which it recrystallized on cooling to -20 °C overnight. This solid was identified as $Et_2AlSC_6F_5$: yield 80%; mp 65-67 °C. ^1H, ^{13}C, and ^{19}F NMR spectral results are presented in Table I.

Reaction of Al(*i*-Bu)$_3$ with Pentafluorothiophenol To Give 1c. The reaction was carried out by using the same procedure as described for **1a**, with pentafluorothiophenol (1 mL, 7.49 mmol) and Al(*i*-Bu)$_3$ (7.49 mL, 7.49 mmol). The solvent was removed exhaustively in vacuo to leave a semisolid. All possible attempts to crystallize this material were unsuccessful. This semisolid was identified as (*i*-Bu)$_2$AlSC$_6$F$_5$, yield 96%. ^1H, ^{13}C, and ^{19}F NMR spectral results are presented in Table I.

Adduct Formation. [Me$_2$Al(μ-SC$_6$F$_5$)]$_2$ was prepared in situ via the procedure used in **1a**, and then 10 mL of tetrahydrofuran was added to the reaction mixture. The reaction mixture was stirred for 2 h, and the solvent was removed under vacuum to leave an oil. Attempts to crystallize the product by dissolving in pentane and cooling to -20 °C failed. The ^1H, ^{13}C, and ^{19}F NMR spectral results (cf. Table I) for this product are consistent with the formula $Me_2AlSC_6F_5$·THF. The synthesis of the diethyl ether adduct was attempted by the same procedure, 10 mL of diethyl ether being substituted for THF. The solvent was removed under vacuum to leave a colorless oil. The attempt to crystallize the product by dissolving in pentane and cooling to -20 °C did not yield a solid. The liquid was identified as $Me_2AlSC_6F_5$·Et_2O. ^1H NMR spectral data: δ 0.62 (Al-CH_3; singlet, 6 H); 0.74 (CH_3; triplet, 6 H); 3.47 (CH_2; quartet, 4 H). ^{13}C NMR spectral data: δ -9.44 (Al-CH_3); 67.85 (CH_2); 13.15 (CH_3).

Reaction with Methyl Benzoate. With the above-described procedure, $AlMe_3$ (3.75 mL, 7.49 mmol) and pentafluorothiophenol (1 mL, 7.49 mmol) gave $Me_2AlSC_6F_5$ in solution. Methyl benzoate (1.0 mL, 8.04 mmol) was syringed into this solution over a period of 5 min, and then the reaction mixture was stirred over a period of 2 h. During addition of each drop of methyl benzoate, a faint yellow solution appeared, which then disappeared rapidly. The solvent was removed in vacuo. The residue, on crystallization from 10 mL of *n*-pentane at -20 °C, was a white solid. This solid was identified as PhC(O)SC$_6$F$_5$, mp 55-58 °C. ^1H NMR spectral data: δ 6.87-7.81 (m). Mass spectral data (EI mode): *m*/*e* = 305, PhC(O)SC$_6$F$_5$ ($MH^{\bullet+}$); *m*/*e* = 199, $SC_6F_5^{\bullet+}$; *m*/*e* = 105, PhC(O)$^{\bullet+}$; *m*/*e* = 77, $Ph^{\bullet+}$. The use of the Al(*i*-Bu)$_3$ (3.75 mL, 3.75 mmol)/C_6F_5SH (0.5 mL, 3.75 mmol)/methyl benzoate (0.5 mL, 4.02 mmol) system and a procedure identical with that described above gave PhC(O)SC$_6$F$_5$. Melting point and ^1H NMR spectral results are identical with those presented above.

X-ray Structure Determination of [Me$_2$Al(μ-SC$_6$F$_5$)]$_2$ (1a). Crystals of [Me$_2$Al(μ-SC$_6$F$_5$)]$_2$ were grown from a pentane solution at -20 °C. A crystal suitable for X-ray diffraction studies was mounted in a thin-walled capillary tube in a drybox; the tube was plugged with grease, removed from the drybox, flame sealed, mounted on a goniometer head, and placed on a P3/V Nicolet diffractometer for data collection. Parameters from the crystal structure determination are presented in Table II.

Table II. Experimental Parameters for the X-ray Diffraction Study of [Me$_2$Al(μ-SC$_6$F$_5$)]$_2$

compd	tetramethylbis(μ-pentafluorobenzenethiolato)dialuminum
formula	$C_{16}H_{12}Al_2F_{10}S_2$
mol wt	513.34
cryst prepn	recrystallized from pentane, -20 °C
cryst color	colorless
cryst syst	monoclinic
space group	$P2_1/a$
cell const constrained from 25 high-angle rflns	
a, Å	14.133 (2)
b, Å	11.146 (2)
c, Å	15.287 (2)
β, deg	116.72 (1)
V, Å^3	2150.8 (0.5)
density (calcd), g cm^{-3}	1.585
Z	4 [Me$_2$Al(μ-SC$_6$F$_5$)]$_2$ units
radiation type	Cu K$\bar{\alpha}$, λ = 1.54184 Å, with a Ni filter
temp, °C	20
type of data collection	θ/2θ scan
2θ scan range, deg	8-110
octants used	$+h,+k,\pm l$
scan rate, deg min^{-1}	variable, 3-8
scan width, deg	0.5
bkgd:scan ratio	1:1.2
std rflns	3 measd every 100 rflns, dev from the std obsd (max dev 7%)
no. of data collected	3173
no. of obsd rflns	1335 with $F_o \geq 2.5\sigma(F)$
linear abs coeff (μ), cm^{-1}	29.79
F(000), e	1024
abs cor	empirical, ψ scans
no. of params refined	276
$R = \sum(\lvert F_o\rvert - \lvert F_c\rvert)/\sum\lvert F_o\rvert$	4.2
$R_w = [\sum(\lvert F_o\rvert - \lvert F_c\rvert)^2/\sum w\lvert F_o\rvert^2]^{1/2}$ [a]	5.8
overall shift/esd	0.000
max shift/esd	0.001
GOF	1.18
resid electron dens, e Å^{-3}	0.34, 1.28 Å from S1

[a] $w = 1.11779/\sigma^2F_o + 0.002(F_o)^2$

The crystal was found to be in the monoclinic cell system. Lattice constants were verified by axial photographs, and the crystal was assigned to the space group $P2_1/a$ (an alternate setting for $P2_1/c$, No. 14) on the basis of the systematic absences *h*0*l* (*h* odd) and 0*k*0 (*k* odd). Data reduction was carried out with use of the SHELXTL program.[9] The direct-methods routine produced an acceptable solution for the structure, yielding positions for all of the non-hydrogen atoms. Full-matrix least-squares refinement was carried out with use of SHELX-76.[10] The usual systematic correction for secondary extinction was applied, and the data were corrected for Lorentz and polarization effects. Scattering factors for neutral carbon and aluminum atoms were used.[11] An empirical correction for absorption was applied. All of the hydrogen atoms

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were placed in calculated positions with a C–H bond distance of 0.96 Å, and all hydrogen atom positional parameters were allowed to ride with their parent carbon atoms during subsequent refinement. A few additional cycles of refinement of the data led to convergence with $R = 4.2\%$ ($R_w = 5.8\%$). The final difference Fourier map showed a maximum electron density of 0.34 e/Å^3, 1.28 Å from S1 with a overall shift/error of 0.000.

Results and Discussion

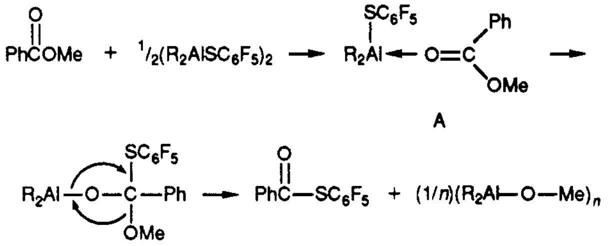
Synthesis. The S–H proton in pentafluorothiophenol reacts rapidly at room temperature with aluminum alkyls in a 1:1 stoichiometry, liberating the alkane and affording the corresponding organoaluminum thiolates, $R_2AlSC_6F_5$, in high yield according to the general reaction scheme given by eq 1. Compounds **1a** and **1b** have been isolated as

$$R_3Al + C_6F_5SH \rightarrow R_2AlSC_6F_5 + RH \qquad (1)$$
$$R = Me\ (\mathbf{1a}),\ Et\ (\mathbf{1b}),\ i\text{-}Bu\ (\mathbf{1c})$$

colorless, transparent crystals, and compound **1c** was isolated as a spectroscopically pure, semisolid material. 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 in both hydrocarbons such as pentane, benzene, and toluene and in donor solvents such as diethyl ether and tetrahydrofuran. The latter solvents appear to form a stable isolable addition compound with disruption of the Al–S–Al bridge bond as indicated in eq 2. This shows the weakness of the sulfur bridge relative to the oxygen bridge, which cannot be disrupted by an ether but requires a stronger base such as pyridine.[1d]

$$R_4Al_2(\mu\text{-}SC_6F_5)_2 + 2\text{base} \rightleftharpoons 2R_2(C_6F_5S)Al\cdot\text{base} \qquad (2)$$

During our studies on the reactions of bases with $R_2AlSC_6F_5$ we also found that $R_2AlSC_6F_5$ (R = Me, i-Bu) reacted with methyl benzoate to give the corresponding thioester $PhC(O)SC_6F_5$ in excellent yield. The reaction presumably proceeds through a two-step sequence. The first stage is the formation of the 1:1 addition complex A,



(3)

indicated by the formation of a yellow intermediate, which rapidly disappeared to yield the final product. In an analogous study, the stable 1:1 yellow addition complex $Et_2AlBHT\cdot MeO_2CC_6H_4Me$ has been prepared and confirmed by X-ray studies.[1i] The results of the present studies are also in full agreement with the established use of an aluminum reagent such as Me_2AlSR (R = CH_3CH_2, $C_6H_5CH_2$, t-C_4H_9) for the preparation of thioesters by its reaction with a variety of functionalized methyl and ethyl esters at room temperature.[4]

NMR Studies. In the ^1H NMR spectrum of $R_2AlSC_6F_5$ (Table I), the absence of the –SH resonance of pentafluorothiophenol and the presence of a sharp ^1H resonance upfield for the alkyl group attached to aluminum in the $-AlR_2$ moiety of $R_2AlSC_6F_5$ provide good evidence for the $-AlR_2$ coordination at the thiolato sulfur. The position of resonances associated with the alkyl groups attached to aluminum are virtually the same as for the corresponding protons in the parent AlR_3. The ^{13}C resonances of the alkyl group in the $-AlR_2$ moiety on complexation are only slightly shifted from the corresponding resonance in the parent AlR_3. In the ^{19}F NMR spectrum the resonances associated with the o-, m-, and p-fluorine atoms are very sharp and the chemical shifts of o- and p-fluorine atoms exhibit appreciable downfield shifts with respect to those of C_6F_5SH, while the signals for the m-fluorine atoms are affected to a much smaller extent. These shift effects probably are associated with the overall electron-withdrawing ability of the R_2AlS- group, which is a strong Lewis acid center. Further, we note that in the 1:1 addition compounds $R_2AlSC_6F_5\cdot B$ (B = Et_2O, THF), the chemical shifts of o- and p-fluorine atoms are upfield with respect to those of $R_2AlSC_6F_5$. Such changes in chemical shifts are attributed to the donation of electron density from these groups to the aluminum atom.

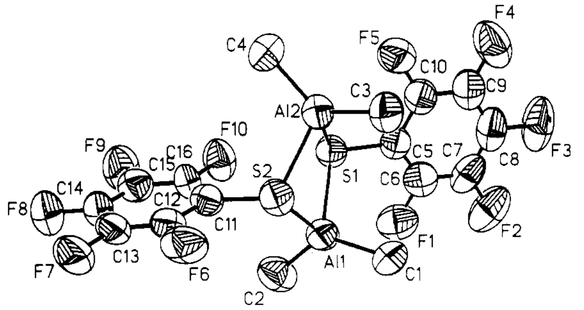


Figure 1. ORTEP diagram (50% thermal ellipsoids) of the $[Me_2Al(\mu\text{-}SC_6F_5)]_2$ molecule (**1a**) showing the atom-labeling scheme. Hydrogen atoms are omitted for clarity.

Table III. Atomic Coordinates and Isotropic Thermal Parameters for the $[Me_2Al(\mu\text{-}SC_6F_5)]_2$ Molecule

atom	x	y	z	U_{eq},[a] Å^2
S1	0.7750 (1)	0.1709 (2)	0.7513 (1)	0.0763 (8)
S2	0.8950 (1)	−0.0188 (2)	0.6591 (1)	0.0797 (8)
Al1	0.9400 (2)	0.1717 (2)	0.7404 (1)	0.077 (1)
Al2	0.7710 (1)	−0.0428 (2)	0.7258 (1)	0.074 (1)
F1	0.9223 (3)	0.3513 (4)	0.8882 (3)	0.115 (2)
F2	0.9675 (4)	0.3914 (5)	1.0770 (4)	0.147 (3)
F3	0.8741 (4)	0.2553 (5)	1.1635 (3)	0.153 (3)
F4	0.7317 (4)	0.0835 (5)	1.0595 (3)	0.139 (3)
F5	0.6871 (3)	0.0444 (4)	0.8713 (3)	0.105 (2)
F6	0.9499 (3)	−0.1227 (4)	0.5118 (3)	0.102 (2)
F7	0.8651 (4)	−0.0801 (4)	0.3188 (3)	0.126 (3)
F8	0.6968 (4)	0.0700 (4)	0.2330 (3)	0.132 (3)
F9	0.6167 (4)	0.1801 (4)	0.3432 (3)	0.124 (2)
F10	0.7043 (3)	0.1439 (4)	0.5372 (3)	0.101 (2)
C1	1.0578 (5)	0.1302 (6)	0.8664 (4)	0.096 (4)
C2	0.9385 (5)	0.2992 (7)	0.6542 (5)	0.106 (4)
C3	0.8617 (5)	−0.1224 (6)	0.8490 (4)	0.094 (4)
C4	0.6334 (6)	−0.0969 (7)	0.6296 (5)	0.108 (4)
C5	0.8063 (5)	0.1943 (7)	0.8754 (4)	0.073 (3)
C6	0.8746 (6)	0.2825 (7)	0.9309 (6)	0.089 (4)
C7	0.8981 (7)	0.3043 (8)	1.0273 (7)	0.102 (5)
C8	0.8503 (8)	0.236 (1)	1.0693 (6)	0.106 (5)
C9	0.7796 (7)	0.1479 (9)	1.0173 (6)	0.097 (5)
C10	0.7591 (6)	0.1305 (7)	0.9224 (6)	0.082 (4)
C11	0.8316 (5)	0.0073 (6)	0.5311 (4)	0.071 (3)
C12	0.8674 (6)	−0.0482 (6)	0.4713 (6)	0.079 (4)
C13	0.8250 (7)	−0.0276 (8)	0.3734 (7)	0.088 (5)
C14	0.7401 (8)	0.0509 (8)	0.3305 (5)	0.093 (5)
C15	0.6999 (6)	0.1051 (6)	0.3847 (6)	0.085 (4)
C16	0.7460 (6)	0.0858 (6)	0.4850 (5)	0.080 (4)

[a] $U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}\, a_i^* a_j^*\, \bar{a}_i\cdot\bar{a}_j$.

Molecular Geometry of the Dimeric $[Me_2Al(\mu\text{-}SC_6F_5)]_2$ (1a). An ORTEP diagram of the dimeric molecular unit of $[Me_2Al(\mu\text{-}SC_6F_5)]_2$ is shown in Figure 1. The positional parameters along with bond lengths and bond angles are listed in Tables III and IV.

The central structural unit of tetramethylbis(μ-pentafluorobenzenethiolato)dialuminum, $[Me_2Al(\mu\text{-}SC_6F_5)]_2$, is a four-membered ring composed of the two aluminum

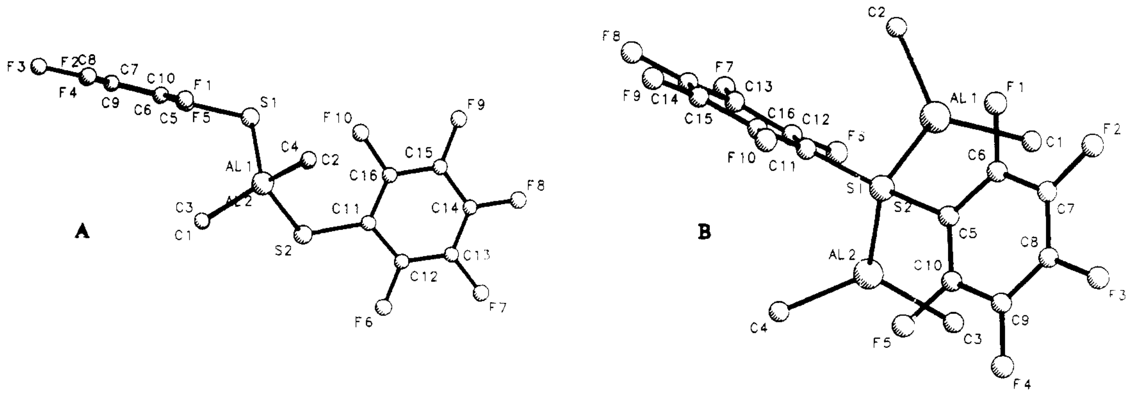


Figure 2. PLUTO diagram showing the orientation of the pentafluorophenyl groups relative to the Al_2S_2 ring in $[Me_2Al(\mu\text{-}SC_6F_5)]_2$: (A) view along the Al–Al axis; (B) view along the S–S axis.

Table IV. Selected Bond Lengths (Å) and Angles (deg) in the $[Me_2Al(\mu\text{-}SC_6F_5)]_2$ Molecule

	Distances		
S1–Al1	2.413 (2)	S2–C11	1.772 (4)
S2–Al1	2.397 (2)	Al1–C1	1.953 (6)
S1–Al2	2.410 (3)	Al1–C2	1.932 (7)
S2–Al2	2.407 (2)	Al2–C3	1.951 (6)
S1–C5	1.762 (4)	Al2–C4	1.933 (7)
	Angles		
S1–Al1–S2	89.61 (8)	C1–Al1–C2	126.2 (3)
S1–Al2–S2	89.41 (8)	C3–Al2–C4	126.4 (3)
S1–Al1–C1	110.6 (2)	Al2–S2–C11	112.5 (2)
S1–Al2–C4	111.9 (2)	Al1–S1–Al2	86.88 (8)
S1–Al1–C2	109.6 (2)	Al1–S1–C5	106.9 (2)
S1–Al2–C3	109.6 (2)	Al1–S2–Al2	87.31 (7)
S2–Al1–C2	112.3 (2)	Al1–S2–C11	108.2 (2)
S2–Al1–C1	102.2 (2)	Al2–S1–C5	107.2 (2)
S2–Al2–C3	99.9 (2)	S1–C5–C6	122.5 (4)
S2–Al2–C4	112.8 (1)	S1–C5–C10	122.6 (5)
S2–C11–C12	120.4 (5)	S2–C11–C16	123.5 (3)

atoms and the two bridging sulfur atoms. The ring is butterfly shaped with an angle between the two planes described by Al1–S1–Al2 and Al1–S2–Al2 of 152.3°. The two pentafluorophenyl groups are in the anti conformation and are oriented so that the plane of ring A (defined by carbon atoms C5–10) is essentially parallel to the Al–Al axis and ring B (defined by carbon atoms C11–16) is perpendicular to the Al–Al axis. These features are clearly seen in Figure 2. This brings the *o*-fluorine atoms F1 and F5 to within 3.1 Å (Al1–F1) and 3.09 Å (Al2–F5) of the aluminum atoms. This close approach (note the sum of the van der Waals radii is 3.91 Å)[12] may indicate some interaction, but no supporting evidence is available. Ring B is essentially orthogonal to ring A with the *o*-fluorine atoms far removed from the Al atoms.

The butterfly geometry of the Al_2S_2 ring may be attributed to the interaction of pentafluorophenyl groups with the aluminum atoms or perhaps to repulsion between the fluorine atoms on the rings and the alkyl groups attached to the metals. The butterfly arrangement is not typical for either carbon- or oxygen-bridged organoaluminum compounds, but distortion of a similar nature is observed for the $[Me_2Al(\mu\text{-}SMe)]_n$ polymer in the solid state,[5] and the distortion for the dimeric molecule $[Me_2AlSMe]_2$ in the gas phase[6] also may be interpreted in terms of this distortion. The only other reported system with a similar distortion of the ring is the hexacyclopropyldialuminum derivative, which adopts this configuration to reduce steric interaction between the cyclopropyl rings.[13]

Table V. Selected Bond Distances (Å) in Organoaluminum Derivatives

compd	Al–S	Al–C	Al–N
$(Me_2AlSC_6F_5)_2$	2.408	1.944	
$(Me_2AlSMe)_n$[a]	2.348 (2)	1.944 (7)	
$(Me_2AlSMe)_2$ (gas phase)[b]	2.370	1.945	
$K(Me_3AlSCNAlMe_3)$[c]	2.489 (2)	1.968 (av)	1.951 (5)
$(AlMe_3)(12)aneS_4$[d]	2.718 (3)	1.949 (av)	
$(Al(i\text{-}Bu)_2(C_6H_5)_2P(S)CP\text{-}(C_6H_5)_2(S)_2)[Al(i\text{-}Bu)_2]$[e]		2.286 (3)	2.033
$(AlMe_3)_4(14)aneS_4$[f]	2.522	1.954 (6)	
$Al_4I_4(SCH_3)_4S_2$[g]	2.18 2.30		
$Al(S_2CNMe_2)_3$[h]	2.395		
$Me_2Al(\mu\text{-}PyS)_2AlMe_2$[i]	2.338 (3)	1.981 (6) (Al1–C) 1.965 (5) (Al2–C)	1.993 (4)

[a] Reference 5. [b] Reference 6. [c] Shakir, R.; Zaworotko, M. J.; Atwood, J. L. *J. Organomet. Chem.* **1979**, *171*, 9. [d] Robinson, G. H.; Sangokoya, S. A. *J. Am. Chem. Soc.* **1988**, *110*, 1494. [e] Robinson, G. H.; Self, M. F.; Pennington, W. T.; Sangokoya, S. A. *Organometallics* **1988**, *7*, 2424. [f] Robinson, G. H.; Zhang, H.; Atwood, J. L. *Organometallics* **1987**, *6*, 887. [g] Boardman, A.; Small, R. W. H.; Worrall, I. J. *Inorg. Chim. Acta* **1986**, *120*, L23. [h] Nöth, H.; Konrad, P. *Chem. Ber.* **1983**, *116*, 3552. [i] Reference 7.

The geometry around the sulfur atom is pyramidal with C5–S1–Al1 = 106.7° and C5–S1–Al2 = Al1–S1–Al2 = 86.9°. This is identical with the values observed in the solid state in $[Me_2Al(\mu\text{-}SMe)]_n$[5] and is only slightly greater than the value observed for the $[Me_2Al(\mu\text{-}SMe)]_2$ dimer in the gas phase.[6]

The geometry around the aluminum 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 IV, and a listing of Al–C and Al–S bond distances for related compounds from the literature is presented in Table V. The one distance worthy of comment is the Al–S distance. In the compound the average value is 2.408 Å, which is slightly longer than that observed in dimeric $Me_4Al_2(\mu\text{-}SMe)_2$ in the gas phase or for the corresponding polymer observed in the solid state. This distance is substantially less than the Al–S bond distance observed in the sulfur addition compound. It now appears reasonable to state that bridging Al–S distances will be close to 2.408 Å and, as noted previously,[5,6] be substantially longer than the 2.22 Å estimated from the sum of the covalent radii.

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Registry No. 1a, 125496-08-4; **1b**, 125496-09-5; **1c**, 125496-10-8; C_6F_5SH, 771-62-0; $AlMe_3$, 75-24-1; $AlEt_3$, 97-93-8; $Al(i\text{-}Bu)_3$, 100-99-2; $Me_2AlSC_6F_5{\cdot}THF$, 125496-11-9; PhC(O)OMe, 93-58-3; $PhC(O)SC_6F_5$, 28078-91-3.

Supplementary Material Available: Listings of anisotropic thermal parameters for the non-hydrogen atoms, positional and isotropic thermal parameters for the hydrogen atoms, torsion angles, least-squares planes and deviations, and all bond distances and angles (12 pages); a listing of the observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

Diphenyl(2,2′-bipyridyl)dioxomolybdenum(VI) and -tungsten(VI): A Comparative Study

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Summary: The structures of $(C_6H_5)_2Mo(O)_2(bpy)$ (**1**) and of the newly prepared tungsten analogue $(C_6H_5)_2W(O)_2(bpy)$ (**2**), where bpy = 2,2′-bipyridyl, are reported. The molybdenum complex **1** exists as two isomers in the same crystal. The orthorhombic unit cell *Pbca* contains 16 molecules in 8 asymmetric pairs of the isomers **1A** and **1B**, which differ primarily with respect to the orientations of the phenyl rings. In **1A**, interactions of the aromatic π-electron systems with one Mo=O bond are maximized; one phenyl ring is almost coplanar with one Mo=O bond and the dihedral angle between the phenyl rings is 20.5°. In **1B**, the phenyl groups adopt a configuration minimizing repulsive interactions with the $Mo(O)_2(bpy)$ moiety; the smallest Mo=O/phenyl dihedral angle is 23°, and the phenyl groups are in a near-orthogonal configuration with a dihedral angle of 75.5°. The combined presence of both modifications allows an especially close-packed molecular arrangement in the crystal. The tungsten complex **2** crystallizes in a monoclinic unit cell with only one type of molecule present, whose structure is intermediate between these of **1A** and **1B**. One phenyl ring is coplanar with a W=O bond; the dihedral angle between the phenyl rings is 46.7°. In solutions of **2** and of the additionally prepared complexes $(4\text{-}CH_3C_6H_4)_2W(O)_2(bpy)$ (**3**) and $(4\text{-}CH_3OC_6H_4)_2W(O)_2(bpy)$ (**4**) evidence for π-type electronic interactions between the aryl substituents and the W=O bond(s) was obtained by UV-vis spectroscopic measurements.

The chemistries of molybdenum and tungsten show striking similarities as well as differences that are still largely unexplained. One approach toward the understanding of these differences is the comparison of chemically analogous compounds of the two elements. In a previous paper[1] we reported comparisons of dialkyl derivatives of the type $R_2Mo(O)_2(bpy)$, where bpy = 2,2′-bipyridyl, with newly prepared analogous complexes of tungsten. We have now extended our studies to the diaryl derivatives of the two elements. Although the synthesis of $(C_6H_5)_2Mo(O)_2(bpy)$ (**1**) and of several substituted derivatives thereof have been described,[2] thus far the structure of only the bis(4-methoxyphenyl) derivative could be determined, as isolation of single crystals of these compounds is difficult. However, we have now succeeded in obtaining single crystals of **1** and completed an X-ray crystallographic structure determination, which produced an unexpected result. In addition, we report the structure of the newly prepared tungsten derivative $(C_6H_5)_2W(O)_2(bpy)$ (**2**). Although the structures of **1** and **2** are different, interactions between the aromatic π electrons and the Mo=O or W=O bonds were observed in both complexes. Furthermore, spectroscopic evidence for similar interactions in solution was also obtained for **2** and the additionally prepared $R_2W^{VI}(O)_2(bpy)$ complexes with R = $4\text{-}CH_3C_6H_4$ (**3**) and $4\text{-}CH_3OC_6H_4$ (**4**).

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer 1330 infrared spectrometer. NMR spectra were measured on a GE QE-300 instrument at 300 MHz (^{1}H) and on a EM 390 instrument at 90 MHz. UV-vis spectra were measured on a Beckman DU-40 spectrophotometer.

Reagents and Chemicals. Complex 1 was prepared as described in ref 2 and recrystallized from CH_2Cl_2/C_2H_5OH. Anal. Calcd for $C_{22}H_{18}MoN_2O_2$: C, 60.28; H, 4.14. Found: C, 59.75; H, 4.25. Mass spectrum (^{96}Mo; m/z (relative intensity, assignment)): 439 (3, M^+); 362 (12, $M^+ - Ph$). $W(O)_2Br_2(bpy)$ (**6**)[3] was dried for 24 h at 100 °C prior to use. Anal. Calcd for $C_{10}H_8Br_2N_2O_2W$: Br, 30.0; W, 34.6. Found, Br, 30.6; W, 34.2. Solutions of the arylmagnesium halides in tetrahydrofuran (THF) were prepared by the usual methods; all aryl bromides were dried over $MgSO_4$ and distilled prior to use.

General Synthesis of Complexes $(aryl)_2W(O)_2(bpy)$ (2-4). To stirred suspensions of 2.5 g (4.7 mmol) of **6** in 5 cm^3 of dry THF was added 10.5 mmol of the respective arylmagnesium halide in 7 cm^3 of THF dropwise under argon at 0 °C over a period of 30 min. The reaction mixtures were warmed to room temperature and were subsequently stirred for 12 h. The brown-black heterogeneous reaction mixtures were treated with 100 cm^3 of cold, saturated aqueous NH_4Cl followed by 100 cm^3 of CH_2Cl_2 and were vigorously shaken in air until the CH_2Cl_2 layer was bright yellow. The CH_2Cl_2 phases were collected, repeatedly washed with water, and dried with $MgSO_4$. The complexes were isolated as pale yellow crystalline solids by evaporating the CH_2Cl_2 solutions to volumes of 5 cm,^{3} adding 10 cm^3 of n-hexane, and cooling to 0 °C. The yields ranged from 60 to 70%, based on **6**. Analytical data are summarized in Table I. Mass spectrum for **2** (^{184}W; m/z (relative intensity, assignment)): 527 (4, M^+); 449 (14, $M^+ - Ph$).

Properties. Complexes 2-4 are air-stable and have higher thermal decomposition points than the corresponding molybdenum compounds (see Table I). On thermolysis at 250 °C, biphenyl and the corresponding biaryls were detected as the main soluble thermolysis products (identified by ^{1}H NMR spectra and melting points).

Structural Analyses. Crystals of 1 and of 2 as obtained from CH_2Cl_2 were suitable for X-ray structural analysis. The structures were solved by conventional Patterson and difference Fourier techniques. Crystallographic data and data collection parameters are given in Table IV. Crystals of approximate sizes given in

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