Synthesis and Spectroscopic Studies on the Thiophene Derivatives of the Group 13 Elements Aluminum and Indium. Crystal and Molecular Structures of $[Me_2M(\mu\text{-}2\text{-}C_4H_3S)]_2$ (M = Al, In) and $\{(2\text{-}C_4H_3S)_2Al[\mu\text{-}N(H)C(H)(C_6H_5)_2]\}_2$

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Trithiophene derivatives $(2\text{-}C_4H_3S)_3M{\cdot}nL$ (M = Al, $n = 1$, L = OEt_2, **1a**; M = In, $n = 2$, L = THF, **1b**) have been prepared by the reaction of the Grignard reagent $2\text{-}C_4H_3SMgBr$ with MCl_3 (M = Al, In) in ether solvents. Compounds **1a,b** undergo exchange reactions with Me_3Al to give a mixture of $[Me_2M(\mu\text{-}2\text{-}C_4H_3S)]_2$ (M = Al, **2a**; M = In, **2b**) and $(2\text{-}C_4H_3S)_2(Me)M{\cdot}L$ (M = Al, L = OEt_2; M = In, L = THF). The aminolysis of **1a** with a primary amine, $(C_6H_5)_2C(H)NH_2$, gives $\{(2\text{-}C_4H_3S)_2Al[\mu\text{-}N(H)C(H)(C_6H_5)_2]\}_2$ (**3**) in excellent yield. The resulting compounds have been characterized by ^1H and ^{13}C NMR spectroscopy. A single-crystal X-ray study of **2a** established that it crystallizes in the monoclinic cell system, space group $P2_1/c$ (No. 14), with cell constants of $a = 14.332(5)$ Å, $b = 14.460(3)$ Å, $c = 16.226(6)$ Å, $\beta = 112.43(2)°$, and $Z = 8$ (dimers); $R = 5.7\%$ and $R_w = 5.5\%$, based on 2709 observed reflections ($I \geq 2.5\sigma(I)$). Compound **2b** crystallizes in the monoclinic space group $C2/c$ (No. 15) with cell constants of $a = 12.999(5)$ Å, $b = 13.421(2)$ Å, $c = 9.522(2)$ Å, $\beta = 105.86(2)°$, and $Z = 4$ (dimers); $R = 2.1\%$ and $R_w = 2.3\%$, based on 1179 observed reflections ($I \geq 2.5\sigma(I)$). The molecular unit in **2a** consists of two Me_2Al moieties bridged symmetrically by thiophene rings. In **2b** the bridge is asymmetric. Compound **3** crystallizes in the triclinic space group $P\bar{1}$ (No. 2) with cell constants of $a = 9.813(5)$ Å, $b = 10.126(5)$ Å, $c = 10.654(5)$ Å, $\alpha = 87.36(4)°$, $\beta = 74.20(4)°$, $\gamma = 72.77(4)°$, and $Z = 1$ (dimer); $R = 7.0\%$ and $R_w = 7.0\%$, based on 1768 observed reflections ($I \geq 2.5\sigma(I)$). The molecular unit in **3** is a nitrogen-bridged, planar dimer with an Al–N bond distance of 1.955(6) Å. In solution at low temperature, **2a** exists as *syn* and *anti* conformers which undergo rapid exchange on the NMR time scale at room temperature with an activation energy of 12 kcal mol^{-1}. The formation of the compound $Me_2Al(\mu\text{-}Me)(\mu\text{-}2\text{-}C_4H_3S)AlMe_2$ has been established by low-temperature NMR spectroscopic studies.

Introduction

Group 13/15 organometallic compounds interest the microelectronics industry because they serve as precursors to semiconductors.[1] The simple organo derivatives of group 13 elements receive particular attention since they are used to deposit metallic films on silicon-based electronic devices.[2] Furthermore, organoaluminum moieties, in combination with transition-metal derivatives, have been used to stabilize reactive organic species.[3-6] Over the past several years we have been involved in the synthesis of organoaluminum compounds and the study of their structure, bonding, and behavior in solution.[7-9] In this paper we report the synthesis of trithiophene derivatives of aluminum and indium by the reaction of the Grignard reagent $2\text{-}C_4H_3SMgBr$ with MCl_3 (M = Al, In) in ether solvents. The reactivity of these trithiophene derivatives with trimethylaluminum and aminodiphenylmethane to give the mixed-ligand organoaluminum and -indium compounds $[Me_2M(\mu\text{-}2\text{-}C_4H_3S)]_2$ (M = Al, In) and the elimination product $\{(2\text{-}C_4H_3S)_2Al[\mu\text{-}N(H)C(H)(C_6H_5)_2]\}_2$ has also been studied. This study includes the determination of the molecular structures of $[Me_2M(\mu\text{-}2\text{-}C_4H_3S)]_2$ (M = Al, In) and of $\{(2\text{-}C_4H_3S)_2Al[\mu\text{-}N(H)C(H)(C_6H_5)_2]\}_2$. The dimeric structure of the indium derivative is unique because it represents the first such observation among structurally characterized triorganoindium derivatives.

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Experimental Section

General Experimental Procedures. All solvents were purified and dried by standard techniques.[10] Argon gas was purified by passing it through a series of columns containing Deox catalyst (Alfa), phosphorus pentoxide, and calcium sulfate. Anhydrous metal chlorides $AlCl_3$ (Aldrich) and $InCl_3$ (Aldrich), 2-bromothiophene (Aldrich), and Me_3Al (Aldrich, 2 M solution in toluene) were used as received. Aminodiphenylmethane (Aldrich) was refluxed over calcium hydride for 24 h and distilled under reduced pressure before use. The Grignard reagent 2-C_4H_3SMgBr was prepared as described previously.[11] All the glassware used in the synthetic work was oven-dried. The compounds are both oxygen and water sensitive; therefore, standard Schlenk-line techniques were employed. ^1H and ^{13}C NMR spectra were recorded either on a General Electric QE-300 NMR or on a GN-300 NMR spectrometer. The chemical shifts were referenced to the residual proton line from benzene-d_6 (δ 7.15 ppm (^1H), 128 ppm (^{13}C)). The variable-temperature NMR spectra were obtained on toluene-d_8 solutions and were referenced to the methyl resonance of toluene (δ 2.09 ppm (^1H), 20.4 ppm (^{13}C)). Mass spectra were run with a MS-80 Autoconsole (Kratos Analytical Instruments) mass spectrometer in the EI mode Melting points were obtained using a Haake Buchler apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

Synthesis of $(2\text{-}C_4H_3S)_3Al\cdot OEt_2$ (1a). A solution of $AlCl_3$ in diethyl ether was prepared by placing $AlCl_3$ (32.71 g, 0.245 mol) in a 250-mL flask and cooling to −78 °C. Diethyl ether (approximately 100 mL) was added slowly with stirring to prevent overheating from the extremely exothermic formation of the $Cl_3Al\cdot OEt_2$ complex. When addition was complete, the solution was brought to room temperature. The $Cl_3Al\cdot OEt_2$ solution was transferred to an addition funnel and added dropwise to the Grignard reagent 2-C_4H_3SMgBr (0.736 mol) in diethyl ether. The reaction mixture was refluxed for 4 h, and the diethyl ether was removed under vacuum. The solid was extracted with a diethyl ether/pentane (1:3; 200 mL) mixture. The supernatant liquid was decanted, and when it was cooled to −20 °C, it gave a white crystalline solid. The extraction was continued until no more solid was obtained. The solid was collected and identified as **1a**. (Note that the ether is readily removed and that the chemical analysis is for $(2\text{-}C_4H_3S)_3Al$.) Yield: 85%. Mp: 82−83 °C. Anal. Calcd for $C_{12}H_9S_3Al$: C, 52.15; H, 3.28. Found: C, 51.69; H, 5.23. ^1H NMR (C_6D_6; δ, ppm): 7.24−7.27 (m, 3H), 7.55−7.57 (m, 3H), 7.74−7.75 (m, 3H) (2-C_4H_3S); 0.57 (t, 6H, $(CH_3CH_2)_2O$); 3.46 (q, 4H, $(CH_3CH_2)_2O$). $^{13}C\{^1H\}$ NMR (C_6D_6; δ, ppm): 128.6, 131.3, 138.2, 142.6 (2-C_4H_3S); 13.2 ($(CH_3CH_2)_2O$); 68.0 ($(CH_3CH_2)_2O$).

Synthesis of $(2\text{-}C_4H_3S)_3In\cdot 2THF$ (1b). $InCl_3$ (15.83 g, 71.557 mmol) was dissolved in tetrahydrofuran (100 mL) and reacted with 2-C_4H_3SMgBr (214 mmol) in diethyl ether by the procedure given for **1a**. The solid was collected and identified as **1b**. Yield: 85%. Mp: 122 °C. (Note that the two THF molecules observed by NMR integration are easily lost and that the analysis is for $(2\text{-}C_4H_3S)_3In$.) Anal. Calcd for $C_{12}H_9InS_3$: C, 39.57; H, 4.14. Found: C, 38.71; H, 4.14. ^1H NMR (C_6D_6; δ, ppm): 7.28−7.31 (m, 3H), 7.56−7.57 (m, 3H), 7.63−7.65 (m, 3H) (2-C_4H_3S); 1.16 (t, 8H, β-H THF); 3.48 (b, 8H, α-H THF). $^{13}C\{^1H\}$ NMR (C_6D_6; δ, ppm): 128.0, 130.7, 136.9, 145.7 (2-C_4H_3S); 24.93 (β-C THF); 70.3 (α-C THF). Mass spectrum (EI mode): *m/e* 284, 84, and 72 corresponding to the fragments $(C_4H_3S)_2In^{\bullet+}$, $C_4H_4S^{\bullet+}$, and $C_4H_8O^{\bullet+}$ were observed.

Synthesis of $[Me_2Al(\mu\text{-}2\text{-}C_4H_3S)]_2$ (2a). $(2\text{-}C_4H_3S)_3Al\cdot OEt_2$ (1.25 g, 3.00 mmol) was stirred in pentane (70 mL), and Me_3Al (3.0 mL, 3.00 mmol) was added over a period of 10 min. The solution was stirred for 3 days to ensure complete reaction. The volume of the solution was reduced to half under vacuum and cooled to −20 °C. The crystalline, colorless solid was collected, washed with 10−15 mL of very cold pentane, dried under vacuum, and identified as **2a**. A better yield (85%) of the product was obtained when the reaction was carried out with a 1:2 ratio of **1a** (2.00 g, 5.71 mmol) to Me_3Al (5.71 mL, 11.42 mmol). Mp: 94 °C. Anal. Calcd for C_6H_9AlS: C, 51.40; H, 6.47. Found: C, 50.60; H, 6.41. ^1H NMR (C_6D_6; δ, ppm): 6.87−6.89 (m, 1H), 7.67−7.69 (m, 1H), 8.16 (b, 1H) (2-C_4H_3S); −0.29 (s, 6H, $AlMe_2$). $^{13}C\{^1H\}$ NMR (C_6D_6; δ, ppm): 127.2, 130.0, 148.5, 160.0 (2-C_4H_3S); −3.9 ($AlMe_2$). Mass spectrum (EI mode): *m/e* 281, 207, 140, 125, 84, and 57 corresponding to the fragments $[Me_2Al(C_4H_3S)]_2^{\bullet+}$, $MeAl(C_4H_3S)_2^{\bullet+}$, $Me_2Al(C_4H_3S)^{\bullet+}$, $MeAl(C_4H_3S)^{\bullet+}$, $C_4H_4S^{\bullet+}$, and $Me_2Al^{\bullet+}$ were observed.

Synthesis of $[Me_2In(\mu\text{-}2\text{-}C_4H_3S)]_2$ (2b). $(2\text{-}C_4H_3S)_3In\cdot 2THF$ (3.25 g, 6.39 mmol) was dissolved in pentane (70 mL) and reacted with Me_3Al (6.39 mL, 12.78 mmol) by the procedure given for **2a**. The solid was collected and identified as **2b**. Yield: 60%. Mp: 100 °C. Anal. Calcd for C_6H_9InS: C, 31.61; H, 3.98. Found: C, 30.36; H, 4.06. ^1H NMR (C_6D_6; δ, ppm): 6.94−6.96 (m, 1H), 7.59−7.61 (m, 1H), 7.80−7.81 (m, 1H) (2-C_4H_3S); −0.15 (s, 6H, $InMe_2$). Mass spectrum (EI mode): *m/e* 296, 281, 213, 145, 130, 115, and 84 corresponding to the fragments $MeIn(C_4H_3S)_2^{\bullet+}$, $In(C_4H_3S)_2^{\bullet+}$, $MeIn(C_4H_3S)^{\bullet+}$, $Me_2In^{\bullet+}$, $MeIn^{\bullet+}$, $In^{\bullet+}$, and $C_4H_4S^{\bullet+}$ were observed.

Synthesis of $\{(2\text{-}C_4H_3S)_2Al[\mu\text{-}N(H)C(H)(C_6H_5)_2]\}_2$ (3). $(2\text{-}C_4H_3S)_3Al\cdot OEt_2$ (2.00 g, 5.71 mmol) was dissolved in toluene (40 mL), and aminodiphenylmethane (0.98 mL, 5.71 mmol) was added dropwise. The solution was refluxed for 12 h and deposited crystalline solid when cooled to room temperature. The product was collected, washed with 10−15 mL of very cold pentane, and dried under vacuum. This solid was identified as **3**. Yield: >90%. Mp: 225 °C. Anal. Calcd for $C_{21}H_{18}AlNS_2$: C, 67.17; H, 4.83; N, 3.73. Found: C, 66.81; H, 5.01; N, 3.59. ^1H NMR (C_6D_6; δ, ppm): 6.77−6.87, 6.96−6.98, 7.10−7.17, 7.21−7.27, 7.49−7.53 (m, 2-C_4H_3S + C_6H_5); 5.59 (1, NH), 3.48 (1, CH); $^2J_{AB}$ = 13.3 Hz; 5.90 (1, NH), 3.18 (1, CH); $^2J_{AB}$ = 13.1 Hz. $^{13}C\{^1H\}$ NMR (C_6D_6; δ, ppm): 126.6, 126.8, 127.5, 128.7, 128.9, 131.6, 131.8, 131.9, 137.5, 138.2, 139.1, 143.7, 143.8 (2-C_4H_3S + C_6H_5); 62.8 (CH). Mass spectrum (EI mode): *m/e* 182, 106, 84, and 77 corresponding to the fragments $(C_6H_5)_2C(H)NH^{\bullet+}$, $(C_6H_5)C(H)NH^{\bullet+}$, $C_4H_4S^{\bullet+}$, and $C_6H_5^{\bullet+}$ were observed. IR (Nujol, cm^{-1}): 3244 w (NH), 3090 w, 3060 w, 3032 w, 3024 w, 2956 br, 2926 br, 1601 w, 1496 m, 1464 s, 1392 s, 1385 s, 1338 w, 1313 w, 1251 w, 1226 w, 1207 s, 1189 m, 1154 w, 1076 m, 1032 m, 997 s, 962 s, 948 s, 916 m, 882 s, 844 m, 828 s, 760 m, 738 s, 720 s, 705 s, 697 s, 679 m, 637 m, 615 w, 608 w, 572 m, 547 s.

X-ray Structure Determination of $[Me_2M(\mu\text{-}2\text{-}C_4H_3S)]_2$ (M = Al, 2a; M = In, 2b) and $\{(2\text{-}C_4H_3S)_2Al[\mu\text{-}N(H)C(H)(C_6H_5)_2]\}_2$ (3). Crystals of $[Me_2M(\mu\text{-}2\text{-}C_4H_3S)]_2$ (M = Al, **2a**; M = In, **2b**) were grown from a mixture of pentane and toluene in a 5:1 ratio at −20 °C and those of **3** from toluene at room temperature. 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 goniometer head, and placed on a Nicolet P3/V diffractometer for data collection. Crystal structure parameters are presented in Table 1.

The crystals of **2a**,**b** were found to be monoclinic. Lattice constants were verified by axial photographs. Compound **2a** was assigned to the space group $P2_1/c$ (No. 14) on the basis of the systematic absences. The space group of **2b** was determined to be $C2/c$ or Cc on the basis of systematic absences and assigned to $C2/c$ (no. 15) on the basis of successful refinement in this space group. The crystal of **3** was found to be triclinic and successfully refined in the space group $P\bar{1}$ (No. 2). Data reduction and calculations were carried out using the SHELXTL program.[12] The direct-methods routine pro-

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Table 1. Experimental Parameters for the X-ray Diffraction Study of $[\mathrm{Me_2Al}(\mu\text{-}2\text{-}\mathrm{C_4H_3S})]_2$ (2a), $[\mathrm{Me_2In}(\mu\text{-}2\text{-}\mathrm{C_4H_3S})]_2$ (2b), and $\{(2\text{-}\mathrm{C_4H_3S})_2\mathrm{Al}[\mu\text{-}\mathrm{N(H)C(H)(C_6H_5)_2}]\}_2$ (3)

	2a	2b	3
formula	C_6H_9AlS	C_6H_9InS	$C_{21}H_{18}AlNS_2$
mol wt	280.37	456.04	758.98
cryst color, habit	colorless, triangular fragment	colorless, diamond shaped	colorless, parallelepipeds
cryst syst	monoclinic	monoclinic	triclinic
space group	$P2_1/c$ (No. 14)	$C2/c$ (No. 15)	$P\bar{1}$ (No. 2)
cell constants obtained from 25, 24, and 25 high-angle rflns			
a (Å)	14.332(5)	12.999(5)	9.813(5)
b (Å)	14.460(3)	13.421(2)	10.126(5)
c (Å)	16.226(6)	9.522(2)	10.654(5)
α (deg)			87.36(4)
β (deg)	112.43(2)	105.86(2)	74.20(4)
γ (deg)			72.77(4)
Z	8 (dimers)	4 (dimers)	1 (dimer)
V (Å^3)	3108.5(1.7)	1598.0(0.8)	972.3(0.7)
density (calcd) (g cm^{-3})	1.198	1.895	1.283
radiation type	Mo K$\bar{\alpha}$ (λ = 0.710 73 Å), with a graphite monochromator	Mo K$\bar{\alpha}$ (λ = 0.710 73 Å), with a graphite monochromator	Mo K$\bar{\alpha}$ (λ = 0.710 73 Å), with a graphite monochromator
temp (°C)	22	22	22
type of data collecn	$\theta/2\theta$ scan	$\theta/2\theta$ scan	$\theta/2\theta$ scan
2θ scan range (deg)	6–50	6–50	6–45
octants used	0 to h; 0 to k; $\pm l$	0 to h; 0 to k; ±1	$0 \pm h$; $\pm k$; $\pm l$
scan rate (deg min^{-1})	variable, 4–25	variable, 3–25	variable, 3–5
scan range	1.0–1.1	1.0–1.0	1.0–1.2
std rflns: 3 measd every 97 rflns	max dev from std <3%	max dev from std <7%	max dev from std <3%
no. of data collected	5922	1611	5308
no. of unique rflns	5452	1403	2558
no. of obsd rflns	2709 ($I \geq 2.5\sigma(I)$)	1179 ($I \geq 2.5\sigma(I)$)	1768 ($I \geq 2.5\sigma(I)$)
linear abs coeff (μ) (cm^{-1})	3.93	30.72	3.09
$F(000)$ (e)	1184	880	924
abs cor	applied, ψ scans	applied, ψ scans	none applied
no. of params refined	293	109	205
data param ratio	9:1	11:1	9:1
$R = \sum(\lvert F_o\rvert - \lvert F_c\rvert)/\sum\lvert F_o\rvert$ (%)	5.7	2.1	7.0
$R_w = [\sum(\lvert F_o\rvert - \lvert F_c\rvert)^2/\sum w\lvert F_o\rvert^2]^{1/2}$ (%)	5.5	2.3	7.0
max shift/esd	0.001	0.001	0.001
residual electron density (e Å^{-3})	0.83	0.42	0.49
transmissn coeff	0.91–0.834	0.499–0.404	

duced an acceptable solution for the structure, yielding positions for some of the non-hydrogen atoms. All other atoms were located from the difference Fourier map after subsequent full-matrix, least-squares refinement using SHELX-76.[13] The data were corrected for Lorentz and polarization effects, and scattering factors for neutral carbon, nitrogen, sulfur, indium, and aluminum atoms were used.[14] In **2a** the bridging thiophene rings are disordered. This has been treated by assigning partial occupancy factors to S1/C6 (87/13), S2/C10 (73/27), S3/C18 (63/37), and S4/C22 (66/34). This disorder can be described by a rotation about a vector passing through the bridging carbon atom and bisecting the bond between the carbon–carbon bond opposite. The two carbon atoms that are interchanged by this process were not treated in any special way. Some increase in the uncertainty of their positions is indicated by the large thermal parameters for these atoms. In **3** the thiophene rings are disordered in the same way and were assigned a 70/30 ratio for the positions designated as S/C. In all cases, the hydrogen atoms have been placed near the position assigned to have a high probability for carbon occupancy. Ten moderately intense reflections were used to correct for absorption effects by collecting ψ scans and varying the diffraction vector from 0 to 180° in 10° increments. Each hydrogen atom was placed in a calculated position with a C–H bond distance of 0.95 Å and assigned isotropic thermal parameters based on the thermal parameters of the carbon atom to which it is bound. The atomic coordinates and isotropic thermal parameters for the non-hydrogen atoms are presented in Tables 2–4, respectively.

Results and Discussion

Syntheses. The trithiophene derivatives $(2\text{-}\mathrm{C_4H_3S})_3\mathrm{Al}\cdot\mathrm{OEt_2}$ (**1a**) and $(2\text{-}\mathrm{C_4H_3S})_3\mathrm{In}\cdot2\mathrm{THF}$ (**1b**) were prepared by the reaction of the Grignard reagent $2\text{-}\mathrm{C_4H_3SMgBr}$ with $\mathrm{MCl_3}$ (M = Al, In) in ether solvents, yielding colorless crystals. The compounds are all sensitive to oxygen and water and decompose quickly when exposed to the atmosphere. The reactivity of **1a** with a primary amine was also investigated by addition of aminodiphenylmethane to **1a** in toluene. On reflux this solution yielded the ether-free complex $\{(2\text{-}\mathrm{C_4H_3S})_2\mathrm{Al}[\mu\text{-}\mathrm{N(H)C(H)(C_6H_5)_2}]\}_2$ (**3**). ^{1}H and ^{13}C NMR spectral data for the addition compounds $(2\text{-}\mathrm{C_4H_3S})_3\mathrm{M}\cdot n\mathrm{L}$ (M = Al, n = 1, L = $\mathrm{OEt_2}$, **1a**; M = In, n = 2, L = THF, **1b**), for the mixed-ligand derivatives $[\mathrm{Me_2M}(\mu\text{-}2\text{-}\mathrm{C_4H_3S})]_2$ (M = Al, **2a**; M = In, **2b**), and for the aminolysis product $\{(2\text{-}\mathrm{C_4H_3S})_2\mathrm{Al}[\mu\text{-}\mathrm{N(H)C(H)(C_6H_5)_2}]\}_2$ (**3**) are presented in the Experimental Section. The ^{1}H NMR spectra of adducts $(2\text{-}\mathrm{C_4H_3S})_3\mathrm{M}\cdot n\mathrm{L}$ are typical of such compounds and confirm the presence of various ligands/groups attached to the metal center. The spectra of **2a,b** and **3** will be discussed in more detail in the following sections.

Compounds **1a,b** undergo exchange with $\mathrm{Me_3Al}$ to give mixtures of $[\mathrm{Me_2M}(\mu\text{-}2\text{-}\mathrm{C_4H_3S})]_2$ (M = Al, **2a**; M = In, **2b**) and $(2\text{-}\mathrm{C_4H_3S})_n(\mathrm{Me})_{3-n}\mathrm{M}\cdot\mathrm{L}$ (M = Al, L = $\mathrm{OEt_2}$; M = In, n = 0, 1, L = THF). At −20 °C the dimeric, thiophene-bridged product crystallized from the solution when either a 1:1 or a 1:2 ratio of **1a**/$\mathrm{Me_3Al}$ is used. With the 1:2 mixture an 85% yield was obtained. Examination of the material remaining in solution by NMR

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Table 2. Atomic Coordinates and Isotropic Thermal Parameters for the Non-Hydrogen Atoms of $[Me_2Al(\mu\text{-}2\text{-}C_4H_3S)]_2$ (2a)

atom[b]	x	y	z	U_{eq}[a] (Å^2)
		Molecule 1		
Al1	0.0003(1)	0.1071(1)	0.7167(1)	0.0523(7)
Al2	−0.0736(1)	0.2721(1)	0.6295(1)	0.0552(8)
C1	−0.0449(5)	0.0415(4)	0.8006(4)	0.075(3)
C2	0.1086(4)	0.0594(4)	0.6831(4)	0.073(3)
C3	−0.0001(5)	0.3074(4)	0.5545(4)	0.083(3)
C4	−0.1810(4)	0.3471(4)	0.6398(4)	0.080(3)
S1/C	0.1592(1)	0.2790(1)	0.7769(1)	0.0709(9)
C1/S	0.1592(1)	0.2790(1)	0.7769(1)	0.0709(9)
C5	0.0377(4)	0.2450(4)	0.7595(4)	0.055(3)
C6/S	0.0103(4)	0.2821(3)	0.8331(3)	0.085(3)
S6/C	0.0103(4)	0.2821(3)	0.8331(3)	0.085(3)
C7	0.0947(6)	0.3340(5)	0.8926(4)	0.085(4)
C8	0.1749(6)	0.3370(4)	0.8691(4)	0.083(3)
S2/C	−0.1185(2)	0.0876(1)	0.5039(1)	0.073(1)
C2/S	−0.1185(2)	0.0876(1)	0.5039(1)	0.073(1)
C9	−0.1270(4)	0.1341(4)	0.5981(3)	0.053(2)
C10	−0.2341(3)	0.1140(3)	0.6007(3)	0.091(2)
S10	−0.2341(3)	0.1140(3)	0.6007(3)	0.091(2)
C11	−0.2864(5)	0.0623(5)	0.5155(5)	0.081(3)
C12	−0.2332(6)	0.0462(4)	0.4642(4)	0.081(4)
		Molecule 2		
Al3	0.4665(1)	0.0214(1)	0.2296(1)	0.0662(9)
Al4	0.3898(1)	−0.1419(1)	0.1417(1)	0.0612(8)
C13	0.5806(5)	0.0789(5)	0.2124(5)	0.119(4)
C14	0.4043(5)	0.0723(5)	0.3080(4)	0.105(4)
C15	0.2743(4)	−0.1985(4)	0.1586(5)	0.096(4)
C16	0.4531(5)	−0.1959(4)	0.0656(4)	0.090(3)
S3/C	0.2356(2)	0.0353(2)	0.0898(2)	0.081(1)
C3/S	0.2356(2)	0.0353(2)	0.0898(2)	0.081(1)
C17	0.3511(4)	−0.0027(4)	0.1015(4)	0.056(3)
C18	0.3765(2)	0.0317(2)	0.0183(2)	0.077(2)
S18	0.3765(2)	0.0317(2)	0.0183(2)	0.077(2)
C19	0.2835(6)	0.0853(5)	−0.0344(4)	0.082(4)
C20	0.2113(5)	0.0865(5)	−0.0015(5)	0.083(3)
S4/C	0.4801(2)	−0.1502(2)	0.3615(2)	0.089(1)
C4/S	0.4801(2)	−0.1502(2)	0.3615(2)	0.089(1)
C21	0.5057(4)	−0.1174(4)	0.2706(4)	0.061(3)
C22	0.6168(3)	−0.1502(3)	0.2781(3)	0.093(2)
S22	0.6168(3)	−0.1502(3)	0.2781(3)	0.093(2)
C23	0.6502(5)	−0.1991(5)	0.3688(6)	0.096(4)
C24	0.5846(7)	−0.2032(5)	0.4105(5)	0.098(4)

[a] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i^*a_j^*\bar{\mathbf{a}}_i\cdot\bar{\mathbf{a}}_j$. [b] S*n*/C and C*n*/S denote disordered sites. Details are described in the text.

Table 3. Atomic Coordinates and Isotropic Thermal Parameters for the Non-Hydrogen Atoms of $[Me_2In(\mu\text{-}2\text{-}C_4H_3S)]_2$ (2b)

atom	x	y	z	U_{eq}[a] (Å^2)
In1	0.11956(2)	0.22425(2)	0.19155(3)	0.0500(1)
S1	0.11275(8)	0.39189(8)	0.4542(1)	0.0625(4)
C1	0.1031(3)	0.2681(3)	0.4063(4)	0.048(1)
C2	0.1024(3)	0.2144(4)	0.5282(5)	0.057(1)
C3	0.1072(3)	0.2714(4)	0.6532(5)	0.072(2)
C4	0.1135(3)	0.3697(4)	0.6296(5)	0.069(2)
C5	0.1699(4)	0.3461(4)	0.0808(6)	0.066(2)
C6	0.1201(4)	0.0667(4)	0.1580(9)	0.078(2)

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

spectroscopy showed several methylaluminum resonances and complex patterns associated with the Et_2O. These results indicate that the process shown in eq 1 shifts far to the left under these conditions and that the exchange of groups is slow on NMR time scale.

$$2[Me_2Al(2\text{-}C_4H_3S)]_2 \rightleftharpoons (Me_3Al)_2 + [Me(\mu\text{-}2\text{-}C_4H_3S)_2Al]_2 \quad (1)$$

The room-temperature ^1H NMR spectrum of **2a** in benzene or toluene shows a single exchange-broadened line for the methyl groups bound to aluminum and broadened resonances for the bridging thiophene groups. Spectra taken at low temperature show additional features of this system that suggest equilibration/exchange processes are occurring. The solid-state structure shows that there are two sets of inequivalent Al−Me groups, with each set distinguished by its relative position to the thiophene groups on the ring (see Figure 1). These results are consistent with a low barrier to rotation about the C-bridge bond of the thiophene groups or a rapid dissociation of the dimer into monomers. In order to explore the nature of this exchange process, three sets of studies were carried out: a variable-temperature study, a concentration study, and a study with Me_3Al added to **2a**. As the temperature is decreased, a number of changes occur. These include the formation of two sets of resonances for all of the spectral regions. The most readily monitored region of the spectrum is that associated with the Al−Me groups. At −65 °C, the Al−Me region of the spectrum shows three lines, and there are two sets of resonances associated for the thiophene groups (see Figure 2). This is consistent with two conformations

Table 4. Atomic Coordinates and Isotropic Thermal Parameters for the Non-Hydrogen Atoms of $\{(2\text{-}C_4H_3)S_2Al[\mu\text{-}N(H)C(H)(C_6H_5)_2]\}_2$ (3)

atom[b]	x	y	z	U_{eq}[a] (Å^2)
Al1	0.5047(2)	0.0327(2)	0.1260(2)	0.0433(7)
N1	0.4010(5)	−0.0699(5)	0.0542(4)	0.048(2)
C1	0.3581(6)	0.1982(6)	0.2247(5)	0.047(3)
S1/C	0.1762(2)	0.2252(3)	0.2597(2)	0.072(1)
C2	0.1295(8)	0.3728(8)	0.3391(7)	0.081(4)
C3	0.244(1)	0.4119(7)	0.3472(7)	0.078(4)
C4/S	0.3959(4)	0.3181(4)	0.2821(4)	0.077(2)
C5	0.6548(6)	−0.0768(6)	0.2081(5)	0.049(3)
C6/S	0.6555(4)	−0.0609(4)	0.3499(4)	0.080(2)
C7	0.792(1)	−0.165(1)	0.3595(9)	0.117(6)
C8	0.8732(9)	−0.2425(9)	0.253(1)	0.106(5)
S2/C	0.8035(3)	−0.2021(2)	0.1325(3)	0.074(1)
C9	0.3965(7)	−0.2090(7)	0.0919(6)	0.063(3)
C10	0.3018(4)	−0.2646(5)	0.0289(4)	0.053(3)
C11	0.3110(4)	−0.4035(5)	0.0499(4)	0.067(3)
C12	0.2354(4)	−0.4678(5)	−0.0090(4)	0.078(4)
C13	0.1505(4)	−0.3930(5)	−0.0890(4)	0.077(4)
C14	0.1414(4)	−0.2540(5)	−0.1101(4)	0.070(3)
C15	0.2170(4)	−0.1898(5)	−0.0511(4)	0.063(3)
C16	0.3489(6)	−0.2196(5)	0.2399(4)	0.065(3)
C17	0.2034(6)	−0.1577(5)	0.3129(4)	0.081(4)
C18	0.1632(6)	−0.1719(5)	0.4478(4)	0.108(5)
C19	0.2684(6)	−0.2480(5)	0.5095(4)	0.110(6)
C20	0.4139(6)	−0.3100(5)	0.4365(4)	0.107(5)
C21	0.4541(6)	−0.2958(5)	0.3017(4)	0.085(4)

[a] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i^*a_j^*\bar{\mathbf{a}}_i\cdot\bar{\mathbf{a}}_j$. [b] S*n*/C denotes a site containing 70% sulfur occupancy and 30% carbon occupancy. C*n*/S indicates 70% carbon and 30% sulfur occupancy.

Figure 1. Computer-generated CHEM-3D diagram of $[Me_2Al(\mu\text{-}2\text{-}C_4H_3S)]_2$ (**2a**) viewed along the Al−Al vector, showing the orientation of thiophene rings.

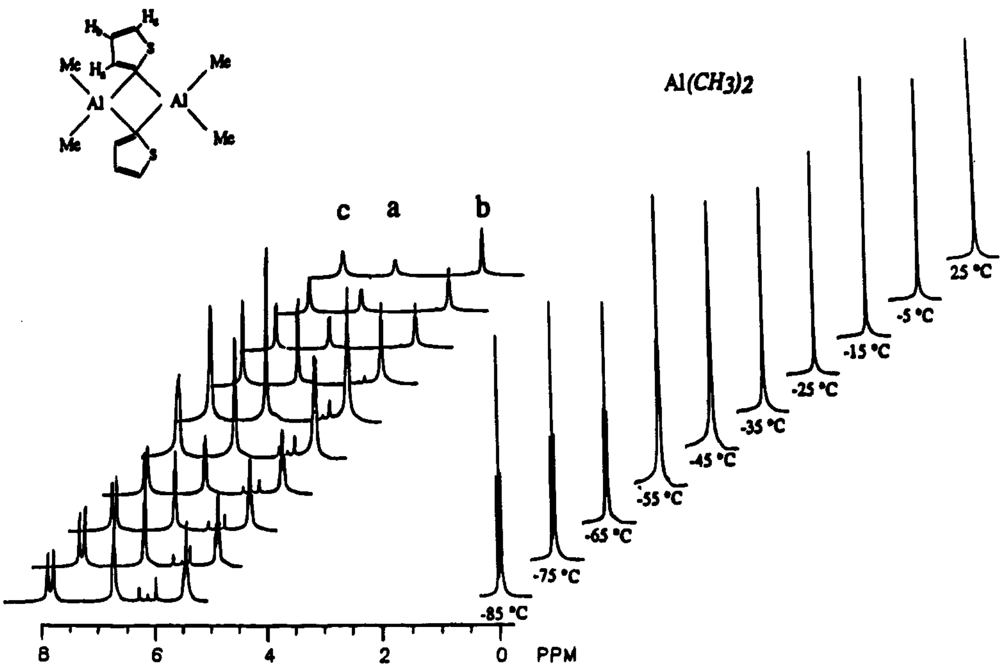
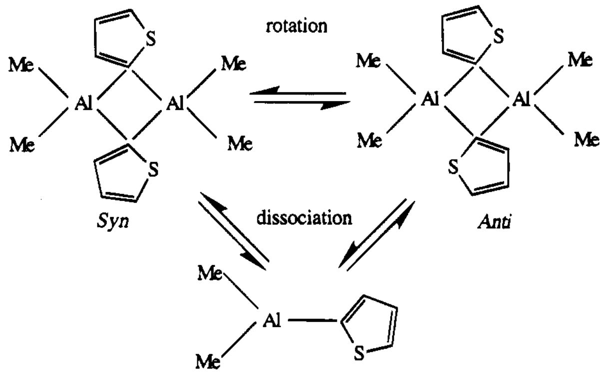


Figure 2. ^1H NMR spectra of $[Me_2Al(\mu\text{-}2\text{-}C_4H_3S)]_2$ (**2a**) as a function of temperature.

Scheme 1



present in solution, *syn* and *anti*.[15,16] The analysis of the data at and below −65 °C shows that the *syn* and *anti* conformations are of nearly equal concentration and, therefore, have equal energy within experimental error. The low-temperature ^{13}C NMR spectrum confirms these results with two sets of resonances, one associated with the *syn* isomer and one with the *anti* isomer. One cannot readily make all of the assignments in the ^{13}C NMR spectrum because of overlap, but for the methyl peaks, the *syn* resonances occur at δ −2.14 and −3.99 ppm and the *anti* methyl resonance occurs at δ −2.98 ppm. At higher temperatures, i.e. above 85 °C, the ^1H resonances associated with the thiophene moiety again broaden, suggesting that a second process occurs. These changes can all be treated in terms of the model shown in Scheme 1. At low temperatures, the *syn* and *anti* conformations are "frozen", leading to spectra for each of these. As the temperature increases, the rate of interchange between the *syn* and *anti* conformations increases and leads to an averaged spectrum. The mechanism of this interchange has not been determined but may be explained by one of three mechanisms proposed for other exchange processes observed for organoaluminum derivatives: the rotation about the carbon bridge,[15−17] a single bridge dissociation followed by rotation,[18] or a dissociation−recombination process similar to that proposed for Me_6Al_2.[19] A line-shape analysis gave a barrier of activation for this process of 12 kcal mol^{-1}. A barrier to rotation of similar magnitude for the cyclopropyl group in $[Me_2Al(\mu\text{-}C_3H_5)]_2$ has been reported.[16] Studies of the concentration dependence were carried out over a 4-fold range and showed no change in the rate of reaction, providing support for the simple rotational process suggested for the *syn* $\rightleftharpoons$ *anti* conversion or, alternatively, the half-bridge mechanism reported for $Me_2Al(\mu\text{-}Me)(\mu\text{-}NPh_2)\text{-}AlMe_2$.[18] Increase of the temperature to 75 °C caused additional line broadening and loss of resolution. This is consistent with a dissociation process with group exchange.

An additional study was carried out in which **2a** was mixed with Me_6Al_2 in a 1:1 ratio to examine the exchange of Me_6Al_2 with **2a** and determine the relative stability of the thiophene vs methyl bridge bond. At room temperature the ^1H NMR spectrum showed broadened lines for all regions of the spectrum and a single line for the methyl groups, indicating fast group exchange on the NMR time scale. Variable-temperature studies revealed that the methyl and thiophene regions were resolved into a number of lines at low temperature. The low methyl region of the spectrum is shown in Figure 3. It is composed of eight lines which can be assigned as indicated in the figure with four species present in solution. Lines A and B are assigned to the *syn* and *anti* dimers, C is assigned to the *syn* and *anti* methyl groups in the pentamethyl derivative, D is assigned to the bridging group in the pentamethyl compounds, and E and F are assigned to the terminal and bridging groups in the trimethylaluminum dimer.

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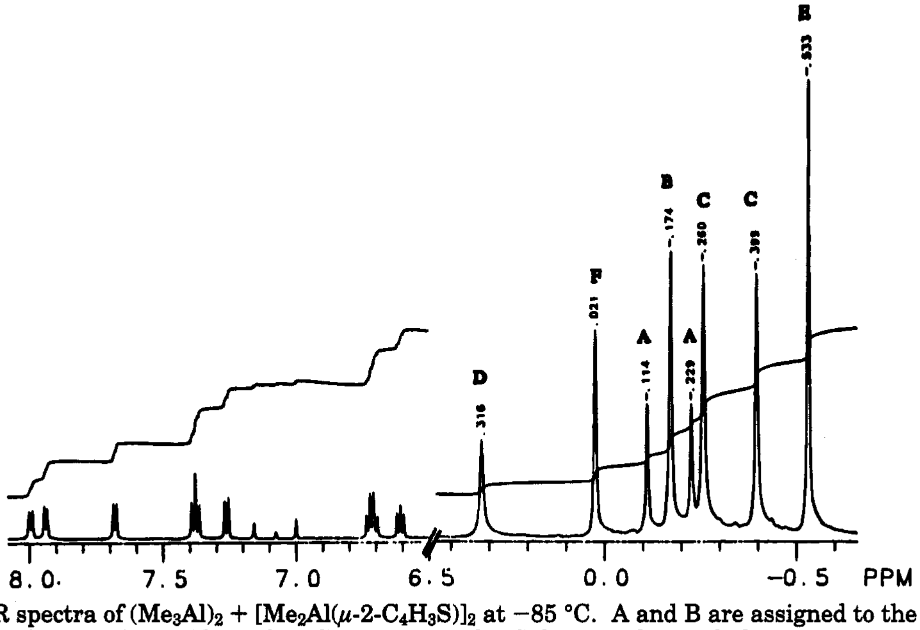
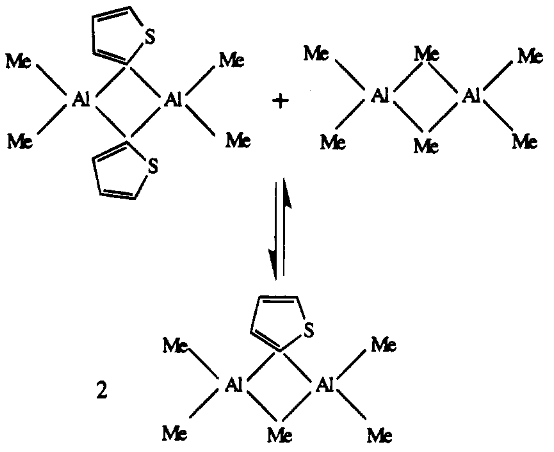


Figure 3. ^1H NMR spectra of $(Me_3Al)_2$ + $[Me_2Al(\mu\text{-}2\text{-}C_4H_3S)]_2$ at −85 °C. A and B are assigned to the methyl resonances for the *syn* and *anti* dimers of $[Me_2Al(\mu\text{-}2\text{-}C_4H_3S)]_2$ respectively, C denotes the methyl groups *syn* and *anti* to the sulfur atom in $Me_2Al(\mu\text{-}2\text{-}C_4H_3S)(\mu\text{-}Me)AlMe_2$, D denotes the bridging methyl group, and E and F are assigned to the bridging and terminal methyl groups in Me_6Al_2, respectively.

Scheme 2



In the thiophene region, the spectrum shows all of the lines associated with **2a** and an additional set of half the intensity, which we have assigned to the pentamethyl derivative.

The integrated intensities of the methyl resonances provided a rough value for the equilibrium constants associated with the reactions shown in Scheme 2. At −85 °C the value of K is 1.8, in which the *syn* and *anti* groups were treated as the same. These results show not only that the thiophene group is preferentially located in the bridging position but also that the differences in energy between the incorporation of two thiophene units vs one in bridging sites favor formation of the symmetrically bridged dimer. This places the thiophene ligand in the same group with other aromatic groups[20] and with other unsaturated bridging ligands. The data available from this study and from earlier work indicate that the stability of the bridge bond increases with greater s orbital contribution from the carbon atom to the bridge bond and with the ability of the bridging group to accept a negative charge, leading to the preferential location of these groups in the bridging site. The observation that symmetrically bridged systems predominate requires that additional stabilization occur in these systems in order to overcome the entropy increase associated with formation of the unsymmetrically bridged compounds. The added stability in the symmetrical species may be a result of reduced ring strain, other steric effects, or electronic factors. The exact nature of these interactions must await a complete theoretical description of the bonding in these systems.

The analogous indium compound $[Me_2In(\mu\text{-}C_4H_3S)]_2$ (**2b**) was studied by VT NMR spectroscopy over the range +75 to −90 °C. These spectra show changes as a function of temperature but are not readily analyzed. The methyl resonance shifts from −0.19 to −0.002 ppm over this temperature range. The region associated with the thiophene ring shows changes in the chemical shifts, line intensities, and line shapes consistent with group exchange and with possible association, but a detailed analysis of this system has not been made.

The enhanced stability of the $[Me_2Al(\mu\text{-}2\text{-}C_4H_3S)]_2$ dimer with bridging thiophene groups provides a system in which the interaction of the thiophene ring with the metal centers may be explored. There are several possible modes of interaction between the thiophene ring and the aluminum center. These are (a) interaction of the thiophene in an η^2 and η^3 fashion similar to that observed in $(Me_2AlCp)_n$,[21] (b) formation of an η^5 complex as observed in $CpAlCl$,[22] (c) interaction with two sites, carbon and sulfur, similar to the bonding observed in the dimethylaluminum pyridine-2-thiolate derivative,[23] and (d) formation of a bridge with a single carbon center involved. In **2a,b** the bonding occurs through a single carbon atom. This mode of bonding may be attributed to the strong interaction of the π electrons of the

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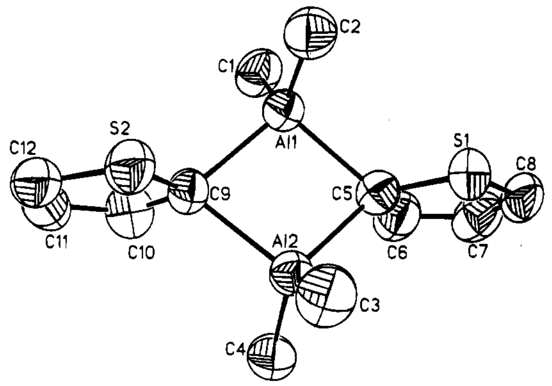

Figure 4. ORTEP diagram (50% thermal ellipsoids) of $[Me_2Al(\mu\text{-}2\text{-}C_4H_3S)]_2$ (**2a**) showing the atom-labeling scheme. Hydrogen atoms have been omitted for clarity.

Table 5. Selected Bond Distances (Å) and Angles (deg) for $[Me_2Al(\mu\text{-}2\text{-}C_4H_3S)]_2$ (2a)

molecule 1		molecule 2	
	Bond Distances		
Al1—C1	1.961(5)	Al3—C13	1.948(7)
Al1—C2	1.957(5)	Al3—C14	1.954(5)
Al1—C5	2.111(6)	Al3—C17	2.133(5)
Al1—C9	2.122(5)	Al3—C21	2.122(6)
Al2—C3	1.957(5)	Al4—C15	1.958(6)
Al2—C4	1.942(6)	Al4—C16	1.951(5)
Al2—C5	2.140(5)	Al4—C17	2.123(5)
Al2—C9	2.127(5)	Al4—C21	2.146(5)
	Bond Angles		
Al1—C5—Al2	81.3(2)	Al3—C17—Al4	80.9(2)
C1—Al1—C2	122.0(2)	Al3—C21—Al4	80.6(2)
C3—Al2—C4	122.7(3)	C13—Al3—C14	123.3(3)
C5—Al1—C9	98.5(2)	C15—Al4—C16	122.9(3)
C5—Al2—C9	97.4(2)	C17—Al3—C21	99.5(2)
Al1—C9—Al2	81.3(2)	C17—Al4—C21	99.0(2)

thiophene with the nonbonded orbitals of the aluminum center. This interaction, in addition to that involving the normal "three-centered" two-electron bridge bonds, adds to the stability of the bridging systems and accounts for the orientation of the thiophene ring in the Al_2C_2 core. These results are consistent with the previous suggestions that in $[Me_2Al(\mu\text{-}R)]_2$ (R = vinyl,[24] phenyl,[25] cyclopropyl,[26] cyclopentadienyl,[21] phenylacetylide[27]) the bridge bonds formed by the ligands rich in π electrons appear to be more stable, both thermodynamically and kinetically, than those formed by simple alkyl groups.

Structures of $[Me_2M(\mu\text{-}2\text{-}C_4H_3S)]_2$ (M = Al, 2a; M = In, 2b). An ORTEP diagram of $[Me_2Al(\mu\text{-}2\text{-}C_4H_3S)]_2$ (**2a**) is shown in Figure 4. Selected bond lengths and bond angles are listed in Table 5.

There are two molecules of **2a** in the asymmetric unit. Each of these is a dimeric unit with π-electron-rich thiophene ligands occupying the bridging site. The main features of the molecular structure of **2a** are similar to those of known organoaluminum compounds. The geometry around the aluminum atoms is distorted tetrahedral, consisting of two methyl carbon atoms and two bridging atoms from the thiophene rings. All of the bond distances and angles of the central ring and the metal—carbon parameters (Table 5) are in the range reported for other organoaluminum derivatives.[7-9] The four-membered Al_2C_2 ring is composed of two aluminum atoms and two bridging carbon atoms in the thiophene ring. The metal—carbon ring is in a butterfly conformation with the angle between the two C—Al—C planes in the ring equal to 14.2°. The butterfly arrangement is not typical for carbon-bridged organoaluminum compounds, but distortion of a similar nature is observed for the $[(c\text{-}C_3H_5)_2Al(\mu\text{-}c\text{-}C_3H_5)]_2$ dimer in the solid state, which adopts this conformation to reduce steric interaction between the cyclopropyl rings.[26] It appears that distortions of this type require only small changes in energy. Such changes appear to be associated with local steric interactions but also may be dependent upon packing forces in the crystal. The thiophene rings are disordered as described in Experimental Section but are predominately in the *syn* conformation and oriented essentially perpendicularly to the Al—Al axis. These features are clearly seen in Figures 1 and 4. The energy difference between the *syn* and *anti* forms and the differences in steric requirements are very small, based on this observation. The butterfly geometry of the Al_2C_2 ring may be attributed to the interaction of the aluminum centers with the suflur atoms, to repulsion between the sulfur atoms and the terminal alkyl groups, or to lattice effects. The data available are not adequate to determine which of these interactions determine the geometry.

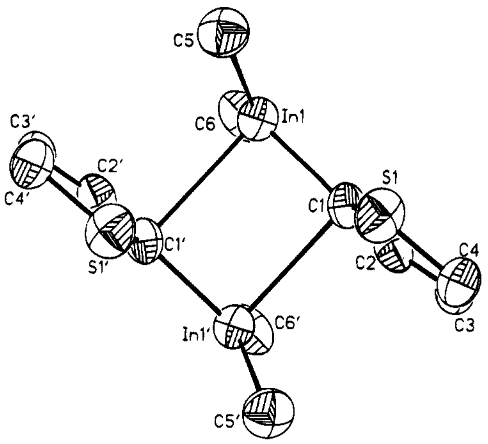

Figure 5. ORTEP diagram (50% thermal ellipsoids) of $[Me_2In(\mu\text{-}2\text{-}C_4H_3S)]_2$ (**2b**) showing the atom-labeling scheme. Hydrogen atoms have been omitted for clarity.

The bridging thiophene ligand is distorted, with C—C and C—S bonds near the aluminum atom slightly longer than the other distances in the thiophene ring. The internal bond angles of the ring at the carbon atom bonded to aluminum are smaller than the other internal ring angles. Similar distortions of the bridging phenyl group in $[R_2Al(\mu\text{-}C_6H_5)]_2$ (R = Me, Ph) have been reported.[25,28] Finally, the overall structure features of molecule 2 are comparable to those of molecule 1.

An ORTEP diagram of the analogous indium derivative $[Me_2In(\mu\text{-}2\text{-}C_4H_3S)]_2$ (**2b**) is shown in Figure 5. Bond lengths and bond angles are listed in Table 6. The three carbon atoms with short In—C bonds are nearly coplanar with the In. The In—C1′ bridge bond is

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Table 6. Bond Distances (Å) and Angles (deg) for $[Me_2In(\mu\text{-}2\text{-}C_4H_3S)]_2$ (2b)

	Bond Distances		
In1−C1	2.194(3)	C1−C2	1.368(5)
In1−C5	2.143(5)	C1−In1′	2.849(3)
In1−C6	2.139(5)	C2−C3	1.402(6)
In1−C1′	2.849(3)	C3−C4	1.344(8)
S1−C1	1.718(3)	In1..In1′	3.576(1)
S1−C4	1.694(4)	C2...In1′	3.069(4)
	Bond Angles		
In1−C1−S1	119.2(2)	C1−In1−C1′	84.3(1)
In1−C1−C2	132.4(3)	C1−S1−C4	94.1(2)
In1−C1−In1′	89.4(1)	C1−C2−C3	115.1(4)
S1−C1−C2	107.5(3)	C2−C1−In1′	85.8(2)
S1−C1−In1′	106.3(1)	C2−C3−C4	112.5(4)
S1−C4−C3	110.7(3)	C5−In1−C6	131.9(2)
C1−In1−C5	112.0(2)	C5−In1−C1′	95.8(2)
C1−In1−C6	114.2(2)	C6−In1−C1′	101.5(2)

perpendicular to this plane with the carbon atom directly above the indium atom. This is seen in Figure 5. The thiophene rings in this molecule were not treated with a disorder model and give ring distances and angles close to those reported in free thiophene.[29] The indium−carbon distances in the primary sphere around indium are close in value and close to the distance observed in monomeric organoindium compounds and in other weakly associated derivatives. This short contact distance between indium and the *ipso* carbon atom in the adjacent $Me_2(2\text{-}C_4H_3S)In$ unit is substantially less than that observed in the weakly associated Me_3In tetramer. In $(Me_3In)_3$, the long-range interactions are 3.038(12) and 3.558(15) Å.[30] Similarly, the interactions in Ph_3In of 3.07 and 3.10 Å have been described as showing weak association in the solid state.[31] Other indium derivatives are monomeric in the solid state, including R_3In (R = mesityl;[32] R = $-C(H)(SiMe_3)_2$[33]). Structural features such as the distorted-tetrahedral geometry around indium, the *syn* conformation of the thiophene rings, the butterfly geometry of the $(InC)_2$ ring (the angle between the planes formed by C1−In1−C1′ and C1−In1′−C1′ is 142.3°), and distortion in the structure of the thiophene rings are similar to those found in **2a**. However, unlike the $Al(\mu\text{-}C)_2Al$ ring, the carbon bridges in **2b** are weak with one normal bond of 2.194(3) and one long bond of 2.849(3) Å. Examination of the packing diagram shown in Figure 6 shows the orientation of the molecules in the lattice. The separation between the dimers is greater than 4.0 Å, showing that dimeric units are separate with no extended interaction in the system.

Structure of $\{(2\text{-}C_4H_3S)_2Al[\mu\text{-}N(H)C(H)(C_6H_5)_2]\}_2$ (3). The molecular structure of the elimination product **3** is shown in an ORTEP drawing (Figure 7). The structure consists of a centrosymmetric dimer with two briding $-N(H)C(H)(C_6H_5)_2$ ligands. The central $Al(\mu\text{-}N)_2Al$ ring is planar, in contrast to the puckered ring found in the thiomorpholine derivative $[Et_2Al(\mu\text{-}NC_4H_8S)]_2$.[34] The two terminal thiophene rings on each aluminum atom are oriented almost perpendicularly to each other. The remaining features of the dimer are normal for organoaluminum compounds.[9] Selected bond distances and angles are listed in Table 7.

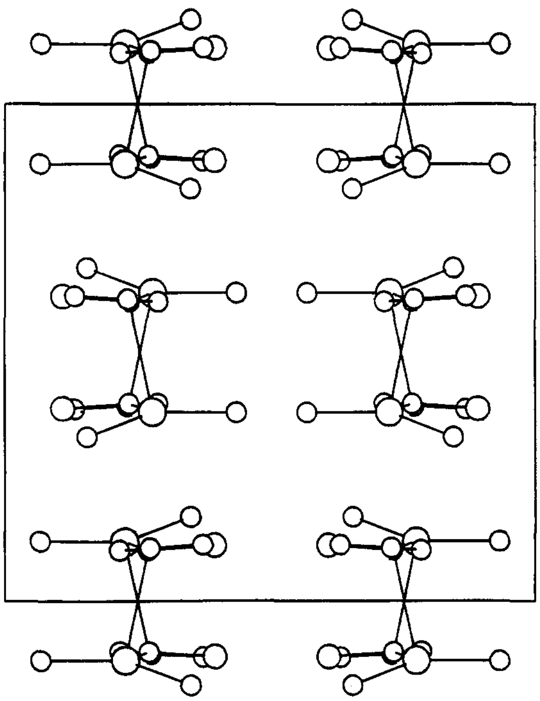

Figure 6. Packing diagram for $[Me_2In(\mu\text{-}2\text{-}C_4H_3S)]_2$ viewed along the *z* axis.

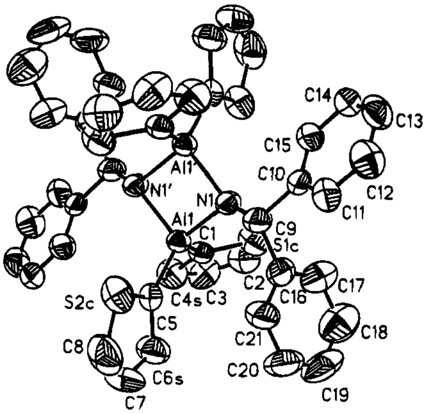

Figure 7. ORTEP diagram (50% thermal ellipsoids) of $\{(2\text{-}C_4H_3S)_2Al[\mu\text{-}N(H)C(H)(C_6H_5)_2]\}_2$ (**3**) showing the atom-labeling scheme. Hydrogen atoms have been omitted for clarity.

Table 7. Selected Bond Distances (Å) and Angles (deg) for $\{(2\text{-}C_4H_3S)_2Al[\mu\text{-}N(H)C(H)(C_6H_5)_2]\}_2$ (3)

	Bond Distances		
Al1−N1	1.955(6)	Al1−C5	1.951(7)
Al1−N1′	1.964(6)	N1−C9	1.46(1)
Al1−C1	1.973(7)	Al1···Al1′	2.827(3)
	Bond Angles		
C1−Al1−C5	117.2(3)	N1−Al1−N1′	87.7(3)
Al1−N1−C9	123.4(5)	N1−Al1−C1	108.8(2)
Al1−C1−S1/C	123.3(4)	N1−Al1−C5	116.2(3)
Al1−C5−C6/S	126.1(4)	N1′−Al1−C1	113.3(3)
Al1−C5−C6/S	126.1(4)	N1′−Al1−C5	110.0(3)
Al1−C5−S2/C	124.6(5)	Al1−N1−Al1′	92.3(3)

The ^1H NMR spectrum of **3** needs a special comment. Two AB quartets of nearly equal intensity associated with the C(H)−N(H) moiety are observed, one set described by δ_A 3.18, δ_B 5.90, and J_{AB} = 13.1 Hz and

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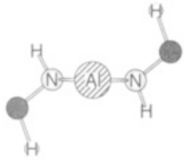
the other by δ_A 3.48, δ_B 5.59, and J_{AB} = 13.3 Hz with the assignment confirmed by selective ^1H decoupling experiments. The observed coupling constants of 13 Hz are large relative to those commonly observed in amines, which are in the range of 6–7 Hz.[35] This implies that the large dihedral H—C—N—H angles of 177 and 168° observed in the solid state are remained in solution with the predominant conformation shown in III. For this



III

conformation, the Karplus relationship predicts a coupling constant on the order of 12–14 Hz, as is observed. There are few examples reported of this type of coupling because of the rapid exchange of protons in amines and the limited number of examples of amines with restricted rotation about the C—N bond.

The independent AB patterns observed at room temperature are retained, even at 76 °C. These results suggest that there are two species, *syn* and *anti* with respect to bridging $-N(H)C(H)(C_6H_5)_2$, present in solution which do not undergo equilibration rapidly on the NMR time scale. Similar results have been reported by Park et al.,[36] who observed slow isomerization of the *trans* derivative $[Me_2Ga(\textit{trans}\text{-}\mu\text{-}N(H)\text{-}t\text{-}Bu)]_2$ to an equilibrium mixture of *cis* and *trans* isomers at 80 °C. Further evidence in support of the presence of both *syn* and *anti* isomers can be deduced from the ^{13}C NMR of **3**. For the *anti* configuration observed in the solid state, 9 ^{13}C resonances, 4 from the thiophene, 4 from the phenyl groups, and 1 from the methylene carbon, are expected. For the *syn* structure, one should observe 13 resonance, 8 from the thiophene ligands, 4 from the phenyl groups of the amido ligands, and 1 from the methylene carbon. In an equilibrium mixture, a total of 22 lines should be observed if there is no overlap. We observed 13 clearly resolved ^{13}C resonances for **3**, which is more than anticipated for the *trans* isomer and is in accord with a mixture of *syn* and *anti* isomers in solution where many of the resonances associated with the phenyl group overlap. A more detailed examination of the spectra shows 6 lines in the region associated with the C2 and C3 atoms of the thiophene ring, exactly the number predicted for a mixture of *syn* and *anti* isomers. Further work exploring the factors which govern isomer stability is planned.

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Supplementary Material Available: Listings of all bond distances and bond angles, anisotropic thermal parameters for the heavy atoms, and hydrogen atom positional parameters for **2a**,**b** and **3** (16 pages). Ordering information is given on any current masthead page.

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