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Article

Organometallic Aluminum Compounds Derived from 2-(1,3,5-Dithiazinan-5-yl)ethanol Ligands[1]

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The reactions of $AlMe_2Y$ (Y = Me or Cl) with new ligands 2-(1,3,5-dithiazinan-5-yl)ethanol (**1**), 2-(1,3,5-dithiazinan-5-yl)-1-methylethanol (**2**), and 2-(1,3,5-dithiazinan-5-yl)-1-phenylethanol (**3**) are described. The ligands are coordinated to aluminum atoms by nitrogen and oxygen atoms, with a nitrogen based spiranic structure. Equimolar reactions gave dimeric structures bearing pentacoordinated aluminum atoms *O*-(AlMeY)-2-(1,3,5-dithiazinan-5-yl)ethanolates (**4**–**7**) as well as monometallic compounds with tetracoordinated aluminum atoms *O*-(AlMeY)-2-(1,3,5-dithiazinan-5-yl)ethanolates (**8**–**9**). Reactions with 2 equiv of the aluminum reagents afforded tetracoordinated dialuminum complexes *O*-(AlMeY)-*O*-($AlMe_2Y$)-2-(1,3,5-dithiazinan-5-yl)ethanolate (**10**–**18**). The structures of the new compounds were determined by NMR (^1H,^{13}C, and ^{27}Al) and complemented by X-ray diffraction of compounds **4**, **10**, and **16**–**18**. Relevant intermolecular interactions C–H···S, C–H···Cl, and C–H···π found in the crystalline network are reported.

Introduction

We are currently investigating the chemistry and the coordinating ability[2,3] of 1,3,5-heterocyclohexanes. The condensation of formaldehyde and primary amines affords oxadiazinanes[2a] or triazinanes;[2c] whereas thiadiazinanes[2b] or dithiazinanes[2c,d] are obtained by adding an aqueous NaSH solution to the mentioned reagents. 1,3,5-Dithiazinanes are heterocycles rich in electron pairs; their rings are easily opened with metal or reducing reagents and, therefore, scarcely studied. These heterocycles react with Lewis acids in various ways which depend on the stoichiometry and the reaction conditions. The borane adducts of the 1,3,5-dithiazinanes have been prepared and were analyzed by NMR and X-ray diffraction. Boron hydrides, $BH_{3-n}X_n$, give N-adducts and borataheterocycles by ring opening reactions.[2b,3e] They differ from the boron analogues in their conformational behavior. Moreover, they crystallize easily. Our results encouraged us to prepare new 1,3,5-dithiazinanes bearing an N-ethanol group which not only acts as a chelating arm also contains an OH group that was expected to form covalent bonds to aluminum. In particular, our efforts were focused on investigating the selectivity and stereochemistry of the coordination reactions with $AlMe_3$ and $AlMe_2Cl$, and their susceptibility to give monomers oligomers or polymers. The ligands 2-(1,3,5)-dithiazinan-5-yl-ethanol (**1**), 2-(1,3,5)-dithiazinan-5-yl-1-methyl-ethanol (**2**), and 2-(1,3,5)-dithiazinan-5-yl-1-phenyl-ethanol (**3**) were prepared from formaldehyde, NaSH, and the corresponding ethanolamines in good yields as described in Scheme 1.

Many reports describe the reaction products of amino alcohols and organoaluminum compounds, and a variety of

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(1) This work is part of the Ph.D. thesis of J. C. Gálvez-Ruiz, Cinvestav, Mexico.

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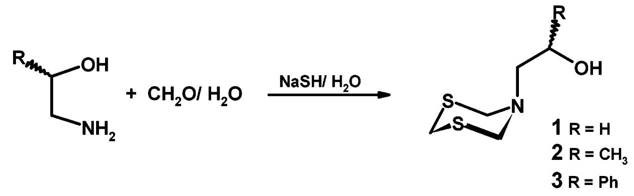
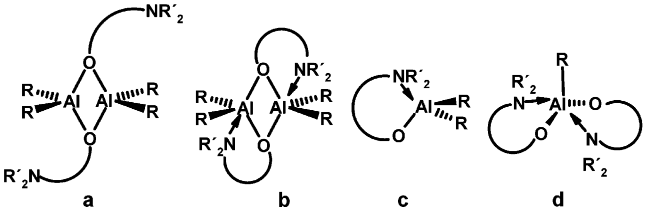
Scheme 1



Scheme 2



structures have been reported indicating a versatile and complex reaction behavior.[4] It is established that four main structures **a**−**d** (Scheme 2) are possible, depending on the stoichiometry, chelate size, basic character of the terminal heteroelement, steric demand of the ligand, and aluminum organic groups. Equilibria in solution between different species make it difficult to establish their structures even with the use of ^{27}Al NMR. Herein, we are reporting new polyfunctional ligands and their reactions with $AlMe_3$ and $AlMe_2Cl$ with the aim to add information about the behavior of thiadiazinanes toward these organoaluminum compounds and their coordination chemistry. We are also interested in the study of interactions in the solid state of organic molecules bearing weakly acidic protons atoms;[5] therefore, we will discuss relevant weak interactions of dithiazinane C−H protons and donors atoms.

Experimental Section

Instrumentation. All solvents were freshly distilled before use. The ^{1}H, ^{13}C, and ^{27}Al NMR spectra were recorded with JEOL GXS-270 (^{1}H 270 MHz) or JEOL Eclipse (^{1}H 400 MHz) and Bruker (^{1}H 300 MHz) instruments. ^{1}H and ^{13}C δ (ppm) are referenced to TMS, and $Al(OH)_6^{3+}$ is the reference for ^{27}Al. Melting points were measured on a Gallenkamp apparatus and are uncorrected. Elemental analyses were performed by Oneida Research Services, Whitesboro, New York.

X-ray Crystallography. Crystal data were obtained with an Enraf-Nonius Kappa CCD or a Siemens-P4 diffractometer both equipped with area detectors. Computations for compounds **4**, **10**, and **16**−**18** were performed by SHELXS-97 (Sheldrick 1990) and SHELXL-97 programs (Sheldrick 1997).[6] Structures of **4**, **10**, **16**, and **17** were obtained at room temperature, and that for **18** was obtainned at −60 °C. Atomic form factors for neutral C, N, O and H were taken from ref 7. Hydrogen atoms were found on difference electron density maps. Crystallographic data (excluding structure factors) have been deposited with the *Cambridge Crystallographic Data Bank* as nos. CCDC216396−CCDC216400. Copies of the data can be obtained free of charge on application to 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: int. Code + 44(1223)336−033. E-mail: deposit@ccdc.cam.ac.uk.] Some crystallographic data and bond lengths and angles are found in Tables 1 and 2.

2-(1,3,5-Dithiazinan-5-yl)ethanol, 1. General Procedure. To a solution of ethanolamine (10 mL, 0.17 mol) in water (50 mL) at 5 °C was slowly added a cool solution (5 °C) of NaSH (27.9 g, 0.50 mol) in aqueous formaldehyde (37%, 62.3 mL, 0.83 mol). The reaction mixture was stirred for 30 min at 0 °C and 24 h at room temperature. The white solids were removed by filtration, washed with water, dissolved in $CHCl_3$, and dried with sodium sulfate. After the evaporation of solvent, compound **1** was obtained as colorless crystals. Yield: 24.6 g, 95.2%. Mp 39 °C. Anal. Calcd for $C_5H_{11}NOS_2$: C, 36.36; H, 6.67; N, 8.48. Found: C, 36.24; H, 6.94; N, 8.44. ^{1}H NMR ($CDCl_3$) δ(ppm) = 4.32 (s, 4H, 2H-4, 2H-6), 3.99 (s, 2H-2), 3.54 (t, ^3J = 5.2 Hz, 2H-8), 3.08 (t, 2H-7, ^3J = 5.2 Hz), 2.67 (s, H9). ^{13}C NMR δ(ppm) = 58.84 (C-8), 58.36 (C4, C6), 51.30 (C7), 33.80 (C2). ^{15}N NMR $\delta = -352.91$.

(±)2-(1,3,5-Dithiazinan-5-yl)-1-methylethanol, 2. Compound **2** was prepared from 2-propanol amine (40 mL, 0.51 mol) following the general procedure. Crystals were obtained from $CHCl_3$. Yield: 69 g, 75%. Mp 70 °C. Anal. Calcd for $C_6H_{13}S_2NO$: C, 40.19; H, 7.31; N, 7.82. Found: C, 40.07; H, 7.79; N, 7.83. ^{1}H NMR ($CDCl_3$): δ = 4.32 (s, 4H, 2H-4, 2H-6), 3.99 (s, 2H-2), 3.54 (qdd, ^3J = 6.2, 9.9, 2.9 Hz, H-8), 3.08 (dd, ^2J = 13.5, ^3J = 2.9 Hz, H-7A), 2.67 (s, 1H-10), 2.4 (dd, ^2J = 13.5, ^3J = 9.9 Hz, H-7B), 1.15 (d, ^3J = 6.2 Hz, 3H-9). ^{13}C NMR ($CDCl_3$): δ = 63.6 (C-8), 58.7 (s br, C-4, C-6), 57.2 (C-7), 33.7 (C-2), 20.1 (C-9). ^{15}N NMR ($CHCl_3$): $\delta = -310.6$.

(±)5-(1,3,5-Dithiazinan-5-yl)-1-phenylethanol, 3. Compound **3** was prepared from 2-phenyl-2-ethanolamine (10 g, 72.9 mmol). Reaction afforded a syrup which crystallized from $CHCl_3$. Yield: 12.3 g, 70%. Mp 56−58 °C. Anal. Calcd for $C_{11}H_{15}NOS_2$: C, 54.74; H, 6.26; N, 5.80. Found: C, 54.44; H, 6.33; N, 5.92. ^{1}H NMR ($CDCl_3$): δ = 7.4−7.2 (s br, 5H), 4.60 (dd, ^3J = 13.5, 2.9 Hz, H-8), 4.31 (s br, 2H-4, 2H-6), 4.00 (s br, 2H2), 3.49 (dd, ^2J = 13.5, ^3J = 2.9 Hz, H-7A), 3.63 (s, H-9), 2.81 (dd, ^3J = ^2J = 13.5 Hz, H-7B). ^{13}C NMR ($CDCl_3$): δ = 141.8 (C*i*), 128.2 (2C*m*), 127.2 (C*p*), 125.6 (2C*o*), 69.5 (C-8), 58.8 (s br, C-4, C-6), 57.1 (C-7), 33.4 (C-2). ^{15}N NMR ($CDCl_3$): $\delta = -333.5$.

General Procedure for the Synthesis of Organoaluminum Compounds 4−7. Using anhydrous conditions, N_2 atmosphere, the aluminum reagent $AlMe_2R$ (R = Me or Cl) [2 M in hexane, 1 or 2 equiv] was slowly added with a hypodermic syringe to a stirred solution of 2-(1,3,5-dithiazinan-5-yl)ethanol **1**−**3** (1 equiv) in toluene at −40 °C. Stirring was continued for 30 min. The resulting mixtures were filtered, and the solvent was evaporated to give crystalline solids.

Preparation of Compounds 4−9: Bis[*O*-dimethylaluminum-2-(1,3,5-dithiazinan-5-yl)-ethanolate], 4. To compound **1** (0.21 g, 1.24 mmol) in toluene (20 mL) was added a solution of $AlMe_3$ (0.76 mL, 2 M in hexane, 1.24 mmol). On standing, crystals

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Table 1. Crystal Data and Data Collection of Compounds **4**, **10**, and **16**−**18**

	4	**10**	**16**	**17**	**18**
formula	$C_{14}H_{32}Al_2N_2O_2S_4$	$C_{10}H_{25}Al_{25}NOS_2 \cdot C_7H_8$	$C_9H_{22}Al_2ClNOS_2$	$C_{10}H_{24}Al_2ClNOS_2$	$C_{15}H_{26}Al_2ClNOS_2$
fw	196.72	192.76	313.81	327.83	403.80
cryst size (mm^3)	0.3 × 0.2 × 0.2	0.4 × 0.3 × 0.2	0.4 × 0.23 × 0.12	0.3 × 0.2 × 0.2	0.2 × 0.2 × 0.2
cryst color	colorless plate	colorless prism	colorless prism	colorless prism	colorless prism
cryst syst	monoclinic	monoclinic	monoclinic	orthorhombic	monoclinic
space group	$P2_1/c$	$P2_1$	$C2/c$	$P2_12_12_1$	$P2_1/c$
a (Å)	9.8132(12)	7.0182(9)	24.776(5)	10.727(2)	9.767(2)
b (Å)	4.7213(17)	13.8168(17)	8.115(2)	11.636(2)	14.021(3)
c (Å)	15.9375(18)	11.9208(12)	17.165(3)	14.411(3)	15.429(3)
β (deg)	107.275(2)	94.602(2)	107.94(3)		96.85(3)
V (Å^3)	2198.5(4)	1152.2(2)	3283.4(12)	1798.8(6)	2097.8(7)
Z	4	4	8	4	4
ρ_{calcd} (Mg/m^3)	1.337	1.111	1.270	1.211	1.279
μ (mm^{-1})	0.522	0.311	0.577	0.530	0.468
F(000)	944	416	1328	696	857
scan type	hemisphere	hemisphere	$\varphi + \omega$ scan	$\varphi + \omega$ scan	$\varphi + \omega$ scan
T (K)	193(2)	193(2)	293(2)	293(2)	293(2)
2θ range, (deg)	3.84−58.06	4.52−58.14	6.90−54.98	7.00−54.94	7.16−54.94
index ranges	$-12 \leq h \leq 12$	$-8 \leq h \leq 8$	$-31 \leq h \leq 26$	$-13 \leq h \leq 13$	$-12 \leq h \leq 11$
	$18 \leq k \leq 19$	$-17 \leq k \leq 17$	$-10 \leq k \leq 10$	$-15 \leq k \leq 15$	$-17 \leq k \leq 18$
	$-18 \leq l \leq 19$	$-10 \leq l \leq 16$	$-21 \leq l \leq 22$	$-18 \leq l \leq 18$	$-20 \leq l \leq 18$
reflns collected	12616	6709	27340	4088	15268
indep reflns	4407	3902	3759	4088	4752
obsd reflns	2131	2132	2707	3284	3226
R(int)	0.1121	0.0650	0.0594	0.0000	0.0453
final R1 (4σ)	R1 = 0.1062	R1 = 0.0613	R1 = 0.0442	R1 = 0.0408	R1 = 0.0581
final wR2	R2 = 0.2409	R2 = 0.1234	R2 = 0.1286	R2 = 0.0869	R2 = 0.1484
GOF	1.045	0.966	0.929	1.032	1.017

separated from the solution which proved to be compound **4**. Yield: 0.26 g, 95%. Mp 208−210 °C. Anal. Calcd for $C_{14}H_{32}Al_2N_2O_2S_4$: C, 37.99; H, 7.29; N, 6.33. Found: C, 38.21; H, 7.39; N, 6.09. ^{1}H NMR (C_6D_6) δ(ppm) = 4.08 (s br, 4H, 4H-2), 4.44 (s br, 4H, 2H-4ax, 2H-6ax), 4.35 (s br, 4H, 2H-4eq, 2H-6eq), 3.74−2.40 (m, 8H, 4H-7, 4H-8), −0.87 (s br, 12H, 4CH_3). ^{13}C NMR δ(ppm) = 56.7 (2C8), 56.2 (2C4, 2C6), 48.5 (2C7), 32.1 (2C2), −1.1 (4CH$_3$). ^{27}Al NMR δ(ppm) = 70 ($\Delta_{1/2}$ = 3240 Hz).

Bis[*O*-dimethylaluminum-1-phenyl-2-(1,3,5-dithiazinan-5-yl)-ethanolate], 5, was prepared from compound **3** (0.33 g, 1.54 mmol) and $AlMe_3$ (0.77 mL, 2 M in hexane, 1.54 mmol). Compound **5** was obtained as a solid. Yield: 0.43 g, 95%. Mp 73−76 °C. Anal. Calcd for $C_{26}H_{40}Al_2N_2O_2S_4$: C, 52.50; H, 6.78; N, 4.71. Found: C, 52.25; H, 7.03; N, 4.92. ^{1}H NMR ($CDCl_3$) δ(ppm) = 4.83 (dd, ^3J = 11.4 and 4.0, 2H, H-8), 4.61 (d br, ^2J = 12.7, 4H, 2H-4ax, 2H-6ax), 4.40 (d br, ^2J = 12.8, 2H, H-2ax), 4.08 (dd, ^2J = 12.7 and ^3J = 4.0, 2H, H-7A), 3.92 (d br, ^2J = 12.7, 4H, 2H-4eq, 2H-6eq), 3.50 (d br, ^2J = 12.8, 2H, H-2eq), 2.73 (dd, ^2J = 12.7 and ^3J = 11.4, 2H, H-7B), −1.05 (s br, 12H, 4CH_3). ^{13}C NMR δ(ppm) = 140.5 (2C*i*), 127.7 (4C*o*), 129.1 (4C*m*), 128.4 (2C*p*), 70.2 (2C8), 58.3 (2C6), 54.6 (2C7), 54.0 (2C4) 32.7 (2C2), −9.56 (s br, 4CH$_3$). ^{27}Al NMR δ(ppm) = 87 ($\Delta_{1/2}$ = 3780 Hz).

Bis[*O*-methylchloroaluminum-2-(1,3,5-dithiazinan-5-yl)ethanolate], 6, was prepared from compound **1** (0.42 g, 2.54 mmol) and $AlMe_2Cl$ (0.24 mL, 2.54 mmol). Compound **6** was obtained as a solid. Yield: 0.55 g, 90%. Mp 170 °C (dec). Anal. Calcd for $C_{12}H_{26}Al_2Cl_2N_2O_2S_4$: C, 29.81; H, 5.42; N, 5.79. Found: C, 30.20; H, 5.82; N, 5.59. ^{1}H NMR ($CDCl_3$) δ(ppm) = 4.97−3.31 (m, 20H, 4H-2, 4H-4, 4H-6, 4H-7, 4H-8), −0.97 (s br, 4CH$_3$). ^{27}Al NMR δ(ppm) = 63 ($\Delta_{1/2}$ = 4550 Hz).

Bis[*O*-methylchloroaluminum-1-phenyl-2-(1,3,5)-dithiazinan-5-yl-ethanolate], 7, was prepared from compound **3** (0.25 g, 1.02 mmol) and $AlMe_2Cl$ (0.1 mL, 1.02 mmol). Compound **7** was obtained as a solid. Yield: 0.31 g, 95%. Mp 80−84 °C. Anal. Calcd for $C_{24}H_{34}Al_2Cl_2N_2O_2S_4$: C, 45.35; H, 5.39; N, 4.41. Found: C, 45.16; H, 5.13; N, 3.95. ^{1}H NMR ($CDCl_3$) δ(ppm) = 7.4−7.3 (m, 10H, Ph), 5.18 (dd, ^3J = 12.1, 4.2, 2H, H-8), 5.13 (d, ^2J = 14.8, 2H, H-6ax), 4.84 (d, ^2J = 13.9, 2H, H-4ax), 4.40 (dd, ^2J = 12.1, ^3J = 4.2, 2H, H-7A), 4.34 (d, ^2J = 13.7, 2H, H-2ax), 4.28 (d br, ^2J = 14.8, 2H, H-6eq), 3.84 (d br, ^2J = 13.9, 2H, H-4eq), 3.40 (d br, ^2J = 13.7, 2H, H-2eq), 2.75 (t, ^2J = ^3J = 12.1, 2H, H-7B), −1.08 (s br, CH_3). ^{13}C NMR δ(ppm) = 138.9 (2C*i*), 127.8 (4C*o*), 128.8 (4C*m*), 128.4 (2C*p*), 69.4 (2C8), 56.8 (2C4), 53.6 (2C6), 53.2 (2C7), 32.0 (2C2), −10.2 (s br, 2CH$_3$). ^{27}Al NMR δ(ppm) = 59 ($\Delta_{1/2}$ = 9260 Hz).

General Procedure for Preparation of Compounds 8 and 9. *O*-Dimethylaluminum-1-methyl-2-(1,3,5-dithiazinan-5-yl)ethanolate, 8. Compound **2** (0.45 g, 2.54 mmol) dissolved in toluene (20 mL) and $AlMe_3$ (1.27 mL, 2 M in hexane, 2.54 mmol) were mixed. A white solid precipitated which was isolated by filtration and recrystallized from toluene. Yield: 0.54 g, 90%. Mp 202−204 °C. Anal. Calcd for $C_8H_{18}AlNOS_2$: C, 40.83; H, 7.71; N, 5.95. Found: C, 41.64; H, 7.81; N, 4.83. ^{1}H NMR ($CDCl_3$) δ(ppm) = 4.48 (s br, 5H, 2H-4, 2H-6, H-8), 4.00 (s br, 1H, H-7A), 3.61 (s br, 2H, H-2), 2.45 (s br, 1H, H-7B), 1.36 (s, 3H, CH$_3$), −0.83 (s br, 6H, 2CH$_3$). ^{13}C NMR δ(ppm) = 63.3 (C8), 58.6 (C4 and C6), 54.5 (C7), 32.8 (C2), 21.8 (CH$_3$), −8.7 (s br, 2CH$_3$). ^{27}Al NMR δ(ppm) = 120 ($\Delta_{1/2}$ = 480 Hz).

***O*-Methylchloroaluminum-1-methyl-2-(1,3,5-dithiazinan-5-yl)ethanolate, 9,** was prepared from compound **2** (0.53 g, 2.95 mmol) and $AlMe_2Cl$ (0.27 mL, 2.95 mmol). Compound **9** was obtained as a solid. Yield: 0.67 g, 89%. Mp 242 °C (dec). Anal. Calcd for $C_7H_{15}AlClNS_2O$: C, 32.87; H, 5.91; N, 5.48. Found: C, 32.60; H, 5.84; N, 5.00. ^{1}H NMR ($CDCl_3$) δ(ppm) = 5.00 (d, ^2J = 14.7, H-6ax), 4.85 (d, ^2J = 14.1, H-4ax), 4.36 (d, ^2J = 13.8, H-2ax), 4.24 (dd, ^2J = 11.5, ^3J = 4.0, H-7A), 4.18 (m, H-8), 3.86 (dd, ^2J = 14.7, ^4J = 2.1, H-6eq), 3.84 (dd, ^2J = 14.1, ^4J = 2.1, H-4eq), 3.44 (dt, ^2J = 13.8, ^4J = 2.1, H-2eq), 2.37 (t, ^2J = ^3J = 11.5, H-7B), 1.21 (d, ^3J = 5.8, 3H, CH$_3$), −0.73 (s br, 3H, CH$_3$). ^{13}C NMR δ(ppm) = 62.8 (C8), 56.9 (C4), 53.5 (C6), 53.1 (C7), 32.0 (C2), 21.0 (CH$_3$), −8.8 (s br, 2CH$_3$). ^{27}Al NMR δ(ppm) = 128 ($\Delta_{1/2}$ = 3520 Hz).

Table 2. Values of Bond Lengths (Å) and Angles (deg) for Compounds **4**, **10**, and **16**−**18**

				4			
S(1)−C(6)	1.806(9)	S(1)−C(2)	1.835(9)	C(6)−S(1)−C(2)	98.2(4)	C(4)−S(3)−C(2)	98.6(4)
S(3)−C(4)	1.798(8)	S(3)−C(2)	1.80(1)	C(12)−S(11)−C(16)	97.3(4)	C(12)−S(13)−C(14)	97.1(4)
S(11)−C(12)	1.798(9)	S(11)−C(16)	1.841(8)	O(19)−Al(1)−O(9)	76.6(2)	O(19)−Al(1)−C(10)	120.9(3)
S(13)−C(12)	1.808(8)	S(13)−C(14)	1.815(8)	O(9)−Al(1)−C(10)	99.4(3)	O(19)−Al(1)−C(9)	114.4(3)
Al(1)−O(19)	1.818(6)	Al(1)−O(9)	1.916(6)	O(9)−Al(1)−C(9)	102.7(3)	C(10)−Al(1)−C(9)	123.7(3)
Al(1)−C(10)	1.977(8)	Al(1)−C(9)	2.000(8)	O(19)−Al(1)−Al(2)	39.0(2)	O(9)−Al(1)−Al(2)	37.57(16)
Al(1)−Al(2)	2.936(3)	Al(2)−O(9)	1.837(5)	C(10)−Al(1)−Al(2)	114.2(3)	C(9)−Al(1)−Al(2)	114.8(2)
Al(2)−O(19)	1.906(6)	Al(2)−C(110)	1.958(8)	O(9)−Al(2)−O(19)	76.4(2)	O(9)−Al(2)−C(110)	119.0(3)
Al(2)−C(19)	1.975(9)	O(9)−C(8)	1.420(9)	O(19)−Al(2)−C(110)	99.6(3)	O(9)−Al(2)−C(19)	116.7(4)
O(19)−C(18)	1.416(9)	N(5)−C(6)	1.43(1)	O(19)−Al(2)−C(19)	99.3(3)	C(110)−Al(2)−C(19)	123.9(4)
N(5)−C(4)	1.48(1)	N(5)−C(7)	1.491(9)	O(9)−Al(2)−Al(1)	39.5(2)	O(19)−Al(2)−Al(1)	36.91(17)
N(15)−C(17)	1.44(1)	N(15)−C(14)	1.48(1)	C(110)−Al(2)−Al(1)	115.2(3)	C(19)−Al(2)−Al(1)	111.4(3)
N(15)−C(16)	1.50(1)	C(2)−H(2A)	0.9900	C(8)−O(9)−Al(2)	126.6(5)	C(8)−O(9)−Al(1)	129.8(5)
				Al(2)−O(9)−Al(1)	102.9(3)	C(18)−O(19)−Al(1)	127.7(5)
				C(18)−O(19)−Al(2)	128.1(4)	Al(1)−O(19)−Al(2)	104.1(3)
				C(6)−N(5)−C(4)	111.9(6)	C(6)−N(5)−C(7)	112.4(6)
				C(4)−N(5)−C(7)	112.9(6)	C(17)−N(15)−C(14)	114.9(6)
				C(17)−N(15)−C(16)	112.6(6)	C(14)−N(15)−C(16)	109.2(6)
				S(3)−C(2)−S(1)	111.8(4)	S(3)−C(2)−H(2A)	109.3
				16			
C(2)−S(3)	1.794(4)	O(9)−Al(2)	1.847(2)	S(3)−C(2)−S(1)	113.1(2)	N(5)−C(6)−S(1)	115.8(2)
C(4)−N(5)	1.495(3)	C(2)−S(1)	1.803(4)	N(5)−C(4)−S(3)	115.9(2)	N(5)−C(7)−C(8)	109.2(2)
C(6)−N(5)	1.494(3)	C(4)−S(3)	1.802(3)	C(6)−N(5)−C(4)	109.6(2)	O(9)−C(8)−C(7)	107.9(2)
C(7)−N(5)	1.497(3)	C(6)−S(1)	1.806(3)	C(4)−N(5)−C(7)	111.2(2)	C(6)−N(5)−C(7)	113.1(2)
C(8)−O(9)	1.446(3)	C(7)−C(8)	1.505(4)	C(4)−N(5)−Al(1)	111.6(2)	C(6)−N(5)−Al(1)	108.5(1)
O(9)−Al(1)	1.827(2)	C(9)−Al(1)	1.938(3)	C(8)−O(9)−Al(1)	113.9(2)	C(7)−N(5)−Al(1)	102.7(2)
Al(2)−Cl(1)	2.178(1)	C(10)−Al(1)	1.945(3)	Al(1)−O(9)−Al(2)	125.7(1)	C(8)−O(9)−Al(2)	120.2(2)
N(5)−Al(1)	2.059(2)	C(11)−Al(2)	1.960(3)	O(9)−Al(1)−C(10)	111.4(1)	O(9)−Al(1)−C(9)	110.6(1)
		C(12)−Al(2)	1.972(3)	O(9)−Al(1)−N(5)	87.43(8)	C(9)−Al(1)−C(10)	123.0(2)
				C(10)−Al(1)−N(5)	110.1(1)	C(9)−Al(1)−N(5)	108.4(1)
				O(9)−Al(2)−C(12)	105.8(1)	O(9)−Al(2)−C(11)	108.0(1)
				O(9)−Al(2)−Cl(1)	102.24(8)	C(11)−Al(2)−C(12)	119.6(2)
				C(12)−Al(2)−Cl(1)	109.6(1)	C(11)−Al(2)−Cl(1)	110.1(1)
				C(2)−S(3)−C(4)	97.8(2)	C(2)−S(1)−C(6)	98.2(2)
				10			
S(1)−C(2)	1.722(8)	S(1)−C(6)	1.807(6)	C(2)−S(1)−C(6)	95.7(3)	C(4)−S(3)−C(2)	96.8(3)
S(3)−C(4)	1.803(6)	S(3)−C(2)	1.804(9)	O(9)−Al(1)−C(10)	112.5(2)	O(9)−Al(1)−C(9)	114.6(3)
Al(1)−O(9)	1.810(4)	Al(1)−C(10)	1.932(6)	C(10)−Al(1)−C(9)	120.7(3)	O(9)−Al(1)−N(5)	86.6(2)
Al(1)−C(9)	1.952(6)	Al(1)−N(5)	2.079(4)	C(10)−Al(1)−N(5)	108.0(2)	C(9)−Al(1)−N(5)	108.7(2)
Al(2)−O(9)	1.892(4)	Al(2)−C(13)	1.973(7)	O(9)−Al(2)−C(13)	104.5(2)	O(9)−Al(2)−C(11)	105.1(2)
Al(2)−C(11)	1.975(6)	Al(2)−C(12)	1.984(6)	C(13)−Al(2)−C(11)	113.1(3)	O(9)−Al(2)−C(12)	101.5(2)
O(9)−C(8)	1.410(7)	N(5)−C(7)	1.455(7)	C(13)−Al(2)−C(12)	113.4(3)	C(11)−Al(2)−C(12)	117.2(3)
N(5)−C(6)	1.464(7)	N(5)−C(4)	1.474(6)	C(8)−O(9)−Al(1)	114.5(4)	C(8)−O(9)−Al(2)	119.2(4)
C(7)−C(8)	1.335(8)	C(14)−C(19)	1.33(1)	Al(1)−O(9)−Al(2)	126.1(2)	C(7)−N(5)−C(6)	113.1(6)
C(14)−C(15)	1.36(1)	C(14)−C(20)	1.51(1)	C(7)−N(5)−C(4)	110.9(5)	C(6)−N(5)−C(4)	109.8(5)
C(15)−C(16)	1.33(25)	C(16)−C(17)	1.34(2)	C(7)−N(5)−Al(1)	102.1(4)	C(6)−N(5)−Al(1)	111.1(3)
C(17)−C(18)	1.35(2)	C(18)−C(19)	1.35(1)	C(4)−N(5)−Al(1)	109.5(3)	S(1)−C(2)−S(3)	113.3(4)
				N(5)−C(4)−S(3)	116.4(4)	N(5)−C(6)−S(1)	116.4(4)
				C(8)−C(7)−N(5)	119.1(6)	C(7)−C(8)−O(9)	115.0(6)
				C(19)−C(14)−C(15)	118.2(8)	C(19)−C(14)−C(20)	121(1)
				C(15)−C(14)−C(20)	121(1)	C(16)−C(15)−C(14)	121.0(9)
				C(15)−C(16)−C(17)	120(1)	C(16)−C(17)−C(18)	120(1)
				C(17)−C(18)−C(19)	119(1)	C(14)−C(19)−C(18)	121.7(9)
				17			
Cl(1)−Al(2)	2.201(1)	S(1)−C(6)	1.799(3)	C(6)−S(1)−C(2)	97.6(2)	C(4)−S(3)−C(2)	98.5(1)
S(1)−C(2)	1.800(5)	S(3)−C(4)	1.797(4)	O(9)−Al(1)−C(10)	116.7(1)	O(9)−Al(1)−C(11)	111.6(2)
S(3)−C(2)	1.810(5)	Al(1)−O(9)	1.845(2)	C(10)−Al(1)−C(11)	120.3(2)	O(9)−Al(1)−N(5)	85.52(9)
Al(1)−C(10)	1.945(4)	Al(1)−C(11)	1.949(4)	C(10)−Al(1)−N(5)	108.1(1)	C(11)−Al(1)−N(5)	108.6(1)
Al(1)−N(5)	2.030(2)	Al(2)−O(9)	1.855(2)	O(9)−Al(2)−C(12)	114.8(1)	O(9)−Al(2)−C(13)	102.7(1)
Al(2)−C(12)	1.959(3)	Al(2)−C(13)	1.974(3)	C(12)−Al(2)−C(13)	118.5(2)	O(9)−Al(2)−Cl(1)	102.10(7)
O(9)−C(8)	1.469(3)	N(5)−C(7)	1.486(4)	C(12)−Al(2)−Cl(1)	106.3(1)	C(13)−Al(2)−Cl(1)	111.3(1)
N(5)−C(4)	1.494(4)	N(5)−C(6)	1.498(3)	C(8)−O(9)−Al(1)	114.2(2)	C(8)−O(9)−Al(2)	122.9(2)
				Al(1)−O(9)−Al(2)	121.2(1)	C(7)−N(5)−C(4)	112.4(2)
				C(7)−N(5)−C(6)	112.7(2)	C(4)−N(5)−C(6)	110.1(2)
				C(7)−N(5)−Al(1)	99.7(2)	C(4)−N(5)−Al(1)	111.9(2)
				C(6)−N(5)−Al(1)	109.7(2)	S(1)−C(2)−S(3)	113.3(2)
				O(9)−C(8)−C(7)	108.2(2)	N(5)−C(4)−S(3)	115.5(2)
				O(9)−C(8)−C(9)	111.2(3)	N(5)−C(6)−S(1)	115.4(2)
				C(9)−C(8)−C(7)	109.8(3)	N(5)−C(7)−C(8)	110.3(2)

Table 2 (Continued)

				18			
C(17)−Al(2)	2.045(8)	C(2)−S(3)	1.801(4)	S(1)−C(2)−S(3)	112.2(2)	O(9)−C(8)−C(7)	107.6(2)
C(17A)−Al(2)	1.969(15)	C(4)−S(3)	1.797(3)	N(5)−C(4)−S(3)	117.0(2)	C(14)−C(9)−C(8)	119.5(3)
C(2)−S(1)	1.802(4)	C(6)−S(1)	1.807(3)	N(5)−C(6)−S(1)	116.2(2)	C(9)−C(10)−C(11)	119.7(3)
C(4)−N(5)	1.484(4)	C(7)−C(8)	1.509(4)	N(5)−C(7)−C(8)	110.1(2)	C(13)−C(12)−C(11)	120.3(4)
C(6)−N(5)	1.493(4)	C(8)−C(9)	1.509(4)	O(9)−C(8)−C(9)	111.9(2)	C(4)−S(3)−C(2)	97.5(2)
C(7)−N(5)	1.491(4)	C(9)−C(14)	1.375(5)	C(9)−C(8)−C(7)	111.7(3)	C(2)−S(1)−C(6)	97.2(2)
C(8)−O(9)	1.458(3)	C(10)−C(11)	1.394(5)	C(14)−C(9)−C(10)	118.8(3)	C(9)−C(14)−C(13)	120.5(4)
C(9)−C(10)	1.392(4)	C(11)−C(12)	1.362(6)	C(10)−C(9)−C(8)	121.7(3)	C(4)−N(5)−C(6)	109.8(2)
C(15)−Al(1)	1.954(4)	C(12)−C(13)	1.355(6)	C(12)−C(11)−C(10)	120.0(3)	C(4)−N(5)−Al(1)	108.5(2)
C(16)−Al(1)	1.940(4)	C(13)−C(14)	1.378(5)	C(12)−C(13)−C(14)	120.6(4)	C(6)−N(5)−Al(1)	111.0(2)
C(18)−Al(2)	1.946(3)	O(9)−Al(1)	1.852(2)	C(4)−N(5)−C(7)	112.8(2)	C(8)−O(9)−Al(2)	121.5(2)
N(5)−Al(1)	2.095(3)	O(9)−Al(2)	1.860(2)	C(7)−N(5)−C(6)	112.4(2)	O(9)−Al(1)−C(16)	119.2(2)
		Al(2)−Cl(1)	2.188(2)	C(7)−N(5)−Al(1)	101.9(2)	C(16)−Al(1)−C(15)	124.0(2)
				C(8)−O(9)−Al(1)	116.6(2)	C(16)−Al(1)−N(5)	103.9(2)
				Al(1)−O(9)−Al(2)	120.2(1)	O(9)−Al(2)−C(18)	116.7(1)
				O(9)−Al(1)−C(15)	109.6(2)	C(18)−Al(2)−C(17A)	125.1(4)
				O(9)−Al(1)−N(5)	85.2(1)	C(18)−Al(2)−C(17)	117.3(3)
				C(15)−Al(1)−N(5)	106.0(2)	O(9)−Al(2)−Cl(1)	93.62(8)
				O(9)−Al(2)−C(17A)	106.8(4)	C(17A)−Al(2)−Cl(1)	100.8(3)
				O(9)−Al(2)−C(17)	104.6(3)	C(18)−Al(2)−Cl(1)	107.9(1)
				C(17A)−Al(2)−C(17)	13.7(3)	C(17)−Al(2)−Cl(1)	114.5(1)

General Procedure for Compounds 10−15. ***O*-Dimethylaluminum-*O*-trimethyl-aluminum-2-(1,3,5-dithiazinan-5-yl)-ethanolate, 10.** Compound **1** (0.36 g, 2.2 mmol) dissolved in toluene (20 mL) and $AlMe_3$ (2.2 mL, 2 M in hexane, 4.4 mmol) were mixed. A white solid was obtained which was recrystallized from toluene at room temperature. Yield: 0.59 g, 92%. Mp 184−186 °C. Anal. Calcd for $C_{10}H_{25}Al_2NOS_2$: C, 40.94; H, 8.59; N, 4.77. Found: C, 40.88; H, 8.18; N, 4.80. ^1H NMR ($CDCl_3$) δ(ppm) = 3.80 (d, $^2J = 13.6$, 2H, H-4ax, H-6ax), 3.51 (d, $^2J = 13.6$, H-2ax), 3.39 (t, $^3J = 5.6$, 2H, H-8), 3.13 (d br, $^2J = 13.6$, 2H, H-4eq, H-6eq), 2.80 (t, $^3J = 5.6$, 2H, H-7), 2.50 (d br, $^2J = 13.6$, H-2eq), −0.58 (s br, 5CH$_3$). ^{13}C NMR δ(ppm) = 58.1 (C8), 55.1 (C4, C6), 48.5 (C7), 30.2 (C2), − 8.4 (br, 5CH$_3$). ^{27}Al NMR δ(ppm) = 156 ($\Delta_{1/2}$ = 4860 Hz).

***O*-Dimethylaluminum-*O*-trimethylaluminum-1-methyl-2-(1,3,5-dithiazinan-5-yl)- ethanolate, 11,** was prepared from compound **2** (0.33 g, 1.82 mmol) and $AlMe_3$ (1.82 mL, 2 M in hexane, 3.64 mmol). Compound **11** was crystallized from toluene. Yield: 0.47 g, 85%. Mp 179−181 °C. Anal. Calcd for $C_{11}H_{27}Al_2NOS_2$: C, 42.98; H, 8.85; N, 4.56. Found: C, 42.68; H, 8.65; N, 4.61. ^1H NMR ($CDCl_3$) δ(ppm) = 4.56 (d, $^2J = 14.1$, H-6ax), 4.49 (d, $^2J = 14.6$, H-4ax), 4.31 (d, $^2J = 14.6$, H-2ax), 4.30 (dd, $^2J = 11.6$, $^3J = 5.9$, H-7A), 4.21 (m, H-8), 3.99 (d br, $^2J = 14.1$, H-6eq), 3.97 (d br, $^2J = 14.6$, H-4eq), 3.49 (d br, $^2J = 14.6$, H-2eq), 2.67 (dd, $^2J = 11.6$, $^3J = 5.9$, H-7B), 1.42 (d, $^3J = 5.9$, CH$_3$), −0.84 (s br, 5CH$_3$). ^{13}C NMR δ(ppm) = 66.8 (C8), 57.8 (C7), 54.8 (C6), 54.7 (C4), 31.5 (C2), 21.4 (CH$_3$), −7.6 (br, 5CH$_3$). ^{27}Al NMR δ(ppm) = 171 ($\Delta_{1/2}$ = 7740 Hz).

***O*-Dimethylaluminum-*O*-trimethylaluminum-1-phenyl-2-(1,3,5-dithiazinan-5-yl)-ethanolate, 12,** was prepared from compound **3** (0.43 g, 1.80 mmol) and $AlMe_3$ (3.6 mL, 2 M in hexane, 7.20 mmol). Compound **12** was crystallized from toluene. Yield: 0.60 g, 90%. Mp 140−144 °C. Anal. Calcd for $C_{16}H_{29}Al_2NOS_2 \cdot 1/2C_7H_8$: C, 52.01; H, 7.91; N, 3.79. Found: C, 52.40; H, 8.33; N, 3.90. ^1H NMR ($CDCl_3$) δ(ppm) = 7.4−7.3 (m, 5H, Ph), 5.17 (dd, $^3J = 8.9$, 5.0, H-8), 4.57 (d, $^2J = 14.3$, H-6ax), 4.51 (d, $^2J = 14.3$, H-4ax), 4.30 (d, $^2J = 13.4$, H-2ax), 4.26 (dd, $^2J = 13.6$, $^3J = 5.0$, H-7A), 4.17 (d br, $^2J = 14.3$, H-6eq), 3.83 (d br, $^2J = 14.3$, H-4eq), 3.47 (d br, $^2J = 13.4$, H-2eq), 3.40 (dd, $^2J = 13.6$, $^3J = 8.9$, H-7B), −1.11 (s, CH$_3$), −0.85 (s, CH$_3$). ^{13}C NMR δ(ppm) = 139.0 (C$_i$), 126.4 (C$_m$), 128.8 (C$_p$), 128.7 (C$_o$), 72.6 (C8), 57.1 (C4), 55.6 (C6), 54.9 (C7), 31.5 (C2), −7.9 (s br, CH$_3$), −7.1 (s br, CH$_3$). ^{27}Al NMR δ(ppm) = 150 ($\Delta_{1/2}$ = 2350 Hz).

***O*-Dimethylchloroaluminum-*O*-methylchloroaluminum-2-(1,3,5-dithiazinan-5-yl)-ethanolate, 13,** was prepared from compound **1** (0.28 g, 1.70 mmol) and $AlMe_2Cl$ (0.32 mL, 3.40 mmol). Compound **13** was crystallized from toluene. Yield: 0.51 g, 90%. Mp 141−144 °C. Anal. Calcd for $C_8H_{19}Al_2Cl_2NOS_2$: C, 28.75; H, 5.73; N, 4.19. Found: C, 28.76; H, 5.68; N, 3.96. ^1H NMR ($CDCl_3$) δ(ppm) = 4.64 (d, $^2J = 13.9$, 2H, H-4ax, H-6ax), 4.40 (d, $^2J = 14.0$, H-2ax), 4.10 (t, $^3J = 5.6$, 2H, H-8), 4.05 (dd, $^2J = 13.9$, $^3J = 2.3$, 2H, H-4eq, H-6eq), 3.77 (t, $^3J = 5.6$, 2H, H-7), 3.55 (dt, $^2J = 14.0$, $^3J = 2.3$, H-2eq), −0.53 (s, 3CH$_3$). ^{13}C NMR δ(ppm) = 59.5 (C8), 55.8 (C4, C6), 47.9 (C7), 31.4 (C2), −10.0 (s br, 3CH$_3$). ^{27}Al NMR δ(ppm) = 129 ($\Delta_{1/2}$ = 3440 Hz).

***O*-Dimethylchloroaluminum-*O*-methylchloroaluminum-1-methyl-2-(1,3,5-dithiazinan −5-yl)-ethanolate, 14,** was prepared from compound **2** (0.36 g, 2.00 mmol) and $AlMe_2Cl$ (0.76 mL, 4.00 mmol). Compound **14** was crystallized from toluene. Yield: 0.73 g, 95%. Mp 103−106 °C. Anal. Calcd for $C_9H_{21}Al_2Cl_2NOS_2$: C, 31.04; H, 6.08; N, 4.02. Found: C, 31.05; H, 6.12; N, 3.82. ^1H NMR ($CDCl_3$) δ(ppm) = 4.62 (d, $^2J = 13.9$, H-6ax), 4.54 (d, $^2J = 14.0$, H-4ax), 4.37 (dd, $^2J = 12.0$, $^3J = 4.0$, H-7A), 4.35 (d, $^2J = 13.9$, H-2ax), 4.34 (ddq, $^3J = 12.0$, 6.5 and 4.0, H-8), 4.07 (dt, $^2J = 14.0$, $^4J = 2.0$, 2H, H-4eq), 3.96 (dt, $^2J = 13.9$, $^4J = 2.0$, H-6eq), 3.48 (dt, $^2J = 13.9$, $^4J = 2.0$, H-2eq), 2.69 (t, $^2J = {}^3J = 12.0$, H-7B), 1.47 (d, $^3J = 6.5$, 3H, CH$_3$), −0.67 (s br, 3CH$_3$). ^{13}C NMR δ(ppm) = 67.2 (C8), 57.7 (C4), 54.7 (C6), 54.2 (C7), 31.4 (C2), 21.2 (CH$_3$), −7.9 (s br, CH$_3$), −7.0 (s br, CH$_3$). ^{27}Al NMR δ(ppm) = 129 ($\Delta_{1/2}$ = 2500 Hz).

***O*-Dimethylchloroaluminum-*O*-methylchloroaluminum-1-phenyl-2-(1,3,5-dithiazinan-5-yl)-ethanolate**, **15,** was prepared from compound **3** (0.43 g, 1.80 mmol) and $AlMe_2Cl$ (0.68 mL, 7.20 mmol). Compound **15** was crystallized from toluene. Yield: 0.63 g, 85%. Mp 96−99 °C. Anal. Calcd for $C_{14}H_{23}Al_2Cl_2NOS_2$: C, 40.98; H, 5.65; N, 3.41. Found: C, 40.44; H, 6.00; N, 3.36. ^1H NMR ($CDCl_3$) δ(ppm) = 7.4−7.2 (m, 5H, Ph), 5.27 (dd, $^3J = 15.0$, 4.0, H-8), 4.68 (d, $^2J = 13.9$, H-4ax), 4.67 (d, $^2J = 14.3$, H-6ax), 4.58 (dd, $^2J = 14.3$, $^3J = 4.0$, H-7A), 4.39 (d, $^2J = 13.9$, H-2ax), 4.31 (dd, $^2J = 14.3$, $^3J = 15.0$, H-7B), 4.10 (d br, $^2J = 13.9$, H-4eq), 3.19 (d br, $^2J = 13.9$, H-2eq), 3.18 (d br, $^2J = 14.3$, H-6eq), −0.39 (s, CH$_3$), −0.30 (s, CH$_3$). ^{13}C NMR δ(ppm) = 136.3 (C$_i$), 129.4 (C$_m$), 128.4 (C$_p$), 127.4 (C$_o$), 73.8 (C8), 57.2 (C4), 53.9 (C6), 54.7 (C7), 31.5 (C2), −9.6 (s br, CH$_3$), −7.6 (s br, CH$_3$). ^{27}Al NMR δ(ppm) = 130 ($\Delta_{1/2}$ = 9370 Hz).

General Procedure for Preparation of Compounds 16−18. *O*-Dimethylchloro-aluminum-*O*-dimethyl aluminum-2-(1,3,5-dithiazinan-5-yl)ethanolate, 16. Compound **16** was obtained two ways: (a) The first way is from compound **1** (0.51 g, 3.07 mmol) in toluene (20 mL) and $AlMe_3$ (1.54 mL, solution 2 M in hexane, 3.07 mmol) at −78 °C. After stirring for 15 min, $AlMe_2Cl$ (0.29 mL, 3.07 mmol) was added. The suspension was stirred for another 15 min and filtered and the solvent evaporated. (b) Alternatively, compound **1** (0.51 g, 3.07 mmol) dissolved in toluene (20 mL) and $AlMe_2Cl$ (0.29 mL, 3.07 mmol) added by syringe were mixed at −78 °C and stirred for 15 min. Then, $AlMe_3$ (1.54 mL, solution 2 M in hexane, 3.07 mmol) was added. After stirring for another 15 min, the suspention was filtered and the solvent evaporated from the filtrate. Compound **16** was obtained as a white solid. Yield: 0.87 g, 90%. Mp 250 °C (dec). Anal. Calcd for $C_9H_{22}Al_2ClNOS_2$: C, 34.45; H, 7.07; N, 4.46. Found: C, 34.68; H, 6.95; N, 4.31. ^1H NMR ($CDCl_3$) δ(ppm) = 4.62 (d, $^2J = 13.8$, 2H, H-4ax, H-6ax), 4.38 (d, $^2J = 14.0$, H-2ax), 4.10 (m, 2H, H-8), 4.00 (dd, $^2J = 13.8$, $^3J = 2.2$, 2H, H-4eq, H-6eq), 3.51 (dt, $^2J = 14.0$, $^3J = 2.2$, 2H, H-2eq), 3.70 (m, 2H, H-7), −0.69 (s, $4CH_3$). ^{13}C NMR δ(ppm) = 58.8 (C8), 55.6 (C4, C6), 48.2 (C7), 31.3 (C2), −9.3 (s br, $4CH_3$). ^{27}Al NMR δ(ppm) = 160 ($\Delta_{1/2} = 7810$ Hz).

***O*-Dimethylchloroaluminum-*O*-dimethylaluminum-1-methyl-2-(1,3,5-dithiazinan-5-yl)ethanolate, 17,** was prepared from compound **2** (0.34 g, 1.92 mmol), $AlMe_3$ (0.96 mL, 2 M in hexane, 1.92 mmol), and $AlMe_2Cl$ (0.18 mL, 1.92 mmol), by the two procedures described for compound **16**. Compound **17** crystallized from $CHCl_3$. Yield: 0.60 g, 95%. Mp 103−106 °C. Anal. Calcd for $C_{10}H_{24}Al_2ClNOS_2$: C, 36.64; H, 7.38; N, 4.27. Found: C, 36.43; H, 7.41; N, 4.61. ^1H NMR ($CDCl_3$) δ(ppm) = 4.64 (d, $^2J = 13.9$, H-4ax), 4.57 (d, $^2J = 14.4$, H-6ax), 4.37 (d, $^2J = 14.0$, H-2ax), 4.34 (m, H-8), 4.41 (dd, $^2J = 11.2$, $^3J = 4.5$, H-7A), 4.12 (dt, $^2J = 14.4$, $^4J = 2.0$, H-6eq), 4.00 (dt, $^2J = 13.9$, $^4J = 2.0$, H-4eq), 3.52 (dt, $^2J = 14.0$, $^4J = 2.0$, H-2eq), 2.71 (dd, $^2J = 11.2$, $^3J = 10.9$, H-7B), 1.51 (d, $^3J = 5.9$, CH_3), −0.66 (s br, $2CH_3$), −0.60 (s br, $2CH_3$). ^{13}C NMR δ(ppm) = 67.1 (C8), 57.6 (C4), 54.5 (C6), 54.1 (C7), 31.4 (C2), 21.1 (CH_3), −8.3 (s br, $2CH_3$), −7.0 (s br, $2CH_3$). ^{27}Al NMR δ(ppm) = 163 ($\Delta_{1/2} = 8330$ Hz).

***O*-Dimethylchloroaluminum-*O*-dimethylaluminum-1-phenyl-2-(1,3,5-dithiazinan-5-yl)ethanolate, 18,** was prepared from compound **3** (0.35 g, 1.40 mmol), $AlMe_3$ (0.72 mL, 2 M in hexane, 1.40 mmol), and $AlMe_2Cl$ (0.13 mL, 1.40 mmol). Compound **18** crystallized from toluene. Yield: 0.46 g, 85%. Mp 106−108 °C. Anal. Calcd for $C_{15}H_{26}NS_2OAl_2Cl$: C, 46.21; H, 6.72; N, 3.59. Found: C, 45.92; H, 7.01; N, 3.41. ^1H NMR ($CDCl_3$) δ(ppm) = 7.5−7.1 (m, 5H, Ph), 5.24 (dd, $^3J = 10.0$, 4.6, H-8), 4.66 (d, $^2J = 13.9$, 2H, H-4ax, H-6ax), 4.50 (dd, $^2J = 13.5$, $^3J = 4.6$, H-7A), 4.34 (d br, $^2J = 13.9$, H-4eq), 3.98 (d, $^2J = 14.0$, H-2ax), 3.95 (d br, $^2J = 13.9$, H-6eq), 3.49 (d br, $^2J = 14.0$, H-2eq), 3.21 (dd, $^2J = 13.5$, $^3J = 10.0$, H-7B), −1.0 (s br, $2CH_3$), −0.4 (s br, $2CH_3$). ^{13}C NMR δ(ppm) = 137.3 (C_i), 126.2 (C_m), 128.9 (C_p), 128.6 (C_o), 73.0 (C8), 57.2 (C4), 54.7 (C6), 54.3 (C7), 31.5 (C2), −9.9 (s br, $2CH_3$), −7.5 (s br, $2CH_3$). ^{27}Al NMR δ(ppm) = 152 ($\Delta_{1/2} = 6260$ Hz).

Results and Discussion

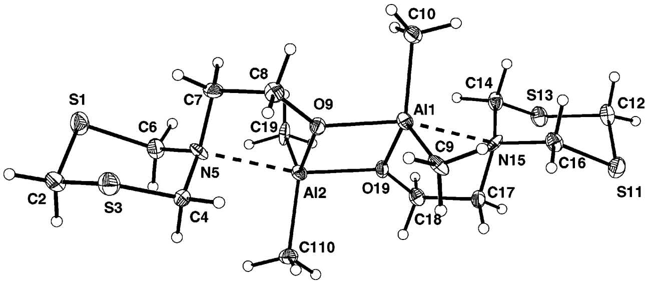
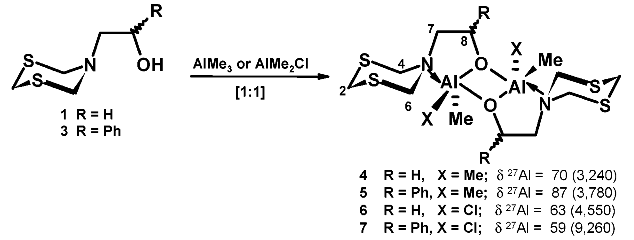


Figure 1. ORTEP representation of compound **4** with coordinated bond lengths of 2.470 Å (N5→Al2) and 2.476 Å (N15→Al1).

Scheme 3



Equimolar Reactions. $AlMe_3$ or $AlMe_2Cl$ was reacted with compounds **1**−**3**, in toluene at −40 °C. Examination by ^{27}Al NMR of the equimolar reaction of compound **1** with $AlMe_3$ gave two signals, one at 9.0 ppm ($\Delta_{1/2} \approx 300$ Hz) which corresponds to an hexacoordinated and symmetrical aluminum atom bonded to oxygen atoms,[8] and a broad signal for a pentacoordinated aluminum atom at 70 ppm ($\Delta_{1/2}$ 3240 Hz). From the toluene solution, crystals were separated that have been characterized by X-ray diffraction as dimeric pentacoordinated aluminum compound **4**, Figure 1 and Scheme 3.

The molecular structure of **4** shows that the aluminum atoms reside in the center of a distorted trigonal bipyramidal, tbp, arrangement with one oxygen and one nitrogen atom in apical positions [O9−Al1−N15, 152.6(3)°; C9−Al1−O19, 116.7(4)°; C9−Al1−C10, 123.7(3)°; C10−Al1−O19, 120.9(3)°]. The oxygen atoms are bridging the aluminum atoms forming a four-membered ring. The apical Al−O bonds are longer (O9−Al1, 1.916(6) Å; Al2−O19, 1.906(6) Å) than the equatorial bonds (O9−Al2, 1.837(5) Å; Al1−O19, 1.818(6) Å). The dithiazinane rings have a chair conformation with the aluminum atoms in equatorial position. The distances N−Al [N5−Al2, 2.470 Å and N15−Al1, 2.476 Å] are exceptionally long with respect to other reported values (2.1−2.3 Å).[4] An explanation can be found in the partial tetrahedral character (70%) of the nitrogen atom that corresponds to a weak base due to the more p character of the nitrogen orbital involved in the coordinative bond, and to the steric effect produced by the dithiazinane cycle. Evidence for a coordinative bond is also based in the direction of the nitrogen lone pair toward the aluminum nuclei and the geometry around the aluminum atoms. The alanoxazolidine rings have an envelope conformation, with C7 and C17 outside the plane. Intermolecular CH···S hydrogen bonds [2.979 Å] were observed, Figure 2. These C−H···S interactions are similar to CH···O interactions which are now accepted as relevant in crystal engineering.[9]

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[8] (a) Akitt, J. W. In *Annual Reports on NMR Spectroscopy*; Mooney E. F., Ed.; Academic Press Inc.: London, 1972; Vol. 5A, p 465. (b) Atwood, D. A.; Jegier, J. A.; Liu, S.; Rutherford, D.; Wei, P.; Tucker, R. C. *Organometallics* **1999**, *18*, 976. (c) Krossing, I. Ph.D. Thesis, Fakultät für Chemie und Pharmazie, Ludwig-Maximilians-Universität, München, Germany, 1997. (d) Kumar, R.; de Mel, V. S. J.; Sierra, M. L.; Hendershot, D. G.; Oliver, J. P. *Organometallics* **1994**, *13* 2079−2083.

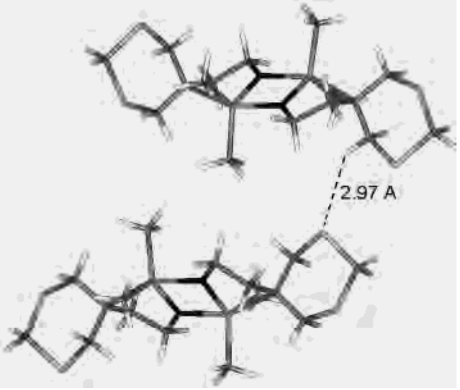
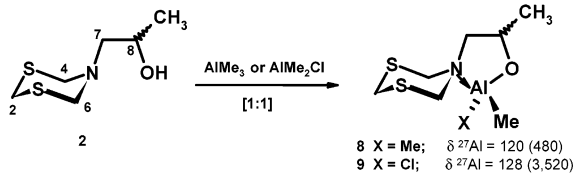


Figure 2. S···H hydrogen bonds (2.97 Å) in the lattice of compound **4**.

Scheme 4



The combination of **1**−**3** and $AlMe_2Cl$ and $AlMe_3$ yields the dimeric pentacoordinated aluminum derivatives **4**−**7** as white powders, Scheme 4. The pentacoordination of the aluminum atom is deduced from the characteristic ^{27}Al resonances (59−87 ppm).[4b,e,10] The ^1H NMR spectra show the absence of the signal for the O−H protons; the H-7 and H-8 atoms show complex coupling patterns of an anchored conformation attributed to the bonding of oxygen and nitrogen atoms to the aluminum centers. Compounds **5** and **7** present the anchored dithiazinane in a chair conformation as is deduced from the different signals for equatorial and axial hydrogen atoms and their coupling patterns. An interesting fact in **5** and **7** is that hydrogen atoms H-7A are deshielded with respect to H-7B (about 1.3−1.6 ppm), and this may be due to their position pointing to sulfur atoms, as found in the solid state structure of compound **4**, Figure 8. The ^{13}C NMR spectra of **5** and **7** (R = Ph) show only one isomer indicating a stereoselective reaction; diasterotopic signals for C4 and C6 of the dithiazinane rings (**5**, $\delta = 58.3$ ppm and 54.0; **7**, $\delta = 53.6$ and 56.8 ppm) are due to the strong N−Al bond and the presence of the stereogenic atom C8, and in **7** to the different substitution at aluminum compound, Scheme 3.

Equimolar reactions of compound **2** (in toluene at −40 °C) with $AlMe_3$ and $AlMe_2Cl$ gave compounds **8** and **9** (Scheme 4). They are stable monomers (structure **c**, Scheme 2), as was established by comparison of their ^{27}Al NMR data ($\delta = 120$ for **8** and 128 for **9**) with those of some tetracoordinated aluminum compounds derived from hydroxypyridine.[4b,e,10b] ^1H and ^{13}C NMR spectra of compounds **8** and **9** indicate only one isomer in each case; therefore, this can be attributed to a stereroselective synthesis or to a dynamic equilibrium toward the more stable isomer. The dithiazinane ring in compound **8** is in conformational equilibrium, whereas **9** is in a anchored conformation with diasterotopic groups C4 and C6. This is attributed to a weaker $N\rightarrow AlMe_2$ bond with respect to $N\rightarrow AlMeCl$. We did not find evidence of dimeric structures of type **b** at room temperature, see a following discussion (Scheme 2). The different behavior of compounds **8** and **9** toward dimerization could be attributed to an electronic effect. For compounds **8** and **9**, methyl (electron releasing) substituted ligand **2** may bind to an aluminum atom with more electronic donation from oxygen to aluminun resulting in a metal atom less electronic deficient that keeps the compounds as monomers.

Reactions with 2 equiv of the Aluminum Compounds. The combination of ligands **1** or **2** with 2 equiv of the aluminum reagents afforded the dimetalated derivatives **10**−**11** and **13**−**14** while ligand **3** was only completely transformed into derivatives **12** and **15** using 4 equiv of aluminum reagents (Scheme 5). The reaction products have one aluminum atom chelated by the aminoalkoxide unit and a second aluminum atom coordinated to the oxygen of the ring.

The structure of compounds **10**−**15** was determined by NMR. They show only one broad signal in the ^{27}Al spectra indicating a fluxional behavior of the aluminum atoms. In the ^1H spectrum of compounds **10**−**15**, the chair preferred conformation of the six-membered ring indicates a strong N→Al bond which inhibits the nitrogen inversion.[3] Compounds **11**, **12**, **14**, and **15** present diasterotopic C4 and C6 atoms due to the coordinative bond and the substitution at C8.

The X-ray diffraction analysis of compound **10**, crystallized from toluene, reveals that the N-coordinated Al atom resides in an equatorial position of the dithiazinane ring, while the $AlMe_3$ unit is bonded to a planar oxygen atom (Figure 3a). The two Al−C bonds of the chelate are eclipsed with N−C4 and N−C6 bonds; the methyl groups of the exocyclic aluminum atom are present in a staggered conformation. The five-membered ring shows an envelope conformation with C8 out of the plane. In the unit cell, one molecule of toluene is present in the asymmetric unit (Figure 3).

An intermolecular arrangement determined by π interactions of protons at C2 and toluene is depicted in Figure 3b. The contact distances in an edge-type interaction are similar to those previously reported, then to three 3 C atoms. Distances to CH2eq are 2.79, 2.74, and 2.80 Å.[9,11]

We have found that some mixed compounds can be prepared by adding $AlMe_2Cl$ to **4**−**5** or by adding 1 equiv of $AlMe_3$ to compound **9**. Reaction of compound **9** with $AlMe_3$ did not give the expected dialuminum derivative **19** but only compound **17** (Scheme 6). The result indicates that the aluminum atoms have exchanged their sites or that a chlorine atom has exchanged its position with a methyl group.[4]

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(9) (a) Desiraju, G. R. *Acc. Chem. Res.* **1996**, *29*, 441−449 and references therein. (b) *The Crystal as a Supramolecular Entity*; Desiraju G. R., Ed.; John Wiley & Sons: Chichester, England, 1996; Vol. 2. (c) *Supramolecular Chemistry*; Steed J. W., Atwood J. L., Eds.; John Wiley & Sons: Chichester, England, 2000. (d) Viswamitra, M. A.; Radhakrishnan, R.; Bandekar, J.; Desiraju, G. R. *J. Am. Chem. Soc.* **1993**, *115*, 4868−4869.

(10) Borrmann, H.; Persson, I.; Sandström, M.; Satålhandske, C. M. V. *J. Chem. Soc., Perkin Trans. 2* **2000**, 393−402.

(11) Koch, U.; Popelier, P. L. A. *J. Phys. Chem.* **1995**, *99*, 9747−9754.

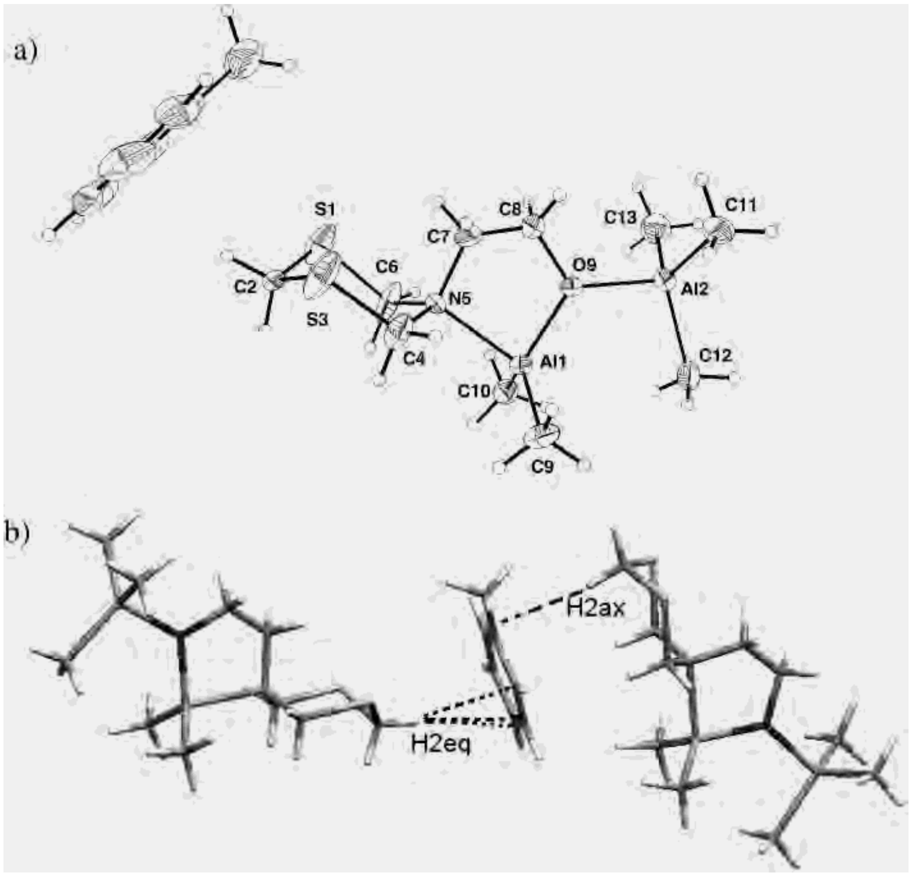
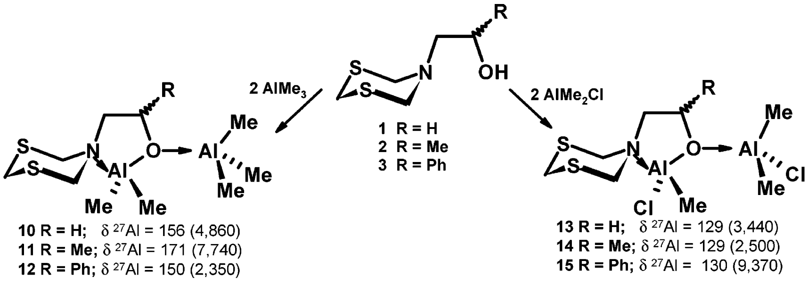


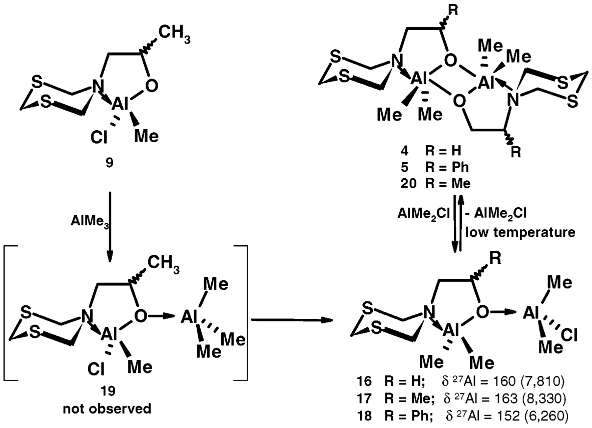
Figure 3. (a) View of compound **10** with a molecule of toluene with the N5→Al1 bond distance of 2.080 Å. (b) Polymeric array of molecules of **10** produced by π interactions of toluene with SCH_2S protons. (The distances from H2eq are the following: to C*ortho*, 2.79 Å; to C*meta*, 2.74 Å; to C*para* 2.80 Å. The distance from H2ax to C*ipso* is 2.75 Å.).

Scheme 5



Some variable temperature NMR experiments were performed for compounds **17** and **18**. By heating (100 °C in toluene), the ^{27}Al NMR spectra showed that the signals become sharp, but their chemical shifts did not change. By cooling in the same solvent, compound **17** at −70 °C did not show, as expected, two different signals for each aluminum atom, but they were completely transformed into the pentacoordinated compound **20** (δ = 54 ppm, $\Delta_{1/2}$ 6400 Hz); the initial aspect of the spectrum was recovered by coming back into room temperature (Scheme 6). The same behavior was observed for compound **18** which was completely transformed at −50 °C into compound **5** (δ = 59 ppm, $\Delta_{1/2}$ 7600 Hz).

Scheme 6



Compounds **16**−**18** crystallized from $CDCl_3$ at room temperature, and their structures were determined by X-ray methods (Figures 4−9). In these three compounds, the heterocyclohexane has a chair conformation with the aluminum atom in equatorial position, and the five-membered ring has an envelope conformation. In compounds **16** and

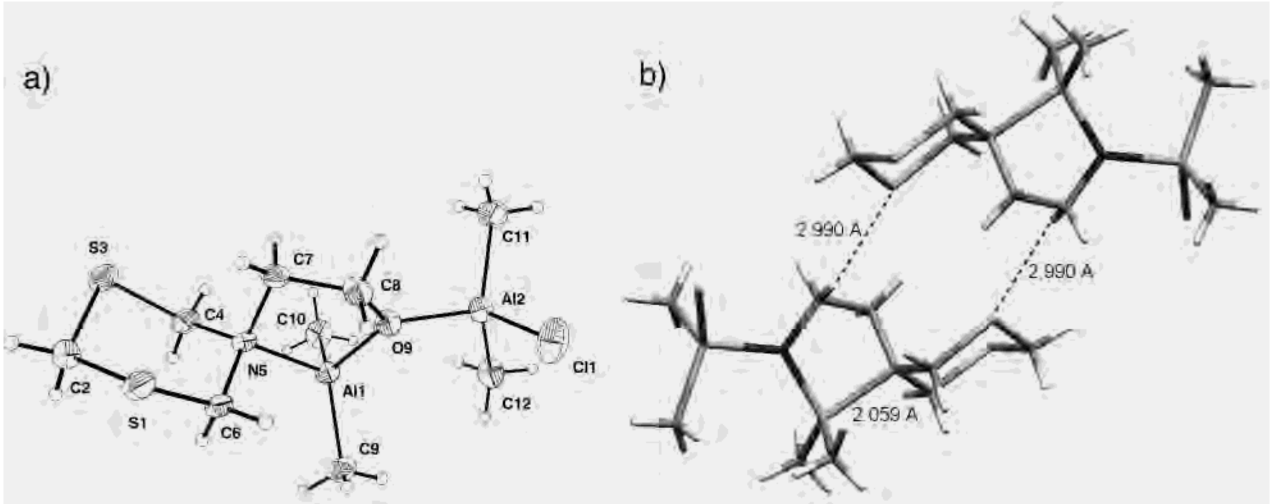


Figure 4. Crystal structure of compound **16**: (a) ORTEP representation and (b) dimeric structure produced by S···H8_{ax} intermolecular interactions and N→Al bond distances.

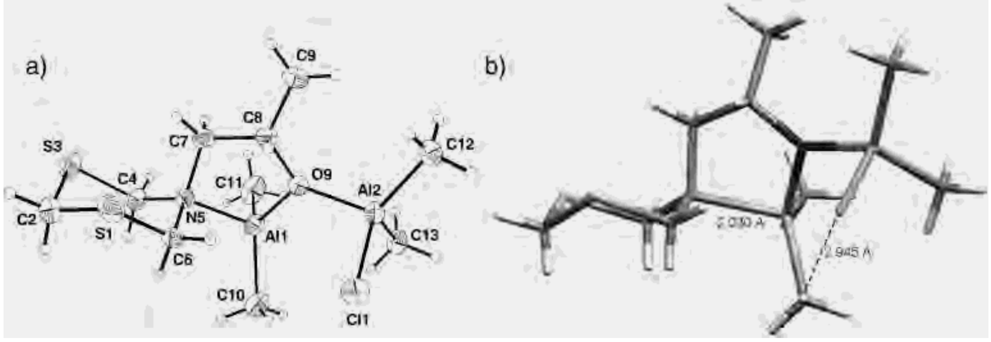


Figure 5. Crystal structure of compound **17**: (a) ORTEP representation and (b) view of the conformation of the five-membered ring.

18, the atom C7 is out of the plane whereas in **17** the N atom deviates from the ring plane. The N−Al bond lengths are short indicating a strong coordinative bond particularly for **16** and **17** (2.059 Å in **16**, 2.030 Å in **17**, and 2.095 Å in **18**); the longest bond length Al−O is the exocyclic bond [in **16**, Al1−O9 1.827(2) Å and Al2−O9 1.847(2) Å; in **17**, 1.845(2) and 1.855(2) Å; and in **18**, 1.852(2) and 1.860(2) Å]. In compound **16**, a dimeric arrangement was produced by two S···H8ax intermolecular hydrogen bonds, 2.99 Å (Figure 4b). The latter is a significant C−H···S hydrogen bond if it is compared with data reported in the literature (3.78 Å) for a similar hydrogen bond.[9]

In compound **17**, the methyl substituent of the five-membered ring is in a pseudoequatorial position (Figure 5). The Al2−Cl bond is directed to a *trans* arrangement with the C−Me bond [Cl1−Al2−C8−C-9, 147.75°]. The chlorine atom Cl1 has an intramolecular hydrogen bond Cl1···H10a, 2.945 Å (Figure 5b).

There are intermolecular cooperative network interactions between three molecules through methylene protons and chlorine atoms [Cl1···H2b′, 2.936 Å and Cl1···H4a′, 2.817 Å] and one Al−CH_3 proton with sulfur [S3···H10c,′ 2.999 Å] (Figure 6).

The solid state structure of compound **18** is shown in Figure 7. It shows short intramolecular contacts of proton H7A and the sulfur atoms of the dithiazinane ring at 2.83 and 2.95 Å (Figure 8).

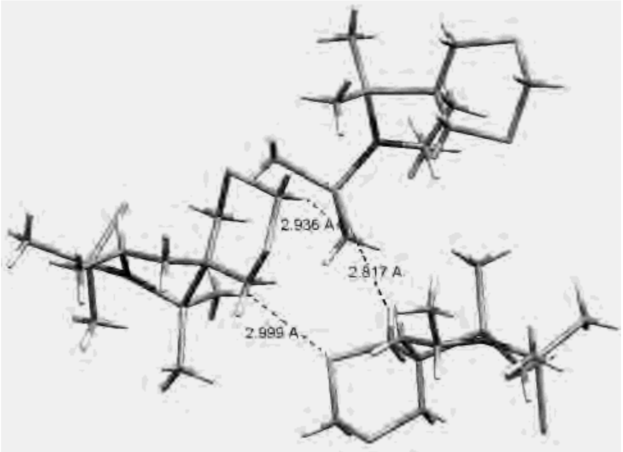


Figure 6. Intramolecular hydrogen bonds Cl···H and S···H10 between three molecules of compound **17**.

A dimeric array is produced by a π interaction centroid type[11] of the phenyl group of one molecule with the H2eq of another molecule [2.760, 2.792, 2.843, and 2.896 Å] (Figure 9). An intermolecular hydrogen bond was found between Cl1···H2ax, 2.77 Å. In the literature, C−H chlorine intermolecular interactions have been proposed for distances of 3.61 Å.[9]

Conclusions

We have reported three new ligands bearing as a coordinating motif a dithiazinane and an ethanol group. They were

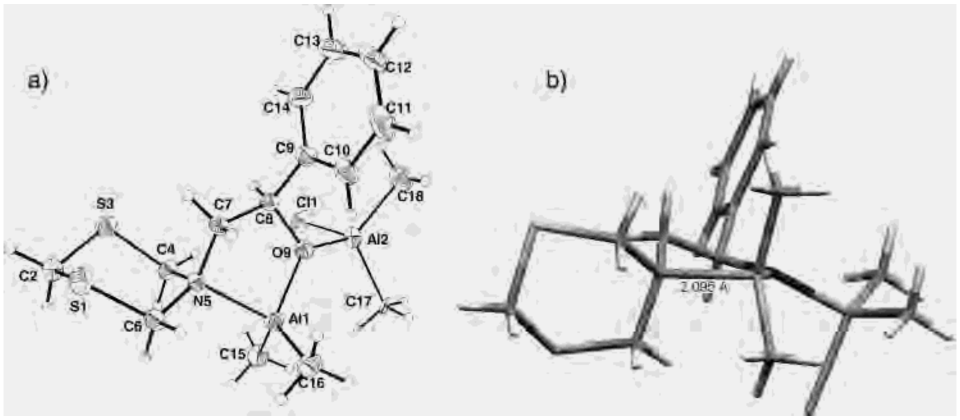


Figure 7. Crystal structure of compound **18**: (a) ORTEP representation and (b) view showing the “heterocyclopentane” conformation.

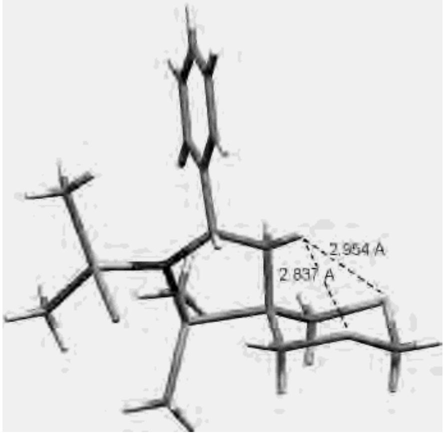


Figure 8. Solid state structure of compound **18** showing the intramolecular contact of proton H7A and the sulfur atoms of dithiazinanyl ring.

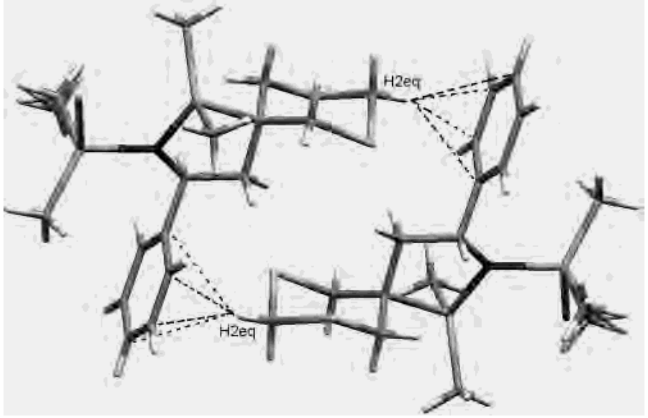


Figure 9. Array of two molecules showing π interactions of compound **18**.

effective coordinating agents for organoaluminum compounds, and the resulting molecules showed different structures depending on the reagent ratio and the substitution at the ethanol arm. Nitrogen and oxygen atoms are involved in the coordination to Al atoms. We have obtained two monomers and four dimers of aminoethanolate aluminum compounds and nine dinuclear derivatives. We have observed neither coordination to sulfur atoms nor opening of the dithiazinanyl ring. We were unable to obtain the bis-aminoethanolate structures **d** or the open structures **a** (Scheme 2). X-ray diffraction studies were helpful in order to establish the actual structures in the solid state and to give evidence of intermolecular interactions C−H····S, C−H····Cl, and C−H····π found in the crystalline network. NMR experiments have shown fluxional behavior for compounds **4**, **6**, and **8** and in others a static conformation of the dithiazinane rings **5**, **7**, and **9**−**18**. The presence of a stereogenic center at the ethanolate group helped to evaluate the N−Al coordination strength making evident the diastereotopism at the methylene carbon atoms C4 and C6. The ^{27}Al NMR spectra indicate the equilibrium between the two alkyl aluminum groups for dinuclear compounds and the preference of the Al−Cl bond in an exocyclic position. Variable temperature experiments indicated a monomer−dimer equilibrium.

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Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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