Organometallics **2002,** *21,* 3471−3476

Methylthiomethyl Compounds of Aluminum, Gallium, and Indium

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Received August 9, 2001

The dimethyl(methylthiomethyl)metal compounds $(Me_2MCH_2SMe)_2$ (M = Al, Ga, In) have been prepared from $LiCH_2SMe$ and the respective dimethylmetal chlorides. Unlike the corresponding lithium compounds, the thiomethyl compounds with $AlMe_2$ and $GaMe_2$ groups are sublimable and well soluble in nonpolar solvents. The compounds $(Me_2MCH_2SMe)_2$ have been characterized by elemental analyses, multinuclear NMR spectroscopy, and, in the cases M = Al and Ga, by single-crystal X-ray crystallography. The Al and Ga compounds are dimeric in the solid and in nondonor solvents, but are cleaved by stronger donors such as ethers and amines. They adopt conformations in which the S-bound methyl groups are placed in equatorial positions of the chair-like six-membered ring systems. Ab initio calculations up to the MP2/6-31G(d) and B3LYP/6-31G(d) levels of theory confirmed these conformations to be the ground states, the one with both S-Me groups in axial position being higher in energy by ca. 25 kJ mol^{-1}. The barriers to inversion of the heterocyclohexane rings in toluene solution (NMR) are 39 kJ mol^{-1} for the Al compound and 36 kJ mol^{-1} for the Ga compound.

Introduction

Organometallic compounds with heteroatoms in geminal position to the metals show a range of different reactivities. Prominent examples from main group chemistry include the carbenoid reactivity of Köbrich's α-halomethyllithium reagents,[1] the reagents for nucleophilic aminomethylation[2] and phosphinomethylation.[3] These examples find their parallels in transition metal systems such as the Seyferth reagent $PhHgCCl_2Br$.[4] The chemistry of heteroorganometal compounds with sulfur in β-position to the metal was developed by Peterson[5] and later continued by Seebach,[6] who introduced thiomethyllithium compounds. Such sulfur systems have been widely applied in heteroatom-promoted metalations in organic synthesis.[7]

Changing the metal in such compounds leads to modified reactivities, but also to variations of the properties of the organometallic reagents such as thermal stability and solubility in nonpolar organic solvents. Only recently have the first thiomethylmagnesium compounds $[Mg(CH_2SR)_2(thf)_3]$ been reported,[8] and a lithium thiomethyl compound was demonstrated to show carbenoid reactivity.[9] Heteroorganometal compounds of the group 13 metals aluminum, gallium, and indium have so far not been investigated in much detail, although they have the potential as new reagents for synthetic applications. The only systems with M−C−S linkages (M = Al, Ga, In) are Oliver's 2-thiophene derivatives of aluminum and indium $[Me_2Al(\mu\text{-}2\text{-}C_4H_3S)]_2$, $[Me_2In(\mu\text{-}2\text{-}C_4H_3S)]_2$, and $\{(2\text{-}C_4H_3S)_2Al[\mu\text{-}N(H)C(H)(C_6H_5)_2]\}_2$ [10] and the reports of polymeric $[Al(CH_2SCH_3)_3]_8$ and dimeric $[Al(CH_3SPh)_3]_2$.[11] Other compounds with donor centers in geminal position relative to a group 13 element exist in various types of possible aggregates, either intramolecular with the formation of three-membered ring systems as in compounds containing BCN,[12] BNN,[13] AlCN,[14] and AlNN[15] units or intermolecular with formation of dimers with cyclohexane-like six-membered rings as in $[(H_2BCH_2NMe_2)_2]$,[16] $[(H_2BCH_2SMe)_2]$,[17] $[Me_2Al(CH_2PMe_2)]_2$ and $[Al(CH_2PMe_2)_3]_2$, [18] and $[(Me_3CCH_2)_2InCH_2PPh_2]_2$.[19]

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10.1021/om0107338 CCC: \$22.00

Aluminum chemistry has recently been predicted to flourish in the areas of catalysis by hypercoordinate compounds and in materials research.[20] Heteroorganoaluminum compounds also contribute to these fields, and we note the first compounds with Al−C−N and Ga−C−N linkages, which have recently been synthesized in our laboratories.[21] These compounds are related to those with donor-functionalized ligands, which have intramolecular donor−acceptor interactions.[22]

In this paper we present the synthesis, conformational behavior, and structural chemistry of the simple methylthiomethyl compounds Me_2MCH_2SMe with M = Al, Ga, In. Our own interest in this chemistry originates from the systematic investigation of main group compounds with geminal donor and acceptor centers with SiON, GeON, and SnON skeletons.[23] Such compounds often reveal surprising structural features, which can serve to explain the unique reactivities of such classes of compounds.

Experimental Section

General Methods. All experiments were carried out under a dry nitrogen atmosphere with standard Schlenk and high-vacuum techniques or in a glovebox operated under argon. Solvents were purified and dried by standard techniques. Pure and donor-free methylthiomethyllithium was obtained by transmetalation of methylthiomethyltri-*n*-butyltin[24] with *n*-butyllithium. CAUTION: Solid $LiCH_2SMe$ spontaneously ignites and burns vigorously on contact with air. Chemical ionization (CI) mass spectra were obtained with a Varian MAT 311A spectrometer. All NMR spectra were recorded on a JEOL JNM-LA400 spectrometer (400.05 MHz ^1H, 100.50 MHz ^{13}C, 104.05 MHz ^{27}Al) in C_6D_6 or toluene-d_8 as solvent dried over K/Na alloy.

Dimethyl(methylthiomethyl)aluminum ($(Me_2AlCH_2SMe)_2$). To a stirred suspension of methylthiomethyllithium (6.17 mmol, 0.42 g) in 50 mL of *n*-hexane was slowly added a solution of dimethylaluminum chloride (6.15 mmol, 6.15 mL of a 1 M solution in *n*-hexane) at −78 °C. The reaction mixture was allowed to warm to room temperature. The solution was filtered and concentrated to 20 mL. Storage at −78 °C yielded colorless crystals. Yield: 0.51 g (70%), mp 64 °C, sublimation point 45 °C (0.01 mbar). CI-MS [*m*/*z* (%)]: 235 (3), [$M^+ - H$]; 221 (100), [$M^+ - Me$]; 207 (12) [$M^+ - 2\ Me$]; 191 (25) [$M^+ - 3\ Me$]; 175 (32) [$M^+ - 4\ Me$]; 118 (13) [$M^+ - Me_2AlCH_2SMe$]; 103 (57) [$Me_2AlCH_2SMe^+ - Me$]. ^1H NMR (C_6D_6): δ −0.48 (s, 12H, $AlCH_3$), 1.10 (s, 4H, $AlCH_2S$); 1.56 (s, 6H, SCH_3). $^{13}C\{^1H\}$ NMR (C_6D_6): δ −11.92 (s, br, $AlCH_3$); 15.35 (s br, $AlCH_2S$); 22.07 (s, SCH_3). ^{27}Al NMR: δ 173 ($\nu_{1/2}$ = 2600 Hz). Anal. Calcd for $C_8H_{22}Al_2S_2$: C 40.65, H 9.38. Found: C 40.06, H 9.41.

Dimethyl(methylthiomethyl)gallium ($(Me_2GaCH_2SMe)_2$). The synthesis and purification of $(Me_2GaCH_2SMe)_2$ is analogous to that used for $[Me_2AlCH_2SMe]_2$ with methylthiomethyllithium (5.58 mmol, 0.38 g) and dimethylgallium chloride (5.58 mmol, 0.75 g). Yield: 0.61 g (62%), mp 67 °C, sublimation point 60 °C (0.01 mbar). CI-MS [*m*/*z* (%)]: 307 (40), [$M^+ - Me$]; 261 (26) [$M^+ - 4\ Me$]; 160 (40) [$M^+ - Me_2GaCH_2SMe$]; 145 (75) [$Me_2GaCH_2SMe - Me$]; 101 (100) [$GaS]^+$. ^1H NMR (C_6D_6): δ −0.12 (s, 12H, $GaCH_3$), 1.36 (s, 4H, $GaCH_2S$), 1.57 (s, 6H, SCH_3). $^{13}C\{^1H\}$ NMR (C_6D_6): δ −8.99 (s, $GaCH_3$); 18.43 (s, $GaCH_2S$); 22.32 (s, SCH_3). Anal. Calcd for $C_8H_{22}Ga_2S_2$: C 29.85, H 6.88. Found: C 29.68, H 6.89.

Dimethyl(methylthiomethyl)indium ($(Me_2InCH_2SMe)_2$). At −78 °C 60 mL of diethyl ether was condensed onto a mixture of methylthiomethyllithium (5.29 mmol, 0.36 g) and dimethylindium chloride (5.29 mmol, 0.95 g). The mixture was allowed to warm slowly to room temperature. The solid residue was separated by centrifugation. Filtration and concentration to 30 mL and storage at −78 °C yielded a colorless powder. Yield: 0.63 g (58%), mp 74 °C. CI-MS [*m*/*e* (%)]: 397 (21), [$M^+ - Me$]; 367(13), [$M^+ - 3\ Me$]; 321 (14) [$M^+ - 6\ Me$]; 206 (7) [$M^+ - Me_2InCH_2SMe$]; 191 (70) [$Me_2InCH_2SMe^+ - Me$]; 176 (4) [$Me_2InCH_2SMe^+ - 2Me$]; 145 (100) [$InS]^+$; 115 (33) [$In]^+$. ^1H NMR (C_6D_6): δ −0.03 (s, 12H, $InCH_3$), 1.36 (s, 4H, $InCH_2S$), 1.62 (s, 6H, SCH_3). $^{13}C\{^1H\}$ NMR (C_6D_6): δ −9.40 (s, $InCH_3$); 16.99 (s, $InCH_2S$); 24.07 (s, SCH_3). Anal. Calcd for $C_8H_{22}In_2S_2$: C 23.32, H 5.38. Found: C 23.10, H 5.31.

Reactions of the Thiomethylaluminum and Thiomethylgallium Compounds with Lewis Bases. The reactions were carried out in an NMR tube and are equilibrium reactions. The products were not isolated, and the characterization of the reaction was carried out by NMR spectrosopy. To a solution of 5 mg of the organometallic compound in 0.4 mL of benzene-d_6 was added 0.4 mL of diethyl ether or triethylamine, and the resulting solution was shaken. After about 5 min the spectra were recorded. $(Me_2AlCH_2SMe)_2 + OEt_2$: ^1H NMR (C_6D_6): δ −0.60 (s, $AlCH_3$), 1.06 (t, $^3J_{HH}$ = 7.0 Hz, OCH_2CH_3), 1.26 (s, $AlCH_2S$); 2.00 (s, SCH_3), 3.27 (q, $^3J_{HH}$ = 7.0 Hz, OCH_2CH_3). ^{27}Al NMR: δ 176 ($\nu_{1/2}$ = 3700 Hz). $(Me_2AlCH_2SMe)_2 + NEt_3$: ^1H NMR (C_6D_6): δ −0.65 (s, $AlCH_3$), 0.92 (t, $^3J_{HH}$ = 7.3 Hz, NCH_2CH_3), 1.26 (s, $AlCH_2S$); 2.07 (s, SCH_3), 2.36 (q, $^3J_{HH}$ = 7.2 Hz, NCH_2CH_3). ^{27}Al NMR: δ 173 ($\nu_{1/2}$ = 3100 Hz). $(Me_2GaCH_2SMe)_2 + NEt_3$: ^1H NMR (C_6D_6): δ −0.22 (s, $GaCH_3$), 0.92 (t, $^3J_{HH}$ = 7.3 Hz, NCH_2CH_3), 1.55 (s, $GaCH_2S$); 2.04 (s, SCH_3), 2.36 (q, $^3J_{HH}$ = 7.2 Hz, NCH_2CH_3).

Crystal Structure Determinations. Single crystals of $(Me_2AlCH_2SMe)_2$ and $(Me_2GaCH_2SMe)_2$ were selected under inert perfluoropolyether oil and fixed onto glass fibers in a small drop of this oil in the cryostream of an Enraf-Nonius Turbo-CAD4 diffractometer with Mo Kα radiation and graphite monochromator. Scattering intensities were measured as ω-scans, and the cell dimensions were deduced from 100 carefully centered reflections (θ-range 19−24°). Structure solution was by direct methods;[25] refinement by full-matrix least-squares methods. No absorption corrections were applied. Non-H atoms were refined with anisotropic thermal displacement parameters; hydrogen atoms were located in difference Fourier maps and refined isotropically. Further crystallographic data are listed in Table 1. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications no. CCDC-168357 [$(Me_2AlCH_2SMe)_2$] and CCDC-168358 [$(Me_2GaCH_2SMe)_2$]. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Results and Discussion

Preparation of the Compounds. The methylthiomethyl compounds $(Me_2AlCH_2SMe)_2$, $(Me_2GaCH_2SMe)_2$, and $(Me_2InCH_2SMe)_2$ were prepared by reacting methylthiomethyllithium $LiCH_2SMe$ with the dimethylmetal

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Table 1. Crystal Data and Refinement Parameters for the Structure Determinations of $(Me_2AlCH_2SMe)_2$ and $(Me_2GaCH_2SMe)_2$

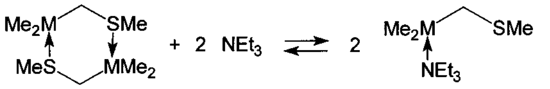
parameter	$(Me_2AlCH_2SMe)_2$	$(Me_2GaCH_2SMe)_2$
formula	$C_4H_{11}AlS$	$C_4H_{11}GaS$
M_r [g mol^{-1}]	118.17	160.91
T [K]	123(2)	148(2)
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$
a [Å]	7.4119(10)	7.419(2)
b [Å]	11.269(5)	11.222(2)
c [Å]	8.7251(9)	8.712(2)
β [deg]	107.677(12)	107.74(3)
V [Å^3]	694.4(3)	690.84
μ [mm^{-1}]	0.469	4.16
Z	4	4
R_1 [$I > 2\sigma(I)$]	0.039	0.021
wR_2 [all data]	0.1031	0.055

chlorides in hexane (eq 1). The crucial point in these syntheses is the application of pure, in particular donor-solvent-free, $LiCH_2SMe$, obtained by transmetalation of Bu_3SnCH_2SMe.[24]

$$2\ MeSCH_2Li + 2\ Me_2MCl \rightarrow (Me_2MCH_2SMe)_2 \qquad M = Al, Ga, In \quad (1)$$

The Al and Ga compounds obtained in this way could be crystallized from hexane at low temperatures, as they are quite soluble in nonpolar solvents such as hexane, pentane, and toluene and even more so in ethers. The indium compound is much less soluble in nonpolar solvents, but dissolves to some extent in diethyl ether and well in THF. The compounds are stable to heating to at least 60 °C, and the aluminum and gallium compounds can be sublimed at 45 °C/60 °C in a vacuum (10^{-2} mbar). All three compounds are sensitive to oxygen and water, but the sensitivity decreases significantly in the series aluminum, gallium, and indium.

Equilibrium Reactions of $(Me_2AlCH_2SMe)_2$ and $(Me_2GaCH_2SMe)_2$. We have explored the reactivity of $(Me_2AlCH_2SMe)_2$ and $(Me_2GaCH_2SMe)_2$ toward ring opening by Lewis bases. Both $(Me_2AlCH_2SMe)_2$ and $(Me_2GaCH_2SMe)_2$ react with diethyl ether and amines such as triethylamine in equilibrium reactions (eq 2), undergoing ring opening and coordination of the ether or amine as the stronger Lewis base to the Al and Ga centers.



(2)

The equilibrium is achieved after a few minutes at ambient temperature, as was shown by NMR experiments. In the NMR experiments employing triethylamine an excess of the base was added to a sample of the methylthiomethyl compound, and ^1H NMR spectra were recorded after a period of about 5 min. In these spectra the $AlMe_2$ signal was shifted to high field (from −0.48 to −0.65 ppm). The other signals were shifted to low field (CH_2 from 1.10 to 1.26 and SMe from 1.56 to 2.07 ppm). This is a striking difference, but comprehensible, as the SMe groups are no longer permanently involved in coordination of the aluminum, but replaced by the stronger base triethylamine. The signal in the ^{27}Al NMR spectrum is found unchanged at 173 ppm, but the half-width increases from 2600 Hz (dimer, no amine added) to 3100 Hz (amine added and coordinated). The ^1H NMR signals of triethylamine (only a single set occurs) remain nearly unchanged, which reflects a rapid exchange between coordinated and free triethylamine. They appear at 0.92 and 2.37 ppm (pure triethylamine 0.91 and 2.36). The results for the reaction of $(Me_2GaCH_2SMe)_2$ with triethylamine are analogous: Upon addition of triethylamine, the ^1H NMR signal for the Me_2Ga group changes from −0.12 to −0.22 ppm, that of the $GaCH_2S$ group from 1.36 to 1.55 ppm, and that of the SMe unit from 1.57 to 2.04 ppm.

Crystal Structures of $(Me_2AlCH_2SMe)_2$ and $(Me_2GaCH_2SMe)_2$. The crystalline phases of the compounds $(Me_2AlCH_2SMe)_2$ and $(Me_2GaCH_2SMe)_2$ are isomorphous, and both belong to the monoclinic space group $P2_1/n$ with $Z = 4$ formula units of the monomer in the unit cell. Both are dimeric with a crystallographic inversion center at the middle of the six-membered $M_2C_2S_2$ rings formed by Al−S and Ga−S donor−accep-

Table 2. Selected Bond Lengths and Angles for $(Me_2AlCH_2SMe)_2$ and $(Me_2GaCH_2SMe)_2$ (Å, deg) as Determined by Single Crystal X-ray Diffraction and by ab Initio Calculations at the MP2/6-31G(d) and B3LYP/6-311G(d) Levels of Theory

	$(Me_2AlCH_2SMe)_2$					$(Me_2GaCH_2SMe)_2$				
conformer:	A, all equatorial			B, all axial		A, all equatorial			B, all axial	
method:	XRD	MP2	DFT	MP2	DFT	XRD	MP2	DFT	MP2	DFT
M−C(1)	2.013(1)	2.023	2.037	2.032	2.036	2.016(2)	2.047	2.051	2.044	2.050
M−C(2)	1.973(1)	1.982	1.983	1.988	1.987	1.980(2)	1.999	2.000	2.007	2.004
M−C(3)	1.978(1)	1.985	1.984	1.985	1.986	1.977(2)	2.007	2.001	2.005	2.005
S−C(1)	1.796(1)	1.800	1.820	1.821	1.845	1.791(2)	1.800	1.817	1.819	1.838
S−C(4)	1.811(1)	1.813	1.832	1.087	1.825	1.805(2)	1.815	1.831	1.809	1.823
M−S′	2.412(1)	2.436	2.479	2.426	2.467	2.460(1)	2.484	2.553	2.481	2.540
∠M−C(1)−S	112.9(1)	112.9	114.5	122.8	123.9	111.6(1)	108.6	113.6	122.1	123.7
∠C(1)−S−M′	103.5(1)	104.9	104.6	106.4	106.2	103.7(1)	101.9	104.6	103.2	106.2
∠C(4)−S−M′	101.4(1)	101.9	102.5	105.0	105.4	100.8(1)	97.8	101.8	102.5	104.9
∠C(1)−M−C(2)	112.9(1)	112.8	112.0	118.8	118.6	113.6(1)	113.8	112.3	121.3	119.9
∠C(1)−M−C(3)	113.7(1)	114.1	114.9	109.3	109.3	114.6(1)	111.6	115.9	108.5	109.7
∠C(2)−M−C(3)	119.3(1)	120.3	119.7	118.9	118.5	120.2(1)	121.4	121.1	118.5	119.2
∠S−M−C(1)	100.5(1)	99.4	99.2	103.9	104.4	99.9(1)	101.8	98.4	105.2	103.3
∠S−M−C(2)	102.4(1)	102.0	102.3	101.1	101.0	100.9(1)	100.8	100.8	99.2	99.9
∠S−M−C(3)	105.0(1)	104.7	105.2	101.6	102.1	103.5(1)	104.1	103.6	100.3	100.6
∠C(1)−S−C(4)	104.4(1)	103.9	104.4	103.3	103.8	103.6(1)	104.0	103.8	102.8	103.6
Σ∠(MC_3)	345.9	347.2	346.6	347.0	346.4	348.4	346.8	349.3	348.3	348.8
ΔE		0.0	0.0	24.4	24.6		0.0	0.0	23.7	25.2

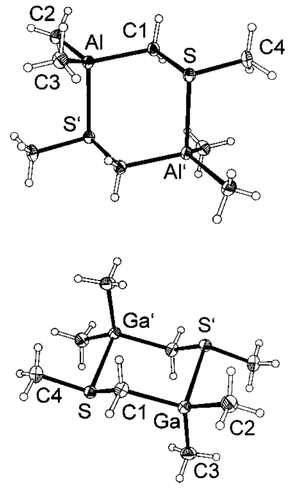
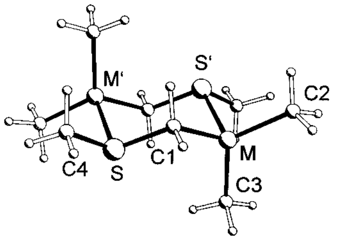
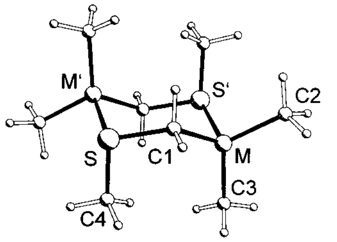


Figure 1. Crystal structures of $(Me_2AlCH_2SMe)_2$ and $(Me_2GaCH_2SMe)_2$. The atoms are displayed at the 50% probability level; the hydrogen atoms as circles of arbitrary size. Geometry parameter values are listed in Table 2.



all-equatorial



all-axial

Figure 2. Calculated molecular structures of the all-equatorial (ground state) and all-axial conformers of $(Me_2AlCH_2SMe)_2$ and $(Me_2GaCH_2SMe)_2$. Calculations were performed at the B3LYP/6-311G(d) level of theory. Geometry parameter values are listed in Table 2.

tor bonds (see Figure 1). This is in variance with the related thiophene compounds $[Me_2M(\mu\text{-}2\text{-}C_4H_3S)]_2$, which form four-membered rings bridged by carbon atoms of the thiophene ring.[10]

The ring systems adopt chair conformations in the solid state with the methyl groups on sulfur being in equatorial positions (compare Figure 2). The sulfur atoms are thus pseudo-tetrahedrally coordinated, while the lone electron pairs point in axial direction. Although further intermolecular contacts would be possible utilizing the remaining lone pair of electrons of the sulfur centers and by increasing the coordination number of the metal centers to five, no such interactions are observed in the crystal phases.

In both compounds $(Me_2AlCH_2SMe)_2$ and $(Me_2GaCH_2SMe)_2$, the endocyclic metal−carbon distances are almost 0.04 Å longer than the exocyclic M−C distances, which are in both cases the same in terms of standard deviations. On the other hand, the endocyclic C−S distances are shorter by 0.014 Å than the exocyclic C−S bonds. A comparison with the C−S bond lengths in Me_2S [1.802(2) Å in the gas phase[26] and 1.794 Å (average) in the crystal phase][27] shows that the data have to be interpreted as a widening of the exocyclic C−S bond rather than shortening of the endocylic one.

The valence angles M−C(1)−S at these endocyclic carbon atoms are somewhat larger (112.9° and 111.6°) than the ideal tetrahedral angle. This proves the absence of structure-determining attractive intramolecular forces between the electronegative S and the electropositive metal centers.

The sum of angles of the primary coordination sphere MC_3 are 345.9° for $(Me_2AlCH_2SMe)_2$ and 348.4° for $(Me_2GaCH_2SMe)_2$, which deviate significantly from the value of 328.4° for an ideal tetrahedron. This is further illustrated by the values for the declination of the vector M−C(1) from the MC(2)C(3) plane, which would be 54.7° for an ideal tetrahedron but is 38.5° for $(Me_2AlCH_2SMe)_2$ and 35.0° for $(Me_2GaCH_2SMe)_2$. The Al−S bond in $(Me_2AlCH_2SMe)_2$ is somewhat shorter (2.412 Å) than that in gaseous $Me_3Al{-}SMe_2$ [2.55(2) Å].[28] As a matter of fact, dative bonds of simple Lewis-acid−base adducts are shorter in the solid state than in the gas phase, due to the interaction of the bond dipole with other dipoles of the surrounding molecules in the crystal.[29] In solid $Me_3Al{-}SMe_2$ the Al−S distance is 2.461 Å on average,[30] which corresponds to a shortening of 0.06 Å in solid $(Me_2AlCH_2SMe)_2$, despite the center of inversion in our molecules, which leads to a complete cancellation of the molecular dipole moments. However, the dative bond on one side of the ring experiences the dipole on the other side, which definitely makes this situation more polar than for an isolated molecule in the gas phase.

Interestingly, the coordination geometry at sulfur in $(Me_2AlCH_2SMe)_2$ and $(Me_2GaCH_2SMe)_2$ is steeply pyramidal, and the declinations of the M−S vectors from the CSC planes are 69.5° and 69.9°. This seemed to be in contradiction to the value of 31(5)° for gaseous $Me_3Al{-}SMe_2$,[29] but is in best agreement with the values of 69.2° and 69.6° for solid $Me_3Al{-}SMe_2$ and $Me_3Ga{-}SMe_2$, which were recently determined in our group.[30]

Spectroscopy. The proton NMR spectra of $(Me_2AlCH_2SMe)_2$, $(Me_2GaCH_2SMe)_2$, and $(Me_2InCH_2SMe)_2$ recorded from C_6D_6 solutions at 21 °C show three singlets with an intensity ratio of 3:2:6. For these three compounds they correspond to the S-bound methyl groups (1.56, 1.57, and 1.62 ppm), the methylene units (1.10, 1.36, and 1.36 ppm), and the two methyl groups bound to the metals (−0.48, −0.12, and −0.03 ppm). The same pattern is observed in the ^{13}C NMR spectra, which

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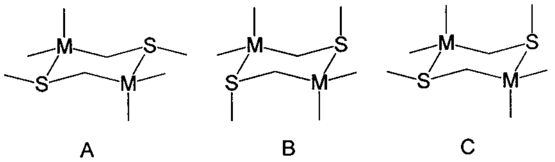
Scheme 1



contain also three signals for S-bound methyl groups (22.07, 22.32, and 24.07 ppm), the methylene unit (15.35, 18.43, and 16.99 ppm), and the two methyl groups bound to the metals (−11.92, −8.99, and −9.40 ppm). Both the ^1H and the ^{13}C NMR data sets reflect the different electronic effects of Al, Ga, and In, but no clear relationship to either the nuclear charge or the electronegativity can be derived.

Noteworthy are the relatively large shifts of the ^1H and ^{13}C NMR signals of the methyl groups on the sulfur atoms (1.56/1.57 and 22.07/22.32 ppm) as compared to the resonances in free Me_2S (1.82 and 17.80 ppm). This observation corresponds to the elongation of this exocyclic bond relative to the C−S bond length in Me_2S (see above).

The ^{27}Al NMR spectrum of $(Me_2AlCH_2SMe)_2$ shows a singlet at 173 ppm, which clearly indicates a coordination number of four at this center in solution.[31]

Molecular Dynamics in Solution. The proton NMR spectra of our three $(Me_2MCH_2SMe)_2$ compounds at ambient temperature consist of three lines in each case. Upon cooling, the signals of the endocyclic methylene units split into two well-resolved doublets. The coalescence temperature for this process is −60 °C. Concurrently the signals of the methyl groups at the metals also split, but only to a small extent, which is only resolved at −80 °C and below.

As depicted in Scheme 1, a mixture of conformers could be expected, with the methyl groups on sulfur either both in equatorial position (as found in the solid state, conformer A), both in axial position (conformer B), or one in axial and one in equatorial position (conformer C).

The first two conformers would be interconverted by rapid inversion of the chair conformation of the M−C−S−M−C−S rings. However, for the mixed conformer C such a process should not be possible and thus should lead to a separate contribution to the NMR spectra.

The resonances of the methyl groups on sulfur, however, do not appear to reflect the dynamic behavior of the molecule, as they appear as singlets down to the lowest temperatures applied (−95 °C). This can only be explained by assuming a very rapid inversion of the tricoordinate sulfur center, which relaxes always in the energetically most favorable equatorial position. The energy barrier for ring inversion can be estimated to be 39.5(20) kJ mol^{-1} (derived from the signals of the CH_2 groups) and 41.2(20) kJ mol^{-1} (derived from the signals of the $AlMe_2$ groups) for the compound $(Me_2AlCH_2SMe)_2$ and 36.4(20) kJ mol^{-1} for the compound $(Me_2GaCH_2SMe)_2$, which is about in the same range as that for cyclohexane (42.6 ± 0.8 kJ mol^{-1}).[32] The occurrence of the splitting of the (metal)methyl resonances at lower temperatures is due to the small split, but the barriers of inversion calculated from both sorts of signals are consistent within the given experimental errors.

To obtain an estimate of the energy difference between the different conformers of $(Me_2AlCH_2SMe)_2$ and $(Me_2GaCH_2SMe)_2$, we optimized the structures of the conformers A and B for these compounds (see Figure 2), which were found to be minima in C_i symmetry. We performed no calculations on the conformer C, as the lower symmetry would have resulted in too long a computational time. The results of these calculations are depicted in Figure 2. In general, the results of the MP2/6-31G(d) and B3LYP/6-311G(d) levels of theory gave geometries that are in good agreement with those obtained from our X-ray diffraction experiments (see Table 1). However, despite the larger basis set, the DFT method was not able to predict the lengths of the Al−S and Ga−S donor bonds correctly and the estimates are 0.04 and 0.07 Å longer at the B3LYP/6-311G(d) level than in the MP2/6-31G(d) calculations. Even in the latter case these parameters are longer than found by crystallography, but this can be rationalized by the different phases, as gaseous molecules of $Me_3Al-SMe_2$ also have longer Al−S bonds than the molecules in the crystal lattice.

The energy differences between conformers A and B are in the range of 25 kJ mol^{-1} for both compounds and for both levels of theory. The contribution of one MeS group can be estimated as half this amount. We could not calculate the energies of the transition states of inversion for the molecules under consideration, but we have done model calculations for the barrier to inversion of the sulfur pyramid in H_3Al-SH_2 and H_3Ga-SH_2 (MP2/6-311G(d), under restriction to C_s symmetry, the symmetry of the ground state), which came out to be 36.5 and 35.7 kJ mol^{-1}. Thus it seems clear that despite that the conformer B is a minimum on the potential hypersurface, the barrier to sulfur inversion is too small to allow the observation of contributions of both conformers in the low-temperature NMR experiments. The higher energy of the conformers B furthermore contributes to a more facile crossing of the inversion barrier and is thus never observed, and the methyl groups on sulfur appear always as single signals in the spectra. The splitting of the other signals reflects that there are two independent dynamic processes, ring inversion and sulfur inversion, taking place at the same time.

We have prepared the first compounds to contain a saturated M−C−S linkage for the metals aluminum, gallium, and indium. The absence of sterically demanding substituents showed that these compounds generally adopt dimeric structures with a chair conformation typical for a six-membered ring system. These structures are highly dynamic with respect to ring inversion, but also concerning the inversion of the tricoordinate sulfur centers. The dimers occur in all phases, the crystals (XRD), the solution (VTNMR), and the gas phase (MS).

By addition of Lewis bases stronger than Me_2S the six-membered rings are opened to give the monomers bound to the Lewis base via the metal atom. This is an equilibrium process in solution. The compounds are also well soluble in noncoordinating solvents such as hydro-

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carbons. This means that they could be applied as nucleophilic thiomethylating reagents in homogeneous solution, which would have some advantages over the corresponding lithium reagents, which are not soluble in hydrocarbons.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the Leonhard-Lorenz-Stiftung. We are grateful to Professor H. Schmidbaur for generous support.

Supporting Information Available: Tables of crystal data, atomic coordinates, equivalent isotropic thermal parameters, and full lists of bond lengths and angles for the compounds $(Me_2AlCH_2SMe)_2$ and $(Me_2GaCH_2SMe)_2$.

OM0107338