

Synthesis and Characterization of Group 13 Compounds of 2-Acetylpyridine Thiosemicarbazone. Single-Crystal Structure of $(i\text{-C}_4\text{H}_9)_2\text{Al}(\text{NC}_5\text{H}_4\text{C}(\text{CH}_3)\text{NNC}(\text{S})\text{NHPh})$

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Novel mononuclear group 13 metal complexes with the formula $(\text{R}_2\text{M})\{\text{NC}_5\text{H}_4\text{C}(\text{CH}_3)\text{NNC}(\text{S})\text{NH}(\text{C}_6\text{H}_5)\}$ ($\text{M}=\text{Al}$, $\text{R}=\text{i-C}_4\text{H}_9$ (**1**); $\text{M}=\text{Ga}$, $\text{R}=\text{i-C}_4\text{H}_9$ (**2**); $\text{M}=\text{Al}$, $\text{R}=\text{CH}_2\text{SiMe}_3$ (**3**); $\text{M}=\text{Ga}$, $\text{R}=\text{CH}_2\text{SiMe}_3$ (**4**)) result when 2-acetyl pyridine 4-phenyl-thiosemicarbazone ligand is mixed with trialkyl aluminum or trialkylgallium. These compounds **1-4** are characterized by microanalysis, NMR (^1H , ^{13}C) spectroscopy, mass spectra, and single-crystal X-ray diffraction. X-ray single-crystal diffraction analysis reveals that **1** is mononuclear metal compound with coordination number of 5 and N, N, S-coordination mode.

Introduction

The terdentate heterocyclic carboxaldehyde thiosemicarbazones have been extensively studied for activity against bacterial¹ and viral² infections, tuberculosis,³ and rheumatism.⁴ Thiosemicarbazones have been shown to form complexes with various transition-metal ions, including Cu(II),⁵ Ni(II),⁶ Co(II),⁷ Fe(II),⁸ and Hg(I).⁹ In particular, gallium(III) complexes of acetylpyridine thiosemicarbazones continue to attract attention due to the fact that the $^{67}\text{Ga}/^{68}\text{Ga}$ may offer a convenient source of γ -ray emitters for positron emission tomography imaging in institutions that do not have a site cyclotron.¹⁰ Although Kepper and co-workers¹¹ developed gallium complexes employing the ligands, which themselves had antiviral and antitumor activity, the coordination chemistry of the thiosemicarbazone ligands with aluminum and gallium remains relatively unexplored.

Recently, we prepared a series of mononuclear group 13 heterocyclic carboxaldehyde thiosemicarbazone complexes $\text{Me}_2\text{M}[\text{NC}_5\text{H}_4\text{C}(\text{CH}_3)\text{NNC}(\text{S})\text{SMe}]$ ($\text{M}=\text{Ga}$, In),¹² dinuclear group 13 complexes $(\text{Me}_2\text{M})[\text{NC}_5\text{H}_4\text{CMe}\text{NNC}(\text{S})\text{NC}_3\text{H}_7](\text{MMe}_2)$ ($\text{M}=\text{Al}$, Ga),¹³ trinuclear group 13 bis(thiosemicarbazone) complexes $(\text{MeM})\{\text{CH}_2[\text{C}(\text{Me})\text{NNC}(\text{S})(\text{NR})]_2\}(\text{MMe}_2)_2$ ($\text{M}=\text{Al}$, Ga ; $\text{R}=\text{Me}$, Et , Ph),¹⁴ and tetranuclear metal complexes with the formula $[(\text{MeM})\{\text{NC}_4\text{H}_3\text{CHNNC}(\text{S})\text{NR}\}(\text{MMe}_2)]_2$ ($\text{M}=\text{Al}$, Ga ; $\text{R}=\text{Me}$, $\text{i-C}_3\text{H}_7$).¹⁵ Since the thiosemicarbazone has the coordination ability that contains one thiol group or one $\text{HN-C}=\text{S}$ donor entity via a tautomerism, the above complexes can be synthesized by the evolution of a methane from the interaction of $\text{AlMe}_3/\text{GaMe}_3$ with N-H/S-H bonds. As part of our continuing studies on the synthetic utility and understanding of the unusual coordination geometry of these ligands with aluminum and gallium complexes, we attempted to react these ligands with bulky alkyl aluminum and gallium instead of methyl group in order to check the bonding mode. We report the synthesis and characterization of group 13 complexes of acetylpyri-

dine thiosemicarbazone and the single-crystal X-ray structure of one of these.

Experimental Section

General Procedures. All experiments were performed in a dry nitrogen atmosphere using standard Schlenk techniques. Toluene and hexane were distilled under an atmosphere of nitrogen from sodium benzophenone ketyl. AlCl_3 and GaCl_3 were purchased from Strem Chemicals. 4-Alkyl-3-thiosemicarbazide($\text{H}_2\text{NNHC}(\text{S})\text{NHR}$) and 2-acetylpyridine were purchased from Aldrich Chemicals and used without further purification. The ligand $[\text{NC}_5\text{H}_4\text{CMe}\text{NNC}(\text{S})\text{NH-C}_6\text{H}_5]$ was prepared according to the literature.¹³ ^1H and ^{13}C $\{^1\text{H}\}$ NMR spectra were collected using a Bruker WH-300 spectrometer. The ^1H and ^{13}C chemical shifts were referenced to benzene- d_6 (^1H , 7.16; $^{13}\text{C}\{^1\text{H}\}$, 128.00). IR spectra were recorded on a Shimadzu FT-IR 8501 spectrometer. Mass spectra were recorded on a high-resolution VG 70-VSEG instrument, and elemental analyses were performed by the Basic Science Center. The compounds $[\text{M}(\text{CH}_2\text{CHMe}_2)_3]$ and $[\text{M}(\text{CH}_2\text{SiMe}_3)_3]$ ($\text{M}=\text{Al}$, Ga) were prepared according to the literature.¹⁶

General Synthesis of $\{\text{M}(\text{CH}_2\text{CCHMe}_2)_2\}(\text{NC}_5\text{H}_4\text{C}(\text{CH}_3)\text{NNC}(\text{S})\text{NHR})$. In a typical synthesis, a solution of 2-acetylpyridine-4-phenylthiosemicarbazones (1.8 mmol) in toluene (20 mL) was treated with MR_3 (3.6 mmol) at room temperature. The stirred mixture was heated to 100-110 °C, during which the suspension dissolved. The resulting yellow solution was stirred at the same temperature for 3-4 h and then allowed to cool to 25 °C. The volatiles were removed under vacuum and washed with hexane (20 mL). The product was extracted with toluene (25 mL) and cooled to -20 °C for 24 hr. The orange solid was collected by filtration and dried under vacuum (65-72% yield). Crystals suitable for x-ray crystallography were obtained by recrystallization from toluene/hexane.

(C_4H_9)₂Al(NC₅H₄C(CH₃)NNC(S)NH(C₆H₅)) (1). Mp: 158-162 °C. ¹H NMR (C₆D₆, 25 °C): δ 8.16-6.47 (m, 9H, Py and Ph), 2.31 (d of sept, *J*=6.32 Hz, 1H, CH), 2.22 (s, 1H, NH), 2.07 (s, 3H, CH₃), 1.30 (d, *J*=6.32 Hz, 6H, CH(CH₃)₂), 1.12 (d, *J*=6.32 Hz, 6H, CH(CH₃)₂), 0.64 (dd, *J*=6.32 Hz and *J*=12.48 Hz, 2H, CH₂), 0.47 (dd, *J*=6.32 Hz, *J*=12.48 Hz, 2H, CH₂). ¹³C{¹H} NMR (C₆D₆, 25 °C): δ 178.23 (CS), 151.01 (C(CH₃)N), 148.63, 146.39, 140.45, 138.98, 135.80, 129.97, 125.64, 123.81, 123.06, 121.16, 119.92 (Py and Ph), 24.78(NCH₃), 20.62 (CHCH₃), 14.43 (CHCH₃), 0.32 (Al(CH₂), 0.12(AlCH₂). IR (KBr pellet; cm⁻¹): 3224 (m), 2992 (w), 2932 (w), 1592 (m), 1534 (m), 1506 (br), 1482 (s), 1438 (s), 1428 (br), 1372 (m), 1336 (w), 1296 (w), 1272 (w), 1264 (w), 1236 (br), 1162 (s), 1126 (m), 1104 (w), 1092 (w), 1066 (w), 1018 (w), 992 (br), 974 (w), 944 (w), 924 (w), 824 (br), 774 (m), 678 (m), 662 (w). MS (EI): *m/z* 410 [M⁺], 353 [M⁺-CH₂CHMe₂]. Anal. Calcd for C₂₂H₃₀AlN₄S: C, 64.46; H, 7.33. Found: C, 64.18; H, 7.18.

(C_4H_9)₂Ga(NC₅H₄C(CH₃)NNC(S)NH(C₆H₅)) (2). Mp: 154-158 °C. ¹H NMR (C₆D₆, 25 °C): δ 8.16-6.54 (m, 9H, Py and Ph), 2.36 (d of sept, *J*=6.28 Hz, 1H, CH), 2.26 (s, 1H, NH), 2.14 (s, 3H, CH₃), 1.36 (d, *J*=6.32 Hz, 6H, CH(CH₃)₂), 1.16 (d, *J*=6.32 Hz, 6H, CH(CH₃)₂), 0.58 (dd, *J*=6.28 Hz and *J*=12.26 Hz, 2H, CH₂), 0.42 (dd, *J*=6.28 Hz, *J*=12.26 Hz, 2H, CH₂). ¹³C{¹H} NMR (C₆D₆, 25 °C): δ 180.22 (CS), 150.92 (C(CH₃)N), 148.01, 146.74, 142.74, 137.94, 135.48, 130.06, 127.86, 124.52, 123.22, 122.02, 120.28 (Py and Ph), 24.22(NCH₃), 18.84 (CHCH₃), 14.28 (CHCH₃), 0.36 (AlCH₂), 0.18 (AlCH₂). IR (KBr pellet; cm⁻¹): 3301 (m), 2995 (w), 2974 (w), 2942 (w), 1590 (m), 1541 (m), 1511 (br), 1480 (s), 1442 (s), 1426 (br), 1374 (m), 1342 (w), 1292 (w), 1276 (w), 1260 (w), 1239 (m), 1164 (s), 1130 (m), 1106 (w), 1088 (w), 1062 (w), 1022 (w), 990 (br), 970 (w), 942 (w), 922 (w), 822 (m), 782 (m), 672 (m), 660 (w). MS (EI): *m/z* 453 [M⁺]. Anal. Calcd for C₂₂H₃₀GaN₄S: C, 58.24; H, 6.62. Found: C, 58.62; H, 6.76.

(CH₂SiMe₃)₂Al(NC₅H₄C(CH₃)NNC(S)NH(C₆H₅)) (3). Mp: 162-165 °C. ¹H NMR (C₆D₆, 25 °C): δ 8.04-6.48 (m, 9H, Py and Ph), 2.31 (s, 1H, NH), 2.08 (s, 3H, CH₃), 2.08 (s, 3H, CH₃), 0.48 (d, *J*=6.02 Hz, 2H, CH₂), 0.36 (d, *J*=6.02 Hz, 2H, CH₂), 0.14 (s, 9H, Si-CH₃), 0.09 (s, 9H, Si-CH₃). ¹³C{¹H} NMR (C₆D₆, 25 °C): δ 178.82 (CS), 150.22 (C(CH₃)N), 147.72, 145.38, 141.97, 136.08, 134.12, 130.24, 128.02, 123.86, 122.36, 120.74, (Py and Ph), 23.96(NCH₃), 0.32 (AlCH₂), 0.22 (AlCH₂), 0.12 (Si-CH₃). IR (KBr pellet; cm⁻¹): 3292 (m), 2992 (m), 2834 (w), 1588 (m), 1564 (m), 1538 (m), 1508 (m), 1476 (s), 1440 (s), 1386 (m), 1338 (m), 1288 (m), 1272 (w), 1233 (m), 1172 (m), 1128 (m), 1082 (w), 1064 (w), 1018 (w), 988 (m), 952 (w), 920 (w), 830 (m), 784 (m), 676 (m), 656 (m). Anal. Calcd for C₂₂H₃₄AlN₄SSi: C, 59.78; H, 7.70. Found: C, 59.26; H, 7.48.

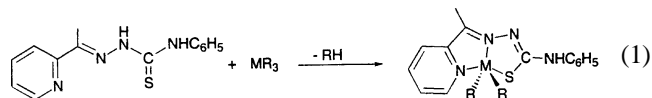
(CH₂SiMe₃)₂Ga(NC₅H₄C(CH₃)NNC(S)NH(C₆H₅)) (4). Mp: 159-166 °C. ¹H NMR (C₆D₆, 25 °C): δ 8.12-6.46 (m, 9H, Py and Ph), 2.28 (s, 1H, NH), 2.14 (s, 3H, CH₃), 0.52 (d, *J*=5.96 Hz, 2H, CH₂), 0.34 (d, *J*=5.96 Hz, 2H, CH₂), 0.14 (s, 9H, Si-CH₃), 0.08 (s, 9H, Si-CH₃). ¹³C{¹H} NMR (C₆D₆, 25 °C): δ 180.22 (CS), 151.04 (C(CH₃)N), 148.04, 146.21,

141.84, 136.64, 134.08, 130.48, 128.66, 124.35, 123.94, 122.06, 120.62 (Py and Ph), 23.26 (NCH₃), 0.28 (GaCH₂), 0.18 (GaCH₂), 0.12 (Si-CH₃), 0.06 (Si-CH₃). IR (KBr pellet; cm⁻¹): 3302 (w), 2986 (m), 2926 (m), 1592 (m), 1558 (m), 1514 (m), 1472 (s), 1442 (s), 1382 (m), 1344 (m), 1282 (w), 1264 (w), 1228 (m), 1168 (m), 1134 (m), 1086 (w), 1062 (w), 1024 (m), 992 (m), 946 (w), 924 (w), 836 (m), 778 (m), 672 (m), 662 (w). Anal. Calcd for C₂₂H₃₄GaN₄SSi: C, 54.39; H, 7.00. Found: C, 54.72; H, 6.82.

X-ray Structure Analysis of Compound 1. Crystals of **1** were grown from toluene-hexane. Diffraction data were collected on a Rigaku/RAXIS IIC area detector by employing graphite-monochromated Mo K α radiation ($\lambda=0.7102$ Å) at 298 K. Indexing was performed from a series of 1 oscillation images with exposures of 5 min/frame. A total of 3998 reflections were measured over the following ranges: 0.0=2 θ =49.9°, 0=h=12, -18=k=17, -9=l=9. Of the reflections measured, a total of 2490 unique reflections with F²>3.0 σ (F²) were used during subsequent structure refinement. The structure was solved by direct methods and refined by full-matrix least-squares techniques based on F to minimize the quantity $\sum w(F_o - F_c)^2$, with $w=1/\sigma^2(F)$. Non-hydrogen atoms were anisotropically refined, and hydrogen atoms were included as constant contributions to the structure factors and were not refined. The structure of **1** was solved using SHELXS-86. Least-squares refinement of scale factors and positional and anisotropic thermal parameters for non-hydrogen atoms was carried out using SHELXL-93. Refinement converged to R(Rw)=0.0670 (0.0459).

Results and Discussion

The reaction of 2-acetylpyridine 4-phenyl-thiosemicarbazone with tri-alkylaluminum or -gallium in toluene at 100-110 °C affords the corresponding mononuclear organoaluminum or gallium complexes in which one hydrogen atom has been lost from the aza hydrogen atom via the alkane elimination reaction according to eq 1.



M=Al, R= C_4H_9 (**1**); M=Al, R=CH₂SiMe₃ (**3**)
M=Ga, R= C_4H_9 (**2**); M=Ga, R=CH₂SiMe₃ (**4**)

The resulting orange products **1-4** were isolated as relatively air-stable, crystalline solids in 65-72% yield. The unusual air stability of this family of group 13 compounds is attributed to steric bulkiness of the alkyl group. These compounds are readily soluble in benzene, toluene, chloroform, and THF.

The ¹H NMR and ¹³C NMR data for **1** support the proposed structure. In particular, the ¹H NMR displayed the characteristic signals of methylene protons at 0.64 ppm and 0.47 ppm (*J*_{H-H}=6.32 Hz and *J*_{H-H}=12.48 Hz) (Figure 1). The spin system of methylene protons is AB, showing a doublet of doublets pattern. The methyl groups of the *iso*-propyl moieties give rise to two doublets at δ 1.30 and 1.12, indicating that the two alkyl groups are in a different environment;

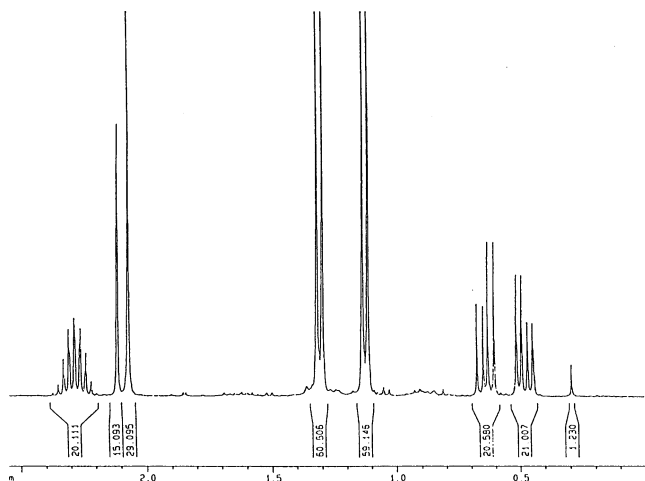


Figure 1. ^1H NMR spectrum of **1** in C_6D_6 .

the methyne CH protons give rise to a doublet of septets resonance at δ 2.31 and the CCH_3 and NH protons give rise to two distinct peaks at 2.07 and 2.22 ppm, respectively. The ^{13}C NMR spectrum of **1** shows two resonances at δ 0.32 and 0.12 ppm, which are due to the carbon atoms of the two Al- CH_2 groups. The carbons (C(10) and C(7)) attached to the CS and imine groups appear at δ 178.23 and 151.01, respectively. The chemical shifts of the two carbons are consistent with prior observations of five-coordinate Al atoms.¹⁷ The ^1H and ^{13}C NMR spectra of the other complexes are well in agreement with those of the compound **1**. The IR spectrum of **1** shows a peak at 1592 cm^{-1} assigned to the ring deformation mode. The stretching mode of $\nu(\text{CS})$ at 774 cm^{-1} is significantly decreased. This could involve a tautomerism for

Table 1. Crystallographic Data for **1**

molecular formula	$\text{C}_{22}\text{H}_{30}\text{AlN}_4\text{S}$
fw	409.55
crystal system	triclinic
space group	P-1
a, Å	10.9160(5)
b, Å	15.5740(9)
c, Å	8.4410(5)
α , deg	100.690(3)
β , deg	107.870(4)
γ , deg	102.740(3)
V, Å ³	1281.7(1)
Z	2
D _{calcd} , gcm ⁻³	1.061
temp, °C	25
radiation (wavelength, Å)	Mo K α (0.7102)
θ_{max} , deg	24.96
limiting indices	$0 \leq h \leq 12, -18 \leq k \leq 17, -9 \leq l \leq 9$
no. of reflns recorded	3998
no. of nonequiv reflns recorded	2490
no. of params refined	299
extinction coef	15.18746
goodness of fit	3.063
R(Rw) ^a	0.0670(0.0459)

$$^a R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}; \text{Rw} = \frac{\sum \omega(|F_o| - |F_c|)^2}{\sum \omega |F_o|^2}^{1/2}$$

Table 2. Selected Bond Distances (Å) and angles (deg) for **1**

S(1)-Al(1)	2.434(2)	N(1)-C(6)	1.365(5)
S(1)-C(10)	1.717(4)	N(8)-N(9)	1.387(4)
Al(1)-N(1)	2.091(4)	N(8)-C(7)	1.304(5)
Al(1)-N(8)	2.051(3)	N(9)-C(10)	1.317(5)
Al(1)-C(19)	1.982(5)	N(11)-C(10)	1.366(5)
Al(1)-C(23)	1.985(5)	N(11)-C(12)	1.417(4)
Al(1)-C(2)	1.316(5)		
Al(1)-S(1)-C(10)	96.0(2)	N(8)-Al(1)-C(23)	129.5(2)
S(1)-Al(1)-N(1)	154.7(1)	C(19)-Al(1)-C(23)	120.4(2)
S(1)-Al(1)-N(8)	79.2(1)	Al(1)-N(1)-C(2)	125.4(3)
S(1)-Al(1)-C(19)	102.6(2)	Al(1)-N(1)-C(6)	116.0(3)
S(1)-Al(1)-C(23)	95.7(1)	C(2)-N(1)-C(6)	118.4(4)
N(1)-Al(1)-N(8)	76.0(1)	Al(1)-N(8)-N(9)	125.5(3)
N(1)-Al(1)-C(19)	90.4(2)	Al(1)-N(8)-C(7)	118.6(3)
N(1)-Al(1)-C(23)	96.3(2)	N(9)-N(8)-C(7)	115.7(3)
N(8)-Al(1)-C(19)	109.6(2)	N(8)-N(9)-C(10)	112.7(3)

semicarbazone-3-thiol, *i.e.*, a 1,3-proton shift. The mass spectrum of **1** showed the presence of a parent ion in addition to species arising from fragmentations of the alkyl groups. Although all the spectra are consistent with the proposed formulation, the bonding mode in **1** is still unclear. Accordingly, the monomeric nature and the coordination geometry of the aluminum were confirmed through single-crystal X-ray diffraction analysis.

Description of the Molecular Structure of 1. Crystals of **1** suitable for an X-ray diffraction study were grown from toluene/hexane at $-20\text{ }^\circ\text{C}$, and the structure of **1** was determined from data collected at $25\text{ }^\circ\text{C}$. Details of the X-ray data collection and structure refinement for compound **1** are presented in Table 1. The molecular structure and atom-numbering schemes for **1** are given in Figure 2. Selected bond distances and angles are given in Table 2. As shown in Figure 1, the molecule consists of a series of one five-membered AlNC_2N and one five-membered AlN_2CS rings.

Several points are worthy of note regarding the structure and bonding in **1**. Compound **1** contains one type of dialkylaluminum fragment, due probably to the steric bulkiness of the alkyl group. When trimethylaluminum was used instead of trialkylaluminum in the reaction of 2-acetylpyridine 4-alkyl-thiosemicarbazone, the product contains two types of dimethylaluminum fragment by further reaction of trimethylaluminum with the aza hydrogen atom. An examination of Al(1) reveals it to be five-coordinate bonded to an axially positioned pyridyl nitrogen, N(1), and thiolato atom, S(1). Atoms N(8), Al(1), C(19), and C(23) constitute an equatorial plane, while the coordination sphere of Al(1) is completed by N(1) and S(1) residing in the axial positions. As the N(1)-Al(1)-S(1) bond angle is $154.7(1)^\circ$ and the sum of the bond angles surrounding the Al atom on the equatorial plane is 359.7° , the coordination may be described as a distorted trigonal bipyramidal (tbp). The distortion is mainly caused by the rigid geometry of the 2-acetylpyridine thiosemicarbazone ligand (bite angle, N(1)-Al(1)-N(8) $70.0(1)^\circ$; N(8)-Al(1)-S(1) $79.2(1)^\circ$), which prevents them from occupying the exact tbp position. The distorted geometry was found in

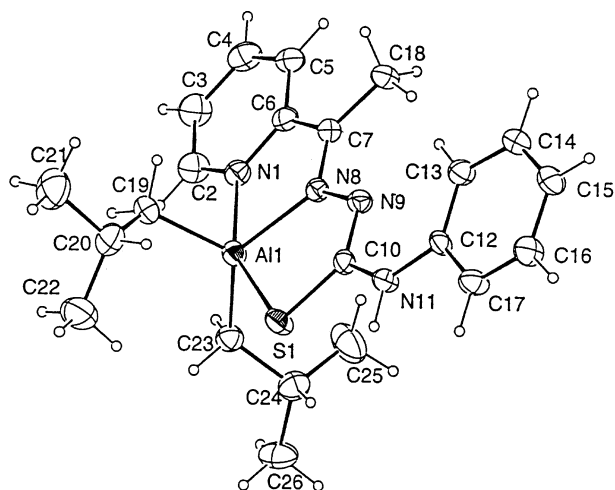


Figure 2. Structure of $(\text{C}_4\text{H}_9)_2\text{Al}(\text{NC}_3\text{H}_4\text{C}(\text{CH}_3)\text{NNC}(\text{S})\text{NH}(\text{C}_6\text{H}_5))$, showing the 30% thermal ellipsoids and atom-labelling scheme.

other structural reports of the neutral five-coordinate organoaluminum complexes.¹⁸ The axial imine Al(1)-N(1) bond distance (2.091(4) Å) is longer than the equatorial imine Al(1)-N(8) distance (2.051(3) Å). The Al(1)-S(1) bond distance (2.434(2) Å) is comparable to those observed for $\text{K}[\text{Al}_2(\text{CH}_3)_6\text{SCN}]$ (2.498(2) Å),¹⁹ and $[\text{Al}(\text{CH}_3)_3]_4[\text{14}] \text{aneS}_4$ (2.522(2) Å).²⁰ The Al(1)-C(19) and Al(1)-C(23) bond distances (1.982(5) Å and 1.985(5) Å) fall well within the range commonly found for five-coordinate aluminum complexes.²¹ The methylene ligands are rotated away from the equatorial nitrogen atom (N(8)), giving an average C-Al-N angle of 119.5(2)°. Two isopropyl groups are located away from each other in order to prevent the steric hindrance.

Conclusion

The four new compounds expand upon the few examples of well-characterized aluminum and gallium complexes of N-heterocyclic carboxaldehyde thiosemicarbazones. The terdentate acetylpyridine thiosemi-carbazones, which have a thiol group via a tautomerism, are valuable for the synthesis of new polynuclear alkylaluminum and -gallium complexes with different coordination environments. In addition, modification of the organic substituents on aluminum and gallium should allow tuning of their steric bulk and, as a result, the derivatives of the product compounds. The reaction of bulky trialkyl aluminum and gallium with thiosemicarbazone gives products displaying complicated bonding modes that require further investigation in order to be understood.

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Supplementry Material Available: Tables of crystal data, atom coordinates, selected bond distances and angles, and anisotropic thermal parameters for compound **1** (12 page). Ordering information is given on any current masthead page.

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