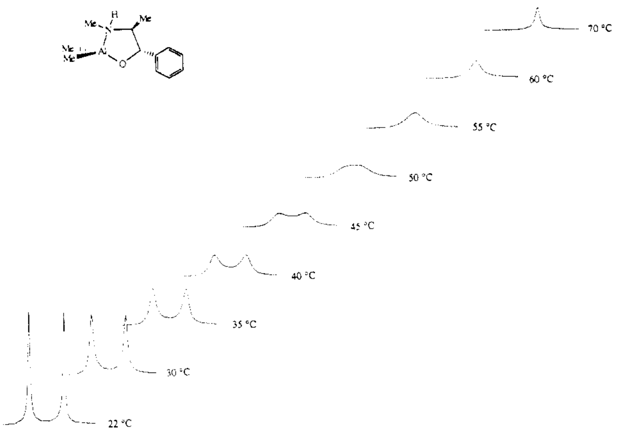

Figure 2. Variable-temperature ^{1}H NMR of 1 (0.205 M, toluene-d_8). Only the region associated with the methyl groups bound to aluminum is shown.

trogen atoms in the unit cell be equivalent. Second this is the first example of a monodentate secondary amine bound to a five-coordinate Al atom and has an unusually long Al–N distance of 2.19 Å. Third, the two methyl groups on aluminum, C1 and C2, are nonequivalent by symmetry. Each of these features influences the behavior of this compound. The first through the induction of the optical activity at the nitrogen already cited, while the second and third are of importance in the dynamic exchange processes associated with this molecule.

The geometry around the aluminum center can be described as distorted trigonal bipyramidal, where both aluminum methyl C atoms and the covalently bound O1 atom of the *l*-ephedrine substituent lie in the equatorial plane. The apical Al1–O1′ distance is significantly longer (1.95 Å) than the equatorial Al1–O1 distance (1.86 Å). Table I compares the Al–O bond distances of several organoaluminum complexes which also contain an Al_2O_2 ring. The apical Al1–N1 dative bond length of 2.19 Å is significantly longer than those reported for other Al–N bonds (see Table I). This observation is in line with the results obtained by van Koten et al.[1] with the lengthening of the Al–N dative bond due to the geometry around the aluminum center and suggests that breaking the nitrogen–aluminum bond should be a relatively low-energy process. A further manifestation of this is seen in the relatively strained five-membered heterocyclic ring Al–O1–C6–C5–N1 which contains a relatively sharp O–Al–N angle of 78.5° and shows some distortion around the carbon atoms with significant deviation from tetrahedral geometry. A discussion of this will be presented in a full paper discussing this and related five-coordinate aluminum derivatives.

The variable-temperature ^{1}H NMR of 1 is shown in Figure 2. At 22 °C the methyl groups are nonequivalent which is consistent with the structure observed in the solid state. As the temperature is increased, the lines associated with these groups broaden and coalesce indicating that the magnetic environment is averaged on the NMR time scale. The energy of activation, ΔE_a, for this process was determined through the use of a deconvolution program[8] and standard line-shape analysis. In complex 1, the energy of activation is 24.4 kcal/mol, the rate of exchange is concentration independent, and the process is reversible. These results can best be interpreted in terms of a dissociate process in which the Al–N bond breaks permitting the two methyl groups to become equivalent on the NMR time scale. At the same time the Al_2O_2 ring remains intact preserving the nature of the complex. When the bulk of the alkyl substituent bound directly to the aluminum is increased, from methyl to ethyl, the ΔE_a appears to decrease with exchange occurring near room temperature. This can be interpreted as a weaker Al–N dative interaction due to the steric interactions between the substituents on the aluminum in complex 2.

In summary, the 100% induction of optical activity at the nitrogen center and the strength of the Al–N dative bond suggest that optically active neutral aluminum complexes, where the aluminum center is optically active, can be synthesized and isolated by simply changing the substituents on the aluminum. Work on the synthesis and structural identification of optically active aluminum complexes is continuing.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research.

Supplementary Material Available: Tables of positional and thermal parameters, complete listings of bond distances and angles, and least-squares planes and deviations (11 pages); a listing of observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.

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[8] General Electric GN 300 NMR spectrometer software, version V-8.

Synthesis and Molecular Structure of Tetramethylbis(μ-pyridine-2-thiolato)dialuminum(III), $[Me_2AlPyS]_2$: An Example of a Unique Head-to-Head Bridged Pyridine-2-thiolato Ligand

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Summary: Reaction of pyridine-2-thiol (PySH) with trialkylaluminum, AlR_3 (R = Me, **1**; R = Et, **2**), affords the crystalline complexes tetramethylbis(μ-pyridine-2-thiolato)dialuminum(III) (**1**) and tetraethylbis(μ-pyridine-2-thiolato)dialuminum(III) (**2**) in quantitative yield. Compound **1** crystallizes in the monoclinic space group $C2/c$ with unit-cell parameters a = 31.651 (3) Å, b = 8.364 (1) Å, c = 14.128 (1) Å, β = 103.84 (1)°, V = 3631.4 (5) Å^3, and D_{calcd} = 1.22 g cm^{-3} for Z = 8. Least-squares refinement based on 1452 observed reflections ($I \geq 2.5\sigma(I)$) converged at R = 4.84% (R_w = 3.52%). The central core of the compound $[Me_2AlPyS]_2$ contains an unusual eight-membered $S_2C_2N_2Al_2$ ring with head-to-head bridging pyridine-2-thiolato ligands. In solution **1** undergoes an exchange process that averages the methyl groups at and above room temperature while at low temperature the methyl groups are fixed on the NMR time scale giving rise to a spectrum consistent with the solid-state structure. The ^{1}H NMR spectrum of the ethyl region of the compound **2**, observed at low temperature, is consistent with formation of diastereotopic methylene groups suggesting that in solution the aluminum atom has a five-coordinate structure. Again at room temperature and above the molecule undergoes exchange process causing the ethyl groups to become equivalent.

Pyridine-2-thiol can serve as a very versatile ligand eliminating hydrogen to form the anion PyS$^-$, which can coordinate through the sulfur, the nitrogen, or both with either formation of a four-membered chelate ring or for-

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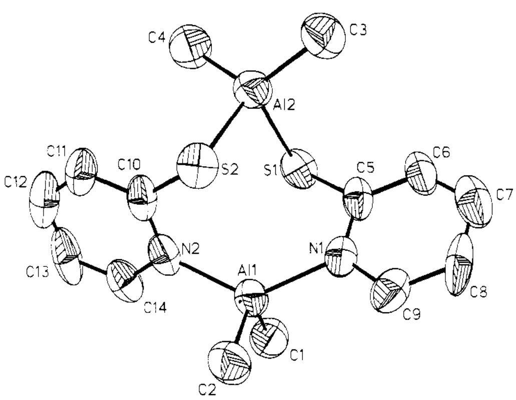

Figure 1. A ORTEP diagram of the $[\mathrm{Me_2AlPyS}]_2$ dimer (1) showing the atom-labeling scheme. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Al1–C, 1.981 (6); Al2-C, 1.965 (5); Al1–N1, 1.993 (4); Al1–N2, 1.992 (4); Al2–S1, 2.335 (3); Al2–S2, 2.341 (3); C5–S1, 1.731 (5); C10–S2, 1.728 (5); C5–N1, 1.375 (8); C9–N1, 1.353 (7); C10–N2, 1.395 (8); C14–N2, 1.366 (7); N1–Al1–N2, 129.5 (2); N1–Al1–C1, 102.0 (2); N1–Al1–C2, 104.5 (2); N2–Al1–C1, 104.0; N2–Al1–C2, 101.0; Al1–N1–C5, 120.7 (3); Al1–N1–C9, 120.1 (4); Al1–N2–C10, 121.2 (3); Al1–N2–C14, 119.9 (4); N1–C5–S1, 116.0 (3); N2–C10–S2, 115.1 (3); S1–Al2–S2, 97.34 (9); S1–Al2–C3, 111.9 (2); S1–Al2–C4, 105.3 (2); S2–Al2–C3, 104.9 (2); S2–Al2–C4, 112.3 (2); C1–Al1–C2, 117.0, C3–Al2–C4, 122.3 (2).

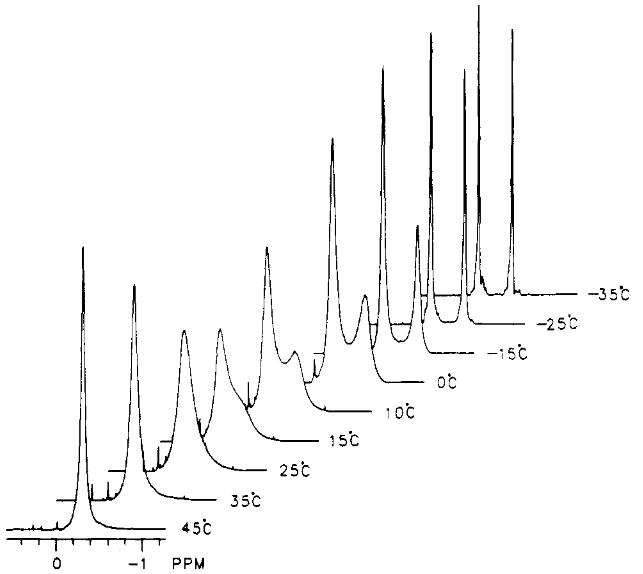

Figure 2. The ^{1}H NMR spectrum of the methyl region of $[\mathrm{Me_2AlPyS}]_2$ (1) as a function of temperature.

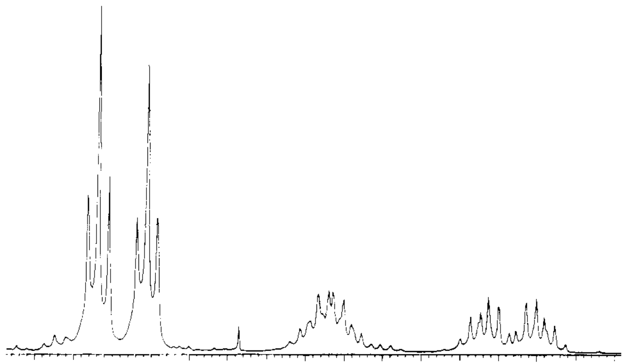

Figure 3. The ^{1}H NMR spectrum of the ethyl region of $[\mathrm{Et_2AlPyS}]_2$ (2) determined at −60 °C.

mation of a three-atom bridging between two metal atoms. All of these forms have been observed for transition-metal complexes.[1] Further, it has been shown that in several of the complexes with bridging PyS ligands rapid intramolecular exchange processes occur with "rotation" of the PyS ligand from head-to-tail to head-to-head.[1] For main-group metals far less is known with no crystallographic studies reported and only very limited spectroscopic information available for the thallium derivatives.[1e]

We have now embarked on an investigation of the interaction of this ligand with simple organoaluminum derivatives to determine how it interacts with these species. Our initial studies have led to several interesting results. Reaction of $\mathrm{Al_2Me_6}$ and $\mathrm{Al_2Et_6}$ with pyridine-2-thiol yields tetramethylbis(μ-pyridine-2-thiolato)dialuminum(III), $[\mathrm{Me_2AlPyS}]_2$ (1), and tetraethylbis(μ-pyridine-2-thiolato)dialuminum(III), $[\mathrm{Et_2AlPyS}]_2$ (2), respectively.[2]

The structure of 1 was determined by single-crystal X-ray diffraction methods and is shown in Figure 1. The structure consists of discrete dimeric unit bridged by the PyS ligand in a head-to-head fashion with formation of an 8-membered ring. The Al–C and Al–N bond distances are normal and comparable to the many examples in the literature.[4] The Al–S distances (average value 2.338 Å) fall

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(2) The compounds are extremely sensitvie to both air and water so standard Schlenk line techniques were employed. Pyridine-2-thiol (1 g, 8.99 mmol) was dissolved in toluene (60 mL), and $\mathrm{AlMe_3}$ (4.50 mL, 8.995 mmol) was syringed as quickly as (ca. 5 min) permitted by the evolution of methane gas. Though the reaction was instantaneous, the solution was left stirring for an additional period of 2 h. The volume of the solution was reduced to ca. 20 mL, and to this solution was added pentane (ca. 50 mL). The resulting solution deposited crystalline product over a period of 24 h at −20 °C. This solid was identified as $\mathrm{AlMe_2PyS}$: yield 90%; mp 114–117 °C. Anal. (Galbraith Laboratories) Calcd for $\mathrm{C_7H_{10}NSAl}$: C, 50.20; H, 5.95; N, 7.98. Found: C, 50.31; H, 5.99; N, 8.38. ^{1}H NMR (δ): benzene-d_6, room temperature all lines are exchange broadened, $\mathrm{AlCH_3}$ 0.22 (s, 6 H), PyS 6.04, 6.25, 7.14, 8.04 (4 exchange broadened singlets, 4 H); −90 °C, toluene-d_8, $\mathrm{AlCH_3}$ −0.32, (s, 3 H), 0.05 (s, 3 H), PyS 5.98 (t, 1 H), 6.40 (t, 1 H), 7.18 (d, 1 H), 7.94 (d, 1 H). The ethyl analogue was prepared by using the same experimental procedures as described above: yield 95%; mp 64–66 °C. ^{1}H NMR (δ): benzene-d_6, room temperature all lines are exchange broadened, $\mathrm{AlCH_2CH_3}$ 0.41 (bs, 2 H), 1.20 (bs, 3 H), PyS 6.2, 6.6, 7.24, 8.0 (4 exchange broadened singlets, 4 H); −90 °C, toluene-d_8, $\mathrm{AlCH_2CH_3}$ 0.26 (m, 2 H), 0.72 (m, 2 H), 1.150 (t, 3 H), 1.30 (t, 3 H), PyS 6.01 (t, 1 H), 6.41 (t, 1 H), 7.28 (d, 1 H), 7.87 (d, 1 H).

(3) Crystal of 1 was mounted in a thin-walled capillary in a drybox and mounted on a goniometer head. X-ray intensity data were collected on Nicolet P3/V diffractometer by using a $\theta/2\theta$ scan with Cu K$\bar{\alpha}$ radiation (λ = 1.54184 Å) at 20 °C. The compound $[\mathrm{Me_2AlPyS}]_2$ crystallizes in the monoclinic space group $C2/c$ with unit cell parameters a = 31.651 (3) Å, b = 8.364 (1) Å, c = 14.128 (1) Å, β = 103.84 (1)°, V = 3631.4 (5) Å^3, and D_{calcd} = 1.22 g cm^{-3} for Z = 8. The structure was solved by direct methods using SHELX-76 and refined based on 1452 observed reflections with intensities ($I \geq 2.5\sigma(I)$). Refinement converged at R = 4.84% (R_w = 3.52%). Anisotropic thermal parameters were used for all non-hydrogen atoms. Hydrogen atoms were placed in idealized positions with assigned isotropic temperatures factors based on the thermal parameters of the carbon atoms to which they are bound.

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into the broad range previously recorded (2.18–2.718 Å),[5] but there are so few examples that a "normal" distance is yet to be defined. The average Al–S distance in the most closely related structure, that of $(\mathrm{Me_2Al}\text{-}\mu\text{-}\mathrm{SMe})_n$, is 2.348 Å in the solid state[6] and 2.370 Å for the dimeric molecule in the gas phase[7] are very close to the values obtained in 1. All of the bond angles in 1 are reasonable for organoaluminum complexes. The one significant feature other than the head-to-head arrangement of the bridging ligands is that the two methyl groups on a given Al atom may be equivalent but differ from those on the other Al center. On the basis of this fact one would anticipate that the ^{1}H NMR spectrum should show two lines for the methyl groups bound to the aluminum.

Examination of the ^{1}H NMR spectra of a sample of 1 in toluene-d_8 shows a broadened resonance line for the methyl groups at room temperature which indicates that some form of exchange process is occurring. A variable-temperature NMR study shown in Figure 2 shows more complex behavior. At high temperature a single sharp line is observed for the Al methyl groups. This broadens and separates into two lines of unequal intensity as the temperature is lowered. A further decrease in temperature leads to a change in the intensity of these lines so that they become of equal intensity within experimental error at approximately −50 °C.

Examination of the ^{1}H NMR spectra of 2 as a function of temperature shows similar results to a first approximation. Closer examination of the low-temperature spectrum shows an additional feature that bears directly on the structure of the compounds in solution. At low temperature the methylene protons of the ethyl groups become diastereotopic as seen in Figure 3. This implies the induction of prochirality at the aluminum center and is identical with the behavior found in $[\mathrm{R_2Al(O\text{-}(\mathit{R})\text{-}CHC_6H_5((\mathit{S})\text{-}CH((\mathit{S})\text{-}NHCH_3)CH_3)}]_2$ which has been shown to have a five-coordinate Al center.[8] Formation of a symmetrical five-coordinate aluminum atoms, however, would make all four ethyl groups identical contrary to their observed behavior. Close examination of the head-to-head structure observed for 1 shows that the ethyl groups in 2 for a molecule of similar structure would be diastereotopic and would account for the observed spectrum.

The conclusions at present are that the pyridine-2-thiol reacts with alkylaluminum derivatives to give new dialkylaluminum thiolates which form head-to-head dimers on crystallization. In solution these dimers undergo rapid rearrangements on the NMR scale near room temperature and above. As the temperature is lowered to intermediate values, there are at least two environments, but of unequal population. This is consistent with formation of two or more species that are undergoing slow exchange. Possible structures include head-to-tail coordination, simple sulfur-bridged derivatives, or more complex species which may involve five- or six-coordinate aluminum centers. At low temperature (<−35 °C) the equilibrium has shifted to two equivalent lines for the methyl groups that can be easily accounted for in terms of the observed solid-state structure. This explanation also accounts for the behavior of the 2, including the observation of diastereotopic methylene protons. Further studies are now in progress to explore the unusual structural properties of aluminum-thiolates and their behavior in solution.

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Supplementary Material Available: Tables of torsion angles, least-squares planes, anisotropic thermal parameters, hydrogen atom positional coordinates, and isotropic thermal parameters (12 pages); a listing of observed and calculated structure factors (11 pages). Ordering information is given on any current masthead page.

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Silyl-Substituted Diphosphenes. Synthesis, Structure, and Modes of Decomposition

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Summary: The first stable silyl-substituted diphosphenes $(2,4,6\text{-}t\text{-}\mathrm{Bu_3C_6H_2)P{=}PSiPh_3}$ (**1**) and $\mathrm{(Me_3Si)_3CP{=}PSiPh_3}$ (**2**) have been synthesized. The structure of **2** has been determined by X-ray crystallography. Compound **1** undergoes slow head-to-head dimerization. The less stable diphosphene $\mathrm{(Me_3Si)_3CP{=}PSiMe_3}$ (**7**) has also been prepared. Compound **7** decomposes to a bicyclobutane-analogous tetraphosphane.

Silyl-substituted diphosphenes of the type $\mathrm{RP{=}PSiR'_3}$ are of potential importance as $\mathrm{RP{=}P}$ unit transfer reagents. A compound of composition $\mathrm{ArP{=}PSiMe_3}$ (Ar = $2,4,6\text{-}t\text{-}\mathrm{Bu_3C_6H_2}$) has, in fact, been implied from spectroscopic data;[1] however, so far no silyl-substituted diphosphene has been isolated. We report the syntheses of the first kinetically stabilized silyl-substituted diphosphenes $\mathrm{ArP{=}PSiPh_3}$ (1) and $\mathrm{(Me_3Si)_3CP{=}PSiPh_3}$ (2) along with an X-ray analysis of 2.

The new lithium phosphide $\mathrm{LiP(SiMe_3)(SiPh_3)}$ (3) was prepared by the following sequence of reactions.[2]

$$\mathrm{NaAl(PH_2)_4} \xrightarrow{\mathrm{Ph_3SiCl}} \mathrm{Ph_3SiPH_2} \xrightarrow{\mathrm{MeLi}} \mathrm{Ph_3SiP(H)Li} \xrightarrow{\mathrm{Me_3SiCl}} \mathrm{Ph_3Si(Me_3Si)PH} \xrightarrow{\mathrm{MeLi}} \underset{\textbf{3}}{\mathrm{Ph_3Si(Me_3Si)PLi}}$$

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