Synthesis and Molecular Structures of 2-Trimethylsilyl-, 2-Trimethylgermyl-, and 2-Trimethylstannyl-pyridines

Frank Riedmiller, Alexander Jockisch, Hubert Schmidbaur*

Anorganisch-chemisches Institut der Technischen Universität München, Lichtenbergstrasse 4, D-85747 Garching, Germany

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Pyridine, 2-Silyl-pyridine, 2-Germyl-pyridine, 2-Stannyl-pyridine, Molecular Structure

5-Methyl-2-trimethylsilyl-pyridine (1) has recently been prepared *via* the "*in situ*" Grignard reaction of 1-bromo-5-methyl-pyridine with magnesium and trimethylchlorosilane in refluxing tetrahydrofuran (thf) and structurally characterized. 2-Trimethylgermyl- (2) and 2trimethylstannyl-pyridine (3) were now obtained from 2-bromo-pyridine through metallation (with *n*-BuLi) and treatment of the intermediates with Me₃GeBr and Me₃SnCl, respectively, in diethylether/ thf at -70°C. The crystal and molecular structure of compound 2 has been determined by low temperature (*in situ*) single crystal X-ray diffraction methods. There is a significant bending of the Me₃Ge substituent towards the nitrogen heteroatom [Ge-C-N = $114.7(2)^{\circ}$]. This phenomenon is known from previous studies of the silicon analogue 1 to be not due to intramolecular (peripheral) Si/Ge—N coordination, but to be rather an intrinsic property of the heteroarene skeleton, as also confirmed by quantum-chemical calculations. Furthermore, there is no evidence for *inter*molecular coordination in the crystals. Such interactions could also be ruled out for the solution state of 2 and 3 through variable temperature multinuclear NMR investigations.

Introduction

Organometallic derivatives of nitrogen heterocycles are useful synthons in preparative organic, organometallic and coordination chemistry [1 - 9]. In the pyridine series the ortho-substituted species are particularly important owing to potential chelating and neighbouring group assistance capabilities [10 - 12]. The molecular structures of these compounds have attracted considerable attention because of alleged evidence for intra- or intermolecular interactions between the heteroatom (E = Si, Ge, Sn etc.) and the nitrogen donor function [13 - 17]. In a recent paper from this laboratory [18] it has been demonstrated that the structural peculiarities do not have their origin in peripheral E-N donor/acceptor interactions (E = Si), but are rather based on intrinsic structural parameters of the pyridine heterocycle. Both experimental and theoretical results are consistent with this interpretation [18].

We have extended these studies now to include representative examples with E = Ge, Sn, together with a silicon compound with a slightly different

* Reprint requests to Prof. Dr. H. Schmidbaur.

substitution pattern. Structural and spectroscopic investigations have been carried out to examine both the crystalline and the solution state.

Preparative Results

The synthesis of 5-methyl-2-trimethyls*ilyl*-pyridine (1) has recently been reported via a method established for other trimethylsilyl-pyridines [13, 18 - 20]. For this preparation the corresponding bromo-pyridine is treated with magnesium and trimethylchlorosilane in refluxing tetrahydrofuran. Standard work-up of the reaction mixture gives a colourless, distillable liquid (b.p. 60 °C at 5 mbar, m.p. -23°C) in 48% yield (eq. (1)).

For the preparation of 2-trimethylgermyl- (2) and 2-trimethylstannyl-pyridine (3) 2-bromo-pyridine is lithiated using *n*-butyllithium in diethylether / tetrahydrofuran at -78°C (-70°C). 2-Lithio-pyridine is then treated *in situ* with trimethylbromogermane or -chlorostannane, respectively. The products are colourless distillable liquids (2: b.p. 135 °C/300 Torr, m.p. -25°C, 45% yield; 3: b.p. 124-127°C/100 Torr, m.p. -37°C, 35% yield) (eq. (2), (3)).

The analytical and spectroscopic data of all three compounds are consistent with the proposed

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composition and structure (Experimental Part). The multinuclear NMR studies included the isotopes ⁷³Ge and ¹¹⁹Sn, which show standard chemical shift data. The values for Sn are in good agreement with data for other trialkylaryltin compounds with tetracoordinate tin atoms. The chemical shift value is not temperature dependent between +25 and -85 °C, and therefore association through Sn \leftarrow N interaction (*inter*molecular) can be ruled out for d⁸-toluene solutions. In the low temperature spectra the ¹¹⁹Sn-¹H spin-spin couplings are well resolved.

While NMR spectroscopy with the ⁷³Ge nuclei is generally very difficult, there is no problem to obtain a well defined ⁷³Ge signal for compound **2** at $\delta = -17.6$ (rel. GeCl₄). In the absence of a suitable collection of reference data, this value must go without comment. The spin-spin couplings ⁷³Ge-¹H are not fully resolved.

The ¹⁴N resonances of the three homologues **1-3** and the corresponding Me₃C-pyridine have chemical shifts of δ = -37.0 (**3**), -43.7 (**2**), -50.7 (**1**), and -64.7 for 2-^{*t*} butyl-pyridine. There is thus a systematic decrease of the shielding of the nitrogen nucleus as the group IV element (C, Si, Ge, Sn) becomes heavier, larger, and less electronegative. This regression is common for the chemical shift of nuclei close to the elements of a given group of the Periodic Table.

Structural Results

Single crystals could be grown from compounds 1 and 2 at low temperature using "*in situ*" crystal growth techniques. The tin analogue 3 did not give suitable crystals (monoedric twins).

As reported previously [18], the structure of 5methyl-2-trimethylsilyl-pyridine (1) shows a tilting of the trimethylsilyl substituent towards the nitrogen atom: The angles Si-C1-N and Si-C1-C2 are 115.8(2) and 124.6(2)°, respectively, meaning for both a deviation from the 120° standard by about 5° in opposite directions. The positioning of the methyl group has no such anomalies, with the angles C6-C4-C3/C5 close to 120° (Fig. 1).

The rotatory position of the Me₃Si group is such that the N atom is staggered relative to the methyl groups with C8 and C9, while the methyl group at C7 is eclipsed relative to the group C2-H1. Note that it is very tempting again to attribute this conformation to a peripheral donor/acceptor interaction $N \rightarrow Si$. It is only after a comparison with the (analogous) structure of 2-methyl-pyridine (2-picoline) and pyridine itself, and also with results from theoretical calculations (MP2/6-31 G* level of theory) [18], that it becomes clear that the observed effect is an intrinsic property of the pyridine heterocycle, and has nothing to do with peripheral coordinative bonding. (ortho-hydrogen atoms and -methyl groups show the same tilt towards the nitrogen atoms.) This correlation qualifies the Si-N coordination as a phantom, which should be rationalized in a different way.

2-Trimethylgermyl-pyridine (2) crystallizes orthorhombically, space group Pbca, Z = 8 (at 133 K). The lattice contains isolated molecules with no crystallographically imposed symmetry. The germanium atom is in the plane of the heterocycle, but the Ge-bound methyl groups are not displaced symmetrically about this molecular plane (Fig. 2, 3).

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Fig. 1. Molecular structure of **1** (ORTEP drawing with 50% probability ellipsoids).



Fig. 2. Molecular structure of 2 (ORTEP drawing with 50% probability ellipsoids). Projection parallel to the plane of the pyridine ring.

The dihedral angle C8-Ge-C1-C2 = 9.1° shows a deviation from a staggered/eclipsed conformation.

The projection down on to the molecular plane shows again a pronounced tilt of the Ge atom towards the N atom with angles Ge-C1-N = 114.7(2) and Ge-C1-C2 124.0(2)°. The Ge–N distance is thus reduced to 2.808 Å. In summary, the disposition is similar to that in **1**, and similar arguments can be used to interpret the results.

The packing of the molecules in the lattice gives no evidence for *inter*molecular contacts other than standard van-der-Waals distances (Fig. 4).

The present results are in full agreement with recent findings for the fully hydrogen-substituted prototypes of the silyl-pyridines [18]. Even for the heavier (and larger) group IV elements, where donor-acceptor interactions are more likely, the structural data are comparable and show no consequences of coordination interactions beyond standard tetracoordination.

Experimental Section

General methods: All experiments were carried out under a dry nitrogen atmosphere. Solvents were approFig. 3. Molecular structure of **2** (ORTEP drawing with 50% probability ellipsoids). Selected bond lengths [Å] and angles [°]: Ge-C1 1.960(2), Ge-C6 1.939(3), Ge-C7 1.948(3), Ge-C8 1.947(3), N-C1 1.351(3), N-C5 1.338(4), C1-C2 1.393(3), C2-C3 1.380(4), C3-C4 1.369(4), C4-C5 1.391(4); C1-Ge-C6 107.92(11), C1-Ge-C7 109.38(12), C1-Ge-C8 107.91(12), C6-Ge-C7 108.82(14), C6-Ge-C8 111.40(14), C7-Ge-C8 111.3(2), N-C1-Ge 114.7(2), Ge-C1-C2 124.0(2), N-C1-C2 121.2(2), C1-C2-C3 120.1(2), C2-C3-C4 118.9(2), C3-C4-C5 118.2(3), C4-C5-N 123.9(3).

priately dried, distilled and saturated with dry nitrogen; glassware was dried in an oven and filled with nitrogen. Starting materials were commercially available.¹H-, ¹³C-, ²⁹Si-, ⁷³Ge-, ¹¹⁹Sn- and ¹⁴N-NMR spectra were recorded with a Jeol JNM-GX 270 spectrometer (¹H at 270.17 MHz, ¹³C at 67.94 MHz, ²⁹Si at 53.67 MHz) or a Jeol JNM-LA 400 spectrometer (¹H at 400.05 MHz, ¹³C at 100.50 MHz, ²⁹Si at 79.38 MHz, ¹⁴N at 28.90 MHz, ⁷³Ge at 13.83 MHz, and ¹¹⁹Sn at 149.10 MHz, the latter with SnMe₄ and GeCl₄ as external references). Mass spectra were recorded with a mass-selective detector HP MS 5971 A (EI-MS 70eV) of an analytical GLC-MS Hewlett Packard 5890 Series II chromatograph (column HP1, crosslinked methylsilicon gum 12 m/0.2 mm, thickness of film 0.33 μ m). IR spectra were recorded on a Midac FT-IR Prospect spectrometer. Elemental analyses



Fig. 4. Packing diagram of 2.

were performed by the Mikroanalytisches Laboratorium des Anorganisch-chemischen Instituts der Technischen Universität München.

5-Methyl-2-trimethylsilyl-pyridine (1)

The synthesis followed the literature procedure for other trimethylsilyl-pyridines[13, 18]. A colourless liquid is obtained in 48% yield (b.p. 60 °C at 5 mbar, m.p. -23 °C). 29 Si-NMR (C₆D₆, 20 °C): δ = -6.21 [s]. $^{-14}$ N-NMR (C₆D₆, 19 °C): δ = -50.7 [bs].

2-Trimethylgermyl-pyridine (2)

To a solution of 2-bromopyridine (4.0 g, 0.025 mol) in 20 ml of diethylether a solution of *n*-butyllithium in hexane (15.8 ml, 1.6 M, 0.025 mol) is added dropwise with cooling (-78 °C). A pale brown solid is formed. After stirring at -78 °C for 30 min a solution of trimethylbromogermane (5.0 g, 0.025 mol) in 15 ml of diethylether is added with vigorous stirring. After 1h of stirring at this temperature the mixture is allowed to warm to room temperature and stirring is continued for about 1h. 30 ml of pentane are added to the mixture and the precipitate is filtered off. After removing the solvent from the filtrate, the product is separated by fractional distillation. A colourless liquid is obtained. Yield 2.23 g (45%; b.p. 135 °C at 300 mbar; m.p. -25 °C). -¹H-NMR (C₆D₆, 23 °C): $\delta = 0.41$ (s, 9H, GeMe₃), 6.68 (dd, ³J_{HH} = 8/5 Hz, 1H, pyridine-H₅), 7.06 (ψ t, ³J_{HH} = 8 Hz, 1H, pyridine-H₄), 7.15 (dm, ${}^{3}J_{\text{HH}} = 8$ Hz, 1H, pyridine-H₃), 8.65 (d, ${}^{3}J_{\text{HH}} =$ 5 Hz, 1H, pyridine-H₆).- $^{13}C{^{1}H}$ -NMR (C₆D₆, 23°C): δ = -2.20 (GeMe₃), 122.33 (C₅), 127.75 (C₃), 133.69 (C₄), 150.42 (C₆), 170.73 (C₂ ipso). -⁷³Ge-NMR (C₆D₆, 23 °C): δ = -17.6 [m]; -16.8 (-85 °C). -¹⁴N-NMR (C₆D₆, 23 °C): δ = -43.7 [bs]. -MS (EI, 70 eV): m/z = 196 [M⁺], 194 [M⁺-2H], 182 [100%, M⁺-CH₃], 166 [M⁺-2CH₃], 152 [M⁺-3CH₃], 118 [GeMe₃⁺], 103 [GeMe₂⁺], 88 [GeMe⁺], 78 [C₅H₄N⁺], 139, 126, 65, 51.

C₈H₁₃NGe (195.7)

Found C 48.8 H 6.8 N 7.1 %, Calcd C 49.1 H 6.7 N 7.2 %.

2-Trimethylstannyl-pyridine (3)

To a solution of 2-bromopyridine (5.0 g, 0.032 mol) in 30 ml of diethylether/thf a solution of n-butyllithium in hexane (22.0 ml, 1.6 M, 0.035 mol) is added dropwise with cooling at -70 °C. After stirring for 30 min a pale brown solid is formed. A solution of trimethylchlorostannane (6.6 g, 0.033 mol) in 25 ml of diethylether is added with vigorous stirring. After stirring for 1h at -70 °C the mixture is allowed to warm to room temperature, and stirring is continued for about 1h. After removing the solvent, the remaining oil is extracted with 30 ml of pentane. The extract is fractionally distilled to give a colourless liquid product. Yield 2.68 g (35%; b.p. 124-127 °C at 100 mbar; m.p. ca. -37 °C). -¹H-NMR (C₆D₆, 23 °C): $\delta = 0.38$ (s, ${}^{2}J_{\text{SnH}} = 53$ Hz, 9H, SnMe₃), 6.78 (dd, ${}^{3}J_{\text{HH}}$ = 7.5/5 Hz, 1H, pyridine-H₅), 7.14 (ψ t, ³J_{HH} = 7.5 Hz, 1H, pyridine-H₄), 7.27 (dm, ${}^{3}J_{HH} = 7.5$ Hz, 1H, pyridine-H₃), 8.77 (d, ${}^{3}J_{\text{HH}} = 5$ Hz, 1H, pyridine-H₆).- ${}^{13}C{}^{1}H{}$ -NMR (C₆D₆, 23°C): $\delta = -9.54$ (SnMe₃), 122.30 (C₅), 131.52 (C₃), 133.34 (C₄), 150.71 (C₆), 173.53 (C₂ ipso). -¹¹⁹Sn-VT-NMR (C₆D₅CD₃, 20 °C): δ = -52.3 [m,²J_{SnH} = 53 Hz], δ = -51.2 (-50 °C), δ = -50.2 (-85 °C). -¹⁴N-NMR (C₆D₆, 23 °C): δ = -37.0 [bs]. -MS (EI, 70 eV): $m/z = 243 [M^++1], 242 [M^+], 228 [100\%, M^+-CH_3],$ 198 [M⁺-3CH₃], 196 [M⁺-2H-3CH₃], 163 [SnMe₃⁺], 144 $[SnMe_2^+]$, 130 $[SnMe^+]$, 78 $[C_5H_4N^+]$, 65, 51.

 $C_8H_{13}NSn (241.8)$

Found C 39.3 H 5.2 N 5.6 %, Calcd C 39.7 H 5.4 N 5.8 %.

Crystal structure determinations

2-Trimethylgermyl-pyridine **2** was condensed into a glass capillary. Single crystals were prepared "*in situ*" on the diffractometer unit by cooling at 1 K h⁻¹. The specimen was used for measurement of precise cell constants and intensity data collection on an Enraf Nonius CAD4 diffractometer (Mo- K_{α} radiation, λ (Mo- K_{α}) = 0.71073 Å). During data collection, three standard reflections were measured periodically as a general check of crystal and instrument stability. No significant changes were observed.

Crystal data for **2**: C₈H₁₃GeN; $M_r = 195.78$; orthorhombic; space group Pbca; a = 8.1284(7); b = 12.1793(7); c = 18.727(2) Å; V = 1853.9(3) Å³; Z = 8; $\rho_{calc} = 1.403$ Mg/m³; F(000) = 800; μ (Mo-K_{α}) = 3.24 mm⁻¹, T = 133 K; 2331 reflections measured, 2017 unique. No absorption correction was applied. The structure was solved by direct methods (SHELXS-86) [21] and completed by full-matrix least-squares techniques against F² (SHELXL-93) [22]. The thermal motion of all nonhydrogen atoms was treated anisotropically. All hydrogen atoms of **2** were found and refined with isotropic contributions. Refinement of 143 parameters for 2016 data converged to a *wR*2 (*R*1) of 0.0785 (0.0310). Residual electron densities: +0.56/-0.60 $e^{A^{-3}}$. Anisotropic thermal parameters, tables of distances and angles, and atomic coordinates have been deposited at Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen. The data are available on request on quoting CSD No. 410417.

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