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Synthesis and characterization of sodium bis(trimethylstannyl) amide and bis(trimethylsilyl) bis(trimethylstannyl) -phospha-tetrazene

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Abstract

Sodium bis(trimethylstannyl)amide NaN(SnMe₃)₂, isolated by the reaction of trimethylstannyldiethylamine with sodium amide, reacts with tris(trimethylsilyl)hydrazino-dichloro-phosphine to form bis(trimethylsilyl)bis(trimethylstannyl)-2-phospha-2-tetrazene, $(Me_3Si)_2N-N=P-N(SnMe_3)_2$. Both the molecules have been isolated and characterized. © 1997 Elsevier Science S.A.

Keywords: Sodium bis(trimethylstannyl)amide; Bis(trimethylsilyl)bis(trimethylstannyl)-2-phospha-2-tetrazene; Synthesis; Characterization

1. Introduction

Lithium bis(trimethylsilyl)amide [1] and other alkali metal bis(silyl)amides [1–4] are well known synthetic intermediates and have been used extensively as ligand transfer reagents, as low coordinative environment reagents, as alkali metal transfer agents and as reagents for introducing covalent character in inorganic systems [1–4]. However, a similar molecule with stannyl moiety in place of silyl is not reported in the literature. With this in view, an attempt has been made to synthesize sodium bis(trimethylstannyl)amide NaN(SnMe₃)₂ and use it as a ligand transfer reagent to synthesize bis(trimethylsilyl)bis(trimethylstannyl)-2-phospha-2-tetrazene (Me₃Si)₂N-N=P-N(SnMe₃)₂.

2. Results and discussion

Trimethylstannyldiethylamine, Me_3SnNEt_2 , formed by the reaction of lithium diethylamide with chlorotrimethylstannane, reacts with sodium amide in the ratio 2:1 in benzene at 40 °C to provide a white crystalline solid, sodium bis(trimethylstannyl)amide, NaN(SnMe₃)₂ (1), subliming at 55 °C/10⁻³ torr. It is also purified by crystallization from diethyl ether at low temperatures.

$$Et_{2}NH + BuLi \xrightarrow{\rightarrow} Et_{2}NLi \xrightarrow{+Me_{3}SnCl} Me_{3}SnNEt_{2}$$

$$2Me_{3}SnNEt_{2} + NaNH_{2} \xrightarrow{40^{\circ}C}_{-2Et_{2}NH} NaN(SnMe_{3})_{2}$$
(1)

Compound (1) was found to be soluble in solvents like benzene, toluene, n-hexane, diethyl ether, tetrahydrofuran, etc. It is sensitive to hydrolysis. In sunlight, it turns yellowish slowly but shows no noticeable decomposition.

The ¹H NMR of (1) in benzene (n-hexane) shows a singlet at 0.20 (0.15) ppm due to stannyl protons. The presence of stannyl group is supported by tin satellites at 55 and 57 Hz due respectively to $J({}^{1}\text{H}-{}^{117}\text{Sn})$ and $J({}^{1}\text{H}-{}^{119}\text{Sn})$. The ¹¹⁹Sn NMR of (1) in deuterated benzene (C₆D₆) shows a signal at 464.4 ppm. This signal is characteristic of tetrahedral tin(IV) [5]. The mass spectrum of (1) shows a molecular ion with relatively low intensity (5%, 70 eV) at m/z 365 and the observed isotopic pattern agrees with that calculated for C₆C₁₈NNaSn₂ (Fig. 1). Besides important fragments at 328 (Me₆Sn₂)⁺, 202 (NaNSnMe₃)⁺, 187 (NaNSnMe₂)⁺ and 165 (Me₃Sn)⁺, a valuable

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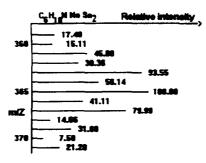
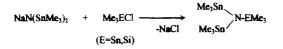


Fig. 1. Observed isotopic pattern of molecular ion in C₆H₁₈NNaSn₂.

metastable transition has been observed to indicate loss of Me_4Sn .

$$365 \xrightarrow[Calc.: 95.8]{m^2 = 96} [NaN = SnMe_2]$$

Formation of NaN(SnMe₃)₂ is also confirmed by its reaction with chlorotrimethylsilane (Me₃SiCl) as well as chlorotrimethylstannane (Me₃SnCl).



The formation of (trimethyl-silyl)bis(trimethylstannyl)amine is confirmed by its ¹H NMR in benzene (n-pentane). The spectrum shows two signals with relative areas 2:1 at 0.24 (0.25) and 0.22 (0.07) ppm. The former is attributed to trimethylstannyl protons due to the presence of side bands at 55 and 57 Hz.

Similarly, formation of tris(trimethylstannyl)amine is indicated by its ¹H NMR in benzene (n-pentane) showing a signal at 0.23 (0.18) ppm with appropriate side bands at 55 and 57 Hz.

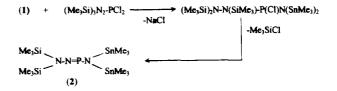
Ligand transfer reaction of (1) has been carried out to synthesize the first ever stannylated sila-phospha-tetrazene (Me₃Si)₂N-N=P-N(SnMe₃)₂.

Compound (1) when treated with an equivalent amount of tris(trimethylsilyl)hydrazino-dichlorophosphine (Me₃Si)₃N₂-PCl₂ [6] gives a light greenish yellow solution. The solution provides a light yellow crystalline solid 4-4'-bis(trimethylsilyl)-1,1'bis(trimethylstannyl)-2-phospha-2-tetrazene (Me₃Si)₂N-N=P-N(SnMe₃)₂ (2), which sublimes at 70°C/10⁻³ torr.

Compound (2) is highly soluble in common organic solvents like benzene, toluene, n-pentane, n-hexane, diethyl ether, tetrahydrofuran, etc. It is purified by crystallization from its solution in n-pentane or n-hexane at low temperatures.

The reaction appears to follow a pathway involving

intermediate formation of phosphine derivative $(Me_3Si)_2N-N(SiMe_3)P(Cl)N(SnMe_3)_2$ which then undergoes elimination of Me_3SiCl to form (2).



Acyclic tetrazenes and phosphatetrazenes can exhibit position isomerism (A) and (B) [7,8].



As already reported for tetrasila-phospha-tetrazene and other organyl-silvl-phospha-tetrazenes, structure (B) is favoured [8,9]. However in the present investigations, disila-distanna-phosphatetrazene (2) exhibits 2-phospha-2-tetrazene arrangement (A). This is supported by NMR studies. ¹H NMR of (B) would have given at least three resonance signals, whereas (2) shows only two signals in benzene at 0.40 and 0.16 ppm with intensity ratio 1:1. The signal at 0.40 ppm is attributed to 2Me₃Sn protons because of the presence of side bands at 55 and 57 Hz. Structure (A) is also supported by ²⁹Si NMR exhibiting only one resonance signal at 7.42 ppm. The ¹¹⁹Sn NMR spectrum is also a singlet at 463.7 ppm. This value is characteristic of tetrahedral tin [5]. The reason for the stabilization of structure (A) for disila-distanna-phospha-tetrazene (2) may be attributed to the reluctance of the Me₃Sn group to undertake 1,3-migration to form (B), probably due to higher steric requirements of the bigger Me₃Sn group compared to the Me₃Si group [8].

³¹ P NMR of (2) in C_6D_6 shows a signal at 301.6 ppm which is characteristic of two-coordinated phosphorus(III)-azene [10].

The mass spectrum of (2) shows a molecular ion with low intensity (3%, 70 eV) at m/Z 547 and the observed isotopic pattern (Fig. 2) agrees with calculated for $C_{12}H_{36}N_3PSi_2Sn_2$. The spectrum shows important fragments at m/Z 460 (M – Me₃SiN)⁺, 328 (Me₆Sn₂)⁺, 297 [(Me₃Si)(Me₃Sn)N₂P]⁺, 165 (Me₃Sn)⁺ and 73 (Me₃Si)⁺. The prominent fragment at m/Z 297 indicating loss of (Me₃Sn)(Me₃Si)N radical is supported by the appropriate metastable.

$$547 \xrightarrow{m^2 = 161}_{\text{Calc.: 161.2}} 297 \left[(\text{Me}_3\text{Si})(\text{Me}_3\text{Sn})\text{N}_2\text{P} \right]_{m/z \ 297}$$

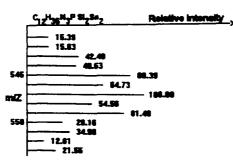


Fig. 2. Observed isotopic pattern of molecular ion in $C_{12}H_{36}N_3PSi_2Sn_2$.

This indicates the possibility of symmetric arrangement of groups in (2), that is $(Me_3Sn)(Me_3Si)N-N=P-N(SiMe_3)(SnMe_3)$ under the conditions.

3. Experimental

3.1. General comments

All investigations were carried out in the absence of air and moisture on a vacuum line connected to a dry nitrogen supply system. Trimethylstannyldiethylamine [11], n-butyl lithium [12], lithium tris(trimethylsilyl)hydrazine [13], tris(trimethylsilyl)hydrazinodichloro-phosphine [6] were prepared as reported. ¹H NMR measurements were recorded on Varian EM 390 and ³¹P, ²⁹Si, ¹¹⁹Sn NMR on Bruker FT NMR 300 MHz. Mass spectra were run on GC mass spectrometer Model 705-205 + (VG). ¹H NMR δ (ppm) in benzene (Et₂O): (Me₃Si)₂N₂H₂, 0.12 (0.07); (Me₃Si)₃N₂H, 0.13, 0.11 (2:1) (0.09); (Me₃Si)₃N₂Li, 0.25 (0.19); (Me₃Si)₃N₂PCl₂, 0.38, 0.20d (0.44, 0.28d) (1:2); Me₃SnNEt₂, 0.13 (0.17); Me₃SnCl, 0.23 (0.60).

3.2. Preparation of sodium bis(trimethylstannyl)amide (1)

Trimethylstannyldiethylamine (4.72 g, 20 mmol) in 10 ml of benzene was added to sodium amide (0.409 g, 10 mmol) suspended in 10 ml of benzene. The reaction mixture was stirred at room temperature for one day. Its ¹H NMR showed a very weak signal at 0.20 ppm attributed to the formation of the bis(stannyl)amide and a strong signal at 0.15 ppm due to unreacted Me₃SnNEt₂. The reaction mixture was then stirred for a further 3 days at room temperature after which the ¹H NMR showed incomplete reaction. The temperature of the reaction mixture was then raised to 40 °C and kept at this temperature for four days. ¹H NMR of the supernatant liquid showed the absence of Me₃SnNEt₂ signal at 0.15 ppm. The solution showed a signal at 0.20 ppm due to NaN(SnMe₃)₂, a triplet at 0.99 ppm and a quartet at 2.41 ppm due to Et_2NH .

After completion of the reaction at 40 °C, the reaction mixture was filtered. The filtrate was then evacuated to give a white powder. It was purified by sublimation into a cooled glass boat at $55 \text{ °C}/10^{-3}$ torr. It was then crystallized from n-hexane at low temperatures. It decomposes without melting on heating at 110 °C. Anal. Found: C, 18.98; H, 4.75; Sn, 51.10. C₆H₁₈NNaSn₂ Calc.: C, 19.75; H, 4.94, Sn, 51.12%.

¹H NMR in benzene (n-hexane) (iTMS) δ (ppm) 0.20 (0.15) [18 H, (Me₃Sn)₂] $J(^{117}Sn-^{1}H)$ and $J(^{119}Sn-^{1}H)$ at 55 and 57 Hz.

¹¹⁹Sn NMR in $C_6 D_6$ (eTMT) 464.4 ppm.

Mass spectrum (70 eV) m/z (assignment; relative intensity %): 365 [(m)⁺; 5], 350 [(m-Me)⁺; 10], 328 [(Me₆Sn)₂⁺; 30], 217 [(Me₄SnNNa)⁺; 9], 202 [(Me₃Sn-NNa)⁺; 10], 188 [(Me₃SnNa)⁺; 10], 179 [(Me₃SnN)⁺; 45], 165 [(Me₃Sn)⁺; 40], 150 [(Me₂Sn)⁺; 21], 97 [(Me₄NNa)⁺; 68], 82 [(Me₃NNa)⁺; 29], 57 [(C₄H₉)⁺; 100].

3.3. Preparation of trimethylsilylbis(trimethylstannyl)amine (Me₃Sn)₂NSiMe₃

Chlorotrimethylsilane (1.080 g, 10 mmol) was added to sodium bis(trimethylstannyl)amide (3.65 g, 10 mmol) in 20 ml benzene in a round bottom flask. The mixture was stirred for 2 h. The clear solution was decanted and its ¹H NMR was taken. The spectrum showed the absence of signals due to NaN(SnMe₃)₂ (0.20 ppm) as well as Me₃SiCl (0.21 ppm). The clear solution was evacuated under high vacuum to get a sticky mass. ¹H NMR (Me₃Sn)₂N(SiMe₃) δ (ppm) in benzene (n-pentane): 0.24 (0.25) [18 H, Me₃Sn] and 0.22 (0.07) [9 H, Me₃Si]. The Me₃Sn signals are supported by the side bands at 55 and 57 Hz.

3.4. Preparation of tris(trimethylstannyl)amine $(Me_3Sn)_3N$

Chlorotrimethylstannane (2.575 g, 5 mmol) solution in 10 ml benzene was added dropwise to a solution of NaN(SnMe₃)₂ (1.855 g, 5 mmol) taken in 20 ml benzene. The reaction mixture was stirred overnight and then filtered to remove a white precipitate of NaCl. The solution was found to contain only one signal at 0.23 ppm. It was evacuated to get a crystalline mass. ¹H NMR in benzene (n-pentane) δ (ppm): 0.23 (0.18) [27 H, 3Me₃Sn]. This signal has side bands at 55 and 57 Hz.

3.5. Preparation of bis(trimethylsilyl)bis(trimethylstannyl)-phospha-tetrazene $(Me_{3}Si)_{2}N-N=P-N(SnMe_{3})_{2}$

Sodium bis(trimethystannyl)amide NaN $(SnMe_3)_2$ (7.290 g, 20 mmol) was dissolved in ether (30 ml) and added dropwise to a solution of $(Me_3Si)_3N_2PCl_2$ (6.980 g, 20 mmol) in ether (25 ml) at -78 °C. The colourless solution was stirred at -78 °C and then allowed to warm up to -30 °C and stirred for 4 h at this temperature. A white precipitate appeared due to formation of NaCl. A sample of this colourless decantate at - 30 °C showed a signal at 167.13 ppm in ³¹P NMR. ¹H NMR of this solution showed three major signals at 0.42 (Me₃Si), 0.20 (2Me₃Si) and 0.23 ppm (2Me₃Sn). The NMR is indicative of an intermediate phosphine, $(Me_3Si)_2N-N(SiMe_3)-P(Cl)-N(SnMe_3)_2$. The reaction mixture was then allowed to come to room temperature, when it started acquiring a greenish yellow colour. It was then stirred at room temperature for 24 h and filtered to remove NaCl. The greenish yellow filtrate was evacuated and ¹H NMR of the trapped liquid contained a signal at 0.40 ppm due to Me₃SiCl which underwent hydrolysis to give a signal at 0.06 ppm due to $(Me_2Si)_2O$. The residual vellowish semi-solid was evacuated and then heated at 65-70 °C/ 10^{-3} torr to obtain a light yellow sublimate (4.90 g, 45% yield). The sublimate could be recrystallized from n-pentane at low temperatures (m.p. 52 °C). The compound is soluble in common organic solvents. It is stable at room temperature but sensitive to air and moisture. Anal. Found: C, 26.16; H, 6.21; N, 7.44. C₁₂H₃₆N₃PSi₂Sn₂ Calc.: C, 26.35; H, 6.59; N, 7.69%.

¹H NMR in benzene δ (ppm) 0.40 (18 H, 2Me₃Sn), $J(^{117}Sn-^{1}H)$ and $J(^{119}Sn-^{1}H)$ at 55 and 57 Hz, 0.16 (18 H, 2Me₃Si).

²⁹Si NMR in $C_6 D_6$ (eTMS) 7.42 ppm.

¹¹⁹Sn NMR in C_6D_6 (eTMT) 463.7 ppm. ³¹P NMR in C_6D_6 (eH₃PO₄) 301.26 ppm.

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