



Synthesis and structural study of *bis*-, *tris*- and *tetra*-[1,3,5]-dithiazinanyl silanes and stannanes

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Conformational study

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ABSTRACT

The synthesis and structural study of 23 new *bis*-, *tris*-, *tetra*-(dithiazinan-2-yl)silanes and stannanes is reported. The compounds were obtained by reaction of 5-alkyl-[1,3,5]-dithiazinanes (alkyl = Me, ⁱPr, ^tBu) with ^tBuLi followed by addition of R'_nSiCl_{4-n} or R'_nSnCl_{4-n} (*n* = 0–2, R' = Me and Ph) in THF. Structures were determined by ¹H, ¹³C, ²⁹Si or ¹¹⁹Sn NMR, mass spectrometry and X-ray diffraction analyses. Conformation of compounds in the solid state is discussed. The silanyl and stannanyl groups are in equatorial position in *bis* and *tris*-dithiazinanyl compounds in solution. The X-ray diffraction of *tetra*-(*N*-isopropyl-dithiazinan-2-yl)stannane showed that the tin atom is bound to two dithiazinanyl groups by equatorial bonds and to other two by axial bonds. Atomic distances indicate sulfur–silicon and sulfur–tin short contacts. NMR data, in particular ²⁹Si and ¹¹⁹Sn chemical shifts and ¹J(¹³C, ¹¹⁹Sn) coupling constants, indicate the presence of weak S...Si and S...Sn interactions in the compounds. *Ab-initio* calculations were performed for (eq,eq,eq,eq), (ax,ax,ax,ax) and (eq,eq,ax,ax) conformers in order to find the most stable structures in *tetra*-(5-methyl-[1,3,5]-dithiazinan-2-yl)silane and *tetra*-(5-methyl-[1,3,5]-dithiazinan-2-yl)stannane.

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1. Introduction

Herein, we describe the synthesis of *bis*-, *tris*- and *tetra*-[1,3,5]-dithiazinan-2-yl)silanes and stannanes. They are analogs to [cyclohexanyl]_nsilanes (*n* = 2–4) and stannanes. The complex conformational equilibria of [cyclohexyl]_nmethanes (*n* = 2–4) due to their fluxional behavior and to the different rotamers of the central bonds. Refs. [1–3] indicated us the interest of the structural analysis of the *bis*-, *tris*-, and *tetra*-(heterocyclohexanyl)silanes and stannanes which could give several conformers of low energy, some of them chiral [4]. The synthesis of methanes and silanes is difficult due to the steric hindrance of the cycles. *Tetracyclohexylmethane* can only be synthesized by catalytic hydrogenation of *tetraphenylmethane* under soft conditions [5]. The synthesis of *tetracyclohexylsilane* has also been reported to be difficult and it was performed by hydrogenation of *tetraphenylsilane* [6], or by reaction of lithium and cyclohexylchloride followed by addition of

tricyclohexylfluorosilane [7]. In contrast, the *tetracyclohexylstannane* has been simply obtained long time ago [8]. The four cyclohexyl groups are easily accommodated due to the bigger size of the metal atom with respect of the carbon and silicon. In contrast of repulsive interactions of cyclohexanyl groups in crowded *tetracyclohexylmethane* or silane, the lone pairs of the two sulfur atoms in [1,3,5]-dithiazinanyl silane and stannane could give attractive contacts with the silicon or tin atoms stabilizing these compounds and affording preferred conformers, as it was found in boron or phosphorus tripodal derivatives of [1,3,5]-dithiazinanes [9], Scheme 1.

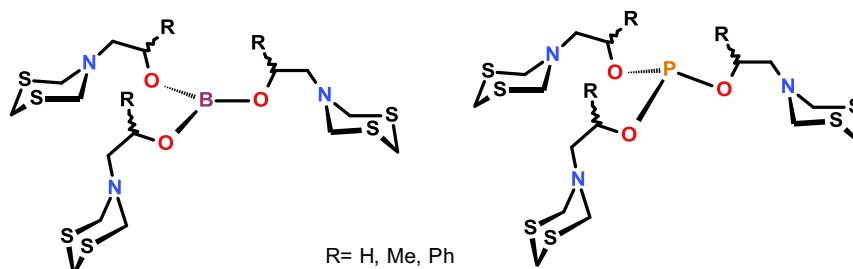
2. Results and discussion

We have already reported tin and silicon compounds bearing one [1,3,5]-dithiazinan-2-yl ring [10], Scheme 2. Due to the structural interest of these new organometallic compounds, we decided to investigate the synthesis of molecules where a central silicon or tin atom bears two, three or four [1,3,5]-dithiazinan-2-yl groups.

[1,3,5]-Dithiazinanes having *N*-methyl (**1**) [11–13] *N*-isopropyl (**2**) [13,14] and *N*-*tert*butyl (**3**) [13] groups have been used as the

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Scheme 1. Boron and phosphorus tripodal compounds derived from *N*-ethanol-[1,3,5]-dithiazinanes [9].

starting heterocycles for building silicon and tin compounds, Scheme 3. Compounds 1–3 are in conformational equilibrium in solution at room temperature, however maintaining the *N*-alkyl group in axial position [14]. This peculiar conformation is due to the electronic repulsions between the free lone pairs of sulfur and the nitrogen atom.

Compounds 1–3 were reacted with $t\text{BuLi}$ in THF in order to form the corresponding lithium derivatives which are reacted *in situ* with silicon and tin halides in THF at low temperature. Reactions afforded compounds 4–26, Scheme 3 [14,15]. In the equimolar reaction of SiMe_2Cl_2 with the lithium derivative of compound 2 in THF, crystals of the disiloxane 27 were obtained as a result of the hydrolysis and dehydration of two (dithiazinan-2-yl)dimethylchlorosilanes. The new compounds 4–27 were characterized by ^1H , ^{13}C , ^{27}Si or ^{119}Sn , NMR, IR, mass and elemental analyses. The structure of compounds 5, 8, 16, 18, 19, 21, 26 and 27 was also determined by X-ray diffraction analyses. Our attempts to obtain the methane analogs of compounds 4–26 were unsuccessful.

2.1. NMR studies

The ^{29}Si NMR spectra of $\text{Me}_2\text{Si}(\text{NR}-[1,3,5]\text{-dithiazinan-2-yl})_2$ (4–6) and $\text{MeSi}(\text{NR}-[1,3,5]\text{-dithiazinanyl})_3$ (16) were obtained and compared with those of $\text{Me}_3\text{Si}(\text{NR}-[1,3,5]\text{-dithiazinanyl})$ (+2.7 to +3.3 ppm) [10]. Data show that in methylsilanes (4–6, 16–17), the [1,3,5]-dithiazinanyl groups slightly shift the silicon resonance to higher frequencies as the number of dithiazinanyl groups increases, due to the low acidity of the silicon and to the weak $\text{S}\cdots\text{Si}$ interactions, as we will discuss later. In phenylsilanes (10–12; 18–20) the effect of the substitution of the phenyl by the dithiazinanyl groups systematically shifts the NMR signals. Therefore, it is possible to calculate the contribution of the dithiazinanyl or phenyl groups to the ^{29}Si chemical shifts in these series of compounds. The chemical shift of the *tetra*-([1,3,5]-dithiazinanyl)silane 25 is –16.9 ppm (Table 1), from this value the contribution to the ^{29}Si chemical shift of each substituent (–4.2 ppm) can be calculated by dividing by 4. On the other side, the chemical shift of the Ph_4Si is –15.0 [16] and therefore the calculated contribution of the phenyl group is –3.7 ppm, similar to that of dithiazinanyl group. The $\text{Ph}_3\text{Si}([1,3,5]\text{-dithiazinanyl})$ appears in the range of –13.4 to –14.0 ppm [10]. The $\text{Ph}_2\text{Si}([1,3,5]\text{-dithiazinanyl})_2$ (10–12) have resonances at –16.2 to –16.5 and $\text{PhSi}([1,3,5]\text{-dithiazinanyl})_3$ (21) at –16.8 ppm. The more important contribution of the [1,3,5]-dithiazinanyl group to the chemical shift in the phenyl series with respect of the methyl

series could be attributed to the electroattractive effect of phenyl group which makes the silicon atoms more acidic.

The ^{119}Sn NMR chemical shifts of tin compounds are more affected by the [1,3,5]-dithiazinanes substitution, than ^{29}Si signals in silane compounds (Table 1). The effect is due to the highest metallic character of tin with respect of silicon atom, and that ^{119}Sn is more sensitive than ^{29}Si to the electronic effect of the substituents [17]. In the methylstannane series, the number of [1,3,5]-dithiazinanyl groups increases the shielding effect of the resonances by the electroattractive effect of the [1,3,5]-dithiazinanyl groups. The more acidic tin atom allows a better $\text{S}\cdots\text{Sn}$ interaction increasing the shifts to lower frequencies. In the phenyl tin series, a systematic contribution of the phenyl groups (–32 ppm) and the [1,3,5]-dithiazinanyl groups (–53 ppm) is found. The ^{119}Sn chemical shift for Ph_4Sn is –128 ppm, whereas that of *tetra* [*N*-*Pr*([1,3,5]-dithiazinanyl)]stannane (26) is –212.5 ppm.

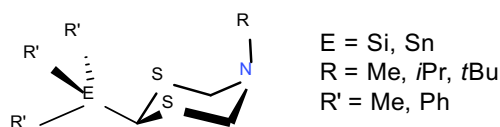
The $^1J(^{13}\text{C}, ^{119}\text{Sn})$ coupling constant values for the SnMe carbon atom are bigger in the tin dithiazinanes (351.2–370.5 Hz) than in the Me_3Sn -cyclohexane (299.4 Hz, Ref. [17]), Table 2. This result clearly indicates that the increase of the constant is due to the sulfur tin weak coordination. The comparison of the $^1J(^{13}\text{C}, ^{119}\text{Sn})$ coupling constant for C2 in the dithiazinanyl- SnMe compounds shows that the values increase with the number of dithiazinanyl substituents. From 281.9 to 291.5 Hz [10] in the monodithiazinanyl compounds to 305.4–309.3 Hz in the *bis*-dithiazinanyl compounds (7–9) and to 331.3–337.2 Hz in the *tris*-dithiazinanyl derivatives (18–20). The increase in the coupling values is proportional to the number of sulfur atoms and therefore this effect can be assigned to weak $\text{S}\cdots\text{Sn}$ interaction. The comparison of the value of these constants in SnMe compounds with those of the SnPh derivatives (Tables 2 and 3) shows that the phenyl groups give bigger constant values due to its electroattractive effect. However, also in the phenyl tin derivatives the coupling constants values are enlarged as the number of dithiazinanes increases. A similar trend is found in the values of the $^2J(^1\text{H}, ^{119}\text{Sn})$ coupling constants with H2 which are discretely increased with the dithiazinane groups.

2.2. X-ray diffraction analyses

2.2.1. Bis-dithiazinanyl compounds

The X-ray diffraction analysis of the $\text{Me}_2\text{Si}(\text{N-isopropyl}-[1,3,5]\text{-dithiazinan-2-yl})_2$ (5) shows that there are two molecules in the asymmetric unit. Due to their similar conformation, only one will be discussed, Fig. 1. Selected bond lengths and angles are in Tables 4 and 5. The silicon atom is *tetracoordinated*, the $\text{CH}_3\text{-Si-CH}_3$ angle (113.08°) is wider than that of $\text{C}_2\text{-Si-C}_2$ (105.42°), which indicates that the [1,3,5]-dithiazinanyl groups do not experience steric repulsion between them. The Si-C_2 bonds present alternated conformations. This solid state conformation is chiral (C2), both enantiomers are found in the cell.

A relevant observation is that the distances between the silicon and the sulfur atoms are very short. They vary between 3.00 and



Scheme 2.

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