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Reaction of *N*-trimethylsilyl derivatives of amides and lactams with chloro(chloromethyl)dimethylstannane: Crystal and molecular structure of 1-(chlorodimethylstannylmethyl)-2-piperidone

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Abstract

A general scheme of reactions between chloro(chloromethyl)dimethylstannane and *N*-trimethylsilylamides and -lactams was established by NMR and IR techniques. The reactions proceed via transmetallation followed by transformation of the *N*-stannylated intermediate (**1**) into (N–Sn)-coordinated *O*-stannylmethyl (**2**) and (O–Sn)-coordinated *N*-stannylmethyl (**3**) derivatives. In the cases of 2-piperidone and 2-hexahydroazepinone these products were isolated as individual compounds (**2b**,**c** and **3b**,**c**). X-ray diffraction study of 1-(chlorodimethylstannylmethyl)-2-piperidone (**3b**) confirmed (3 + 2)-coordination state of the tin atom and axial positions of oxygen and halogen atoms. The experimental and quantum-chemically calculated structural parameters are discussed in comparison with those of related trigonal bipyramidal (TBP) silicon, germanium and tin derivatives. Calculation at the MP2/LanL2DZ/D95 level reveals that the stability of the (O–M)chelates increases in the following order: (O–Si) < (O–Ge) < (O–Sn).

Keywords: Tin; Synthesis; Intramolecular coordination; ^{1}H, ^{13}C, ^{15}N and ^{119}Sn NMR spectra; X-ray study; MP2/LanL2DZ/D95 calculations

1. Introduction

The interest in penta- and hexacoordinated organotin derivatives, in particular compounds with intramolecular coordination, results from their high reactivity, structural and stereodynamic diversity. These properties have been used for modelling of the pathways of nucleophilic substitution at the tin atom [1]. However, at present only few examples of pentacoordinated tin derivatives with intramolecular O–Sn coordination have been reported [1].

As part of a systematic study of hypervalent silicon [2], germanium [3], and tin [4] derivatives containing *N*-amidomethyl and *N*-lactamomethyl C,O-chelating ligands, we have shown earlier that the reaction of *N*-trimethylsilyl (*N*-TMS) derivatives of amides and lactams with $ClCH_2MMe_2Cl$ (M = Si, Ge) [5] proceeds through more than one step [6]. NMR monitoring data indicate that the first step is a transmetallation reaction producing Me_3SiCl [6]. In the case of $ClCH_2SiMe_2Cl$ [M = Si], the transmetallation step is rapid, and is complete within a few minutes even at low temperatures (from −60 to −80 °C). When

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the temperature increases ($-30 < T < -20$ °C), the *N*-[chloromethyl(dimethyl)silyl] intermediates (Si analogs of **1**, Si-**1**, Scheme 1) undergo intramolecular *O*-silylmethylation to yield the corresponding *O*-(chlorodimethylsilylmethyl)imidates (Si-**2**) which subsequently isomerize to *N*-silylmethylated products (Si-**3**) upon further increase in temperature (up to 0–25 °C). In the case of $ClCH_2GeMe_2Cl$ similar transformations occur under more severe conditions [7]. The formation of the transmetallation intermediates (Ge-**1**) is observed at ~ -20 °C, whereas their transformation into *O*-germylmethylated compounds (Ge-**2**) proceeds between −10 and 10 °C, and the following isomerization into the final *N*-germylmethylated (Ge-**3**) at 60 °C or higher temperatures. Here, we discuss the reactions of chloro(chloromethyl)dimethylstannane with *N*-TMS derivatives of amides and lactams and present the X-ray structure of **3b**. Quantum-mechanical calculations (MP2/LanL2DZ/D95) were employed to study the structure and thermodynamic stability of **3b** as well as its Si- and Ge-analogs.

2. Results and discussion

2.1. Synthesis and NMR studies

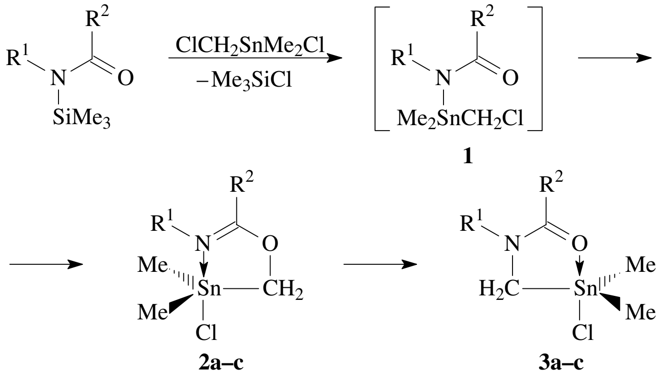
The reactions of $ClCH_2SnMe_2Cl$ with *N*-TMS-amides and -lactams require more drastic conditions than those necessary for the silicon and germanium analogs [8].

NMR monitoring of a mixture of equimolar amounts of $ClCH_2SnMe_2Cl$ and *N*-TMS-*N*-methylacetamide in $CDCl_3$ shows initially only the formation of an intermolecular (1:1) complex of the reactants at −30 to −60 °C, and no noticeable transmetallation product, as is evident from the absence of Me_3SiCl formation. Formation of similar molecular adducts between Me_2SnCl_2 and Me_3SnBr with donor solvents (including DMF) has been reported previously [9a]. The adduct formation is indicated by a large upfield shift of the corresponding ^{119}Sn NMR signal, from 112.3 ppm (in $CDCl_3$, characteristic of $ClCH_2SnMe_2Cl$), to −1.5 ppm at 20 °C, assigned to the 1:1 adduct. The latter signal is temperature dependent, −50 ppm at −50 °C. A small amount of the unstable transmetallation product **1a** ($R^1 = R^2 = Me$) appears and is observed in the NMR spectra for 2 h at −20 °C and for 5 min at 20 °C, perhaps as DA-complexes with $ClCH_2SnMe_2Cl$, before reacting further to **2**. The formation of products **2a** and **3a** (in a 2:7 population ratio) is complete at room temperature within 80 h. At 70 °C, the reaction is complete within 5 h and leads to a different product ratio, **2a**:**3a** = 1:10. The NMR parameters of compounds **1a**–**3a** are collected in Table 1.

Interestingly, the analogous reactions of $ClCH_2SnMe_2Cl$ with *N*-triethylgermyl- and *N*-trimethylstannyl-*N*-methylacetamides in $CDCl_3$ solutions were found to proceed faster. NMR monitoring revealed that these reactions are complete within 20–25 min at 60 °C to yield 7:3 and 5:4 ratios of the products **2a**:**3a** for *N*-germylated and *N*-stannylated amides, respectively.

These results suggested a synthetic strategy for the preparation of compounds **2a** and **3a**: the (*N*–Sn)-chelate **2a** was prepared in 62% yield by stirring an equimolar $CDCl_3$ solution of $ClCH_2SnMe_2Cl$ and *N*-triethylgermyl-*N*-methylacetamide at 20 °C for 48 h, followed by crystallization from *n*-heptane. Heating of a similar solution in *n*-heptane to 100 °C for 24 h, followed by crystallization from ether, afforded the (O–Sn)-chelate **3a** as a yellowish amorphous product (m.p. 220 °C), which contained a few percent of the isomeric **2a**.

Preparation of the *N*-lactamomethyl derivatives **3b**,**c** as individual compounds requires even higher temperatures. Similar to their silicon [6] and germanium [7] analogs, tin derivatives **2b**,**c** and **3b**,**c** can be characterized in the IR spectra by the adsorption bands at ~1655 (average intensity) of the C=N adsorption and ~1590 and 1500 cm^{-1} (strong) of the NCO fragment. In the IR spectrum of the solution of *N*-TMS-caprolactam and $ClCH_2SnMe_2Cl$ in an inert solvent (*o*-xylene), both types of these absorptions were found to appear simultaneously at 80–100 °C. Refluxing the reaction mixture (144–145 °C) noticeably increases the absorption at 1590 cm^{-1}, although the band of the lac-



Scheme 1.

Table 1
^1H, ^{13}C, ^{14}N, ^{119}Sn NMR chemical shifts (spin-coupling constants, Hz) of compounds **1a**–**3a**

Compound		δ (ppm)				
		$(CH_3)_2Sn$	CH_3C	CH_3N	$SnCH_2$	OCN
1a[a]	^1H	0.43	2.04	2.91	3.28	
	^{119}Sn	8.7				
2a	^1H	0.63	2.02	2.93	3.92	
	^{13}C	0.23	15.71	32.94	57.75	171.9
		$^1J_{CSn}$ 566 Hz			$^1J_{CSn}$ 632 Hz	
	^{14}N	−186.06				
	^{119}Sn	−73.50				
3a	^1H	0.67	2.12	3.22	2.87	
	^{13}C	0.87	20.10	39.11	40.14	174.4
		$^1J_{CSn}$ 546 Hz			$^1J_{CSn}$ 552 Hz	
	^{14}N	−278.16				
	^{119}Sn	−40.60				

[a] The ^{14}N chemical shifts are given from CH_3NO_2.