THREE-MEMBERED RINGS WITH A COORDINATION BOND

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1965

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Abstract

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UDC 542.957

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(Presented by Academician N. N. Semenov, 1 VII 1965)

In previous communications we discussed the "lateral" electronic interaction in the system

$$>\mathrm{N}-\mathrm{C}-\mathrm{X},$$

where X is an atom with an unshared electron pair (^{1,2}). Most naturally, the N–X interaction in this system may be represented when atom X has vacant orbitals. In this case a three-membered ring with a coordination bond is possible in principle:

$$\begin{array}{c} >\mathrm{N} \\ \downarrow \\ \mathrm{X} \end{array}$$

An unambiguous proof of such an effect is of interest not only in itself. It would have far-reaching consequences for considering numerous transformations of geminal systems in a unified way.

By the method described earlier (^{3}), we obtained and studied a series of geminal derivatives with a tin atom (Table 1). The structure of the products was confirmed by NMR data (Table 2), IR and mass spectra (Fig. 1)*.

Table 1

Compound	Yield, %	B.p., °C/mm Hg	n_D^{20}	d_4^{20}	MRD found	MRD calc.	C, % found	C, % calc.	H, % found	H, % calc.	N, % found	N, % calc.	Sn, % found	Sn, % calc.
I	81.0	66.2–67.0/1.2	1.4998	1.3207	58.30	58.59	36.42; 36.72	36.40	7.42; 7.53	7.25	–	–	44.49; 44.80	44.97
II	94.4	192.8–193 m.p.	–	–	–	–	26.70; 26.85	26.63	5.82; 5.86	5.46	3.70; 3.77	3.45	28.55; 29.05	29.24

Compound	Yield, %	B.p., °C/mm Hg	n_D^{20}	d_4^{20}	MRD found	MRD calc.	C, % found	C, % calc.	H, % found	H, % calc.	N, % found	N, % calc.	Sn, % found	Sn, % calc.
III	96.5	106.6–107.8 m.p.	—	—	—	—	32.33; 32.40	31.98	7.13; 7.14	6.71	—	—	—	—
IV	58.7	54–55.5/20	1.4820	1.3104	47.84	47.51	33.36; 33.39	32.77	7.21; 7.21	6.88	6.17; 6.35	6.37	53.64; 53.71	53.98
V	74.2	55.7–56/0.8	1.5279	1.3511	55.60	54.27	39.31; 39.40	39.39	6.42; 6.46	6.20	—	—	48.35; 48.46	48.66
VI	45.8	59.2–59.5/65	1.4570	1.3190	43.13	42.90	29.26; 29.27	28.75	7.04; 7.09	6.76	—	—	—	—
VII	60.0	68–69/15	1.4754	1.2462	56.90	56.85	38.32; 38.32	38.29	8.13; 2.28	8.03	—	—	—	—
VIII	70.0	49.8–50.0/1.0	1.4760	1.2730	54.50	54.85	38.84; 38.96	39.07	7.72; 8.05	6.97	—	—	47.39; 47.65	48.27
IX	52.3	61.2–62.6/16	1.4662	1.3991	46.91	47.36	30.02; 30.92	30.42	6.04; 6.13	5.96	—	—	—	—
X	72.2	48.5–50/10	1.4874	1.3299	60.37	61.30	38.54; 38.74	38.75	7.51; 7.60	7.23	—	—	—	—
XI*	80.6	46.5–48/18	1.4893	1.5071	40.99	41.31	—	—	—	—	—	—	—	—
XII	32.6	97–101/745	1.4443	1.4328	36.51	36.24	—	—	—	—	—	—	—	—

Compounds: I. $(CH_3)_3SnCH_2N$(morpholine), II. $(CH_3)_3SnCH_2N^+(CH_3)$(morpholine) I^-, III. $(CH_3)_3SnCH_2{-}N^+H$(morpholine) Cl^-, IV. $(CH_3)_3SnCH_2N$(aziridine), V. $(CH_3)_3SnCH_2N$(pyrrole), VI. $(CH_3)_3SnCH_2OCH_3$, VII. $(C_2H_5)_3SnCH_2OCH_3$, VIII. $(C_2H_5)_3SnCH_2CN$, IX. $(CH_3)_3SnCH_2OCOCH_3$, X. $(C_2H_5)_3SnCH_2OCOCH_3$, XI. $(CH_3)_3SnCH_2Cl$, XII. $(CH_3)_3SnCH_2F$.

* Literature data: b.p. 44–48/15; n_D^{20} 1.4860; d_4^{25} 1.5560 (4).

Determination of the basicity of aminomethylstannanes (Table 3) shows that the basicity constant (K_b) is 4 orders of magnitude lower than in the corresponding carbon analogs. A less pronounced decrease in K_b is observed for aminomethylgermanes (5) and contradictory data for silanes (5,6). Lower–

* In the first spectrum of Fig. 1 the maximum peak is reduced 10-fold.

Table 2

Chemical shifts in NMR spectra relative to the signal of hexamethyldisiloxane (measured on a JNM-C-60 instrument) and in nuclear gamma-resonance (NGR) spectra
relative to SnO_2 (10)

Compound	δ_{CH_3-Sn}	δ_{CH_2}	$J[H'_3(C-Sn^{117,119})]$, Hz	$J[H'_2(C)-Sn^{117,119}]$, Hz	δ of other protons	NGR (10) δ, mm/sec	NGR (10) Δ, mm/sec
I	0,06	2,25	50,4	28,8	CH_2N 2,17; CH_2O 3,45	1,38	0,0
II	0,19	3,19	57,6	–	CH_2N 3,24; CH_2O 3,81	1,17	0,0
IV	0,05	2,08	52,8	30,0	CH_3N 3,02	1,32	0,0
IVa	–	2,08	–	–	cycl.: 0,73; 1,53	1,32	0,0
V	–0,04	3,52	50,4	26,4	cycl.: 0,70; 1,51	1,38	0,0
VI	0,025	3,53	52,8	16,2	αH 5,97; βH 6,33; CH_3O 3,16	1,38	0,0
VII	–	–	–	–	–	1,35	0,0
VIII	–	–	–	–	–	1,29	0,0
IX	0,03	3,99	49,8	15,6	CH_3CO 1,87	1,35	0,0
X	–	–	–	–	–	1,35	0,0
XI	0,30	2,84	55,8	19,8	–	1,32	0,0
XII	–0,09	4,77	48,0	48,0	–	1,38	0,0
$(CH_3)_4Sn$	–0,01	–	53	–	–	1,30	0,0

Table 3

Basicity of aminomethylstannanes, -germanes, and -silanes (determined by potentiometric titration with respect to pH during half-neutralization in aqueous dioxane, $C \sim 10^{-2}$ mole/l at 20° on an LPU-01 instrument)

Compound	pK	K_b
$(C_2H_5)_3SnCH_2N(CH_3)_2$	7,73	$1,86 \cdot 10^{-8}$

Compound	pK	K_b
$(CH_3)_3SnCH_2N(CH_2CH_2)_2O$	7,03	$9,33 \cdot 10^{-8}$
$(CH_3)_3GeCH_2N(C_2H_5)_2$	5,15	$7,10 \cdot 10^{-6}$ (5)
$(CH_3)_3SiCH_2N(C_2H_5)_2$	4,10	$7,90 \cdot 10^{-5}$ (5)
$(CH_3)_3SiCH_2NH_2$	3,0–3,3	$5,0—9,6 \cdot 10^{-4}$ (6)
$(CH_3)_3CCH_2NH_2$	3,8	$1,6 \cdot 10^{-4}$ (6)

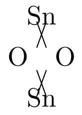
···tion of the basic properties is manifested in the iodomethylation reaction of I, which proceeds with an almost quantitative yield only after 27 days (28 hr, 37.6%; 94 hr, 67.6%; 195 hr, 80%; 648 hr, 94.4%). Aminomethylgermanes and silanes are iodomethylated completely in 8-10 hr (5).

A considerable decrease in the basic properties of nitrogen can be explained by a change in the coordination number of tin and by the formation of an intramolecular coordination bond N → Sn, with some transfer of the unshared electron pair of nitrogen to the vacant orbital of tin with partial sp^3d character.

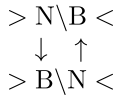
From the decrease in basicity one can estimate the upper limit of the strength of the N → Sn bond. From

$$\frac{k_1}{k_2} = \exp\left(-\frac{\Delta\Delta E}{RT}\right); \qquad \Delta\Delta F = \Delta\Delta H - T\Delta\Delta S^\circ,$$

neglecting the change in the entropy term, we obtain $\Delta\Delta H \sim 5.5$ kcal/mole. A close value (4.5 kcal/mole) was found for the energy of the O → Sn interaction in a distannoxane of the type



(7) and N → B in dimers of aminomethyldimethylborane (4.49 kcal/mole) (8):



$$\begin{array}{c} >N\backslash B< \\ \downarrow \quad \uparrow \\ >B\backslash N< \end{array}$$

The N → Sn interaction is confirmed by the slowing of nitrogen inversion in ethyleneiminomethylstannanes. For a change in configuration in this case, in addition to overcoming the inversion barrier, rupture of the coordination bond is necessary.

Fig. 1

Fig. 1

Figure 1: Fig. 1

Coalescence of the doublet signal of the ethyleneimine protons in the spectra of IV is observed at $t_c > 140^\circ$, whereas in N-alkylethyleneimines the signals coalesce into a narrow singlet at $t_c = 60$—80° (^{2}). The inversion barrier in N-alkylethyleneimines is 10 kcal, which is close to the barrier of hindered rotation in dimethylformamide (7 kcal) and dimethylacetamide (12 kcal; $t_c = 63^\circ$), while in nitrosodimethylamine $t_c = 193^\circ$ and the rotational barrier is 23 kcal. Estimation of the strength of the $N \to Sn$ bond from these data leads to a value of the same order as from the decrease in basicity.

In the UV spectra of aminomethylstannanes, in contrast to tetraalkylstannanes, a small bathochromic shift and a significant increase in the extinction coefficient are observed (Table 4).

The possibility of intermolecular interaction with the formation, for example, of a dimer

$$\begin{array}{cc} > N & Sn < \\ \downarrow & \uparrow \\ > Sn & N < \end{array}$$

is excluded by the constancy of the molecular weight when it is determined for compound I by the cryoscopic method (in benzene at concentrations of $0.2 \div 2.8\%$) and by the electrothermal method (^{9}) (in cyclohexane and methyl ethyl ketone in the range $1.2 \div 11\%$).

The absence of quadrupole splitting and the small changes in chemical shifts in the Mössbauer spectra (Table 2) (^{10}) can be explained by insufficient sensitivity of the method to weak interactions. Thus, for the limiting cases, when the coordination number of tin is 4 in the case of $(CH_3)_3SnCl$, $\delta = 1.40$, $\Delta = 3.09$, and for the corresponding complex with pyridine, when the coordination number is 5, $\delta = 1.42$; $\Delta = 3.35$ (^{11}). In addition, dialkyldicarboxylates of tin in the δ and Δ values differ hardly at all from the analogs of distannoxanes $^{(12)}$, for which the presence of an O $\to$ Sn interaction has been clearly proved $^{(7)}$; in the NMR spectra the effect appears only when the number of distannoxane units in the molecule is increased $^{(10)}$.

Thus, despite the absence of convincing data on the coordinating ability of tetraalkylstannanes, it must be admitted that in aminomethylstannanes there is an intramolecular coordination interaction, energetically close to a hydrogen bond. The phenomenon is evidently due to the fixed arrangement of the tin and nitrogen atoms (position effect), which favors interaction with a partial change in hybridization and configuration and with the approach of N $\to$ Sn from the initial state:

Sn ·········· N

2.18 Å 109°28′ 1.47 Å
Sn·············N

3.00 Å

An analogous interaction can explain the increase in the mobility of halide in trialkylchloromethylstannanes (3,5). The effect increases in the presence of electronegative substituents at tin; thus, in trichloromethylchlorostannane (ν_{CH}3015 cm^{-1}) and in halomethyltrihalogermanes ($\nu_{CH} > 3000$ cm^{-1}) (5), the valence vibrations of the $C-H$ bonds lie in the region characteristic of a three-membered ring. It is interesting that the chemical shift of the protons of the CH_2 group of aminomethyldimethylborane lies in the region characteristic of three-membered rings (7). The ejection of difluorocarbene from $(CH_3)_3SnCF_3$ can likewise be explained by an F → Sn interaction (13).

Table 4

UV spectra in hexane

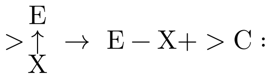
Compound	λ_{max}, mμ	ε
$(CH_3)_4Sn$	215.2	4.8
$(CH_3)_3SnCH_2F$	211.5	24.2
$(CH_3)_3SnCH_2N$with a three-membered N-heterocycle	216.4	194
$(CH_3)_3SnCH_2N$with a six-membered morpholine-type N, O-heterocycle	217.0	558

The reason for the enhancement of the effects in the series

$$Sn > Ge > Si$$

should evidently be sought not in the difference in the electronegativities of the elements (which is too small!), but in an increase in coordinating ability (14).

The formation of an intramolecular coordination bond is evidently a general property of geminal systems with atoms (E) having vacant *p*- or *d*-orbitals and unshared electron pairs (X): for $BCH_2N <$ there is evidence in favor of an N → B interaction (8), while in $-ZnCH_2X$ (15), $-HgCH_2X$ (16), $> SiCH_2X$ (17), $> PCH_2X$ (18) one may propose a unified mechanism of carbene ejection:



$$>\overset{E}{\underset{X}{\uparrow}}\rightarrow E-X+>C:$$

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Received
30 VI 1965

CITED LITERATURE

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Note: Figure translations are in progress. See original paper for figures.