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## SHORT COMMUNICATION

### Some infrared studies of organometallic pseudohalogen\*

As part of a detailed investigation into the structure, bonding, and chemical properties of pseudohalogen groups attached to organometallics, we have prepared the series of compounds  $(\text{CH}_3)_3\text{MX}$  ( $\text{M} = \text{Si, Ge, Sn, Pb}$ ;  $\text{X} = \text{NCO, NCS, N}_3$ ), and studied their infrared spectra from 4000 to  $300\text{ cm}^{-1}$ . While many of these compounds have been previously prepared, detailed infrared spectra have been reported only for the azides<sup>1</sup>. The compounds studied in this investigation are listed in Table I.

Investigation concentrated on the three vibrational modes internal to the pseudohalogen group (two stretching, one bending) and the metal-pseudohalogen

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TABLE I  
COMPOUNDS PREPARED AND SOME OF THEIR INFRARED ABSORPTIONS

Compound	Syn. Meth. <sup>a</sup>	M. p.	B. p.	$\nu_{\text{as}}(P_s)$ <sup>b</sup>	$\nu_{\text{sym}}(P_s)$ <sup>b</sup>	$\delta(P_s)$ <sup>b</sup>	$\nu(M-P_s)$ <sup>b</sup>	Ref.
<i>Azides</i>								
$(CH_3)_3SiN_3$	1, 3, 4	-95°	96°	2145	1336	685	528	1
$(CH_3)_3GeN_3$	2, 3	-65°	136°	2102	1290	675	456	1, 17
$(CH_3)_3SnN_3$	2	121-2°		2045 (2088) <sup>c</sup>	1286	665	462 (401) <sup>c</sup>	1, 14
$(CH_3)_3PbN_3$	2	dec. 105°		2034	1279	655		1
<i>Isocyanates</i>								
$(CH_3)_3SiNCO$	3, 4	-49°	91°	2290	1435	616	521	5
$(CH_3)_3GeNCO$	3, 4		122°	2240	1415	606	454	
$(CH_3)_3SnNCO$	4	105-7°		2215 (2243) <sup>c</sup>	1375 (?)	618	400	
$(CH_3)_3PbNCO$	4	dec. 220°		2190	1325 (?)	606		
<i>Isothiocyanates</i>								
$(CH_3)_3SiNCS$	3	-32.8°	143°	2080	956	470	436	5
$(CH_3)_3GeNCS$	4, 5		191.5-93°	2075	892	476		18
$(CH_3)_3SnNCS$	3	107-10°		2073	1065	478		19
$(CH_3)_3PbNCS$	3	dec. 145°		2090	1030 1005	464		

<sup>a</sup> Synthetic methods: 1.  $(CH_3)_3Si_2NH + HN_3$ ; 2.  $(CH_3)_3M(OH) + HN_3$ ; 3.  $(CH_3)_3MCl + AgX$ ; 4.  $(CH_3)_3MCl + AgX$ ; 5.  $(CH_3)_3GeCN + S$ .  
<sup>b</sup> P<sub>s</sub> = pseudohalide; M = metal; <sup>c</sup> Run in CH<sub>2</sub>Cl<sub>2</sub> or CHCl<sub>3</sub> solution.

stretching mode. These are listed in Table 1. Infrared peaks arising from vibrations of the organic group do not differ appreciably from those reported elsewhere (see Ref. 1 and papers cited therein), and are not given here. Raman spectra for  $(\text{CH}_3)_3\text{SiNCO}^2$ ,  $(\text{CH}_3)_3\text{SiNCS}^3$ , and  $(\text{CH}_3)_3\text{SiN}_3^4$  have been reported; peak assignments for both infrared and Raman spectra of these compounds are given in Table 2.

Bands arising from the metal-pseudohalogen stretching mode appear in the KBr-CsBr region of the infrared; a previous assignment of Si-N<sub>3</sub> and Ge-N<sub>3</sub> bands to 880 cm<sup>-1</sup> and 796 cm<sup>-1</sup> respectively is in error<sup>1</sup>. No bands arising from this vibrational mode could be found in the trimethyllead compounds or in  $(\text{CH}_3)_3\text{SnNCS}$ . The metal-thiocyanate bands appear at considerably lower frequency than the corresponding bands of the other two series, at present, no explanation can be offered for this. These values are in good agreement with previously reported work<sup>2-4,6-13</sup>.

Since both cyanate and thiocyanate are capable of bonding isomerism, the question arises as to which form exists in these compounds. For silicon, there is strong evidence that both the cyanate and thiocyanate bond through nitrogen<sup>2,3,6-11</sup>, making them iso compounds. Similar evidence, though less complete, also exists germanium<sup>10</sup> and tin<sup>12</sup> compounds. There is no strong evidence one way or the other for lead compounds, but the spectra of trimethyllead (iso)cyanate and (iso)thiocyanate strongly resemble those of their lighter homologs, suggesting that the iso structure is the correct one.

In common with many other trimethyltin derivatives,  $(\text{CH}_3)_3\text{SnN}_3$  has been reported to have a bridging azide group in the solid state<sup>1,14</sup>.  $\nu_{as}(\text{N}_3)$  shifts to higher frequency when  $(\text{CH}_3)_3\text{SnN}_3$  goes into solution, while  $\nu(\text{Sn-N}_3)$  shifts to lower frequency under the same conditions. These shifts are consistent with such a bridging group.  $(\text{CH}_3)_3\text{SnNCO}$  shows a similar shift under the same conditions. X-ray studies of  $(\text{CH}_3)_3\text{SnCN}$  indicates the presence of a bridging cyanide group<sup>15</sup>.

$(\text{CH}_3)_3\text{SnN}_3$  forms yellowish solid complexes with  $(\text{C}_2\text{H}_5)_3\text{N}$  and  $\text{C}_3\text{H}_5\text{N}$ , probably with 1:1 stoichiometry. These complexes dissolve in  $\text{CH}_2\text{Cl}_2$  without dis-

TABLE 2  
INFRARED AND RAMAN DATA OF TRIMETHYLSILYL PSEUDOHALIDES

Assignment	$(\text{CH}_3)_3\text{SiN}_3$		$(\text{CH}_3)_3\text{SiNCO}$		$(\text{CH}_3)_3\text{SiNCS}$	
	Infrared	Raman <sup>4</sup>	Infrared	Raman <sup>2</sup>	Infrared	Raman <sup>3</sup>
$\nu_{as}$ CH	2990	2970	2985	2963	2980	2968
$\nu_{sym}$ CH	2912	2905	2915	2901	2900	2905
$\nu_{as}$ Pseud.	2145	2141	2290		2080	2066
$\delta_{as}$ CH <sub>3</sub>	1430, 1405	1414	1415	1412	1415	1416
$\nu_{sym}$ Pseud.	1332	1324	1435	1435	956	993
$\delta_{sym}$ CH <sub>3</sub>	1259	1264	1255	1260	1259	1295
$\rho_{as}$ CH <sub>3</sub>	849	853	850	850	840	854
$\rho_{sym}$ CH <sub>3</sub>	755	761	755	761	758	764
$\nu_{as}$ SiC <sub>3</sub>	693	700	690	701	690	706
$\delta$ Pseud.	685		616		470	467
$\nu_{sym}$ SiC <sub>3</sub>	620	620	642	644	630	632
$\nu$ Si-Pseud.	528	534	521	528	436	433
$\delta$ CSiN		287		280		277
$\delta_{sym}$ SiC <sub>3</sub>		206		208		214
$\delta_{as}$ SiC <sub>3</sub>		117		151		151

sociation.  $\nu_{as}(\text{N}_3)$  appears at  $2060\text{ cm}^{-1}$  in both complexes, and shows no positional shift when the complexes go into solution.

Both  $(\text{CH}_3)_3\text{SiN}_3$  and  $(\text{CH}_3)_3\text{SiNCO}$  have anomalously high stretching bands compared to their organic analogs<sup>1,16</sup>; dative  $\pi$ -bonding between silicon and nitrogen has been suggested as the cause for this. The steady bathochromic shift in these as the central atom changes to germanium, tin, and lead is probably due to a decrease in this  $\pi$ -bonding, plus a mass effect. The isothiocyanates do not show a regular pattern, but there is other evidence to indicate considerable dative  $\pi$ -bonding between silicon and nitrogen<sup>3,6,8,11</sup>.

### Experimental

*General.* The compounds in Table I were prepared by standard synthetic methods elsewhere described<sup>1,5,19</sup>. Only those compounds not previously reported will be described here.

*Isocyanatotrimethylgermane.* A solution of 0.644 g (0.00325 moles)  $(\text{CH}_3)_3\text{GeBr}$  in 5 ml diethyl ether was refluxed over 0.579 g (0.00386 moles)  $\text{AgOCN}$  for 24 h. Fractional distillation gave 0.142 g (27.4%)  $(\text{CH}_3)_3\text{GeNCO}$ , a clear, colorless liquid boiling at  $120\text{--}122^\circ$ . Purity was established through infrared spectroscopy.

*Trimethyltin isocyanate.* A solution of 2.0 g (0.010 moles)  $(\text{CH}_3)_3\text{SnCl}$  in 50 ml benzene was refluxed for 10 h over 1.7 (0.011 moles)  $\text{AgOCN}$ . The resulting mixture was filtered while hot, and the filtrate evaporated to yield the crude product. Recrystallization from diethyl ether gave 1.0 g (48%)  $(\text{CH}_3)_3\text{SnNCO}$ , m.  $105\text{--}7^\circ$ . (Found: C, 23.27; H, 4.67.  $\text{C}_4\text{H}_9\text{NOSn}$  calcd.: C, 23.34; H, 4.41%.)

*Trimethyllead isocyanate.* A solution of 2.9 g (0.010 moles)  $(\text{CH}_3)_3\text{PbCl}$  in 50 ml benzene was refluxed for 11 h over 2.0 g (0.013 moles)  $\text{AgOCN}$ . The resulting mixture was filtered while hot, and the filtrate evaporated to yield the crude product. Recrystallization from benzene gave 0.3 g (10%)  $(\text{CH}_3)_3\text{PbNCO}$ , dec.  $210^\circ$ . (Found: C, 16.55; H, 3.23.  $\text{C}_4\text{H}_9\text{NOPb}$  calcd.: C, 16.32; H, 3.08%.)

*Trimethyllead isothiocyanate.* A solution of 2.9 g (0.010 moles)  $(\text{CH}_3)_3\text{PbCl}$  in 50 ml benzene was refluxed for 12 h over 1.1 g (0.011 moles)  $\text{KSCN}$ . The resulting mixture was filtered while hot and allowed to stand in a closed container. Crystal formation occurred after 24 h. The solid was recrystallized from benzene to give 1.1 g (34%)  $(\text{CH}_3)_3\text{PbNCS}$ , dec.  $145^\circ$ . (Found: C, 15.48; H, 3.00.  $\text{C}_4\text{H}_9\text{NSPb}$  calcd.: C, 15.48; H, 2.92%.)

*Amine complexes of trimethyltin azide.* Solutions of  $(\text{CH}_3)_3\text{SnN}_3$  in  $\text{CH}_2\text{Cl}_2$  were treated with approximately equimolar quantities of  $(\text{C}_2\text{H}_5)_3\text{N}$  or  $\text{C}_5\text{H}_5\text{N}$ . The mixtures were allowed to stand for 24 h, after which the solvent was stripped off under vacuum.  $(\text{CH}_3)_3\text{SnN}_3 \cdot \text{N}(\text{C}_2\text{H}_5)_3$ , m.  $125\text{--}128^\circ$ , and  $(\text{CH}_3)_3\text{SnN}_3 \cdot \text{NC}_5\text{H}_5$ , m.  $136\text{--}137^\circ$ , are yellowish solids, stable to air but rapidly decomposed by moisture.

*Infrared work.* Infrared spectra were run on Perkin-Elmer Model 21 Recording Spectrophotometers having NaCl and CsBr prisms. All compounds were run as solutions (5–10%) in  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ , or  $\text{CCl}_4$ , and as neat liquids or mulls. Polystyrene bands at  $1603$  and  $906\text{ cm}^{-1}$  were used to calibrate spectra in the NaCl region. Peak positions are accurate to  $\pm 5\text{ cm}^{-1}$  in the NaCl range,  $\pm 2\text{ cm}^{-1}$  in the CsBr range.

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## PRELIMINARY NOTES

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### Synthesis of some pentasilyl-substituted cyclohexenes

Earlier reports from these Laboratories<sup>1-3</sup> have shown that the reaction of certain chlorosilanes with lithium and chlorotrimethylsilane in tetrahydrofuran (THF) is a convenient method for a one-step preparation of some trimethylsilyl-substituted silanes. By this procedure, silicon tetrachloride gave high yields of tetrakis(trimethylsilyl)silane<sup>1</sup>. Methyltrichlorosilane<sup>2</sup>, dimethyldichlorosilane and methylethyldichlorosilane<sup>3</sup> afford very good yields of tris(trimethylsilyl)methylsilane, octamethyltrisilane and 2-ethylheptamethyltrisilane, respectively.

As a result of studies designed to determine the scope of this *in situ* type reaction, we are now reporting that phenyl-substituted chlorosilanes react with lithium and chlorotrimethylsilane to give, in addition to the normal coupling products, pentasilyl-substituted cyclohexenes. Thus, phenyltrichlorosilane gave the known<sup>4</sup> tris(trimethylsilyl)phenylsilane (I) and 2-[(tetra(trimethylsilyl)cyclohexen-1-yl]-2-trimethylsilylhexamethyltrisilane (II), m.p. 222-227°. (Found: mol. wt., 617.  $\text{C}_{27}\text{H}_{63}\text{Si}_5$ . Calcd.: mol. wt., 617.5.)

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