Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

REACTIONS OF GROUP IV ORGANOMETALLIC COMPOUNDS XXIII*. SOME ADDITION REACTIONS OF ASYMMETRIC HEPTAMETHYLDIMETALLAZANES: $Me_3M{-}NMe{-}M'Me_3$ WITH HETEROCUMULENES

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(Received June 21st, 1971)

SUMMARY

The structures of the addition products of heptamethylsilagermazane and heptamethylsilastannazane with isocyanates or isothiocyanates have been elucidated spectroscopically. The substituents on the heterocumulenes, the migratory aptitudes of the Me_3M groups ($Me_3Si > Me_3Ge > Me_3Sn$), and the affinity of each metal for the nitrogen, oxygen, or sulphur atom determines which of the possible isomeric structures is favoured in each case.

INTRODUCTION

The chemical reactions of heptamethyldimetallazane and related compounds, especially the reactions with a number of unsaturated bonds, can be interpreted in terms of addition–elimination processes[2–7]. The direction of the β-eliminations from the addition products are mainly determined by the affinity of the metal atom towards the nitrogen, oxygen, or sulphur atoms, and from sets of addition–elimination reactions such as those in Eqn. 1–8:

$$(Me_3Si)_2NMe + Ph{-}N{=}C{=}O \xrightarrow{\Delta} (Me_3Si)_2O + Ph{-}N{=}C{=}N{-}Me^2 \quad (1)$$

$$(Me_3Si)_2NMe + Ph{-}N{=}C{=}S \rightleftharpoons (Me_3Si)_2NPh + Me{-}N{=}C{=}S \rightleftharpoons$$
$$\rightleftharpoons (Me_3Si)_2S + Ph{-}N{=}C{=}N{-}Me^3 \quad (2)$$

$$(Me_3Si)_2NMe + S{=}C{=}S \xrightarrow{\Delta} (Me_3Si)_2S + Me{-}N{=}C{=}S^3 \quad (3)$$

$$(Me_3Ge)_2NMe + Ph{-}N{=}C{=}S \xrightarrow{\Delta} (Me_3Ge)_2S + Ph{-}N{=}C{=}N{-}Me^4 \quad (4)$$

$$(Me_3Ge)_2O + Ph{-}N{=}C{=}S \xrightarrow{\Delta} (Me_3Ge)_2S + Ph{-}N{=}C{=}O^4 \quad (5)$$

$$(Me_3Sn)_2NMe + Ph{-}N{=}C{=}S \longrightarrow (Me_3Sn)_2S + Ph{-}N{=}C{=}N{-}Me^{3-5} \quad (6)$$

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* For part XXII see ref. 1.

$$(Bu_3Sn)_2O + Ph\text{-}N{=}C{=}S \rightarrow (Bu_3Sn)_2S + Ph\text{-}N{=}C{=}O^6 \quad (7)$$

$$(Bu_3Sn)_2N\text{-}Ar + Cl_3C\text{-}CH{=}O \rightarrow (Bu_3Sn)_2O + Cl_3C\text{-}CH{=}N\text{-}Ar^7 \quad (8)$$

the following affinity orders were established for the Me_3M groups:

Me_3Si; $O > S \geqslant N$

Me_3Ge: $S > O \simeq N$

Me_3Sn: $S > O > N$

These orders would be expected to correlate with the relevant bond energies, soft–hard characters, and electronegativities, but such correlations have not been established, and the orders remain essentially empirical.

In this paper, the addition reactions of asymmetric Group IV dimetallazanes with isocyanates and isothiocyanates are considered; such reactions involving the asymmetric compounds have been little studied previously[8].

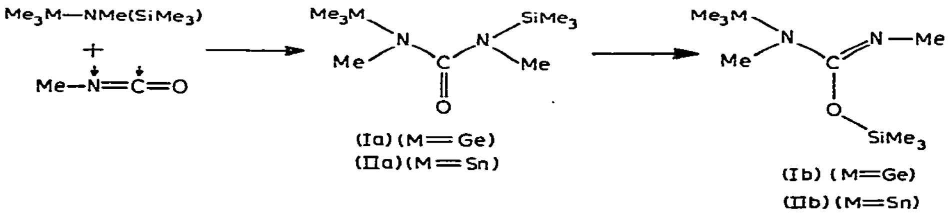
RESULTS AND DISCUSSIONS

The addition products obtained from the reactions of heptamethylsilagermazane, $Me_3Si\text{-}NMe\text{-}GeMe_3$, or heptamethylsilastannazane, $Me_3Si\text{-}NMe\text{-}SnMe_3$, with methyl or phenyl isocyanate and isothiocyanates are mostly more stable than those from the symmetric dimetallazanes or from related compounds, as shown in Eqn. 1–8, from which β-eliminations frequently occurred. Detailed investigation of the structures of the addition products should assist understanding the affinities of the trimethylmetallyl groups for the heteroatoms in the intermediate 1/1 adducts.

Cleavage of the metal–nitrogen bond might be expected to occur readily in the order, Sn–N > Ge–N > Si–N, based on Abel's basicity scales derived from $\Delta\nu$(C–D) (cm^{-1}, $CDCl_3$)[9]; for $Me_3Sn\text{-}NEt_2$ the value of $\Delta\nu$(C–D) is 90, for $Me_3Ge\text{-}NEt_2$, 82, and for $Me_3Si\text{-}NEt_2$, 64 cm^{-1}.

Addition reactions of $Me_3Si\text{-}NMe\text{-}MMe_3$ (M = Ge and Sn) with isocyanates

The addition reactions of heptamethylsilagermazane and heptamethylsilastannazane with methyl isocyanate took place exothermally, and the 1/1 adducts; (I) and (II), were isolated by distillation. The adduct from heptamethylsilagermazane (I) could possibly have two isomeric structures, (Ia) and (Ib), between which interconversion would be possible by a 1,3-migration of the Me_3Si group. The fact that the NMR spectra of (I) did not change even at low temperatures suggests that only one isomer is present and a strong absorption for ν(C=N) at 1608 cm^{-1} indicated that this was (Ib). Similarly, the adduct from heptamethylsilastannazane, has the

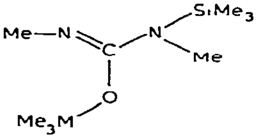


(Ia) (M=Ge)
(IIa) (M=Sn)

(Ib) (M=Ge)
(IIb) (M=Sn)

structure (IIb), as indicated by the infrared and NMR spectra; the infrared spectrum had ν(C=N) at 1613 vs and ν(C=O) at 1645 vw, consistent with structure (IIb).

The possibility of the structures (Ic) and (IIc) was excluded by the relatively high chemical shifts of CH_3–M protons, since the CH_3 protons of CH_3–M–N bonds have higher chemical shifts than those of CH_3–M–O or CH_3–M–S bonds.



(Ic) (M=Ge)
(IIc) (M=Sn)

In addition, the appearance of satellites bands due to ^{117}Sn and ^{119}Sn in one of the two CH_3–N proton signals (τ 7.17 with J 31 Hz) provided strong evidence in favour of structure (IIb) since (IIc) should exhibit both CH_3–N proton signals without the appearance of any satellites. Structures (Ib) or (IIb) are in agreement with the known affinity of the trimethylsilyl group to oxygen atoms, whilst the absence of structures (Ic) or (IIc) indicates that 1,3 migrations of Me_3M groups occur readily in the order, $Me_3Si \gg Me_3Ge$ or Me_3Sn, therefore, selective migration of the Me_3Si group yielding (Ib) or (IIb).

When phenyl isocyanate was used as an acceptor molecule, somewhat more complicated behaviour was observed since the introduction of a phenyl group in the adduct molecule increases the number of possible isomers in the system.

The NMR spectrum of adduct (III), purified by distillation after preparation by the instantaneous reaction between heptamethylsilagermazane with phenyl isocyanate, showed the apparent presence of two isomers in the ratio 2.5/1, with two strong assignable ν(C=N) absorptions at 1610 and 1590 cm^{-1}. This infrared evidence suggests the presence of iminoether structures, the extremely high migratory ability of the trimethylsilyl group in comparison with the trimethylgermyl group suggesting the existence of a Me_3Si–O bond in both possible isomers, similar to that in structure (Ib).

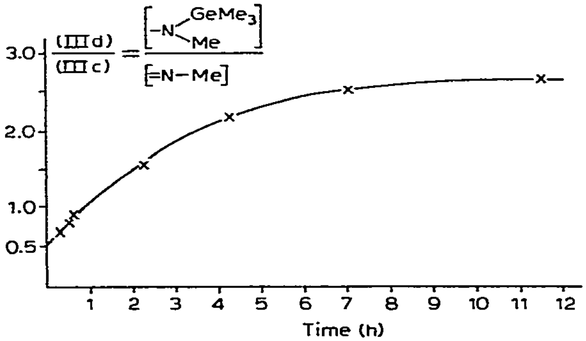
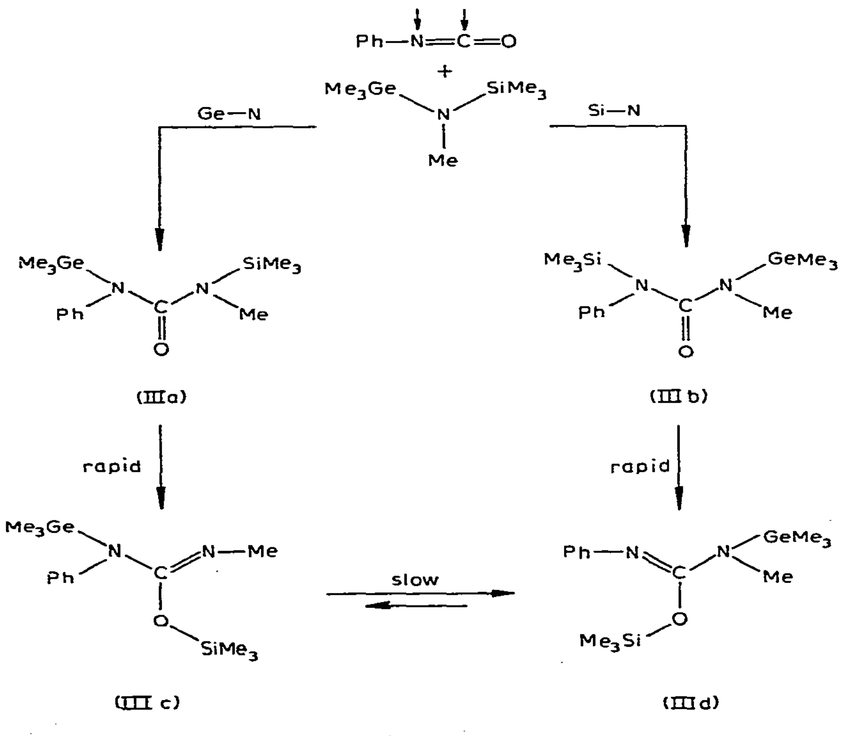


Fig. 1. Variation of the ratio [IIId]/[IIIc] during the reaction of Me_3Si–NMe–$GeMe_3$ with Ph–N=C=O in CCl_4 at 25°.

More interestingly, the intensity ratios among the two isomers in the reaction mixture changed from 0.5/1 to 2.5/1 with time as shown in Fig. 1, despite the fact that the addition reaction was apparently completed instantaneously. This variation must be ascribed to a rearrangement between the two isomers of a similar sort to that of of the 1,3-migration of either Me_3Ge or Me_3Si groups. The 1,3-migration of the Me_3Si group occurs very rapidly[10] and therefore the rearrangement observed in this case must be due to the 1,3-migration of the Me_3Ge group. The extrapolated value (0.5) at zero time, which corresponds to the completion of the addition reaction is consistent with the reactivity ratio Ge–N/Si–N as estimated by the ratio of the competitive reactions of $Me_3Ge–NMe_2$ and $Me_3Si–NMe_2$ towards phenyl isocyanate (=2/1).

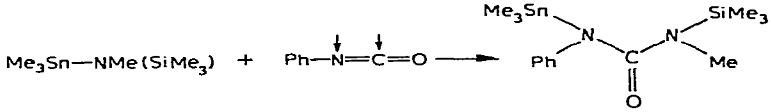
These observations may be reasonably explained in terms of the following scheme in which both (IIIc) and (IIId) contribute towards the final structure of the 1/1 adduct (III). Initially, the conversion (IIIa)$\rightarrow$(IIIc), involving Ge–N bond cleavage, occurs at nearly twice the rate of the conversion (IIIb)$\rightarrow$(IIId), which involves Si–N bond cleavage, and leads to an isomer ratio [(IIId)]/[(IIIc)] 0.5/1. Subsequently, due to the gradual migration of the Me_3Ge group from N–Ph to N–Me this isomer ratio is modified to 2.5/1, a value in complete agreement with that observed for the distilled adduct.

The reaction of phenyl isocyanate with heptamethylsilastannazane occurs instantaneously to yield the 1/1 adduct (IV). The NMR spectrum of (IV) shows the



[(IIIc)] / [(IIId)] = 1 / 2.5

presence of only one isomer and the CH_3–N proton signal (τ 7.72) gave no indication of any satellite bands due to ^{117}Sn or ^{119}Sn. The chemical shifts of both CH_3–Si and CH_3–Sn, observed at τ 9.80 and 9.75, respectively, suggest that the attachment of both Group IV organometallyl groups is to nitrogen. These results may be explained on the basis of the amide structure (IVa) which is produced by the selective cleavage of the Sn–N bond in heptamethylsilastannazane because the nucleophilicity of Sn–N bonds is considerably higher than that of Si–N bonds, a conclusion in agreement with Abel's basicity scale[9].



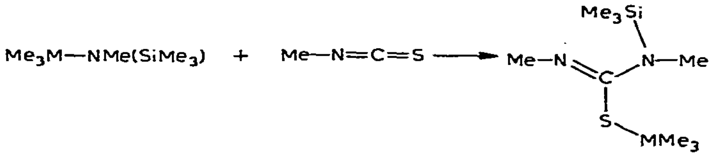
(IVa)

Structure (IVa) is also consistent with the observed infrared measurements in which a strong absorption ascribed to ν(C=O) was observed at 1665 cm^{-1}. The absence of 1,3-migration of the Me_3Si group in (IV) is somewhat difficult to explain, although either a weak coordination of the carbonyl oxygen atom to the trimethyltin moiety or the existence of steric hindrance in the iminoether structure would tend to inhibit the transfer of the silicon atom from the nitrogen to the oxygen atom.

Addition reactions of Me_3SiNMe–MMe_3 (M = Ge and Sn) with isothiocyanates

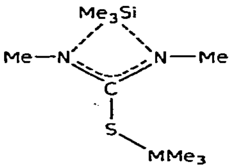
The addition reactions of methyl or phenyl isothiocyanates with heptamethylsila-germazane or -stannazane proceeded more slowly than the reactions with the corresponding isocyanates, and for this reason the rate differences between Si–N and M–N (M = Ge, Sn) bond cleavage are higher in the case of isothiocyanates.

Both heptamethylsilagermazane and heptamethylsilastannazane gave the stable 1/1 adducts (V) and (VI), respectively, with methyl isothiocyanate. The NMR spectra of either (V) or (VI) exhibit quite low chemical shifts for the CH_3–M proton signals, viz., τ 9.48 for M = Ge and τ 9.54 for M = Sn, which strongly suggests that (V) and (VI) possess Me_3M–S linkages. The strong affinities of both Me_3Ge and Me_3Sn groups for sulphur atoms, as discussed earlier, support the preferential formation of germanium– or tin–sulphur bonded structures as depicted below.



(V) (M = Ge)
(VI) (M = Sn)

However, the observation that the CH_3–N proton signals appeared as singlets in both cases (τ 7.05 for M = Ge and τ 7.02 for M = Sn) indicates that migration of the Me_3Si group between the two chemically equivalent N–Me groups takes place over the NMR time scale. For this reason, the structures of these compounds are best represented as (Va) or (VIa), the appearance of ν(C=N) at 1608 and 1603 cm^{-1}, for M=Ge and M=Sn, respectively, in the infrared spectra providing further evidence for the proposed structure*.

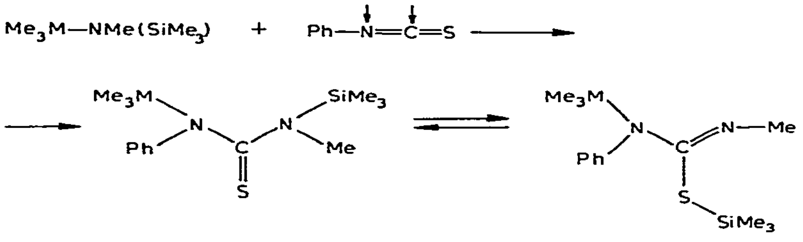


(Va) (M=Ge)
(VIa) (M=Sn)

Reactions of phenyl isothiocyanates with these heptamethylsilametallazanes result in the adducts (VII) and (VIII) with considerably different structures from those of (Va) and (VIa) discussed above. In addition, the thermal stability of the 1/1 adduct (VIII) obtained from the reaction between heptamethylsilastannazane and phenyl isothiocyanate was extremely low, the adduct decomposing readily during distillation to give methylphenylcarbodiimide and a mixture of bis(organometallic) sulphides.

The chemical shifts of the respective CH_3–M proton signals were τ 9.73 for (VII) (M=Ge) and τ 9.80 for (VIII) (M=Sn), both being quite high field values indicating that bonding between the Me_3M groups and the nitrogen atoms should occur. The absence of any satellites due to ^{117}Sn and ^{119}Sn in the spectrum of adduct (VIII) suggests the existence of a Me_3Sn–N(Ph)– linkage. The chemical shifts of the CH_3–Si proton signals in both adducts occurred at surprisingly low field values, *viz.*, around τ 9.70, being lower than the corresponding CH_3–M proton signals associated with the N–Ph groups.

The NMR and the infrared results mentioned above, in which both ν(C=N) and ν(C=S) occurred with considerable intensity, may be explained by the existence of two interconvertible structures, *i.e.*,



(VIIa) (M=Ge)
(VIIIa) (M=Sn)

(VIIb) (M=Ge)
(VIIIb) (M=Sn)

Interconversion involving 1,3-migration of Me_3Si groups occurs over the NMR time scale, since the affinity of Me_3Si groups for nitrogen and sulphur atoms is similar. The low chemical shifts observed for the CH_3–Si proton signals may be

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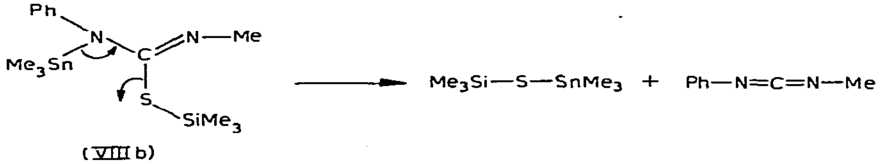
* The time scale of measurements by infrared spectroscopy is much shorter than that of measurements by NMR spectroscopy.

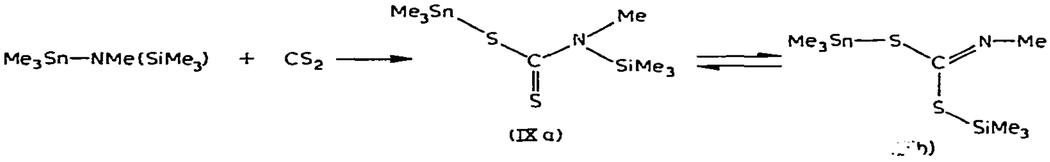
ascribed to the partial contributions of the two structures (VIIb) and (VIIIb) to the overall system.

The thermal instability of the 1/1 adduct (VIII) may be reasonably explained in terms of the proposed structure (VIIIb). The pyrolysis products were methylphenylcarbodiimide, trimethylsilyltrimethylstannyl sulphide, bis(trimethylstannyl) sulphide, and bis(trimethylsilyl) sulphide, the latter three Group IV organometallic sulphides being obtained by thermal disproportionation. From this it follows that the decomposition of adduct (VIII) proceeds via the β-elimination of Me_3Si–S–MMe_3 from structure (VIIIb) to give methylphenylcarbodiimide, the soft S–$SiMe_3$ group readily attacking the soft Me_3Sn moiety.



This kind of β-elimination has already been extensively studied as illustrated by Eqns. 1, 2, 4 and 6.

Adduct (IX), formed by the addition reaction of heptamethylsilastannazane and carbon disulphide, was stable. Its structure may also be represented in solution as an isomeric mixture of (IXa) and (IXb) since the chemical shifts of CH_3–Si and N–CH_3 (τ 9.58 and τ 6.85, respectively[6–8]) are close to those of (VIII).



CONCLUSIONS

The affinity orders of Group IV organometallyl groups, from the basis of their addition–elimination reactions, are closely correlated with the type of bonds between the organometallyl moieties and to the particular heteroatoms in the addition products formed. For this reason, β-elimination during addition–elimination reactions is controlled by the nature of the isomers preferentially formed amongst the 1/1 adducts. Bond formations for the Group IV organometallyl groups studied were found to occur in the following order: R_3Si: $O > S \simeq N$; R_3Ge: $S > O \simeq N$; R_3Sn: $S > O > N$.

It has been found that the 1,3-migration of trimethylmetallyl groups is an important factor in determining the structure of the predominant species formed during the reaction. In general, as has been shown previously, these migrations were found to be extremely rapid in terms of the NMR time scale at room temperature. During the conversion (IIIc)→(IIId), however, the migration of the Me_3Ge group was found to be quite slow and no clear evidence for the migration of the Me_3Sn group has been obtained from the reactions studied in this present investigation. It appears,

TABLE 1

NMR SPECTRA OF ADDUCTS AND PREDOMINANT STRUCTURES

Adduct	Components		Chemical shift (τ, ppm)[a]				Coupling constant (Hz)		Predominant structure
	Acceptor	Addendum	CH_3-Si	CH_3-M	CH_3-N	CH_3-N=C	$J(^{119}Sn-H)$	$J(^{117}Sn-H)$	
(I)	Me-N=C=O	Me_3Si-NMe-$GeMe_3$	9.82[b]	9.61[b]	7.28	7.25			(Ib)
(II)	Me-N=C=O	Me_3Si-NMe-$SnMe_3$	9.84	9.73	7.17[c]	7.22	57.5	54.8	(IIb)
(III)	Ph-N=C=O	Me_3Si-NMe-$GeMe_3$	9.82	9.63	7.87				(IIId)
			9.85	9.59		7.73			(IIIc)
(IV)	Ph-N=C=O	Me_3Si-NMe-$SnMe_3$	9.80	9.75	7.72[d]		58.5	55.7	(IVa)
(V)	Me-N=C=S	Me_3Si-NMe-$GeMe_3$	9.84[b]	9.48[b]		7.05			(Va)
(VI)	Me-N=C=S	Me_3Si-NMe-$SnMe_3$	9.88	9.54		7.02[d]	57.5	54.8	(VIa)
(VII)	Ph-N=C=S	Me_3Si-NMe-$GeMe_3$	9.70[b]	9.73[b]		7.02			(VIIa) ⇄ (VIIb)
(VIII)	Ph-N=C=S	Me_3Si-NMe-$SnMe_3$	9.71	9.80		7.05[d]	56.9	54.3	(VIIIa) ⇄ (VIIIb)
(IX)	CS_2	Me_3Si-NMe-$SnMe_3$	9.58	9.45		6.85[d]			(IXa) ⇄ (IXb)

[a] Measured in CCl_4 relative to internal $(CH_3)_4Si$ at τ 10.00 ppm. [b] Peak assignments between CH_3-Si and CH_3-Si and CH_3-Ge were made on the basis of differences in the ^{13}C satellites; $J(H-^{13}C)$ 15 ~ 124 for Me_3Si and $J(H-^{13}C)$ 125 ~ 130 Hz for Me_3Ge. [c] $J(H-C-^{117,119}Sn)$ 30.6 Hz. [d] No satellite due to $^{117,119}Sn$ was observed.

therefore, that the ease of 1,3-migration amongst Me_3M groups occurs in the series $Si \gg Ge > Sn$.

EXPERIMENTAL

Heptamethylsilagermazane and heptamethylsilastannazane were prepared by the method proposed by Scherrer[11] in 75% yield (b.p. 39–40°/12 mm) and 55% yield (b.p. 69–70°/30 mm) respectively. All reactions and measurements of NMR spectra were performed under an argon atmosphere. NMR spectra were recorded using a JEOL-C-60HL model spectrometer, infrared spectra being measured by means of a JASCO-DS-403G spectrometer.

Addition reaction of methyl isocyanate with $Me_3Si-NMe-GeMe_3$ (I)

Methyl isocyanate (229 mg; 4.02 mmoles) was gradually added to a solution of heptamethylsilagermazane (835 mg; 3.80 mmoles) in carbon tetrachloride (0.8 ml). An exothermic reaction took place after a few seconds. After removal of the low boiling fractions under reduced pressure (0.1 mm), the pure 1/1 adduct (I) was isolated in 70% yield by vacuum distillation; b.p. 48–49°/0.08 mm. (Found: C, 39.10; H, 8.88. $C_9H_{24}N_2OSiGe$ calcd.: C, 39.03; H, 8.73%.) IR (CCl_4), $\nu(C{=}N)$ 1608 vs and $\nu(C{=}O)$ 1640 vw cm^{-1}. NMR spectroscopic data for all the adducts studied in this investigation are summarized in Table 1.

Addition reaction of methyl isocyanate with $Me_3Si-NMe-SnMe_3$ (II)

Methyl isocyanate (218 mg; 3.83 mmoles) was slowly added to heptamethylsilastannazane (1.04 g; 3.92 mmoles) dissolved in 0.7 ml of carbon tetrachloride at 0°. An extremely violent exothermic reaction occurred and the 1/1 adduct (II) was isolated in 69% yield by distillation under vacuum; b.p. 54–55°/0.08 mm. (Found: C, 33.59; H, 7.39. $C_9H_{24}N_2OSiSn$ calcd.: C, 33.46; H, 7.49%.) IR (CCl_4), $\nu(C{=}N)$ 1613 vs and $\nu(C{=}O)$ 1645 vw cm^{-1}.

Addition reaction of phenyl isocyanate with $Me_3Si-NMe-GeMe_3$ (III)

Phenyl isocyanate (329 mg; 2.76 mmoles) was added to heptamethylsilagermazane (636 mg; 2.89 mmoles) in 0.7 ml of carbon tetrachloride, the solution being cooled in a dry ice/acetone bath. An instantaneous reaction occurred and the characteristic absorption maximum of phenyl isocyanate at 2250 cm^{-1} completely vanished within one minute. After removal of the low boiling fractions by evaporation under vacuum the adduct (III) was obtained in 78% yield by distillation; b.p. 70–73°/0.06 mm. (Found: C, 49.75; H, 7.58. $C_{14}H_{26}N_2OSiGe$ calcd.: C, 49.60; H, 7.73%.) IR (CCl_4), $\nu(C{=}N)$ 1610 vs and 1590 vs, $\nu(C{=}O)$ 1655 w cm^{-1}.

The interconversion between (IIId) and (IIIc) was studied by mixing equimolar amounts of both components in carbon tetrachloride solution in aNMR tube which was sealed under an atmosphere of argon. The ratio of (IIIc) to (IIId) was measured in terms of the two CH_3-N proton signals at τ 7.87 and 7.83 respectively at appropriate time intervals at 25°.

Competitive reactions of Me_3SiNMe_2 and Me_3GeNMe_2 with $Ph-NCO$. To a mixture of Me_3SiNMe_2 (544 mg; 4.63 mmoles) and Me_3GeNMe_2 (739 mg; 4.58

mmoles) in 0.8 ml of carbon tetrachloride at 0°, 512 mg (4.30 mmoles) of phenyl isocyanate was added. After the disappearance of the characteristic infrared absorption maxima of phenyl isocyanate the molar ratio of the two 1/1 adducts, Me_3Si–NPhCO–NMe_2 and Me_3Ge–NPhCO–NMe_2, was measured in terms of the two CH_3–M proton signals.

Addition reaction of phenyl isocyanate with Me_3Si–NMe–$SNMe_3$ (IV)

Phenyl isocyanate (400 mg; 3.33 mmoles) was added to a soltuion of heptamethylsilastannazane (1.05 mg; 4.00 mmoles) in carbon tetrachloride (0.8 ml) at 0°. After the evolution of heat had ceased, the 1/1 adduct (IV) was isolated in 69% yield by distillation under reduced pressure; b.p. 93°/0.08 mm. (Found: C, 44.77; H, 6.63. $C_{14}H_{26}N_2OSiSn$ calcd.: C, 44.58; H, 6.8%.) IR (CCl_4), $\nu(C{=}O)$ 1663 vs and $\nu(C{=}N)$ 1595 m cm^{-1}.

Addition reaction of methyl isothiocyanate with Me_3Si–NMe–$GeMe_3$ (V)

Methyl isothiocyanate (323 mg; 4.42 mmoles) was gradually added to heptamethylsilagermazane (998 mg; 4.53 mmoles) and the mixture was kept for 24 h at room temperature. Adduct (V) was recovered in 63% yield by distillation under reduced pressure; b.p. 59–61°/0.04 mm. (Found: C, 36.72; H, 8.25. $C_9H_{24}N_2SSiGe$ calcd.: C, 36.89; H, 8.26%.) IR (CCl_4), $\nu(C{=}N)$ 1608 s cm^{-1}.

Addition reaction of methyl isothiocyanate with Me_3Si–NMe–$SnMe_3$ (VI)

Dropwise addition of methyl isothiocyanate (235 mg; 3.22 mmoles) to a carbon tetrachloride (0.9 ml) solution of heptamethylsilastannazane (922 mg; 3.45 mmoles) cooled in a dry ice/acetone bath resulted in a violent reaction. The temperature was slowly raised up to room temperature and the 1/1 adduct (VI) was obtained in 79% yield by distillation under vacuum, b.p. 70°/0.12 mm. (Found: C, 32.01; H, 7.28. $C_9H_{24}N_2SSiSn$ calcd.: C, 31.87; H, 7.13%.) $\nu(C{=}N)$ in CCl_4 1603 s cm^{-1}.

Addition reaction of phenyl isothiocyanate with Me_3Si–NMe–$GeMe_3$ (VII)

Phenyl isothiocyanate (410 mg; 3.03 mmoles) was gradually added to heptamethylsilagermazane (692 mg; 3.14 mmoles) at 0°. The mixture was kept at room temperature overnight when the 1/1 adduct (VII) was isolated in 60% yield by distillation; b.p. 87–88°/0.05 mm. (Found: C, 47.50; H, 7.31. $C_{14}H_{26}N_2SSiGe$ calcd.: C, 47.35; H, 7.38%.) IR (CCl_4), $\nu(C{=}N)$ 1580 s and $\nu(C{=}S)$ 1335 cm^{-1}.

Adduct (VII) was hydrolysed by atmospheric moisture to give *N*-methyl-*N'*-phenylthiourea in quantitative yield, the latter compound being identified by means of mixed melting point measurements with an authentic sample (m.p. 115–116°) and by comparison of the infrared spectrum with that of the authentic sample.

Addition reaction of phenyl isothiocyanate with Me_3Si–NMe–$SnMe_3$ (VIII)

A spontaneous reaction occurred when phenyl isothiocyanate (444 mg; 3.10 mmoles) was added to heptamethylsilastannazane (926 mg; 3.48 mmoles) dissolved in CCl_4 (0.8 ml) at 0°. Evaporation of the low boiling components under vacuum (0.1 mm) left 1.32 g (99%) of the crude 1/1 adduct (VIII). The IR spectrum of adduct (VIII) exhibited $\nu(C{=}N)$ 1590 m and $\nu(C{=}S)$ 1285 s cm^{-1}. The NMR data recorded in Table 1 support the formation of the 1/1 adduct. An attempt to purify the crude adduct by high vacuum distillation, however, caused complete decomposition of (VIII) whilst hydrolysis of (VIII) by atmospheric moisture gave quantitatively the demetallated, *N*-methyl-*N'*-phenylthiourea; m.p. 116°.

Pyrolysis of 1/1 adduct(VIII). Adduct(VIII) completely decomposed at 100° in 1 h. Distillation of the mixture gave the following products (1) methylphenylcarbodiimide (30%; based on the total N–Me fragment): (2) hexamethyldisilthiane (10%), hexamethylsilastannathiane (20%) and hexamethyldistannathiane (55%); all yields of metal sulphides were estimated based on the total S fragments. Poly(methylphenylcarbodiimide) remained as distillation residue. All of the above materials were identified by the comparison of their NMR and infrared spectra with those of authentic samples.

Addition reaction of carbon disulphide with Me_3Si–NMe–$SnMe_3$ (IX)

Carbon disulphide (376 mg; 4.94 mmoles) reacted exothermally with heptamethylsilastannazane (1.22 g; 4.60 mmoles) at room temperature. After the evolution of heat had ceased, the whole reaction mixture was converted into a light yellow solid. After 30 min. the 1/1 adduct (IX) was recrystallized from dry n-hexane to give the pure colourless compound in 43% yield; m.p. 67–69°. (Found: C, 27.61; H, 6.60. $C_8H_{21}NS_2SiSn$ calcd.: C, 28.09; H, 6.19%.)

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