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Azomethine Derivatives. Part XVII.[1,2] Some New Methyleneamino-derivatives of Silicon, Germanium, and Tin

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The new hydrolytically sensitive yellow methyleneamino-derivatives $M(N{:}CPh_2)_4$ (M = Ge or Sn), $Ge(N{:}CR_2)_4$, $SiMe(N{:}CR_2)_3$, and $SiMe_2(N{:}CR_2)_2$ (R = *p*-tolyl) and $GeBr_3(N{:}CBu^t_2)$, $GeX_2(N{:}CBu^t_2)_2$ (X = Cl or Br), and $GeCl(N{:}CBu^t_2)_3$ have been prepared from Group 4 halides and methyleneaminolithium derivatives. Features of their i.r., ^1H n.m.r., and mass spectra, and of the structures of the compounds $M(N{:}CPh_2)_4$, are reported and discussed.

THIS paper describes some new methyleneamino-derivatives of silicon, germanium, and tin, which were prepared in order to obtain further information on the mode of attachment of imino-groups, $R_2C{:}N$, to Group 4 elements. Earlier studies on $M(N{:}CR_2)_xX_y$ derivatives of the Group 2 or 3 elements Be,[3] B,[4-8] or Al[9] had shown their i.r. and ^1H n.m.r. spectra to be useful guides to the shapes (linear or bent) of their C=N–M skeletons, whereas similar studies on methyleneamino-derivatives of silicon,[1,8,10-12] germanium,[11-13] and tin[11,12,14,15] afforded little structural information. While the 'high' azomethine stretching frequencies and singlet ^1H t-butyl resonances of di-t-butylmethyleneaminosilanes $Si(N{:}CBu^t_2)X_3$ may signify that these compounds have the linear C=N–Si skeletons that would allow maximum $N \Rightarrow Si$ π bonding,[1] the electronic[11] and ^1H n.m.r. spectra[13] of diarylmethyleneamino-derivatives of these Group 4 elements support structures with bent C=N–M skeletons. We have accordingly prepared some new methyleneamino-derivatives, explored their spectra for further structural information, and obtained a series of crystalline derivatives suitable for *X*-ray crystallographic study, a preliminary account of which has already appeared.[2]

RESULTS AND DISCUSSION

The new compounds are listed in the Table. The diphenylmethyleneamino-derivatives $M(N{:}CPh_2)_4$ (M = Ge or Sn) were prepared to provide, with the previously prepared silicon compound $Si(N{:}CPh_2)_4$,[10] a series of crystalline compounds suitable for *X*-ray crystallographic study. The di-*p*-tolyl- and di-t-butyl-methyleneamino-compounds were prepared to see whether their ^1H n.m.r. spectra, by demonstrating the equivalence or non-equivalence of their tolyl or butyl groups, would establish their shapes. They were prepared by adding suitable proportions of the Group 4 chloride or bromide to frozen (−196 °C) solutions of the appropriate lithium derivative $Li(N{:}CR_2)$ in diethyl ether–hexane or –pentane mixtures, and allowing the mixture to warm to room temperature, when reaction was normally complete. Attempts to prepare the di-t-butylmethyleneaminogermanes $GeBr(N{:}CBu^t_2)_3$ and $Ge(N{:}CBu^t_2)_4$ from

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$GeBr_4$ and $Li(N{:}CBu^t_2)$ (3 or 4 mol equivalents) were unsuccessful. Three di-t-butylmethyleneamino-groups could be attached to the same germanium atom, however, by use of $GeCl_4$ as the starting material, though heating to *ca.* 70 °C was needed to attach the third methyleneamino-group, and the product was still $GeCl(N{:}CBu^t_2)_3$, not $Ge(N{:}CBu^t_2)_4$, even when an excess of $Li(N{:}CBu^t_2)$ was used. Greater difficulty in attaching $Bu^t_2C{:}N$ groups as opposed to $Ph_2C{:}N$ groups has also been found in studies on silicon [1] and boron [16] systems, the difference being attributable to steric factors. In this connection, it appears significant that whereas only one $Bu^t_2C{:}N$ group could be attached to a silicon atom,[1] three such groups can be attached to the slightly larger germanium atom.

Compound	M.p., θ_c/°C [b.p., θ_c/°C (P/mmHg)]	$\tilde{\nu}$(C=N) cm^{-1}	$\tilde{\nu}$(M–N) cm^{-1}	τ(Me) [a]	Analysis [b] (%) C	H	N	Cl or Br	M [b,c]
$SiMe_2[N{:}C(C_6H_4Me\text{-}p)_2]_2$		1 643	860	7.83	79.9	7.4	5.8		453
					(81.0)	(7.2)	(5.9)		(474)
$SiMe[N{:}C(C_6H_4Me\text{-}p)_2]_3$		1 642	857	7.83	80.4	7.0	6.5		613
					(82.8)	(6.8)	(6.3)		(667)
$Ge(N{:}CPh_2)_4$	188	1 601 [e]	700 [e,f]		77.5	5.0	7.1		754
	(decomp.) [d]				(78.9)	(5.1)	(7.1)		(793)
$Ge[N{:}C(C_6H_4Me\text{-}p)_2]_4$	60	1 598 [e]	707 [e]	8.43	79.5	6.3	6.0		869
	(decomp.) [g]				(79.6)	(6.2)	(6.2)		(905)
$GeCl(N{:}Bu^t_2)_3$		1 652	731	8.73	61.9	10.7	7.6	6.8	473
					(61.4)	(10.2)	(8.0)	(6.7)	(528)
$GeCl_2(N{:}CBu^t_2)_2$	[120 (0.5)]	1 645	741	8.75	50.1	8.7	6.6	17.1	398
					(51.0)	(8.5)	(6.6)	(16.8)	(424)
$GeBr_2(N{:}Bu^t_2)_2$	[120 (0.2)]	1 646	736	8.70	41.3	7.4	5.5	31.2	483
					(42.1)	(7.0)	(5.5)	(31.2)	(513)
$GeBr_3(N{:}CBu^t_2)$	48 [h]	1 624	731	8.81	23.5	3.7	2.9	53.8	428
					(23.9)	(4.0)	(3.1)	(53.0)	(453)
$Sn(N{:}CPh_2)_4$	170—180	1 590 [e]	654		75.5	5.2	7.0		[j]
	(decomp.) [i]				(75.3)	(4.8)	(6.7)		

[a] ^1H N.m.r. data relate to benzene solutions. [b] Calculated values are given in parentheses. [c] Determined by cryoscopy in benzene solutions. [d] Recrystallised from toluene–hexane. [e] Nujol mull; the remaining i.r. data relate to liquid films. [f] Tentative assignment, obscured by phenyl absorption. [g] From light petroleum. [h] From toluene–light petroleum. [i] From toluene. [j] Not soluble enough in benzene to allow cryoscopic determination of M.

The identities of the new derivatives were confirmed by elemental analyses (Table), and their monomeric state of association in benzene was established by cryoscopy. All nine compounds are yellow moisture-sensitive substances which need to be manipulated and stored *in vacuo*, or under a dry atmosphere: their reaction with moist air can be followed by the rapid fading of the yellow colour, by fuming in the case of the halides, and by the appearance of new absorptions, attributable to hydrolysis products, in their i.r. spectra. For example, Nujol mulls of the diarylmethyleneamino-derivatives, after brief exposure to air, characteristically absorb in the range 3 220—3 280 [ν(N–H)] and 1 650—1 660 cm^{-1} [ν(C=N)].

Diarylmethyleneaminosilicon halides $SiX_{4-n}[N{:}C(aryl)_2]_n$ tend to disproportionate readily, *e.g.* as in

$$2\ SiMe_2(Cl)(N{:}CPh_2) \longrightarrow SiMe_2(N{:}CPh_2)_2 + SiMe_2Cl_2 \quad (1)$$

equation (1).[8,11] Problems with similar disproportionations caused us to abandon the synthesis of di-*p*-tolylmethyleneaminosilicon chlorides $SiCl_{4-n}[N{:}C(C_6H_4Me\text{-}p)_2]_n$ and related germanium chlorides and bromides after preliminary experiments led to products of variable composition. The di-t-butylmethyleneaminogermanium halides $GeCl_{4-x}(N{:}CBu^t_2)_x$ (x = 1—3) and $GeBr_2(N{:}CBu^t_2)_2$ by contrast proved surprisingly stable to disproportionation. The dihalides, for example, are oils which can be purified by distillation under low pressure at 120—150 °C (Table), and their mass spectra contained no peaks attributable to products of disproportionation. The fragmentation of $GeX_2(N{:}CBu^t_2)_2$ (X = Cl or Br) in the mass spectrometer led to no $Ge(N{:}CBu^t_2)_3$ or GeX_3 units, and no $Ge(N{:}CBu^t_2)_2$ or $GeBr_4$ units were detected in the mass spectrum of $GeBr_3(N{:}CBu^t_2)$. Fragmentation followed the usual pattern for such derivatives:[1] progressive cleavage of M–N and M–X bonds; loss of substituents R from methyleneamino-groups $R_2C{:}N$; and occasional migration of substituents R from the azomethine carbon atom to the metal.

An *X*-ray crystallographic study [2] of the compounds $M(N{:}CPh_2)_4$ (M = Si,[10] Ge, or Sn) has shown their C=N–M units to be bent, the angle at nitrogen averaging 137° for M = Si, 127° for Ge, and 121° for Sn, indicating a decreasing degree of $N \xrightarrow{} M$ π bonding in this sequence. Their 'short' M–N bonds [Si–N, 172(1); Ge–N, 187(1); and Sn–N, 206(4) pm] also indicate significant $N \xrightarrow{} M$ π bonding, at least in the case of the silicon and germanium compounds; the uncertainty in the length of the Sn–N bond is too great to allow firm conclusions to be drawn about its order.

These structures may usefully be compared with those of isocyanate, isothiocyanate, and carbodi-imide derivatives of these same elements. The following C=N–M angles have been found in structural studies on Group 4 isocyanates, *etc.*: $Si(NCO)_4$, 180,[17] 146;[18] $Si(NCS)_4$, 180;[19]

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$\mathrm{SiH_3(NCO)}$, $\mathrm{SiH_3(NCS)}$, 180;[20,21] $\mathrm{SiMe_3(NCO)}$, 150;[22] $\mathrm{SiMe_3(NCS)}$, 154;[22] $\mathrm{SiF_3(NCO)}$, 161;[23] $\mathrm{SiCl_{\mathit{x}}(NCO)_{4-\mathit{x}}}$ *ca.* 140;[24] $\mathrm{GeH_3(NCO)}$, $\mathrm{H_3GeNCNGeH_3}$, *ca.* 140;[25] $\mathrm{SnMe_3(NCS)}$, 173;[26] $\mathrm{SnMe_2(NCS)_2}$, 164;[27,28] $\mathrm{Me_3SnNCNSnMe_3}$, 118;[29] and $\{[\mathrm{(SCN)Me_2Sn}]_2\mathrm{O}\}$, 170°.[30] These bond angles, and the M–N bond lengths in these compounds, are suggestive of $\mathrm{N} \Longrightarrow \mathrm{M}$ π bonding in most cases, especially when it is borne in mind that the bent structures found by electron-diffraction studies on the silyl pseudohalides[18,22–24] may really reflect the ease of deformation of floppy linear Si(NCX) units.[21,31]

The structures of the methyleneamino-derivatives may also be compared with those of similar derivatives of neighbouring elements. The phosphorus compound $\mathrm{P(N{:}CPh_2)_3}$ has bent C=N–P units (average CNP angle, 123°),[32] indicating little if any dative π bonding, whereas approximately linear C=N–M units have been found attaching the terminal imino-groups of $\{\mathrm{Be(N{:}CBu^t{}_2)_2}\}_2$ to three-co-ordinate beryllium (CNBe angle, 161°),[33] of $\mathrm{B(C_6H_2Me_3\text{-}2,4,6)_2(N{:}CPh_2)}$ to three co-ordinate boron (CNB angle, 173°),[34] and of $\mathrm{Li[Al(N{:}CBu^t{}_2)_4]}$ to four-co-ordinate aluminium (CNAl angle, 167°).[35]

We believe that the di-*p*-tolylmethyleneamino-compounds $\mathrm{SiMe_2(N{:}CR_2)_2}$, $\mathrm{SiMe(N{:}CR_2)_3}$, and $\mathrm{Ge(N{:}CR_2)_4}$ (R = *p*-tolyl), like the diphenylmethyleneamino-compounds $\mathrm{M(N{:}CPh_2)_4}$, contain bent C=N–M units, although we have been unable to confirm this by our spectroscopic studies. Their ^{1}H n.m.r. spectra contain only singlet absorptions (see Table for τ values) attributable to the tolyl methyl groups, even at −80 °C, the lowest temperature at which satisfactory spectra could be obtained. When Cook and Mislow[13] demonstrated the bent C=N–Ge unit of the compound $\mathrm{GeMe_3\{N{:}CPh(C_6H_4CF_3\text{-}\mathit{p})\}}$ by the overlapping doublet structure of its $\mathrm{GeMe_3}$ resonance they found it necessary to cool their solutions to −110 °C. Clearly, whether the preferred structure is linear or bent, the barrier to inversion at nitrogen in many of these C=N–M systems is low. The ^{1}H n.m.r. spectra of the new di-t-butylmethyleneaminogermanes $\mathrm{GeX_{4-\mathit{n}}(N{:}CBu^t{}_2)_{\mathit{n}}}$ contained only singlet t-butyl absorptions at or above −80 °C. (The parent imine, $\mathrm{Bu^t{}_2C{:}NH}$, gives a well resolved doublet at −60 °C.[9]) Again, structures with bent C=N–Ge units inverting rapidly at nitrogen appear likely.

The i.r. spectra of the new methyleneamino-derivatives also appear consistent with bent C=N–M structures in that the azomethine stretching absorptions have frequencies (Table) little different from those of the parent imines [$\mathrm{Ph_2C{:}NH}$ has ν(C=N) at 1 607, $(p\text{-}\mathrm{MeC_6H_4})_2\mathrm{C{:}NH}$ at 1 610, and $\mathrm{Bu^t{}_2C{:}NH}$ at 1 610 cm^{-1}].[36] Coupling of the C=N and N–M vibrations of linear C=N–M units would be expected to cause a marked increase in ν(C=N) relative to the parent imine, as has been found for derivatives of beryllium,[3] boron,[4–8] aluminium,[9] and gallium,[37] although this effect decreases as the mass of M increases. Detailed interpretation of the azomethine stretching frequencies in the Table is complicated by the varying number of imino-groups present. Coupling of the azomethine stretching vibrations is to be expected for derivatives with more than one imino-group attached to the same central Group 4 atom [*i.e.* for all the compounds in the Table except $\mathrm{GeBr_3(N{:}CBu^t{}_2)}$], and the frequencies listed in the Table relate to the relatively sharp maximum of what in many cases is a broad absorption with pronounced shoulders *ca.* 10—30 cm^{-1} to either side, further complicated, in the case of the species with aryl substituents, by the presence of the characteristic ring mode at *ca.* 1 575 cm^{-1}.

In the Table, we also list the frequencies of bands assignable to M-N stretching vibrations. Lappert and Palmer,[12] in their study of compounds $\mathrm{MMe_{4-\mathit{x}}[N{:}C(CF_3)_2]_{\mathit{x}}}$ (M = Si, Ge, or Sn) assigned absorptions at *ca.* 950—960 cm^{-1} to the M–N stretching vibrations, the frequencies surprisingly not varying significantly with M.[38] Our own assignments, which must be regarded as tentative in view of the complexity of the spectra in the 500—950 cm^{-1} region, relating to only one of the two M–N stretching absorptions expected for most of these compounds, show the expected variation with M, and appear to be in line with the frequencies of other M–N absorptions.[38]

EXPERIMENTAL

The methods used to prepare the methyleneaminolithium reagents, and the manipulative techniques used for the moisture-sensitive products, were as described in earlier parts of this series.[1] I.r. spectra were recorded on a Perkin-Elmer 457 instrument. ^{1}H N.m.r. spectra were obtained at 60 MHz on a Varian A56/60D spectrometer.

Details of the i.r. spectra of the new compounds are in Supplementary Publication No. SUP 21594 (4 pp.).*

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* For details see Notice to Authors No. 7, *J.C.S. Dalton*, 1974, Index issue (items less than 10 pp. are supplied as full-size copies).

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