Alkylideneamido-derivatives of Metals and Metalloids. Part IV.[1] 1,1-Bis(trifluoromethyl)methyleneamido-complexes of Group IVB Metals

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The twelve bis(trifluoromethyl)methyleneamido-complexes of the Group IVB elements have been synthesised, $Me_{4-n}M[N{:}C(CF_3)_2]_n$ (M = Si, Ge, or Sn; n = 1—4). They are relatively volatile, colourless (Ge) or yellow (Si or Sn) liquids. I.r. and ^1H and ^{19}F n.m.r. spectra are reported. More selective data are also available on u.v. and photoelectron spectra.

In Part III,[1] the synthesis and chemistry of some alkylideneamino(trimethyl)stannanes $Me_3SnN{:}CR_2$ was reported. This work has now been extended to the twelve compounds $Me_{4-n}M[N{:}C(CF_3)_2]_n$ (I) (M = Si, Ge, or Sn; n = 1—4), of which ten have previously not been reported. $Me_3SnN{:}C(CF_3)_2$ was described in Part III,[1] and $Me_3SiN{:}C(CF_3)_2$ by Chan and Rochow.[2]

The compounds were prepared in all cases by LiCl elimination. B.p.s and sensitivity towards hydrolysis increased in the series $M = Si < Ge < Sn$ and $n = 1 < 2 < 3 < 4$.

An aspect of interest concerns geometry and bonding. Thus there are reports in the literature both of bent MNC (for M = Sn [2] and Ti [3]), which require sp^2 hybridised nitrogen, and linear MNC (for M = B [4-6] and Mo [7]) assemblies, involving sp hybridisation at N and $M \rightleftharpoons N$ π-bonding. Accordingly the twelve compounds have been investigated spectroscopically, particularly using ^{19}F n.m.r. and photoelectron (p.e.) spectra.

Characterisation of the Group IVB bis(trifluoromethyl)methyleneamido-complexes $Me_{4-n}M[N{:}C(CF_3)_2]_n$

Compound	Colour	^{19}F n.m.r. (Hz) [c]	^1H n.m.r. (τ)	$J_{^{117}Sn-Me}$ (Hz)	$J_{^{119}Sn-Me}$ (Hz)	U.v. $\lambda(n \rightarrow \pi^*)$ (nm) [d]	B.p. (°C, mmHg)	Yield (%)	I.r. data (cm^{-1}; liquid films) ν(C=N)	ν(M–N)	ρ(M–R)	$\nu_{as}\nu_s$ (M–R)	Analytical data C	H	N	M
$Me_3SiN{:}C(CF_3)_2$ [a]	Yellow	6900	9·61 [e]				70—72, 500	65	1765 [a]	955	852, 804	629	30·5 (30·4)	4·0 (3·8)	6·1 (5·9)	237 [h]
$Me_2Si[N{:}C(CF_3)_2]_2$	Yellow	6970	9·51 [e]			342	84—85, 207	70	1770	957	811	667	25·0 (24·9)	1·7 (1·6)	7·2 (7·2)	386,[h] 412 [i]
$MeSi[N{:}C(CF_3)_2]_3$	Yellow	7060	9·06				87—89 90	72	1774	959	841, 793		22·7 (22·4)	0·7 (0·6)	7·9 (7·9)	
$Si[N{:}C(CF_3)_2]_4$	Yellow	7100					93—95, 88	67·5	1786	959			21·1 (21·1)	0·2 (0·0)	8·3 (8·2)	282 [h]
$Me_3GeN{:}C(CF_3)_2$	Colourless	7100	9·48				31—33, 40	66·7	1730	955	840	618, 578	25·7 (25·6)	3·3 (3·2)	5·1 (5·0)	
$Me_2Ge[N{:}C(CF_3)_2]_2$	Colourless	7180	9·18 [f]			321	80—83, 66	77	1730	957	831	639, 598	22·0 (22·3)	1·6 (1·4)	6·3 (6·5)	580 [h]
$MeGe[N{:}C(CF_3)_2]_3$	Colourless	7230	8·80 [e]				77—79, 35	69	1733	961	832	628	20·5 (20·7)	0·7 (0·5)	7·1 (7·3)	
$Ge[N{:}C(CF_3)_2]_4$	Colourless	7335					90—94, 70	72	1730	961			19·7 (19·8)	0·3 (0·0)	7·7 (7·7)	
$Me_3SnN{:}C(CF_3)_2$ [b]	Yellow	6850	9·48 [f]	59	56·5		51, 31	84	1720	948	787, 774	548, 521	22·1 (22·0)	2·9 (2·8)	4·1 (4·3)	477[h]
$Me_2Sn[N{:}C(CF_3)_2]_2$	Yellow	6870	9·19 [g]	71·5	67·5	329sh	121—122, 130	83	1719	949	791, 777	561,532	20·4 (20·2)	1·4 (1·3)	5·9 (5·9)	
$MeSn[N{:}C(CF_3)_2]_3$	Yellow	6840	8·88 [e]	93·5	89		91, 27	63	1717	956	804, 781	552, 538	19·0 (19·2)	0·6 (0·5)	6·5 (6·7)	
$Sn[N{:}C(CF_3)_2]_4$	Yellow	7370					81—83, 23	94	1717	957			18·7 (18·6)	0·2 (0·0)	7·1 (7·2)	

[a] *Cf.*, ref. 2 (^{19}F n.m.r. data are new) ν(C=N) 1780 cm^{-1}. [b] See ref. 1. [c] Shift upfield from $CFCl_3$ as external standard. [d] Vapour phase spectrum. [e] Using benzene as internal standard. [f] Using THF as internal standard. [g] Using TMS as internal standard. [h] Parent ion in mass spectrum. [i] Determined cryoscopically in benzene.

Chan and Rochow [2] investigated the u.v. spectra of a large number of alkylideneamino-organosilanes and a few germanium and tin analogues and concluded that these types of molecule contained a non-linear arrangement at N. It was considered that in a linear structure π-electron-donating substituents on silicon should appreciably affect the $n(N) \longrightarrow \pi^*$ transition energy, whereas experimentally all compounds were found to absorb in the narrow range 363 ± 3 nm. The significant shifts in $n \longrightarrow \pi^*$ transition energy with changing central metal atom were attributable to a balance between the amount of excited state π-bonding (in the order $Si > Ge > Sn \gg Pb$) and the inductive effect (where electropositivity follows the order $C < Si \sim Ge < Sn < Pb$). Thus for a given series, the resultant of these two effects produces an order of $n \longrightarrow \pi^*$ transition energy $Si < Sn < Ge$. This analysis is consistent not only with our u.v. data (Table), but also with the colour of our compounds; the silicon and tin complexes are pale yellow, whereas the alkylideneaminogermanes are colourless.

The ^1H n.m.r. spectrum of each of the nine compounds (I) (M = Si, Ge, or Sn; n = 1, 2, or 3) exhibits a singlet (Table). This may be due to linearity at N; however, this is not inevitable because for a bent system there is, almost certainly, essentially free rotation about the M–N bond. Increasing n leads, as expected, to increased deshielding of the residual methyl groups.

All twelve compounds [(I); n = 1—4] show a singlet

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[1] Part III, M. F. Lappert, J. McMeeking, and D. E. Palmer, preceding paper.

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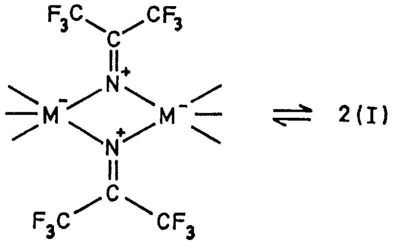
in their ^{19}F n.m.r. spectra (Table). This may be explained either by a linear $M{-}N{=}C\!<$ arrangement, or by a rapid (on the n.m.r. time scale) inversion process at nitrogen. The latter might arise from a rapid equilibration between monomer and dimer (II); the electron-withdrawing CF_3 groups make dimeric structures (II) unlikely. Some of the compounds (Table) were shown to be monomeric in the vapour phase and in solution. Many alkylideneamido-compounds are known to exist in dimeric form (II), including the cases of M=B,[4,8,9] Be,[9] and Mo.[10] It has recently been reported that $Me_3GeN{:}C(Ph)C_6H_4{\cdot}CF_3$-*p* shows a singlet Me_3Ge ^1H signal down to −70°, but from studies at lower temperatures $\Delta G^{\ddagger}_{-108^\circ} = 9{\cdot}2$ kcal mol^{-1} is calculated for inversion at nitrogen.[11]



(II)

The C:N bond stretching mode seems to be fairly sensitive to the nature of the metal and also, in the case of silicon, to the number of alkylideneamido-substituents. Thus, $\nu(C{:}N)$ increases for the series Sn < Ge < Si and for Si: $n = 1 < 2 < 3 < 4$ (Table). The latter effect is in agreement with findings for $Ph_{4-n}Si(N{:}CPh_2)_n$;[2] the result of Summerford and Wade for $Si[N{:}CPh_2]_4$ is, however, inconsistent.[12] It is concluded that the electronegativity of the central metal M has a role and that electronic effects may be transmitted through M, although whether this involves π- as well as σ-mechanisms remains an open question.

The p.e. spectra of $HN{:}C(CF_3)_2$ and $Me_3MN{:}C(CF_3)_2$ do not support the West model[13] on the effect of metalloid substitution on the π, n, and π^* energy levels. The first vertical ionisation potential, referring to the non-bonding pair of electrons on the nitrogen, is reduced from 11·83 eV in the case of the free alkylideneamine to 9·21—9·68 eV for the Group IVB metal compounds. This work will be discussed fully in a further publication.[14]

EXPERIMENTAL

Diethyl ether was distilled from sodium–benzophenone immediately before use and was rigorously degassed under vacuum. Manipulations were conducted under high vacuum or using apparatus filled with dry oxygen-free nitrogen. Products were distilled through a small-scale distillation apparatus, incorporating a 4 in. Vigreux column.

The chlorides Me_3SiCl, Me_2SiCl_2, $MeSiCl_3$, $SiCl_4$, Me_2GeCl_2, $MeGeCl_3$, $GeCl_4$, and $SnCl_4$ were obtained commercially and redistilled; purity was checked by g.l.c. Me_3GeCl was prepared from Me_2GeCl_2 and MeLi and was purified by slow distillation through a spinning-band column.[15] Me_3SnCl, Me_2SnCl_2, and $MeSnCl_3$ were prepared by metathesis: $3Me_4Sn + SnCl_4$;[16] $Me_4Sn + SnCl_4$;[16] and $Me_4Sn + 2SnCl_4$ (spinning-band separation from Me_2SnCl_2).[17]

Analyses were carried out by Alfred Bernhardt, West Germany. I.r. spectra were recorded using a Perkin-Elmer 457 instrument and ^1H n.m.r. using a Varian T60 machine. ^{19}F n.m.r. spectra were recorded by Mr. A. Alexander on a JEOL JNM 100 instrument: a machine with external lock was necessary as the tin compounds reacted with internal standards, $CFCl_3$ and C_6F_6. The He^{I} p.e. spectra were obtained on a Perkin-Elmer PS16 instrument by Mr. B. T. Wilkins.[13] U.v. spectra were recorded on a Cary 14 machine.

Preparation of Bis[1,1-*bis*(*trifluoromethyl*)*methyleneamino*]-*dimethylstannane*.—1,1-Bis(trifluoromethyl)methyleneamine (3 ml, *ca.* 30 mmol) was distilled into a flask containing an ethereal solution of methyl-lithium (22·6 ml of 1·15M solution, 26 mmol) under vacuum at −196°. Nitrogen was admitted into the system and the stirred solution was allowed to warm to 0°, to give a yellow solution of $LiN{:}C(CF_3)_2$ with evolution of methane. Dichlorodimethylstannane (2·85 g, 13 mmol) in diethyl ether (30 ml) was added dropwise to the stirred solution at 0°. The mixture was stirred for ½ h whilst slowly warming to room temperature. Lithium chloride was filtered off, and the pale yellow solution was distilled to give diethyl ether and then *bis*[1,1-*bis*(*trifluoromethyl*)*methyleneamino*]*dimethylstannane* (5·13 g, 83%).

The Other Syntheses.—This general technique was employed for the series of compounds. Reactions were normally conducted on a smaller scale, *ca.* 5 mmol; the lower quoted yields (Table) were accounted for by loss upon distillation. There was no indication that reactions proceeded other than quantitatively.

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