Pentafluoro-orthotellurates of Silicon, Germanium, and Tin

By Friedrich Sladky* and Holger Kropshofer

(*Institut für Anorganische und Analytische Chemie der Universität, A* 6020 *Innsbruck, Innrain* 52*a, Austria*)

Summary Reaction of Me_4Sn, $Me_3(Si,Ge,Sn)Cl$, and $SiCl_4$ with $HOTeF_5$ or $AgOTeF_5$ gives $Me_3(Si,Ge,Sn)OTeF_5$ and $Si(OTeF_5)_4$; $Me_3SiOTeF_5$ has been tested as a reagent for the transfer of the F_5TeO group in metathetical reactions with fluorides and the structure of the adducts of $Me_3SnOTeF_5$ with MeCN and Me_2SO has been studied by i.r. and n.m.r. spectroscopy.

The F_5TeO group is an extremely versatile ligand for main group elements ranging from boron to xenon.[1] Owing to the high electronegativity and apolarity of this group, some of the pentafluoro-orthotellurates show interesting chemical behaviour [*e.g.* $B(OTeF_5)_3$ is superior to BF_3 in its Lewis acidity, and $Xe(OTeF_5)_2$ is the most stable xenon(II) comexcept XeF_2].

Reaction of $HOTeF_5$ with $Me_3(Si,Sn)Cl$ at room temperature affords $Me_3(Si,Sn)OTeF_5$:

$Me_3SiCl + HOTeF_5 \rightarrow HCl + Me_3SiOTeF_5$ (b.p. 94 °C at 714 mmHg)

$Me_3SnCl + HOTeF_5 \rightarrow HCl + Me_3SnOTeF_5$ (b.p. 48 °C at 0·1 mmHg).

Alternatively the latter compound can be prepared by protonation of Me_4Sn:

$Me_4Sn + HOTeF_5 \rightarrow CH_4 + Me_3SnOTeF_5$

Interestingly Me_3GeCl does not interact with $HOTeF_5$, but $Me_3GeOTeF_5$ can be prepared by use of $AgOTeF_5$ in acetonitrile solution:

$Me_3GeCl + AgOTeF_5 = AgCl + Me_3GeOTeF_5$ (b.p. 45 °C at 12 mmHg).

The same route affords $Si(OTeF_5)_4$:

$SiCl_4 + 4\ AgOTeF_5 \rightarrow 4\ AgCl + Si(OTeF_5)_4$ (m.p. 37 °C)

$Me_3SiOTeF_5$ has been tested as a reagent for the transfer of the F_5TeO group in metathetical reactions with covalent halides, such as PF_5, AsF_3, SF_4, and TeF_6:

$Me_3SiOTeF_5 + E{-}F \rightarrow Me_3SiF + E{-}OTeF_5$

With the exception of TeF_6 (no reaction) and AsF_3, fluorination of the F_5TeO group takes place:

$Me_3SiOTeF_5 + PF_5,SF_4 \rightarrow Me_3SiF + TeF_6 + POF_3,SOF_2$

AsF_3 initially affords $F_2AsOTeF_5$ which dismutates on distillation to AsF_3 and $As(OTeF_5)_3$:

$Me_3SiOTeF_5 + AsF_3 \rightarrow Me_3SiF + F_2AsOTeF_5$

$3\ F_2AsOTeF_5 \rightarrow 2AsF_3 + As(OTeF_5)_3$ (b.p. 35 °C at 0·1 mmHg).

The co-ordination chemistry of $Me_3SnOTeF_5$ is of interest because of the ligand behaviour of the F_5TeO group. The coupling constants $J(^{119,117}Sn\text{-}Me)$ at 58·1 and 55·2 Hz respectively are within the established range for four-co-ordinate tin[2] and indicate together with the presence of

$\nu_{sym}(SnC_3)$ at 512 cm^{-1} a non-bridging, covalently bound F_5TeO ligand. Interaction of $Me_3SnOTeF_5$ with an excess of MeCN or Me_2SO increases the tin–proton coupling constants by *ca.* 10 Hz, to values diagnostic of five-coordinate tin.[3] The disappearance of $\nu_{sym}(SnC_3)$ in addition proves these adducts to be based on a trigonal bipyramidal geometry in which the methyl groups occupy the equatorial positions. Comparison of $R(= J_{AB}/\nu_0\delta_{AB})$-values of the AB_4 type ^{19}F n.m.r. spectra of these adducts with $Cs^+F_5TeO^-$ allows a differentiation between the two possible structures $Me_3Sn(L)OTeF_5$(I) and $[Me_3SnL_2]^+[F_5TeO]^-$(II). In accord with the lower donor strength of L = MeCN structure (I) is indicated for the acetonitrile adduct, whereas the stronger base L = Me_2SO promotes complete ionization of the F_5TeO group and formation of structure (II).

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