Tris(trimethylsilyl)methyl-polyselenides and -polytellurides. *X*-Ray Structure of $(Me_3Si)_3CTeTeTeC(SiMe_3)_3$

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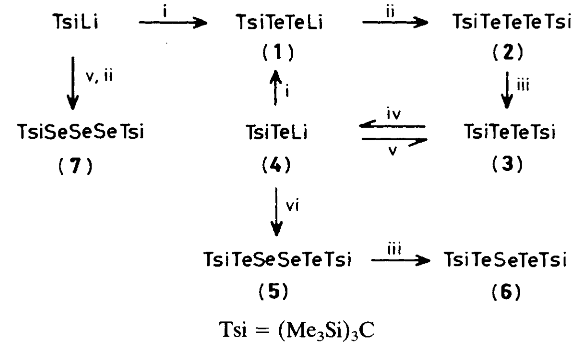
Novel polyselenides and polytellurides have been prepared by means of the stabilizing tris(trimethylsilyl)methyl group; $[(Me_3Si)_3C]_2Te_3$, the first compound containing a three tellurium atom chain, crystallizes as a *trans*-rotamer with a bonding angle of 103.8(1)° at the central tellurium atom and Te–Te bond distances of 2.710(1) Å.

The propensity for catenation is greatly diminished in going from sulphur to tellurium. The only examples of a Te–Te moiety existing between two other elements are given by the the diorganyl ditellurides. Longer chains of tellurium atoms have only been reported for polyatomic tellurium anions and cluster cations.[1] The ability of the very bulky tris(trimethylsilyl)methyl group (trisyl group, Tsi) to give compounds of unusual properties is well documented.[2]

Tris(trimethylsilyl)methyl-lithium[3] is the first reported carbanion to undergo insertion (exothermically) of two equivalents of tellurium with the formation of a yellow–brown solution [tetrahydrofuran (THF)] of $TsiTeTe^-$ (**1**) (Scheme 1, Table 1). Adding water and bubbling O_2 through such a solution leads, after extraction with pentane, to red–black crystals of bis[tris(trimethylsilyl)methyl]tritelluride (**2**) (60% yield relative to TsiH).

The structure of (**2**) is confirmed by *X*-ray crystallography† (Figure 1). Compound (**2**) crystallizes as a *trans*-rotamer with a torsion angle of 105.2(2)°. The molecule resides on a crystallographic twofold axis passing through the central tellurium atom. The bonding angle at the central tellurium atom is 103.8(1)° and the Te–Te and Te–C bond lengths are 2.710(1) and 2.213(7) Å, respectively. An interesting feature of the structure is that silicon (and hydrogen) atoms are disordered into two sets of positions [Si(1,2,3) and Si(4,5,6)] whereas the positions of the carbon atoms are identical for both sets. The molecular structure suggests that no extraordinary bonding parameters are responsible for the existence of (**2**) but that the effective steric shielding of the tellurium atoms 1,1′ is. Regarding the chemical reactivity, (**2**) can be looked upon as an activated diorganyl monotelluride.



Scheme 1. *Reagents:* i, Te; ii, H_2O, O_2; iii, Hg; iv, Li; v, Se; vi, Se_2Cl_2.

Compound (**2**) is stable against air and light and decomposes above 160 °C without melting. Analogous reactions with other bulky organyls like t-butyl-lithium or 2,4,6-tris(t-butyl)phenyl-lithium only lead to ditellurides.[4] Stirring (**1**) with water only affords, besides (**2**) as the main product, bis[tris(trimethylsilyl)methyl]ditelluride (**3**) (35% yield relative to TsiH). We propose for this reaction the intermediate formation and decomposition of the tellurole TsiTeTeH. Compound (**3**) can easily be separated from (**2**) by fractional crystallization from pentane, in which (**3**) is *less* soluble than (**2**). Compound (**3**) forms green–black crystals which decompose above 150 °C without melting; it is the first ditelluride which is not orange or red. By shaking a pentane solution of (**2**) with mercury until the colour changes from red to green, (**3**) is obtained selectively. It can be reduced with lithium in THF to a yellow solution of $TsiTe^-$ (**4**); (**4**) does not undergo insertion of selenium with formation of $TsiTeSe^-$, instead oxidation occurs to (**3**). Se_2Cl_2 however reacts with (**1**) or (**4**) with formation of TsiTeSeSeTeTsi (**5**) which can be converted into TsiTeSeTeTsi (**6**) by shaking a pentane solution of (**5**)

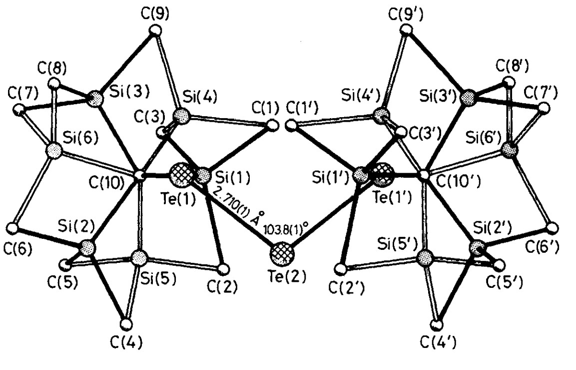


Figure 1. The structure of $(Me_3Si)_3CTeTeTeC(SiMe_3)_3$ projected onto the Te_3 plane.

Table 1. Characteristic n.m.r. data for tris(trimethylsilyl)methyl-selenides and -tellurides.

Compound[c]	$\delta(^{125}Te)$[a]/p.p.m.	$\delta(^{77}Se)$[b]/p.p.m.
TsiTeLi (**4**)[d]	−287	
TsiTeTeLi (**1**)[d]	−32, −191	
TsiTeTeTsi (**3**)	+331	
TsiTeTeTeTsi (**2**)	+480, +332	
TsiTeSeTeTsi (**6**)	+933	+186
TsiTeSeSeTeTsi (**5**)	+921	+517
TsiSeSeSeTsi (**7**)		+560, +651
TsiSeSeLi[d]		+570, +415
TsiSeLi[d]		+188

[a] Relative to Me_2Te. [b] Relative to Me_2Se. [c] In pentane. [d] In THF.

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† *Crystal data* for (**2**): $C_{20}H_{54}Si_6Te_3$, $M = 845.96$, orthorhombic, space group *Pnab*, $a = 12.639(3)$, $b = 12.960(4)$, $c = 22.392(4)$ Å, $U = 3667.9$ Å^3, $Z = 4$, $D_c = 1.532$ g cm^{-3}. The structure analysis is based on 2336 independent reflections (Mo-K_α) and $R = 0.045$. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

with mercury. Diaryltellurenylmonoselenides have been reported previously[5] but (**5**) is a new type of compound.

Reactions analagous to the formation of (**1**) and (**2**) with selenium instead of tellurium afford bis[tris(trimethylsilyl)-methyl]triselenide (**7**) [red crystals, isomorphous and isostructural with (**2**), m.p. 204 °C]. In contrast to a few poorly characterized and unstable diorganyl triselenides,[6] (**7**) is again stable against air and light.

Although the existence and stability of the first diorganyl tritelluride (**2**) can certainly be attributed to the steric shielding by the Tsi groups, (**2**) is surprisingly reactive as a ligand. It interacts readily with $HgCl_2$ with formation of a 1 : 1 complex and replaces ethylene from $(Ph_3P)_2PtC_2H_4$ below room temperature and one Ph_3P group at elevated temperatures.

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