1,3-Migration of a Methyl Group from Tin to Silicon *via* a Cationic Intermediate

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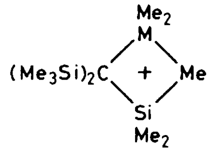
Reactions of $(Me_3Si)_2C(SnMe_3)(SiMe_2I)$ with AgY ($Y = O_2CMe$, O_2CCF_3, or O_3SCF_3) give exclusively $(Me_3Si)_3CSnMe_2Y$; *i.e.* 1,3-migration of an Me group from an Sn to an Si atom occurs, apparently within an intermediate cation in which an Me group bridges between these atoms.

It has been shown previously that 1,3-migrations of an Me group between silicon centres can take place when a compound of the type $TsiSiR_2I$ [$Tsi = (Me_3Si)_3C$] reacts with silver salts, the rearranged product $(Me_3Si)_2C(SiMe_2Y)(SiR_2Me)$ being formed either exclusively (*e.g.*, R = Ph) or (*e.g.*, R = Et) with the unrearranged $TsiSiEt_2Y$ (*e.g.*, $Y = O_2CMe$, O_2CCF_3, NO_3, OCN, *etc.* from AgY, and Y = F from $AgBF_4$).[1] Similar migrations, but from Ge to Si, take place when the compound $(Me_3Si)_2C(GeMe_3)(SiMe_2Br)$ reacts with AgY, mixtures of the rearranged $TsiGeMe_2Y$ and the unrearranged $(Me_3Si)_2C(GeMe_3)(SiMe_2Y)$ being formed.[2] The reactions are thought to involve formation of Me-bridged cations (I) which are then attacked by a nucleophile Y^- at either end of the bridge, attack at the least sterically hindered centre usually being favoured. We have now observed similar migration from Sn to Si.



(I)

When the tin chloride $TsiSnMe_2Cl$ was treated with AgO_2CMe in CH_2Cl_2, filtration and evaporation of the solution left $TsiSnMe_2O_2CMe$, m.p. 255 °C (decomp.); δ_H (CH_2Cl_2) 0.24 (27 H, s, $SiMe_3$), 0.73 [6H, s, ^2J (^1H–^{119}Sn) 55.8 Hz, $SnMe_2$], and 1.96 (3H, s, CMe); δ_C ($CDCl_3$) 4.6 (s, $SiMe_3$), 4.5 (s, $SnMe_2$), 49.5 (s, C*Me*), and 175 (s, CO); δ (^{119}Sn) ($CDCl_3$) 101.1 p.p.m. (s); ν (CO) 1674 cm^{-1}; *m*/*z*

425 ([M − Me]$^+$). The same product was formed, apparently exclusively (though <5% of the unrearranged isomer would have escaped detection), when the silicon iodide $(Me_3Si)_2C(SnMe_3)(SiMe_2I)$ (the corresponding chloride did not react under the conditions used) was treated in the same way with AgO_2CMe; *i.e.* migration of an Me group from Sn to Si had taken place. Identical products, $TsiSnMe_2Y$, were likewise obtained from $TsiSnMe_2Cl$ and $(Me_3Si)_2C(SnMe_3)(SiMe_2I)$ in reactions in CH_2Cl_2 with AgO_2CCF_3 or AgO_3SCF_3.†

When $AgBF_4$ was used in CH_2Cl_2, the initial product from $TsiSnMe_2Cl$ was the tetrafluoroborate $TsiSnMe_2BF_4$, which could be isolated, but decomposed to the fluoride $TsiSnMe_2F$ on prolonged stirring of the product mixture or addition of Et_2O. When $AgBF_4$ was used with $(Me_3Si)_2C(SnMe_3)(SiMe_2X)$ ($X = Br$ or I) in CH_2Cl_2, the product was apparently exclusively the rearranged fluoride $TsiSnMe_2F$ [δ_F (in $CDCl_3$–CH_2Cl_2 relative to external $CFCl_3$), −203.6 p.p.m., s, $^1J(^{19}F-^{119}Sn)$ 2376 Hz; δ_{Sn} ($CH_2Cl_2/CDCl_3$ relative to internal $SnMe_4$), 146.9 p.p.m. (d)], but when the solvent was 1 : 1 v/v CH_2Cl_2–Et_2O the product was exclusively the unrearranged $(Me_3Si)_2C(SnMe_3)(SiMe_2F)$ [δ_F −142.0 p.p.m., septet, $^3J(^1H-^{19}F)$ 6.8 Hz, $^1J(^{19}F-^{29}Si)$ 285 Hz; δ_{Sn} ($CDCl_3$) 7.0 (s)]. The fact that this exceptional behaviour is found in fluoride formation may be associated in part with the very high affinity of silicon for fluorine. It is possible that the BF_4^- anion transfers an F^- ion to Si more readily when Et_2O is present to complex with the BF_3 formed, and so the nucleophilic attack at the silicon centre in the intermediate cation can take place before the BF_4^- liberated by the formation of AgX can diffuse away and attack selectively at the less hindered tin atom. [Change from CH_2Cl_2 to Et_2O as solvent has previously been shown to affect the course of the reaction of TsiSiPhHI with $AgBF_4$; in CH_2Cl_2 the product is a *ca.* 60 : 40 mixture of the rearranged $(Me_3Si)_2C(SiPhHMe)(SiMe_2F)$ and the unrearranged TsiSiPhHF, whereas in Et_2O only the latter is formed.[3]]

It can reasonably be assumed that the reactions of the $(Me_3Si)_2C(SnMe_3)(SiMe_2X)$ compounds proceed through a bridged cation (I, M = Sn), the incoming nucleophile Y^- then attacking at the less hindered end of the bridge, as is usually the case. Presumably because of the large size of the tin atom, the product is exclusively that of attack at tin, whereas for the cation (I, M = Ge) attacks at Ge and Si occur to comparable extents.[2] The results do not permit a firm conclusion on whether the reactions of $TsiSnMe_2Cl$ also proceed through cations (I, M = Sn), but we think it more likely that they involve some type of direct substitution at the M–Cl bond, as appeared to be the case for reactions of $(Me_3Si)_3CGeMe_2Cl$.[2]

Preparation of the compounds $(Me_3Si)_2C(SnMe_3)(SiMe_2X)$ involved use of the reagent $(Me_3Si)_2(Me_3Sn)CLi$, which was made by reaction of $(Me_3Si)_2C(SnMe_3)_2$ with a one-molar proportion of MeLi in tetrahydrofuran. The $(Me_3Si)_2C(SnMe_3)_2$ (*cf.* ref. 4) was unexpectedly obtained as the sole product when $(Me_3Si)_2CCl_2$ was treated with either a one- or two-molar proportion of Me_3SnLi in tetrahydrofuran.

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† All products mentioned gave satisfactory analyses and spectra, including mass spectra.