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INSERTION REACTIONS OF THERMALLY GENERATED STANNYLENES R_2Sn INTO Sn-X (X = Cl, Br, SPh) AND Sn-Sn BONDS

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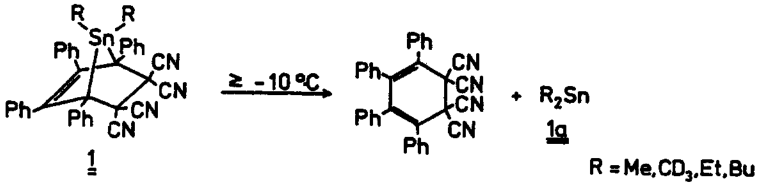
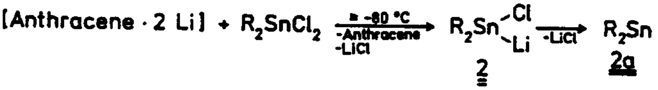
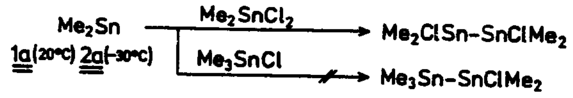
Summary: Thermally generated stannylenes R_2Sn insert efficiently into Sn-X bonds (X = Cl, Br, SPh) as well as into electron deficient Sn-Sn bonds e.g. in $Me_2(Hal)Sn-Sn(Hal)Me_2$, but not into hexaalkyldistannanes R_6Sn_2 under the same conditions; stannylenes R_2Sn always behave as nucleophiles here.

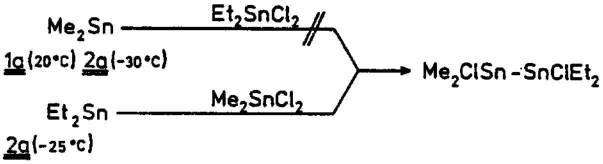
During our studies on heavy carbene analogues R_2M[3], we found two convenient thermal stannylene sources: The 7-stannanorbornene derivative 1[4] gives at and above -10°C a free stannylene 1a via an unimolecular splitting. On the other hand, 2a (^{13}C-NMR, -55°C, THF: δ = 13.32 ppm (s)) is formed from dilithio anthracene as indicated via 2, which exists in two forms (δ = 11.73 and 10.14 ppm (2s, 1:1), 14.53 and 14.87 ppm (2s, 1:1))[5]:





Now we wish to report a smooth insertion of R_2Sn, R= Me, Et(the figures 1a and 2a indicating the method of generation) into the Sn-Cl bond of Me_2SnCl_2, but not of Me_3SnCl[6] and Et_2SnCl_2. Clearly both polar and steric effects on the Sn-Cl bond are of influence, the higher electron deficiency of the tin atom in Me_2SnCl_2 seems to be important supposing a nucleophilic behaviour of the stannylenes R_2Sn:





Scavengers with one Me residue, $MeRSnCl_2$, always give insertion into the Sn-Cl bond, but yields decrease with increasing bulkiness of R. Because of similar solubilities, redistributions, and high sensibilities against temperature and light the resulting distannane dihalides could not be isolated but have been identified and determined by ^1H- and ^{119}Sn-NMR, see table, and alkylation to hexaalkyldistannanes. Both stannylene sources and all analytical methods yield quite consistent results.

Table: Insertion of Me_2Sn 1a or 2a into the Sn-Cl bond of $MeRSnCl_2$

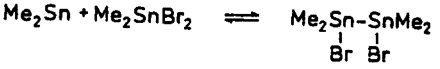
Products $Me_2(Cl)Sn-Sn(Cl)MeR$

R=	Yields in % with 1a(20°C)	2a(-30°C)	^1H-NMR[a)] of MeSn groups (28°C)	^{119}Sn-NMR[b)] (-80°C)
Me	100	100	0.80(12H)	-138.8($SnMe_2$)
Et	93	90	0.79(6H), 0.73(3H)	-136.4($SnMe_2$),-120.0(SnEtMe)
Pr	∿45	78	0.79(6H), 0.75(3H)	--
tBu	∿45	65	0.78(6H), 0.67(3H)	--
Ph	∿100	∿100	0.80(6H), 0.95(3H)	--

a) in THF, δ in ppm, standard TMS; similar values are recorded in CH_2Cl_2.
b) in THF containing LiCl, δ in ppm, standard Me_4Sn.

Similar insertions have been established for the Sn-Br and Sn-SPh bonds generating the corresponding distannanes 3 and 4. Since the latter prepared independently proved to be thermal stannylene sources[2], the following equilibria are resulting:

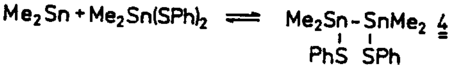
^1H-NMR (C_6H_6), standard TMS



$$Me_2Sn + Me_2SnBr_2 \rightleftharpoons \underset{Br}{Me_2Sn}-\underset{Br}{SnMe_2}$$

3

δ = 0.67 ppm (s, $^2J(Sn-H)$ = 50/53 Hz, $^3J(Sn-H)$ = 14 Hz)



$$Me_2Sn + Me_2Sn(SPh)_2 \rightleftharpoons \underset{PhS}{Me_2Sn}-\underset{SPh}{SnMe_2}$$

4

δ = 0.35 ppm (s, $^2J(Sn-H)$ = 48/51 Hz, $^3J(Sn-H)$ = 14 Hz)

Further strong evidence for these equilibria is given by their shift by excess Me_2SnBr_2 or, resp., $Me_2Sn(SPh)_2$ towards higher contents of 3 (Fig. 1) or, resp., 4 (Fig. 2) (^1H-NMR):

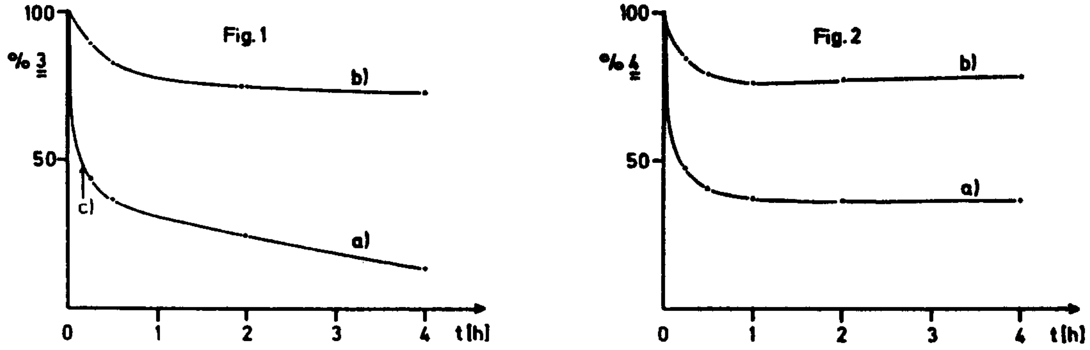
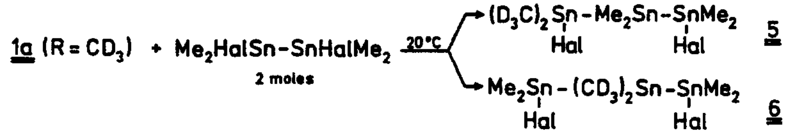


Fig. 1+2: a) Stannylene extrusion/insertion with pure 3 or 4 in benzene at 80°C. b) in presence of 5 moles of Me_2SnBr_2 or $Me_2Sn(SPh)_2$ per mol 3 or 4. c) slow deposition of elemental tin.

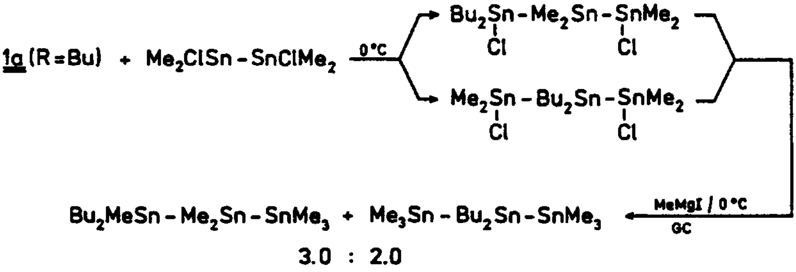
By the way, these experiments show clearly the reversibility of the polymerization of Me_2Sn[7,8], competing with the insertions under the conditions mentioned above.

In hexaalkyldistannanes $R_3Sn\text{-}SnR_3$ the Sn-Sn bond apparently is rather inert towards thermal stannylene insertion: Neither 1a (R = Me, 0°C) nor 2a (R = Me, Et, -20°C) gave us insertions into Me_6Sn_2[9] and Et_6Sn_2. Only above 100°C an insertion of R'_2Sn into R_6Sn_2 giving $R_3Sn\text{-}R'_2Sn\text{-}SnR_3$ has been observed[12,13].

Therefore, we were surprised that dihalo distannanes $Me_2HalSn\text{-}SnHalMe_2$, at 20°C or even 0°C, clearly gave a stannylene insertion into their Sn-Sn bond, besides the expected Sn-Cl insertion (estimation by ^1H-NMR):



Hal=	5 (%)	6 (%)	^1H-NMR (CH_2Cl_2), standard TMS
Cl	62	38	0.83 (s, Me_2SnCl), 0.70 ppm (s, Me_2Sn)
Br	66	34	0.97 (s, Me_2SnBr), 0.73 ppm (s, Me_2Sn)



Whereas with $(D_3C)_2Sn$ the overall yield of 5 + 6 is nearly quantitative, with Bu_2Sn an overall insertion of only 2% is found: Steric influences are seen to be important also in this case.

The high activity of the Sn-Sn bond in the halo distannanes can be derived from its electron deficiency compared with the Sn-Sn bond in the peralkylated distannanes. This is confirmed by the high activity of another electron deficient distannane[14], the product being identified by ^{1}H-NMR (CH_2Cl_2, $\delta = 0.30$ (s, 9H), 0.67 ppm (s, 6H)) and degradation by iodine:

$$\underline{\underline{\mathbf{1a}}}\,(R{=}Me) + Me_3Sn{-}Sn(C_6F_5)_3 \xrightarrow{20^\circ C} Me_3Sn{-}Me_2Sn{-}Sn(C_6F_5)_3$$

Again, the thermally generated stannylenes R_2Sn behave as nucleophiles as they did during insertion into Sn-X bonds, see above. This is in accordance with the assumption of singlet species R_2Sn:, whose paired electrons act as donors. It is of interest that a singlet ground state is found for stannylenes also by quantum chemical calculations[16].

References:

1) R.Moser, Dissertation Univ. Dortmund 1980.

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3) W.P.Neumann and M.Schriewer, Tetrahedron Lett. 21, 3273 (1980), B.Mayer and W.P.Neumann, ibid. 4887. Further references are given there.

4) W.P.Neumann, Ch.Grugel, and M.Schriewer, Angew. Chem. Internat. Edit. 18, 543 (1979).

5) A full report of the corresponding ^{119}Sn- and ^{13}C-NMR investigations of R_2Sn[1] will be given elsewhere.

6) Other authors[11] suggest, however, insertion into the Sn-Cl bond of Me_3SnCl forming Me_5Sn_2Cl and polystannanes $Me_{2n+1}Sn_nCl$ from other R_2Sn sources.

7) Transient $(Me_2Sn)_n$ formation and degradation can be observed (^{1}H-NMR: δ = 0.72 or 0.47 ppm) during the thermolysis of 3 or, resp., 4.

8) This is consistent with older findings that $(Ph_2Sn)_n$ gives Ph_2Sn insertion into Ph_2SnCl_2 at 140°C yielding first (presumably) $Ph_2ClSn{-}SnClPh_2$ decomposing to Ph_3SnCl and other products: H.G.Kuivila and E.R.Jakusik, J. Org. Chem. 26, 1430 (1961).

9) Under other conditions, a Me_2Sn insertion into Me_6Sn_2 giving Me_8Sn_3 is mentioned[10] but not confirmed in later investigations[11].

10) D.P.Arnold, M.J.Cuthbertson, and P.R.Wells, J.Organomet.Chem. 184, 39 (1980)

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13) Ch.Grugel, W.P.Neumann, and P.Seifert, Tetrahedron Lett. 1977, 2205.

14) Neither $Me_2(C_6F_5)Sn{-}Sn(C_6F_5)Me_2$ nor $Me_2(AcO)Sn{-}Sn(OAc)Me_2$ did react under the same conditions, the latter certainly because of the strong pentacoordination between Sn atoms and the acetyl residues[15].

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16) G.Olbrich, Chem. Phys. Lett. 73, 110 (1980), and private communication.

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