The First Application of Samarium(II) Diiodide for the Formation of Group 14 Element Catenates: Synthesis of Tri- or Poly-germanes and Polystannanes

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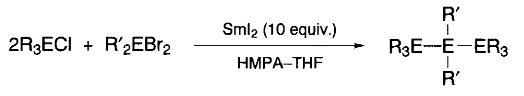
Some Group 14 element catenates such as tri- or poly-germanes and polystannanes are synthesized by use of the one-electron reducing agent SmI_2.

The Group 14 element catenates such as polysilanes, polygermanes, and polystannanes have attracted increasing attention owing to their unique physical, chemical and optical properties, and their engineering applications.[1–9] Much attention is therefore being directed towards the development of synthetic routes. The most practical methods for synthesizing the Group 14 element catenates is a Wurtz-type polycondensation of Group 14 element dihalides with an alkali metal (Kipping method). These reactions are usually carried out under vigorous conditions and often lead to low yields of the polymers because of their heterogeneous nature. Moreover, such reactions, in which moisture-sensitive alkali metals are used, can be hazardous. Therefore, much milder, safer and more efficient methods are desirable. We report here a new synthetic procedure for the formation of Group 14 element catenates by use of SmI_2. This reaction is particularly useful for the synthesis of polygermanes and polystannanes which are difficult to obtain in high yields by the Kipping method. SmI_2 is known to be a mild one-electron reducing agent and it has been applied in a wide variety of carbon–carbon bond formation reactions.[10]

Table 1 Syntheses of various trigermanes and analogues

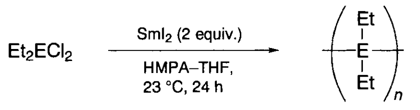


$$2R_3ECl + R'_2EBr_2 \xrightarrow[\text{HMPA–THF}]{SmI_2\ (10\ \text{equiv.})} R_3E{-}E(R')_2{-}ER_3$$

Entry	Product[a]	Conditions[b]	Yield[c] (%)
1	$Et_3GeGePh_2GeEt_3$	A	94
2	$Et_3GeGePh_2GeEt_3$	B	90
3	$Et_3GeGePh_2GeEt_3$	C	89
4	$Et_3GeGePh_2GeEt_3$	D	83
5	$Et_3GeGePh_2GeEt_3$	E	74
6	$Me_3GeGePh_2GeMe_3$	A	87
7	$Bu^n{}_3GeGePh_2GeBu^n{}_3$	B	87
8	$Pr^i{}_3GeGePh_2GePr^i{}_3$	A	30
9	$Et_3GeGeMePhGeEt_3$	A	70
10	$Et_3SiGePh_2SiEt_3$	A	50
11	$Et_3SnGePh_2SnEt_3$	B	42

[a] All products were characterized by ^1H NMR and GC-MS. [b] A, see text. B, c = 3 mmol dm^3. C, c = 15 mmol dm^3. D, THF solutions of substrates were reacted for 1 h. E, reaction carried out at 0 °C. [c] Isolated yields.

Table 2 Polymerization of Et_2ECl_2 by use of SmI_2



$$Et_2ECl_2 \xrightarrow[\text{HMPA–THF, 23 °C, 24 h}]{SmI_2\ (2\ \text{equiv.})} \left(E(Et)_2\right)_n$$

Entry	E	λ_{max}/nm	$\overline{M}_w$[a]	$\overline{M}_n$[a]	M_w/M_n[a]	Yield[b] (%)
1	Ge	289	2380	2030	1.17	19
2[c]	Ge	288	1562	1393	1.12	63
3	Sn	368	4820	3980	1.21	74
4[d]	Sn	367	4100	3570	1.15	76

[a] Determined by GPC based on polystyrene standard. [b] Isolated yield. [c] Reaction was carried out at reflux temperature for 7.5 h. [d] Reaction was carried out at reflux temperature for 5 h, in the absence of HMPA.

Initially, a trigermane was chosen as a catenated model compound and reactions were carried out under a variety of conditions (Table 1). When a THF solution (40 ml) of Et_3GeCl (25.7 mg, 0.13 mmol) and Ph_2GeBr_2 (23.3 mg, 0.06 mmol) was added to a THF–HMPA (12 : 1) solution of SmI_2 [0.6 mmol; prepared from Sm and diiodoethane in THF (0.1 mol dm^{-3})] at room temp. under an argon atmosphere for 2 h and stirred for 1 h, the corresponding trigermane was obtained in 94% yield (entry 1). Many types of trigermanes and analogues could be synthesized in moderate to good yields under mild conditions (entries 6–11). If concentrated solutions of substrates were added to SmI_2, a tetragermane, $Et_3Ge(GePh_2)_2GeEt_3$, was obtained as a by-product (entries 2 and 3). This result prompted us to apply SmI_2 to the synthesis of polymers containing Group 14 elements.

In Table 2, some results of polymerization of Et_2GeCl_2 and Et_2SnCl_2 are summarized, and as can be seen, SmI_2 is an efficient agent for the synthesis of polygermanes and polystannanes. The resulting polymers had narrow molecular mass distributions ($\overline{M}_w/\overline{M}_n$ = 1.12–1.21). In particular, polystannanes were obtained in good yields, and had high molecular masses (entry 3). Moreover, when reactions were carried out at reflux temperature in the absence of HMPA, polystannanes were obtained in 76% yield (entry 4).

Consequently, SmI_2 is a new and useful agent for the synthesis of polygermanes and polystannanes in good yields under mild conditions.

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