Ruthenium-Catalyzed Demethanative Coupling of $HGeMe_3$: A High Yield Route to Polygermanes

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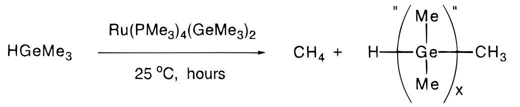
As a result of "σ-conjugation", polymers with extended backbones of the heavier group 14 elements exhibit unique electronic and optical properties not normally associated with saturated polymers, including a red shift of λ_{max} with increasing chain length, narrow emission bands, and semiconducting behavior. Potential applications of these polymers as photoconductors, photoresists, and nonlinear optical materials have been suggested.

As a class, polysilanes have been extensively studied, but polygermanes have received limited attention. Similar to polysilanes, the principal method for preparing polygermanes is the Wurtz-type coupling of dichlorogermanes with molten sodium, which typically produces high molecular weight polymers, but in extremely low (5−26%) yields.[2] More recently, Mochida and co-workers have developed an alternative strategy based on the reaction of germanium diiodide with Grignard or lithium reagents,[2d,3] which produces lower molecular weight polymers, but in better yields (≤60%). Over the last decade, transition metal catalyzed dehydrogenative coupling of organosilanes has become well-established for the preparation of polysilanes[4] and polycarbosilanes.[5] Although successfully applied to secondary stannanes,[6] the use of catalytic routes to polygermanes has been limited.[7] We now report an efficient catalytic process for preparing permethyl polygermanes in high yields from trimethylgermane. This appears to be the first example of a catalytic *demethanative* coupling, in which element−element bonds are produced with the concurrent elimination of CH_4.

The catalytic coupling of $HGeMe_3$ in the presence of 0.01−1.0 mol % of $Ru(PMe_3)_4(GeMe_3)_2$ (**1**) proceeds at 25 °C in hydrocarbon solvents or neat germane to yield long-chain polygermanes. The initial products of the reaction are identified by ^1H NMR as CH_4 and discrete oligogermanes, including $HGeMe_2GeMe_3$. In an NMR tube scale reaction, all $HGeMe_3$ has been consumed within 10 min. After ca. 1 h at 25 °C, the sharp resonances of oligogermanes are replaced with two broad peaks (δ 0.70 and 0.51) identified as the Ge−Me groups of the polygermane. Ge−H resonances are no longer observed in the ^1H NMR. The gross shape of the peaks is invariant with further reaction time. The reaction solution remains very pale yellow and free of any visible precipitate. On preparative scales, the polygermane is isolated as a colorless gum or flexible solid in 80−90% yield.



As catalyst **1** is synthesized from $HGeMe_3$ and $Ru(PMe_3)_4Me_2$ (**2**),[8] it is not surprising that the latter can be used directly as a precatalyst. A short induction period (≤15 min) is observed following addition of 0.01−1 mol % of **2** to neat $HGeMe_3$, after which methane evolution ensues. This induction period is associated with conversion of **2** to **1**, the active species.

Molecular weights of the polygermanes were determined by GPC using two methods (Table 1). Use of either **1** or **2** had no significant effect on the molecular weight distribution. The common method of refractive index detection and calibration against polystyrene standards yields $M_n \approx (1-4) \times 10^4$ and $M_w \approx (2-7) \times 10^4$ for the polygermanes. In a previous study of poly(methylphenyl)silanes using SEC/light scattering, it was concluded that the molecular weight of this particular *linear* polysilane is accurately determined with polystyrene calibrants.[9] However, polystyrene is not always a reliable model for inorganic polymers; it has been suggested that the molecular weights of polysilanes can be underestimated by this method.[1a] The use of an inline viscometer is a more accurate technique which can yield absolute values of molecular weight for each retention volume.[10] In the present study, M_w values for the polygermanes determined by SEC/viscometry range from 2×10^4 to 2×10^5; these M_w values are up to 3-fold larger than those determined using polystyrene standards.

The polygermanes obtained via Ru-catalyzed demethanative coupling appear to possess highly branched structures, with pendant $(GeMe_2)_xGeMe_3$ groups rather than only linear $GeMe_2$ subunits. Previous studies of polygermanes have suggested that even short linear poly(dimethylgermane) chains are insoluble in most solvents.[11] In contrast, these polygermanes are freely soluble in common hydrocarbon solvents. In addition, the appearance of two distinct broad peaks in the ^1H NMR is not consistent with simple linear $GeMe_2$ chains, instead indicating two significantly different Ge−Me environments.

Conclusive evidence for a highly branched structure is found in the intrinsic viscosities and also in a dynamic light-scattering experiment. The polygermanes have extremely low intrinsic viscosities (0.03−0.06 dL/g), commonly exhibited by high polymers with small hydrodynamic volumes resulting from branched microstructures. Absolute measurement of hydrody-

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(1) For reviews, see: (a) West, R. *J. Organomet. Chem.* **1986**, *300*, 327−346. (b) West, R. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley and Sons: New York, 1989; pp 1207−1240. (c) Miller, R. D.; Michl, J. *Chem. Rev.* **1989**, *89*, 1359−1410.

(2) (a) Trefonas, P.; West, R. *J. Polym. Sci.* **1985**, *23*, 2099−2107. (b) Miller, R. D.; Sooriyakumaran, R. *J. Polym. Sci., Polym. Chem. Ed.* **1987**, *25*, 111−125. (c) Hayashi, T.; Uchimaru, Y.; Reddy, N. P.; Tanaka, M. *Chem. Lett.* **1992**, 647−650. (d) Mochida, K.; Chiba, H. *J. Organomet. Chem.* **1994**, *473*, 45−54.

(3) The formation of oligomeric alkylgermanes by related methods has also been previously reported: (a) Nefedov, O. M.; Kolesnikov, S. P. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1964**, 773−774. (b) Glockling, F.; Light, J. R. C. *J. Chem. Soc., Chem. Commun.* **1968**, 1052−1053.

(4) For recent reviews, see: (a) Harrod, J. F. In *Inorganic and Organometallic Polymers*; Zeldin, M., Wynne, K. J., Allcock, H. R., Eds.; ACS Symposium Series 360; American Chemical Society: Washington, DC, 1988; pp 89−100. (b) Corey, J. Y. In *Advances in Silicon Chemistry*; Larson, G., Ed.; JAI Press: Greenwich, CT, 1991; Vol. 1, pp 327−387. (c) Tilley, T. D. *Acc. Chem. Res.* **1993**, *26*, 22−29.

(5) (a) Procopio, L. J.; Berry, D. H. *J. Am. Chem. Soc.* **1991**, *113*, 4039−4040. (b) Procopio, L. J.; Mayer, B.; Plössl, K.; Berry, D. H. *Polym. Prepr.* **1992**, *33*, 1241−1242.

(6) (a) Imori, T.; Tilley, T. D. *J. Chem. Soc., Chem. Commun.* **1993**, 1607−1609. (b) Imori, T.; Lu, V.; Cai, H.; Tilley, T. D. *J. Am. Chem. Soc.* **1995**, *117*, 9931−9940.

(7) Aitken, C.; Harrod, J. F.; Malek, A. *J. Organomet. Chem.* **1988**, *349*, 285−291.

(8) (a) Andersen, R. A.; Jones, R. A.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1978**, 446−453. (b) Jones, R. A.; Real, R. M.; Wilkinson, G.; Galas, A. M. R.; Hursthouse, M. B.; Malik, K. M. A. *J. Chem. Soc., Dalton Trans.* **1980**, 511−518.

(9) Devaux, J.; Daoust, D.; De Mahieu, A.-F.; Strazielle, C. In *Inorganic and Organometallic Oligomers and Polymers*; Harrod, J. F., Laine, R. M., Eds.; Kluwer Academic: Dordrecht, The Netherlands, 1991; pp 49−60.

(10) Kuo, C. Y.; Provder, T.; Koehler, M. E. *J. Liq. Chromatogr.* **1990**, *13*, 3177−3199.

(11) (a) Carberry, E.; Dombek, B. *J. Organomet. Chem.* **1972**, *36*, 61−70. (b) Kolesnikov, S. P.; Mitenina, T. L.; Shteinshneider, A. Y.; Nefedov, O. M. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1982**, 942−943.

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Table 1. Summary of $HGeMe_3$ Polymerization Data[a]

catalyst (mol %)	yield (%)	GPC−polystyrene 10^4M_w	GPC−polystyrene 10^4M_n	viscometry 10^4M_w	viscometry 10^4M_n	viscometry $[\eta]$ (dL/g)
1[b] (1.0)	85	5.4	2.8	14.4	0.5	0.06
1 (0.1)	97	6.6	1.8	8.0	0.8	0.05
2 (1.0)	82	3.8	1.9	8.4	1.4	0.06
2 (0.1)	92	7.4	3.7	20.5	1.0	0.06
2[c] (1.0)	81	2.0	0.9	2.5	0.5	0.03

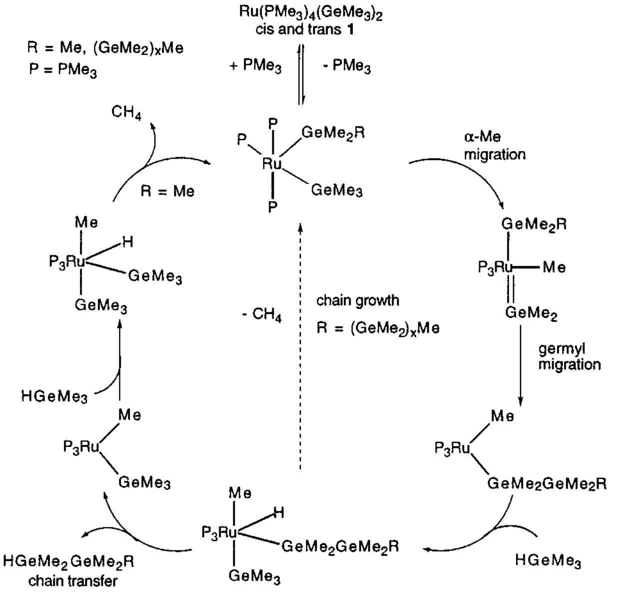
[a] All reactions run in neat $HGeMe_3$ in glass bombs equipped with Teflon valves at 25 °C for 1 week (except where noted). [b] Time = 1 day. [c] $T = 60$ °C.

namic diameter (D_h) of the material in entry 1 of Table 1 by dynamic light scattering confirms a small D_h value of the polymer (5 nm) relative to that of linear polystyrene of comparable molecular weight ($D_h = 11$ nm). Furthermore, the high degree of branching implied by the small D_h explains why the M_w values determined relative to linear polystyrene calibrants are low compared with the values from SEC/viscometry. The large polydispersity index and high M_z (data not listed in Table 1) are not fully understood, but may indicate the presence of a small fraction (<1%) of microgel in the polymers. In addition, the GPC traces do not indicate the presence of cyclic oligomers.

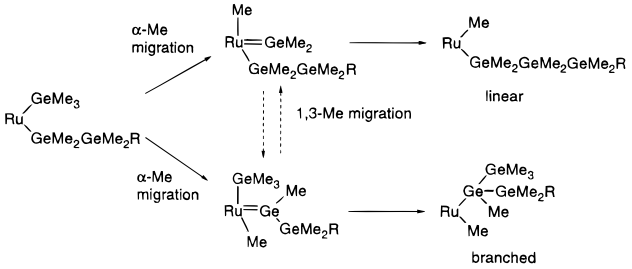
The active catalyst **1** is not stable in solution at room temperature in the absence of $HGeMe_3$ and converts to $HGeMe_3$, oligogermanes, and $Ru(PMe_3)_3(\eta^2\text{-}CH_2PMe_2)(GeMe_3)$ **(3)**[12] in which a methyl group on a phosphine ligand has been metalated. Both the catalytic activity of **1** and the decomposition of **1** to **3** are strongly inhibited in the presence of excess PMe_3, suggesting that the initial step in the catalytic process is loss of a labile phosphine ligand from the coordinatively saturated **1**.

The catalytic coupling of $HGeMe_3$ by **1** involves the cleavage of Ge−C bonds and the formation of Ge−Ge bonds. Intermolecular cleavage of a Ge−C bond by direct oxidative addition of a free germane is unprecedented. However, Ge−C cleavage could be accomplished by an α-methyl migration from a germyl ligand to form a metal−methyl−germylene complex. This type of process has been observed in other organometallic systems, including α-migrations of hydrogen[13] and carbon[14] from alkyls yielding alkylidene complexes. Analogous organosilicon and -germanium systems also provide evidence for the intermediacy of silylene and germylene metal complexes via α-elimination mechanisms.[15] The most direct route to Ge−Ge bond formation, reductive elimination, seems to be precluded by the absence of detectable amounts of Ge_2Me_6 in the reaction mixture.[16] As an alternative, Ge−Ge bond formation could be accomplished by the reverse of an α-migration step: germyl to germylene migration. An analogous process, silyl to silylene migration, has been proposed in the photolysis of transition metal substituted disilanes[17] and in the reversible scrambling of a CD_3 group between silicon atoms in $(dcpe)Pt(H)(SiMe_2SiMe_3)$.[18] In addition, the migration of a silyl group from a tantalum center to an alkylidene has been observed.[19] The reverse of this process has also been indicated in many instances.[15] These key steps are illustrated in the mechanism proposed in Scheme 1. The $Ge{-}CH_3$ cleavage by α-migration followed by germyl migration yields a digermyl methyl complex. Addition of $HGeMe_3$ produces a seven-coordinate methyl hydride complex, from which CH_4 loss regenerates a bis(germyl) species. Alternatively, exchange of $HGeMe_3$ for $HGeMe_2GeMe_2R$ corresponds to a chain transfer step.

Scheme 1. Proposed Mechanism for Linear Germane Chain Growth by Demethanative Coupling



Scheme 2. Proposed Mechanism for Formation of Linear or Branched Polygermanes



The catalytic cycle can lead to either linear or branched polygermanes (Scheme 2). The structure of the polymer will be influenced by the site of the α-Me migration: either a $GeMe_3$ or an oligogermyl ($Ge\mathit{Me}_2GeMe_2R$) group. Interconversion via 1,3-migration in the germyl−germylene complex could also lead to branching. Related redistributions of alkyl groups in bis(silyl) and mixed germyl silyl systems have been observed and are thought to proceed via 1,3-migrations of substituents in intermediate silylene (or germylene) complexes.[20]

In summary, demethanative coupling of a tertiary germane produces nearly quantitative yields of highly branched, high molecular weight polygermanes under very mild conditions.

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Supporting Information Available: Experimental procedures and characterization of **1** and **3** (3 pages). See any current masthead page for ordering and Internet access instructions.

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(12) Compound **3** could not be isolated free of the oligogermanes which are formed concurrently. Spectroscopic data is listed in the supporting information.

(13) (a) Cooper, N. J.; Green, M. L. H. *J. Chem. Soc., Chem. Commun.* **1974**, 761−762. (b) Turner, H. W.; Schrock, R. R.; Fellmann, J. D.; Holmes, S. J. *J. Am. Chem. Soc.* **1983**, *105*, 4942−4950.

(14) Yang, J.; Yin, J.; Abboud, K. A.; Jones, W. M. *Organometallics* **1994**, *13*, 971−973 and references cited therein.

(15) For a recent review, see: Pannell, K. H.; Sharma, H. K. *Chem. Rev.* **1995**, *95*, 1351−1374.

(16) In addition, Ge_2Me_6 has been shown to be stable under the catalytic reaction conditions.

(17) Pannell, K. H.; Sharma, H. *Organometallics* **1991**, *10*, 954−959.

(18) Recatto, C. A. Ph.D. Thesis, Tulane University, 1994.

(19) Berry, D. H.; Koloski, T. S.; Carroll, P. J. *Organometallics* **1990**, *9*, 2952−2962.

(20) For example, see: (a) Pannell, K. H.; Cervantes, J.; Hernandez, C.; Cassias, J.; Vincenti, S. *Organometallics* **1986**, *5*, 1056−1057. (b) Pestana, D. C.; Koloski, T. S.; Berry, D. H. *Organometallics* **1994**, *13*, 4173−4175. (c) Figge, L. K.; Carroll, P. J.; Berry, D. H. *Organometallics* **1996**, *15*, 209−215.