

# Catalytic Approach to Germanium-Functionalized Silsesquioxanes and Germasilsesquioxanes

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**ABSTRACT:** Silsesquioxanes have attracted considerable attention in recent years due to their unique hybrid structure and versatile properties. Herein, we report the first catalytic approach to the synthesis of completely and partially condensed germaniumfunctionalized silsesquioxanes as well as germasilsesquioxanes, mediated by scandium(III) triflate. We provide a solution for introducing germyl functionalities into various types of silsesquioxanes under mild conditions with excellent yields. This methodology turns out to be a highly efficient and selective synthesis route to obtaining novel germanium-containing silsesquioxanes. These new multielement POSS derivatives may have great potential for further applications as valuable multifunctional building blocks in material chemistry.

## REFERENCES:

- (1) Cordes, D. B.; Lickiss, P. D.; Rataboul, F. *Chem. Rev.* 2010, 110, 2081–2173.
- (2) Yan, Z.; Xu, H.; Guang, S.; Zhao, X.; Fan, W.; Liu, X. Y. *Adv. Funct. Mater.* 2012, 22, 345–352.
- (3) Ayandele, E.; Sarkar, B.; Alexandridis, P. *Nanomaterials* 2012, 2, 445–475.
- (4) Phillips, S. H.; Haddad, T. S.; Tomczak, S. J. *Curr. Opin. Solid State Mater. Sci.* 2004, 8, 21–29.
- (5) Olivero, F.; Carniato, F.; Bisio, C.; Marchese, L. *J. Mater. Chem.* 2012, 22, 25254–25261.
- (6) Chan, K. L.; Sonar, P.; Sellinger, A. *J. Mater. Chem.* 2009, 19, 9103–9120.
- (7) Yang, X.; Froehlich, J. D.; Chae, H. S.; Harding, B. T.; Li, S.; Mochizuki, A.; Jabbour, G. E. *Chem. Mater.* 2010, 22, 4776–4782.
- (8) Kamino, B. A.; Bender, T. P. *Chem. Soc. Rev.* 2013, 42, 5119–5130.
- (9) Seurer, B.; Coughlin, E. B. *Macromol. Chem. Phys.* 2008, 209, 1198–1209.
- (10) Murugavel, R.; Voigt, A.; Walawalkar, M. G.; Roesky, H. W. *Chem. Rev.* 1996, 96, 2205–2236.
- (11) Feher, F. J.; Budzichowski, T. A.; Ziller, J. W. *Inorg. Chem.* 1997, 36, 4082–4086.
- (12) Lorenz, V.; Edelmann, F. T. *Advances in Organometallic Chemistry. Metallasilsesquioxanes*; Elsevier: Magdeburg, Germany, 2005; pp 101–153.
- (13) Levitsky, M. M.; Yalymov, A. I.; Kulakova, A. N.; Petrov, A. A.; Bilyachenko, A. N. *J. Mol. Catal. A: Chem.* 2017, 426, 297–304.

- (14) Feher, F. J.; Newman, D. A.; Walzer, J. F. *J. Am. Chem. Soc.* 1989, 111, 1741–1748.
- (15) Pach, M.; Macrae, R. M.; Carmichael, I. *J. Am. Chem. Soc.* 2006, 128, 6111–6125.
- (16) Kamitani, M.; Fukumoto, K.; Tada, R.; Itazaki, M.; Nakazawa, H. *Organometallics* 2012, 31, 2957–2960.
- (17) Risen, W. M.; Wang, Y. Z., Jr.; Honore, A. U.S. Patent 2001/ 6248852, 2001.
- (18) Gadzała-Kopciuch, R.; Pypowski, K.; Chrzascik, I.; Kluska, M. *Crit. Rev. Anal. Chem.* 2010, 40, 187–193.
- (19) Carpenter, J.; Lukehart, M.; Henderson, D. O.; Mu, R.; Jones, B. D.; Glosser, R.; Stock, S. R.; Wittig, J. E.; Zhu, J. G. *Chem. Mater.* 1996, 8, 1268–1274.
- (20) Lin, Q.; Bu, X.; Mao, C.; Zhao, X.; Sasan, K.; Feng, P. *J. Am. Chem. Soc.* 2015, 137, 6184–6187.
- (21) Nedež, C.; Choplin, A.; Basset, J. M.; Benazzi, E. *Inorg. Chem.* 1994, 33, 1094–1098.
- (22) Rzonsowska, M.; Dudziec, B.; Marciniak, B. *Dalton Trans.* 2016, 45, 17187–17194.
- (23) Frąckowiak, D.; Żak, P.; Spolnik, G.; Pyziak, M.; Marciniak, B. *Organometallics* 2015, 34, 3950–3958.
- (24) Żak, P.; Frąckowiak, D.; Grzelak, M.; Bołt, M.; Kubicki, M.; Marciniak, B. *Adv. Synth. Catal.* 2016, 358, 3265–3276.
- (25) Frąckowiak, D.; Żak, P.; Marciniak, B. U.S. Patent 2016/ 9249167, 2016.
- (26) Grzelak, M.; Frąckowiak, D.; Marciniak, B. *Eur. J. Inorg. Chem.* 2017, 2017, 3337–3342.
- (27) Puff, H.; Bockmann, M. P.; Kok, T. R.; Schuh, W. J. *Organomet. Chem.* 1984, 268, 197–206.
- (28) Ignatovich, L.; Muravenko, V.; Grinberga, S.; Lukevics, E. *Chem. Heterocycl. Compd.* 2006, 42, 268–271.
- (29) Hreczycho, G.; Frąckowiak, D.; Pawluć, P.; Marciniak, B. *Tetrahedron Lett.* 2011, 52, 74–76.
- (30) Hreczycho, G.; Kuciński, K.; Pawluć, P.; Marciniak, B. *Organometallics* 2013, 32, 5001–5004.
- (31) Hreczycho, G.; Pawluć, P.; Marciniak, B. *New J. Chem.* 2011, 35, 2743–2746.
- (32) Hreczycho, G. *Eur. J. Inorg. Chem.* 2015, 67–72.
- (33) Kuciński, K.; Hreczycho, G. *ChemCatChem* 2017, 9, 1868–1885.

- (34) Frąckowiak, D.; Walkowiak, J.; Hreczycho, G.; Marciniak, B. *Eur. J. Inorg. Chem.* 2014, 3216–3220.
- (35) Kuciński, K.; Hreczycho, G. *ChemSusChem* 2017, 10, 4695-4698.
- (36) Kaźmierczak, J.; Kuciński, K.; Hreczycho, G. *Inorg. Chem.* 2017, 56, 9337.
- (37) Kaneko, Y.; Coughlin, E. B.; Gunji, T.; Itoh, M.; Matsukawa, K.; Naka, K. *Int. J. Polym. Sci.* 2012, 2012, 1–2.
- (38) Sharma, I.; Wurst, J. M.; Tan, D. S. *Org. Lett.* 2014, 16, 2474– 2477.
- (39) Dzudza, A.; Marks, T. J. *Chem. Eur. J.* 2010, 16, 3403–3422.
- (40) Dang, T. T.; Boeck, F.; Hintermann, L. *J. Org. Chem.* 2011, 76, 9353–9361.
- (41) Roesky, H. W. *Efficient Methods for Preparing Silicon Compounds*; Elsevier: Göttingen, Germany, 2016; pp 143–159.
- (42) Duchateau, R.; Abbenhuis, H. C. L.; van Santen, R. A.; Thiele, S. K. H.; van Tol, M. F. H. *Organometallics* 1998, 17, 5222–5224.