

Catalysis by titanocene-functionalized polymer-supported dendrimers

Patrick E. Berget, Jacqueline M. Teixeira, John L. Jacobsen and Neil E. Schore*

Department of Chemistry, University of California, Davis, CA 95616, USA

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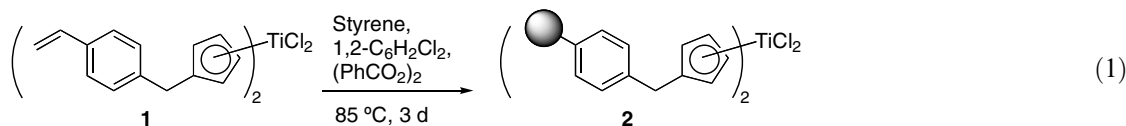
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Abstract—A series of variously-functionalized first-, second-, and third-generation dendrimers have been prepared and linked via a biphenyl core to a bis-styryl moiety suitable for use as a crosslinker in polymerization. Attachment of titanocene moieties to the first-generation system and copolymerization with styrene affords polymeric disks that exhibit catalytic properties superior to comparable solution-phase systems in a multicomponent coupling of chlorosilanes with Grignards to give bis-allylic silanes.

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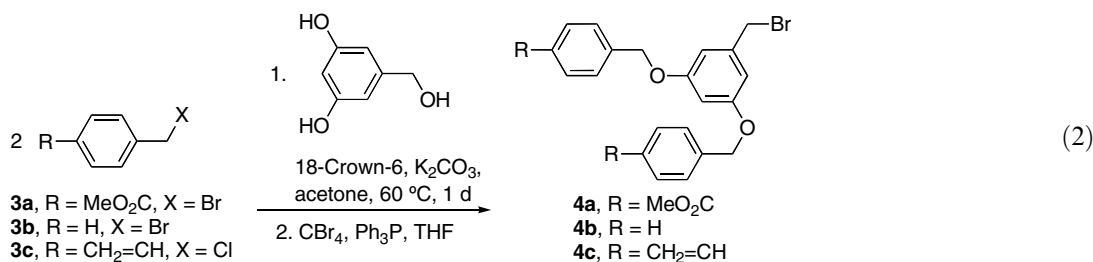
Our recent successful synthesis and polymerization of the titanocene dichloride crosslinker (**1**) gave titanocene disks **2** that were catalytically active and recyclable to a limited extent, Eq. 1.¹ However, we were

known,² as are dendrimers peripherally functionalized with both ferrocene³ and monocyclopentadienyltitanium.⁴ Preliminary results of our studies are presented herein.



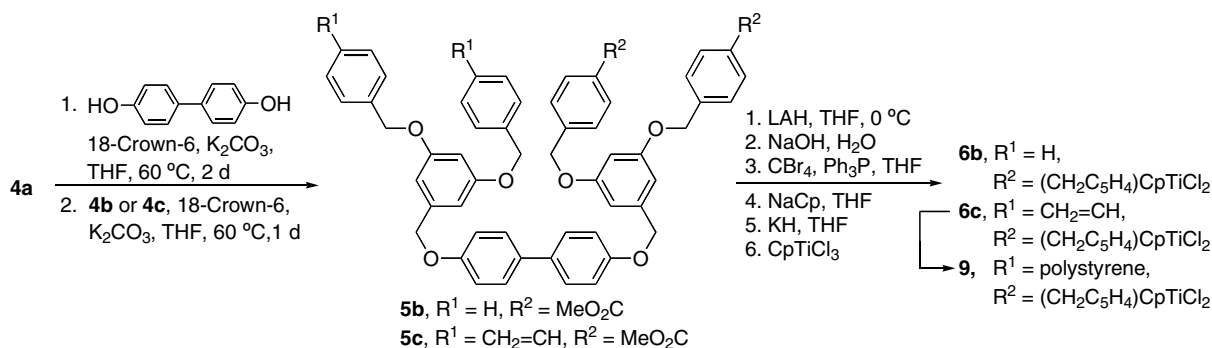
unable to synthesize more lightly crosslinked disks that might more accurately mirror a solution phase environment. In addition, disks with higher loading (and crosslinking) performed poorly. As a result we chose to investigate the use of dendrimers as a means of increasing loading while maintaining low crosslinking. Dendrimers bearing titanocene at the core are

Following the general synthetic approach of Fréchet,⁵ we first prepared intermediates **4a–c**, Eq. 2. We then proceeded to build a first-generation dendrimer about a biphenyl core using **4a** and **4b**. Using straightforward methodology we completed a preparation of bis-titanocene **6b** with reasonable efficiency (Scheme 1, 73% from **4a** and **4b**).



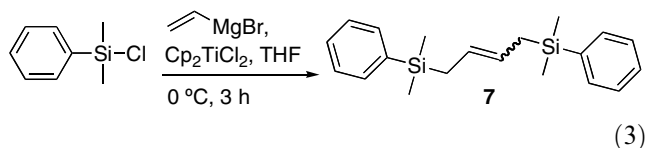
Keywords: Dendrimers; Polymer-supported synthesis; Titanocene catalysis; Multicomponent coupling.

* Corresponding author. Tel.: +1 530 752 6263; fax: +1 530 754 7610; e-mail: neschore@ucdavis.edu



Scheme 1. Synthesis of first-generation titanocene dendrimers.

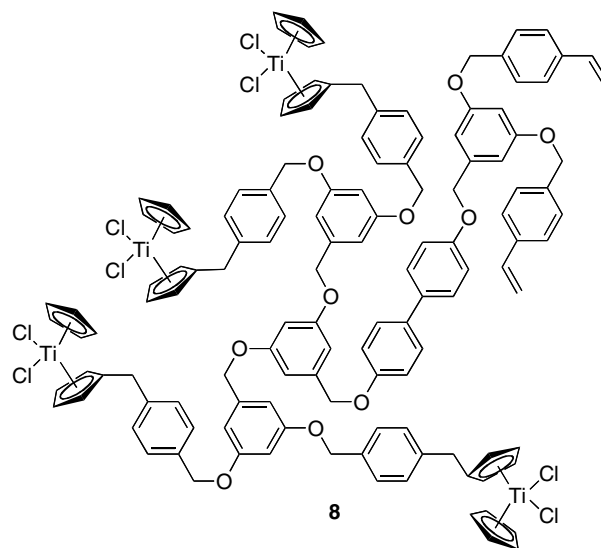
We had previously employed the multicomponent butene synthesis described by Watabe et al., Eq. 3,⁶ as a test for the catalytic activity of titanocenes such as **1**. We found that in THF solution, monomeric dendrimer **6b** functioned identically to Cp₂TiCl₂, giving butene **7** in 96% yield by ¹H NMR as an 87:13 *E/Z* mixture. The same results were obtained in isopropylbenzene, indicating that the reaction is compatible with a polystyrene framework. The sole byproduct in all applications of this process is dimethylphenylvinylsilane, which results from the uncatalyzed reaction that competes with the Ti-catalyzed butene synthesis.



A number of styryl-functionalized dendrimers that function as polymerization monomers are known.⁷ In a manner similar to the synthesis of **6b** we prepared first-generation crosslinking bis-titanocene monomer **6c** in 44% overall yield from **4c**. We also constructed small amounts of second-generation tetrakis-titanocene **8**. We prepared the third-generation octabromo species, but got no further as subsequent steps gave only intractable material. The intermediates in these syntheses were stable as solids but sensitive toward polymerization in solution. The first-, second-, and third-generation brominated species proved to be easiest to handle and to obtain pure.

To evaluate the access of reagents to the interior of polymerized dendrimeric disks we polymerized styrene and brominated dendron **4c** in a 5 mm ID test tube. The resulting disks, 0.85% crosslinked assuming complete reaction of vinyl groups, swelled nearly twice as much in THF as did disks of 1% DVB-crosslinked polystyrene.

Polymerization of **6c** gave disks of **9** (Scheme 1) containing 0.113 mmol/g Ti, corresponding to 0.64% crosslinking, much lower than disks **2** (0.312 mmol/g Ti). Yet disks **9** significantly outperformed disks **2**. In our low-tech batch-flow reactor,¹ disks **9** gave significant catalytic activity, and, like disks **2**, could be recycled through three runs after which reactivity dropped. Both polymers



initially gave 80% yield of butene product. Product removal and addition of more substrate in both cases gave 75% conversion in a second run and 60% in a third. A fourth run gave 22% butene using **2** and 8% from **9** (remainder Me₂PhSiCH=CH₂). As discussed previously,¹ we suspect that the reduction in reactivity derives from at least two causes: formation of Ti complexes of unknown structure that cannot reenter the catalytic cycle and buildup of salts within the polymer that inhibit substrate-catalyst interaction, allowing the uncatalyzed solution-phase vinylsilane formation to compete.

Significantly, the lightly loaded disks **9** gave aggregate turnover numbers four times greater than disks **2**: 2.7 mmol substrate was converted to product by 0.017 mmol Ti in **9** (TON = 159) versus 2.9 mmol converted by 0.074 mmol Ti in **2** (TON = 39). Evidently the lower crosslinking in **9** more than offsets the reduced Ti loading relative to **2**, giving rise to much improved catalytic efficiency. Indeed, the results from **9** also exceed the TON reported for the original solution-phase Cp₂TiCl₂-based system by nearly a factor of three (Table 1). In contrast, heavily loaded Wang-derived titanocene dichloride-containing beads gave very poor results: <10% in each of the two runs, corresponding essentially to stoichiometric activity. It is possible that the monolith polymer environment is protecting the organometallic from deactivation under the reaction

Table 1. Titanocene dichloride-catalyzed butene synthesis

Catalyst	Loading (mmol/g)	Crosslinking %	Aggregate TON
Cp ₂ TiCl ₂	—	—	53.6
Wang resin	0.70	1.0	2.4
Disks 2	0.31	3.6	38.8
Disks 9	0.11	0.64	159.3

conditions. Although too little of second-generation **8** was obtained to permit preparation of polymeric second-generation dendrimers, the monomer itself displayed solution-phase catalytic activity identical to that of either **6b** or Cp₂TiCl₂.

In summary, dendrimeric titanocene derivatives behave in solution identically to the simple system. Polymer attachment gives rise to enhanced reactivity at low loading levels, possibly a consequence of a protective environment. Additional applications of polymeric dendrimers in other synthetic contexts are under study and will be reported in due course.

Acknowledgments

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Supplementary data

All experimental and characterization information. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.tetlet.2007.09.115](https://doi.org/10.1016/j.tetlet.2007.09.115).

References and notes

- Berget, P. E.; Schore, N. E. *Tetrahedron Lett.* **2005**, *46*, 8869, *General procedure*: four 0.060 g disks **2** (0.074 mmol Ti) or four 0.040 g disks **9** (0.017 mmol Ti) in 4 mL THF were shaken for 6 h at 0 °C with 1.2 mmol CH₂=CHMgBr (added in 3 portions) and 1.2 mmol Me₂PhSiCl. The product solution was decanted and the disks retreated similarly for each successive run.
- Andrés, R.; de Jesús, E.; de la Mata, F. J.; Flores, J. C.; Gómez, R. *Eur. J. Inorg. Chem.* **2002**, 2281.
- Köllner, C.; Pugin, B.; Togni, A. *J. Am. Chem. Soc.* **1998**, *120*, 10274.
- Arévalo, S.; de Jesús, E.; de la Mata, F. J.; Flores, J. C.; Gómez, R. *Organometallics* **2001**, *20*, 2583.
- (a) Hawker, C.; Fréchet, J. M. J. *J. Chem. Soc., Chem. Commun.* **1990**, 1010; (b) Hawker, C. J.; Wooley, K. L.; Fréchet, J. M. J. *J. Chem. Soc., Perkin Trans. 1* **1993**, 1287.
- Watabe, H.; Terao, J.; Kambe, N. *Org. Lett.* **2001**, *3*, 1733.
- (a) Rheiner, P. B.; Seebach, D. *Polym. Mater. Sci. Eng.* **1997**, *77*, 130; (b) Rheiner, P. B.; Sellner, H.; Seebach, D. *Helv. Chim. Acta* **1997**, *80*, 2027; (c) Sellner, H.; Seebach, D. *Angew. Chem., Int. Ed.* **1999**, *38*, 1918; (d) Sellner, H.; Rheiner, P. B.; Seebach, D. *Helv. Chim. Acta* **2002**, *85*, 352; (e) Sellner, H.; Faber, C.; Rheiner, P. B.; Seebach, D. *Chem. Eur. J.* **2000**, *6*, 3692; (f) Sellner, H.; Karjalainen, J. K.; Seebach, D. *Chem. Eur. J.* **2001**, *7*, 2873.