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Catalytically active, recyclable polymeric titanocene disks: a batch-flow reactor

Patrick E. Berget and Neil E. Schore*

Department of Chemistry, University of California, Davis, One Shields Avenue, Davis CA 95616, USA

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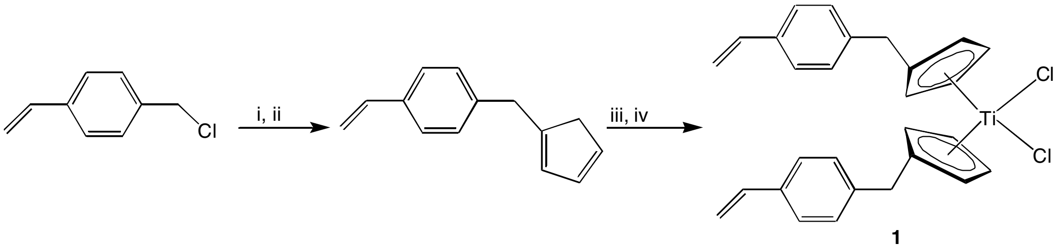
Abstract—Dichlorotitanocene bound within porous polystyrene disks catalyzes the coupling of vinylmagnesium chloride and chlorosilanes to form 1,4-bis(silyl)-2-butenes. A simple batch-flow reactor permits catalyst reuse by repeated addition of fresh reagents and decantation of products.

The strategy of affixing a soluble catalyst to an insoluble polymer support has considerable potential,[1] including the very attractive possibility of use in a continuous flow manner.[2] Flow-through processes utilizing monolithic materials such as polymer rods and disks have been described.[3] In addition, flow reactors have been developed for microwave-promoted, photochemical, enzyme-catalyzed, and metal-catalyzed syntheses.[4]

We have developed a procedure to incorporate dichlorotitanocene into a polymer matrix, specifically at the crosslink position, and have found it to be active in a catalytic batch-flow-through carbon–carbon bond-forming reaction system.

Positioning transition metals at crosslinks provides the opportunity for robust metal binding through chelation by multiple polymer-linked ligand moieties. Although no titanocene-derived crosslinking reagents were known at the start of this work, we applied our earlier experience with zirconocene systems to the synthesis of bis(*p*-vinylbenzylcyclopentadienyl)dichlorotitanocene (**1**) (Scheme 1).[5]

As with zirconocenes, the hydrolytic sensitivity of titanocenes precludes the use of suspension-polymerization methods. We thus prepared Sherrington-style titanocene-crosslinked polymer rods[3d] using the methodologies we first used for the synthesis of polymer-bound zirconocene. Titanocene **1** was dissolved into a solution of styrene and 1,2-dichlorobenzene using gentle warming. The mixture was then transferred into a silanized Pyrex test tube containing 2 wt % benzoyl peroxide—initial polymerization attempts had given materials that adhered to the tube interiors, thus necessitating pretreatment with dichlorodimethylsilane. The capped tube was placed in an 85 °C oil bath; argon was bubbled through the solution for 1 h to ensure good initial



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Scheme 1. Reagents and conditions: (i) NaCp, NaI, THF; (ii) aq HCl; (iii) NaH, THF, 0 °C; (iv) 0.5 equiv $TiCl_4$, THF.

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

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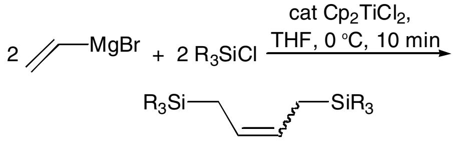
mixing. For polymerization of a mixture containing 2.5 mol % **1**, 2–3 days was required for the process to go to completion (as judged to be the case when the polymer rod had completely pulled away from the test tube walls). For a 5.0 mol % crosslinked polymer 7–8 days was necessary. Upon complete polymerization the test tubes were carefully broken and the rods removed intact. The deep red rods, which have a rubbery consistency, were then sliced with a razor into bright red disks 1–3 mm thick. Since the sole crosslinking monomer is titanocene **1**, the degree of crosslinking is the same as the titanium loading. To ensure that the disks were free from unreacted monomer they were subjected to Soxhlet extraction with hot THF. Evaporation of the extracts under reduced pressure showed only 1,2-dichlorobenzene and trace amounts of styrene by NMR. There was no evidence of any soluble titanocene-derived species.

Watabe et al. have reported that multicomponent coupling of two molecules of vinylmagnesium bromide and two of various chlorosilanes in the presence of catalytic Cp_2TiCl_2 gives 1,4-disilyl-2-butenes, essentially bis(allyl)-silanes (**2**, Eq. 1).[6] This rapid, high-yield reaction appeared to be an interesting and attractive one to study in order to evaluate recyclable disk methodology.



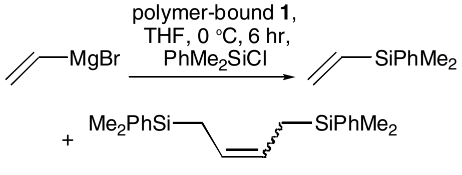
2

(1)

The mechanism proposed[6] for this process is illustrated in Scheme 2. Keys to the success of the process include efficient conversion of divinyltitanocene into a titanacyclopentene, which proceeds via the butadiene π-complex, and a fortuitous selectivity for chlorosilanes to react more rapidly with allylic than with vinylic Grignard reagents.

Initial experiments revealed that the competing uncatalyzed conversion of vinylmagnesium bromide and chlorosilane into a vinylsilane, which in the solution phase version of the process has negligible impact (<5%), was going to be a problem (Eq. 2). Although formation of the desired 1,4-disilylbutene was observed, the reduced overall rate of this polymer-supported catalyzed process allowed vinylsilane formation to compete.

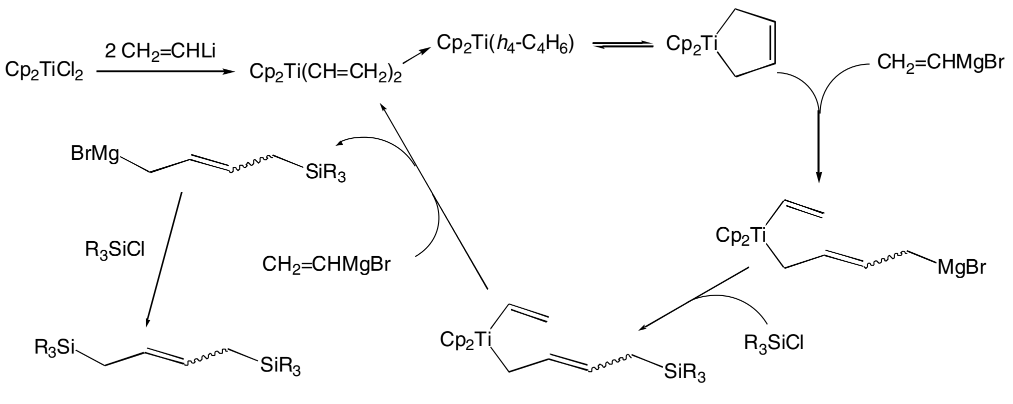
After extensive experimentation we found that a procedure involving addition of excess Grignard in portions provided the best results.



(2)

We designed a simple flow reactor from a dual chamber Schlenk recrystallizing tube and charged one chamber with several 2.5% crosslinked disks which were then swollen with THF and cooled to 0 °C. Vinylmagnesium bromide (8 equiv relative to polymer-bound Ti) was added, followed after 10 min by 10 equiv of chlorodimethylphenylsilane. After 2 and 4 h two additional 8 equiv aliquots of Grignard were added. After the total 6 h of reaction time the supernatant was decanted through the frit into the second chamber, from which it was removed for analysis maintaining an argon atmosphere. Fresh reagents were added to the side containing the disks and the sequence repeated through several runs, giving the results in Table 1 for two separate but similarly prepared batches of disks. In each run carried out as described above, conversion of chlorosilane to the mixture of silylated products was 100%. Through three runs (i.e., an initial run plus two recyclings) yields of **2** averaged better than 70%, the remainder being vinylsilane. In addition, the 87/13 (or better) *E*/*Z* ratio was an improvement over the solution-phase 74/26 result. Despite these encouraging results, catalytic reactivity dropped precipitously after the third run, and vinylsilane formation predominated.

We also carried out a set of runs using disks loaded with 5.0% of the crosslinking monomer to determine whether the higher loading would improve catalytic reactivity



Scheme 2. Mechanism proposed by Watabe et al.[6]

Table 1. Preparation of 1,4-bis(dimethylphenylsilyl)-2-butene, **2**, using 2.5% crosslinked disks

Run	%Yield[a]	*E*/*Z*
Batch 1		
1	82	88/12
2	72	88/12
3	79	87/13
4	29	87/13
5	13	90/10
Batch 2		
1	80	89/11
2	74	91/9
3	62	89/11
4	22	88/12

[a] Remainder dimethylphenylvinylsilane.

despite the increased crosslinking. Using the same procedure as that described above, we found that 5% of crosslinked disks could be reused through four or five runs, but gave rather lower yields (50–60%) of **2**. Again, catalytic reactivity dropped precipitously thereafter.

To further evaluate these results, we compared the total number of moles of product produced through all of the runs with the number of moles of polymer-bound catalyst, obtaining overall turnover numbers. The two batches of 2.5% crosslinked disks gave aggregate turnover numbers of 39.2 and 40.5, through five and four runs, respectively. For comparison, using 5.0% crosslinked disks a total turnover number of 17.9 was obtained. The analogous solution-phase process is reported to give a turnover number of 53.6.[6]

The detrimental effect of higher crosslinking implies that, despite the higher loading, the rate of catalysis using the 5% crosslinked resin is reduced compared with the 2.5%, allowing the solution-phase vinylsilane-producing side reaction to compete more effectively. Our observations do not directly address the reason behind the reduced effectiveness of the more highly-crosslinked resin, but both reduced rates of encounter between substrates and catalyst as well as changes in chemical environment of the resin interior with increased crosslinking may contribute. It is also not clear what causes deactivation of the catalyst after several cycles of use. To address the latter we set out to investigate whether or not the disks could be regenerated.

Based upon work of Fürstner and Hupperts[7] as well as our own in a related system,[8] we first examined regeneration methods in the solution phase. The proposed mechanism (Scheme 2) suggested that divinyltitanocene was the likely Ti-containing species at the end of a cycle. We therefore tested the efficacy of several reagents at converting divinyltitanocene back to titanocene dihalide. We found that I_2, $SOCl_2$, and ClCOCOCl in THF all gave quantitative conversion to Cp_2TiX_2 (X = Cl or I) in under 2 h at 25 °C. In attempting to adopt these methods to recycle our titanocene-functionalized disks, we exposed samples of the latter to THF solutions of each of these reagents at 25 °C. After a period of time that ranged from 1.5 h for ClCOCOCl to 18 h for I_2, the initially dark disks lightened to an amber color rather than the expected red for a titanocene dihalide, and they were found to be completely inactive. These experiments suggest that neither divinyltitanocene nor any other simple Cp_2TiR_2 is present at the end of a catalytic run. Another complicating issue is the formation over the course of the catalysis of several equivalents of inorganic salts that may impede reactivity. Procedures designed to extract and/or coordinate and remove these salts from the disks have been carried out without reactivity being restored. Experiments are currently underway to ascertain directly what is the nature of the Ti-containing species and on that basis to design a practical regeneration procedure. Our results will be reported in due course.

Acknowledgements

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