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Catalytically Active, Recyclable Zirconocene Supported at Cross-Links within Porous Polymer Disks

Saphon Hok, Jenny Vassilian, and Neil E. Schore*

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

neschore@ucdavis.edu

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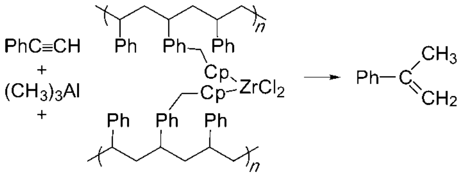
ABSTRACT



Copolymerization of bis(4-vinylbenzylcyclopentadienyl)zirconium dichloride and styrene in a test tube, followed by extraction of the bulk polymer and slicing into "disks" 1 mm thick and 5 mm in diameter, gives a supported zirconocene species that exhibits both stoichiometric and catalytic chemical activity. The disks catalyze reaction of trimethylaluminum and phenylacetylene to give α-methylstyrene with modest turnover numbers and are active over at least six recyclings.

We are interested in developing novel methods of tethering organometallic species of use in organic synthesis to insoluble polymer supports, with the goal of overcoming various shortcomings associated with their practical use. In this context, we sought to construct a robust attachment between a cross-linked polymer and a zirconocene moiety that would be active both stoichiometrically and catalytically, would be readily recyclable for repeated use, and would be less prone to loss of desired chemical reactivity due to processes such as hydrolysis or redox-mediated dimerization than are monomeric analogues.

The symmetry of the zirconocene system also afforded us an opportunity to consider the infrequently employed strategy of situating the functional moieties at the polymer cross-links themselves.[1,2] To this end, we constructed a zirconium derivative with the appropriate vinyl substitution to permit incorporation into a polystyrene-based system *during the polymerization process itself*. This strategy contrasts with the preparation of previous zirconocene-bearing polymers, in which a Zr moiety was attached after polymerization.[3,4]

Treatment of *p*-vinylbenzyl chloride with cyclopentadienylsodium in THF containing a catalytic amount of

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(1) Examples of ligands for organometallic species copolymerized *as cross-links*: (a) De, B. B.; Lohray, B. B.; Dhal, P. K. *Tetrahedron Lett.* **1993**, *34*, 2371. (b) De, B. B.; Lohray, B. B.; Sivaram, S.; Dhal, P. K. *Tetrahedron*: *Asymmetry* **1995**, *6*, 2105. (c) Minutolo, F.; Pini, D.; Salvadori, P. *Tetrahedron Lett.* **1996**, *37*, 3375. (d) Minutolo, F.; Pini, D.; Petri, A.; Salvadori, P. *Tetrahedron*: *Asymmetry* **1996**, *7*, 2293. (e) Rheiner, P. B.; Sellner, H.; Seebach, D. *Helv. Chim. Acta* **1997**, *80*, 2027. (f) De, B. B.; Lohray, B. B.; Sivaram, S.; Dhal, P. K. *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 1809. (g) Sellner, H.; Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 1918. (h) Sellner, H.; Faber, C.; Rheiner, P. B.; Seebach, D. *Chem. Eur. J.* **2000**, *6*, 3692. (i) Yang, X.-W.; Sheng, J.-H.; Da, C.-S.; Wang, H.-S.; Su, W.; Wang, R.; Chan, A. S. C. *J. Org. Chem.* **2000**, *65*, 295. (j) Sellner, H.; Karjalainen, J. K.; Seebach, D. *Chem. Eur. J.* **2001**, *7*, 2873 and refs. therein; (k) Altava, B.; Burguete, M. I.; García-Verdugo, E.; Luis, S. V.; Vincent, M. J.; Mayoral, J. A. *React. Funct. Polym.* **2001**, *48*, 25 and references therein.

(2) (a) Wilson, M. E.; Wilson, J. A.; Kurth, M. J. *Macromolecules* **1997**, *30*, 3340. (b) Wilson, M.; Paech, K.; Zhou, W.-J.; Kurth, M. J. *J. Org. Chem.* **1998**, *63*, 5094. (c) Halm, C.; Kurth, M. J. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 510.

(3) Via covalent bonding through polymer-bound Cp-type ligands. Linked to polystyrene: (a) Nishida, H.; Uozumi, T.; Soga, K. *Macromol. Rapid Commun.* **1995**, *16*, 821. (b) Kitagawa, T.; Uozumi, T.; Soga, K.; Takata, T. *Polymer* **1997**, *38*, 615. (c) Hong, S. C.; Terenishi, T.; Soga, K. *Polymer* **1998**, *39*, 7153. (d) Hong, S. C.; Ban, H. T.; Kishi, N.; Jin, J.; Uozumi, T.; Soga, K. *Macromol. Chem. Phys.* **1998**, *199*, 1393. (e) Stork, M.; Koch, M.; Klapper, M.; Müllen, K.; Gregorius, H.; Rief, U. *Macromol. Rapid Commun.* **1999**, *20*, 210. Linked to silica: (f) Iiskola, E. I.; Timonen, S.; Pakkanen, T. T.; Härkki, O.; Lehmus, P.; Seppälä, J. V. *Macromolecules* **1997**, *30*, 2853. (g) Schneider, H.; Puchta, G. T.; Kaul, F. A. R.; Raudaschl-Sieber, G.; Lefebvre, F.; Saggio, G.; Mihalios, D.; Herrmann, W. A.; Basset, J. M. *J. Mol. Catal. A: Chem.* **2001**, *170*, 127.

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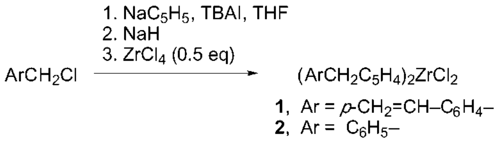
tetrabutylammonium iodide gave a 59% yield of *p*-vinylbenzylcyclopentadiene as a mixture of double-bond isomers.[5] Anticipating that this material would be rather prone to Diels−Alder dimerization, we proceeded immediately to subject it to deprotonation with NaH, followed immediately by reaction with $ZrCl_4$ in THF. The product, bis(*p*-vinylbenzylcyclopentadienyl)zirconium dichloride (**1**), was characterized fully spectroscopically (IR, ^1H and ^{13}C NMR) and by elemental analysis.[6] For solution-phase reactivity comparison purposes, the known[7] bis(benzylcyclopentadienyl) analogue (**2**) was similarly prepared (Scheme 1).

Scheme 1. Preparation of Monomeric Zirconocenes

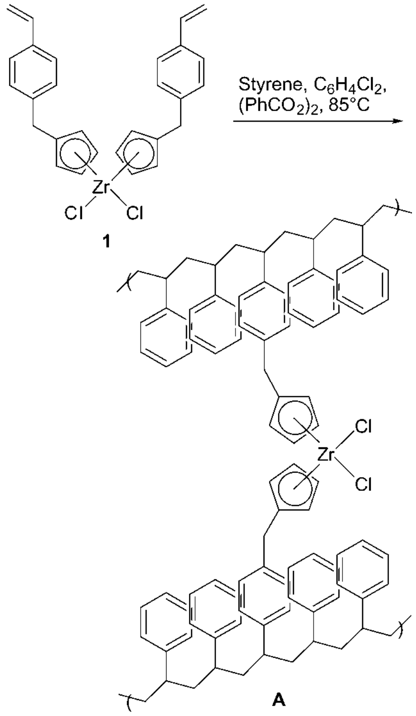


$$ArCH_2Cl \xrightarrow{\text{1. } NaC_5H_5\text{, TBAI, THF; 2. NaH; 3. } ZrCl_4 \text{ (0.5 eq)}} (ArCH_2C_5H_4)_2ZrCl_2$$

1, Ar = *p*-CH_2=CH–C_6H_4–
2, Ar = C_6H_5–

As expected, attempts to generate polymer beads by conventional suspension copolymerization of mixtures of **1** and styrene instead gave rise to beads containing hydrolyzed zirconocene species of the general formula $[(ArC_5H_4)_2ZrCl]_2O$. As an alternative, following Sherrington's strategy,[8] we submitted **1** to bulk copolymerization with styrene under air- and water-free conditions, both with and without added *p*-divinylbenzene. Varying concentrations of **1**, styrene, and divinylbenzene were mixed with dichlorobenzene and warmed until homogeneous. The solution was transferred to a 5 mm i.d. Pyrex test tube charged with benzoyl peroxide, heated to 85 °C, and agitated and purged with Ar bubbling until polymerization rendered the mixture viscous. Bubbling was stopped, and polymerization was allowed to continue at 85 °C for 2−3 days. After cooling, the tube was broken, and the flexible, light brown polymer rod was sliced into disks approximately 1 mm in thickness. The disks were extracted (Soxhlet) with THF for several days, followed by drying under vacuum at 50 °C, becoming translucent and light orange in color. Two sets of disks were eventually prepared for investigation: one (disks **A**) nominally containing 2.4 mol % Zr as both functional unit and sole cross-linker and another (disks **B**) nominally containing 2.3 mol % Zr and 2.7 mol % *p*-divinylbenzene as additional cross-linker (Scheme 2).

Scheme 2. Preparation of Polymer Disks **A**



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A

We initially attempted stoichiometric hydrozirconation[9] experiments as a test for the qualitative presence of active Zr residues in disks **A**. Using a one-pot procedure,[10] the disks were combined with Red-Al (Aldrich) and styrene in THF and allowed to stand for 8 h under Ar. After exposure to *t*-BuOOH for an additional 4 h, the disks were extracted, and the residue after solvent evaporation was examined by reversed-phase HPLC and ^1H NMR. The presence of both 1- and 2-phenylethanol in the same ratio obtained from solution-phase hydrozirconation with either Cp_2ZrClH or the bis(benzyl) analogue was thus confirmed, although the total amount was too small to allow absolute determination of yield (Scheme 3).

Given this positive result, we turned to a catalytic system, alkyne carbometalation based on Negishi's method.[11] In a typical experiment, 0.5 g of Zr-cross-linked and function-

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(4) Via noncovalent linkages. Impregnation: (a) Soga, K.; Kaminaka, M. *Makromol. Chem., Rapid. Commun.* **1992**, *13*, 221. (b) Soga, K.; Kaminaka, M. *Makromol. Chem.* **1993**, *194*, 1745. Ionic salt: (c) Roscoe, S. B.; Gong, C.; Fréchet, J. M. J.; Walzer, J. F. *J. Polym. Sci. Pt. A: Polym. Chem.* **2000**, *38*, 2979. (d) Kishi, N.; Ahn, C.-H.; Jin, J.; Uozumi, T.; Sano, T.; Soga, K. *Polymer* **2000**, *41*, 4005. σ-Coordination: (e) Musikabhumma, K.; Uozumi, T.; Sano, T.; Soga, K. *Macromol. Rapid Commun.* **2000**, *21*, 675. (f) Koch, M.; Stork, M.; Klapper, M.; Müllen, K.; Gregorius, H. *Macromolecules* **2000**, *33*, 7713.

(5) Anal. Calcd for $C_{14}H_{14}$: C, 92.26; H, 7.74. Found: C, 92.19; H, 7.81. ^1H and ^{13}C NMR indicate the presence of the expected two major double-bond isomers of the cyclopentadiene ring in a ca. 1.2:1.0 ratio.

(6) Anal. Calcd for $C_{28}H_{28}Cl_2Zr$: C, 64.10; H, 4.99; Cl, 13.52; Zr, 17.39. Found: C, 63.78; H, 5.05; Cl, 13.62; Zr, 17.90. ^1H NMR (C_6D_6, 300 MHz) δ: 3.97 (s, 4H), 5.07 (d, $J = 11$ Hz, 2H), 5.60 (d, $J = 18$ Hz, 2H), 5.63 (m, 4H), 5.87 (m, 4H), 6.58 (dd, $J = 11$, 18 Hz, 2H), 7.03 (d, $J = 8$ Hz, 4H), 7.20 (d, $J = 8$ Hz, 4H). ^1H NMR ($CDCl_3$) δ: 3.99 (s, 4H), 5.10 (d, $J = 11$ Hz, 2H), 5.71 (d, $J = 18$ Hz, 2H), 6.22 (m, AA′BB′, 8H), 6.68 (dd, $J = 11$, 18 Hz, 2H), 7.16 (d, $J = 8$ Hz, 4H), 7.34 (d, $J = 8$ Hz, 4H). ^{13}C NMR (C_6D_6) δ: 36.2, 112.4, 113.4, 117.1, 126.8, 129.4, 133.5, 136.2, 136.9, 140.0. ^{13}C NMR ($CDCl_3$) δ: 35.7, 112.5, 113.3, 116.8, 126.2, 128.8, 133.4, 135.7, 136.2, 149.2.

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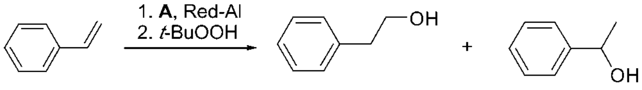
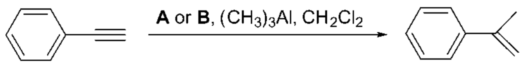
Scheme 3. Hydrozirconation with Disks **A**



alized disks were preswelled in 8 mL of CH_2Cl_2 and then treated successively with 10-fold molar excesses of 2 M trimethylaluminum in hexane and then phenylacetylene. Reactions were allowed to proceed at room temperature for 4−7 days, followed by decantation of the now reddish-orange solutions from the disks, washing of the disks with additional CH_2Cl_2, and workup of the combined filtrates (Scheme 4). The disks were collected, dried in vacuo, and reused up to six times.

Scheme 4. Catalytic Carbometalation with Disks **A** or **B**



Although yields were generally determined by NMR, we did carry out a careful gravimetric yield determination with one fresh polymer batch. A total mass balance of 88% was obtained, including 17% of α-methylstyrene, corresponding to a turnover number of 3.3 over a 4 day reaction time. Thus there is only minimal material loss to handling or other processes. Turnover numbers, based upon the ratio of α-methylstyrene product to recovered phenylacetylene (^{1}H NMR), ranged from 0.5 to 6. Best overall results were obtained with disks **A** (Table 1): turnover after 6 days rose from 2.6 in the first run to 6.0 in the second and then dropped and leveled off through run 5. At this point, these disks were stored dry under an inert atmosphere for 6 months and then reused successfully for two more 4-day runs. During the course of these recyclings, the disks displayed fragility, cracking upon repeated swelling and deswelling and in some cases fracturing to somewhat smaller pieces, which nonetheless were still large enough to cause no difficulty in use or handling (decantation, filtration, or other manipulation). By way of comparison, under comparable solution-phase conditions using the analogous soluble catalyst **2**, a turnover number of 6.4 was realized after 2 days of reaction. Thus, the solution-phase reaction proceeds some 3−10 times faster than its solid-phase counterpart.

Table 1. Carbometalation of Phenylacetylene Using Disks **A** in CH_2Cl_2

cycle no.	run time (days)	turnover no.
1	6	2.63
2	6	6.05
3	6	3.19
4	7	1.63
5	7	1.59
6[a]	4	2.43
7	4	1.36

[a] Six months elapsed time between runs 6 and 7.

Similar experiments using the more highly cross-linked disks **B** displayed reduced reaction rates and correspondingly lower turnover numbers over the duration of each run (Table 2).

Table 2. Carbometalation of Phenylacetylene Using Disks **B** in CH_2Cl_2

cycle no.	run time (days)	turnover no.
1	6	1.70
2	6	2.03
3	7	2.20
4	7	1.03
5[a]	4	0.69
6	4	0.57

[a] Six months elapsed time between runs 5 and 6.

Finally, a series of experiments was run using a fluorous solvent, perfluorohexane, in conjuction with CH_2Cl_2, based upon reports that fluorous solvents can under certain circumstances enhance catalyst activity and accelerate polymer-supported reactions.[12] We found little effect on the results of these processes (Table 3).

Table 3. Carbometalation of Phenylacetylene Using Disks **A** in 1:1 n-C_6F_{14}/CH_2Cl_2

cycle no.	run time (days)	turnover no.
1	4	1.86
2	4	1.04
3	4	1.20

From these results, one can conclude that the highest reactivity is found in the polymer with the least cross-linking and that reactivity increases in cycles immediately following the first. The latter may result from the presence of any of several complexes involving the polymer-bound zirconocene and the excess $AlMe_3$ used in the first cycle, which may reduce or eliminate an induction period.[11] A detailed analytical investigation of the species present throughout the active "life" of such disks is underway to address this issue.

In summary, we have developed the first cross-link-bound zirconocene-functionalized polymer system via what we

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believe is the first example of zirconocene incorporation as a polymerization monomer. We have also demonstrated that bulk polymerization of an otherwise sensitive organometallic can give rise to polymer-bound species exhibiting both catalytic activity and recyclability, provided that the polymerization process is suitably controlled. We are currently looking at ways to make more physically robust disks and to expand the range of organometallic species that can be bound within them. These efforts will be described in due course.

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Supporting Information Available: Detailed descriptions of experimental procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

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