Krickemeyer, H. Bögge, M. Schmidtmann, C. Beugholt, P. Kögerler, C. Lu, *Angew. Chem.* **1998**, *110*, 1278; *Angew. Chem. Int. Ed.* **1998**, *37*, 1220; d) A. K. Powell, S. L. Heath, D. Gatteschi, L. Pardi, R. Sessoli, G. Spina, F. Del Giallo, F. Pieralli, *J. Am. Chem. Soc.* **1995**, *117*, 2491; e) A. Müller, F. Peters, M. J. Pope, D. Gatteschi, *Chem. Rev.* **1998**, *98*, 239.

[6] a) B. Hasenknopf, J.-M. Lehn, B. O. Kneisel, G. Baum, D. Fenske, *Angew. Chem.* **1996**, *108*, 1987; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1838; b) B. Hasenknopf, J.-M. Lehn, N. Boumediene, A. Dupont-Gervais, A. Van Dorsselaer, B. O. Kneisel, D. Fenske, *J. Am. Chem. Soc.* **1997**, *119*, 10956; c) B. Olenyuk, A. Fechtenkötter, P. J. Stang, *J. Chem. Soc. Dalton Trans.* **1998**, 1707; d) M. Withersby, A. J. Blake, N. R. Champness, P. Hubberstey, W.-S. Li, M. Schröder, *Angew. Chem.* **1997**, *109*, 2421; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2327; e) J. S. Fleming, K. L. V. Mann, C.-A. Carraz, E. Psillakis, J. C. Jefferey, J. A. McCleverty, M. D. Ward, *Angew. Chem.* **1998**, *110*, 1315; *Angew. Chem. Int. Ed.* **1998**, *37*, 1279; f) R. Vilar, D. M. P. Mingos, A. J. P. White, D. J. Williams, *Angew. Chem.* **1998**, *110*, 1323; *Angew. Chem. Int. Ed.* **1998**, *37*, 1258.

[7] a) R. W. Saalfank, I. Bernt, E. Uller, F. Hampel, *Angew. Chem.* **1997**, *109*, 2596; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2482; b) R. W. Saalfank, N. Löw, S. Kareth, V. Seitz, F. Hampel, D. Stalke, M. Teichert, *Angew. Chem.* **1998**, *110*, 182; *Angew. Chem. Int. Ed.* **1998**, *37*, 173; c) R. W. Saalfank, N. Löw, F. Hampel, H.-D. Stachel, *Angew. Chem.* **1996**, *108*, 2353; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2209; d) D. L. Caulder, R. E. Powers, T. N. Parac, K. N. Raymond, *Angew. Chem.* **1998**, *110*, 1940; *Angew. Chem. Int. Ed.* **1998**, *37*, 1840.

[8] a) A. Pajunen, S. Pajunen, *Acta Crystallogr. Sect. B* **1982**, *38*, 3093; b) A. Nakahara, H. Yamamoto, H. Matsumoto, *Bull. Chem. Soc. Jpn.* **1964**, *37*, 1137.

[9] A. J. Blake, D. M. J. Doble, W. S. Li, M. Schröder, *J. Chem. Soc. Dalton Trans.* **1997**, 3655.

[10] a) Synthesis of [Ni(L)]: Reaction of 1,3-diaminopropane (0.074 g, 1 mmol) with sodium pyruvate (0.220 g, 2 mmol) and $Ni(BF_4)_2 \cdot 6H_2O$ (0.340 g, 1 mmol) in MeOH (40 mL) under reflux for 2 h resulted in a blue-green solution. This was reduced in volume and eluted through a Sephadex LH-20 column. Slow diffusion of Et_2O vapor into the resulting solution yielded green crystals of $[Ni(L)(MeOH)_2] \cdot 2MeOH$. The structure of this complex has been confirmed by single-crystal X-ray diffraction.[11b] b) The method for the synthesis of [Ni(L)] was also used in the synthesis of [Mn(L)].

[11] a) Satisfactory elemental analyses were obtained for **1**, **2**, and **3**. Single-crystal X-ray analyses: All fully occupied non-hydrogen atoms were refined using anisotropic displacement parameters, and disordered atoms were refined isotropically over partially occupied sites. All hydrogen atoms were allowed to ride on their respective parent atoms. **1**: $C_{54}H_{72}N_{12}O_{36}Cl_3Ni_6La$, $M_r = 2062.76$, trigonal, space group $P\bar{3}$, $a = 12.4549(11)$, $c = 12.736(2)$ Å, $V = 1711$ Å^3, $T = 150(2)$ K, $\rho_{calcd} = 2.002$ g cm^{-3}, $Z = 1$. Data were collected at 200(2) K on a Stoe Imaging Plate Diffractometer System (IPDS). Of the 2031 data collected ($2\theta_{max} = 50°$, $-14 \leq h \leq 12$, $0 \leq k \leq 14$, $0 \leq l \leq 15$), 1988 were unique ($R_{int} = 0.140$) and 1670 had $F \geq 4\sigma(F)$. All non-hydrogen atoms were located using heavy-atom and difference-Fourier methods.[13] $R_1 = 0.0748$ ($F \geq 4\sigma(F)$), and $wR_2 = 0.226$ (all data) for 179 parameters, $(\Delta/\sigma)_{max} = 0.02$, the largest difference Fourier extrema of 3.04 and -1.53 e Å^{-3} both lay near the La atom. **2**: $C_{92.5}H_{150.3}N_{18}O_{61.65}Cl_4Na_4Ni_9$, $M_r = 3663.16$, monoclinic, space group $P2_1/n$, $a = 17.735(4)$, $b = 27.149(5)$, $c = 28.938(6)$ Å, $\beta = 100.22(3)°$, $V = 13711(5)$ Å^3, $T = 200(2)$ K, $\rho_{calcd} = 1.581$ g cm^{-3}, $Z = 4$. Data were collected as for **1**. Of the 78620 data collected ($2\theta_{max} = 52.26°$, $-21 \leq h \leq 21$, $-33 \leq k \leq 31$, $-35 \leq l \leq 35$), 25638 were unique ($R_{int} = 0.109$) and 20268 had $F \geq 4\sigma(F)$. All non-hydrogen atoms were located using direct and difference Fourier methods.[13] $R_1 = 0.0549$ ($F \geq 4\sigma(F)$), and $wR_2 = 0.1634$ (all data) for 1752 parameters, $(\Delta/\sigma)_{max} = 0.08$, largest Fourier extrema: 0.84 and -0.95 e Å^{-3}. **3**: $C_{58}H_{93}N_{12}O_{38.5}Cl_2Mn_6$, $M_r = 2029.92$, cubic, space group $Pa\bar{3}$, $a = 25.523(3)$ Å, $V = 16625.9$ Å^3, $T = 150(2)$ K, $\rho_{calcd} = 1.622$ g cm^{-3}, $Z = 8$. Data were collected as for **1**. Of the 8599 data collected ($2\theta_{max} = 50°$, $0 \leq h \leq 30$, $0 \leq k \leq 21$, $0 \leq l \leq 30$), 4467 were unique ($R_{int} = 0.138$) and 2195 had $F \geq 4\sigma(F)$. All non-hydrogen atoms were located using direct and difference Fourier methods.[13] $R_1 = 0.1053$ ($F \geq 4\sigma(F)$), and $wR_2 = 0.249$ (all data) for 358 parameters, $(\Delta/\sigma)_{max} = 0.02$, largest Fourier extrema: 0.87 and -0.88 e Å^{-3}. b) Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-104533 ($[Ni(L)(MeOH)_2] \cdot 2MeOH$), CCDC-104534 (**1**), CCDC-104535 (**2**), and CCDC-104536 (**3**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[12] Y. Yukawa, S. Igarashi, A. Yamano, S. Sato, *Chem. Commun.* **1997**, 711.

[13] G. M. Sheldrick, SHELXS-96, *Acta Crystallogr. Sect. A* **1990**, *46*, 467;[7] G. M. Sheldrick, SHELXL-97, Universität Göttingen, Germany, **1997**.

Dendritically Cross-Linking Chiral Ligands: High Stability of a Polystyrene-Bound Ti-TADDOLate Catalyst with Diffusion Control**

Holger Sellner and Dieter Seebach*

Polymer-bound reagents and catalysts[1] have received renewed attention in connection with combinatorial synthetic methods.[2] Besides the classical approach of grafting a functional group or ligand to a given polymer (e.g. the Merrifield resin), there have recently also been examples of incorporation of the groups of interest through copolymerization.[3] Both methods have already been applied to TADDOL, a versatile ligand or ligand precursor for EPC synthesis[4] (see **1** in Scheme 1).[5] Two years ago we incorporated for the first time a dendritically modified TADDOL (**2**) with copolymerizable groups at the periphery as cross-linker in polystyrene, and obtained an enantioselective catalytic efficiency with the resulting Ti complex which was similar to that of the homogeneous analogues.[6] Before starting to test this surprising effect with other ligands, we had to investigate its origin, and the stability of this new type of catalyst in multiple applications had to be analyzed.

By cross-linking suspension copolymerization with styrene of dendrimer **2** and—for comparison—of TADDOLs **3**–**5**, bearing shorter and longer, more or less flexible spacers, we have generated beads of p-**2**, p-**3**, p-**4**, and p-**5** (Scheme 1),[7] having a diameter of about 400 µm in the non-solvent-swollen state. Upon treatment with $Ti(OCHMe_2)_4$, polymer-bound diisopropoxy-Ti-TADDOLates were obtained, as illustrated in Scheme 2. Elementary analysis of the p-**2** derivative with a loading of 0.1 mmol g^{-1} showed that 85 % of the chiral diol moieties within the polymer had been complexed with Ti ions.

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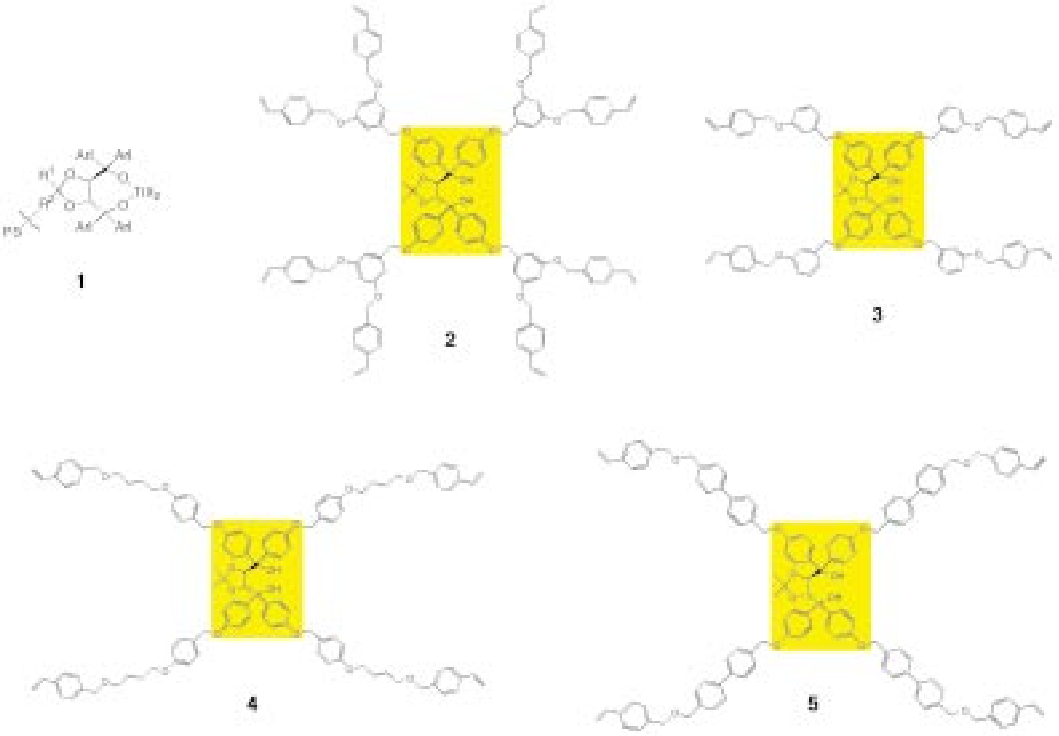
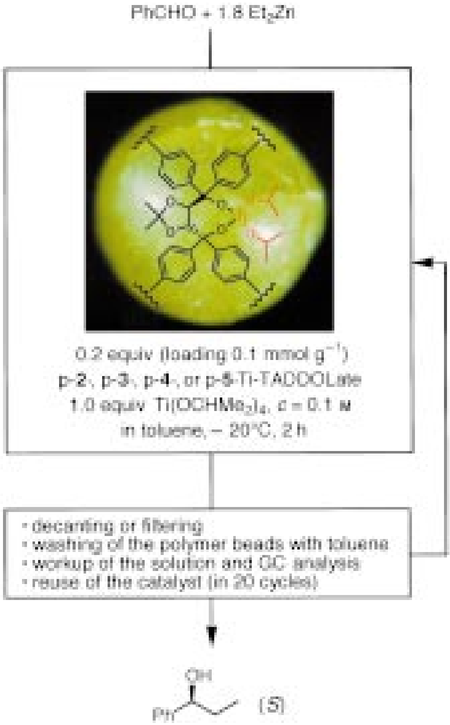
[**] This work was supported by the Schweizerischer Nationalfonds (projects nos. 20–50674.97 and 2027–048157).



Scheme 1. Polymer-bound Ti-TADDOLate **1** and styryl-substituted TADDOL derivatives **2**–**5**, which as cross-linkers were radically suspension-copolymerized with styrene to give p-**2**, p-**3**, p-**4**, and p-**5**. Loading: 0.1–0.6 mmol g^{-1}.[7]



Scheme 2. Enantioselective addition of diethylzinc to benzaldehyde using polymer-bound Ti-TADDOLates from p-**2**–p-**5** (Scheme 1) under standard conditions. With 0.20, 0.05, and 0.02 equiv of p-**2** · Ti-TADDOLate the *S*/*R* selectivity in the formation of 1-phenylpropanol is 98/2, 96/4, and 90/10, respectively (GC analysis[5a]). For results of 20 cycles, see Figure 1.

The polymer-bound Ti-TADDOLates were employed 20 times in the catalysis of the nucleophilic addition of diethylzinc to benzaldehyde[4] under the conditions specified in Scheme 2. The results are presented in Figure 1.

The following features are remarkable:

1) While the enantioselectivity is above 9:1 with all polymers of low loading (0.1 mmol TADDOL per g polymer), only the dendritic polymer gives rise to a constant selectivity of 98:2 in 20 sequential applications (Figure 1 a, b).
2) The catalytic performance drops from p-**3** to p-**4** to p-**5**, that is, with increasing chain length of the spacers between the TADDOL core and polymer backbone. Besides the decline in enantioselectivity there are erratic results with respect to both kinetics and conversion with the simply elongated derivatives (Figure 1 a).[8]
3) The same is true for polymers of higher degree of loading (Figure 1 b).
4) The low-loaded dendritic p-**2** beads keep their high swelling properties (ca. 2.5-fold) even after 20 runs, while all others do not swell as well after multiple reuse.
5) The rate of reaction is the same with and without stirring when p-**2** beads are employed (which fill the whole reaction volume under standard conditions). Thus, free diffusion of reactants and products to and from the active center is obtained.
6) The monomeric, soluble dendritic diisopropoxy-**2** · Ti-TADDOLate and the derived polymeric p-**2** · Ti-TADDOLate show virtually identical kinetics; it even looks like the polymer is slightly faster (Figure 1 c).[9]

Conclusion: It is worthwhile to dendritically modify other *preferred* ligands with peripheral styryl groups, to incorporate them in a cross-linking manner into polymers, and to investigate the performance of the resulting immobilized catalysts.

Received: February 1, 1999 [Z 12980 IE]
German version: *Angew. Chem.* **1999**, *111*, 2039–2041

Keywords: asymmetric catalysis · dendrimers · immobilizations · polymers · titanium

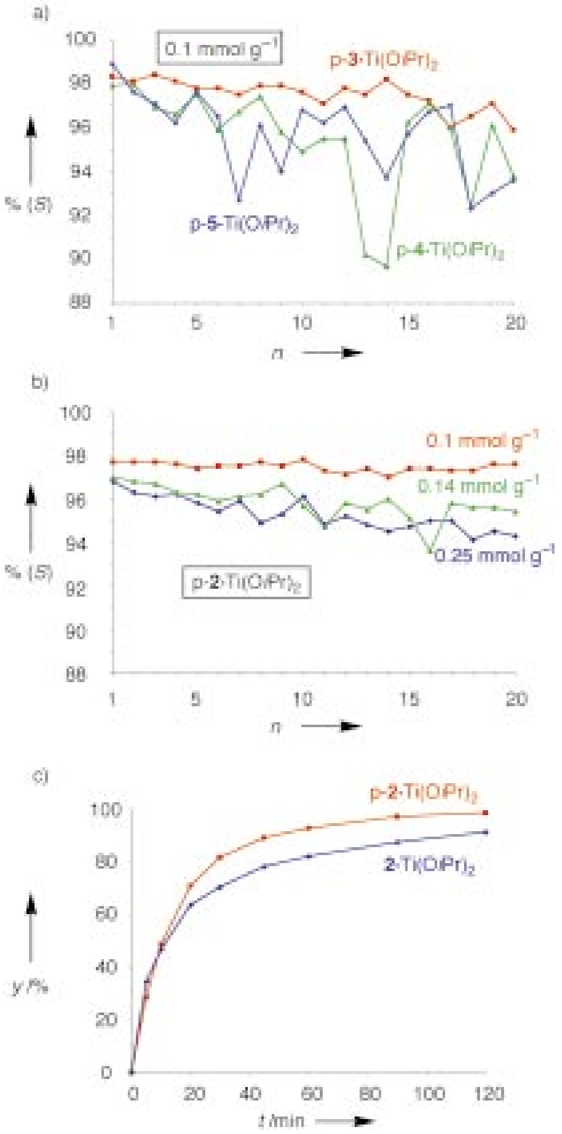


Figure 1. Enantioselectivities in the formation of (S)-1-phenylpropanol in n catalytic cycles a) with p-**3** · Ti-TADDOLate, p-**4** · Ti-TADDOLate, and p-**5** · Ti-TADDOLate under standard conditions (Scheme 2) and b) with p-**2** · Ti-TADDOLate using loadings of 0.1, 0.14, and 0.25 mmol g^{-1}; c) comparison of reaction kinetics with polymer-bound (red) and with homogeneous (blue) dendritic Ti-TADDOLate (y = conversion).[9]

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[1] Early review article: A. Patschornik in *Modern Synthetic Methods, Vol. 1* (Ed.: R. Scheffold), Sauerländer, Aarau, **1976**, pp. 113–168.

[2] S. R. Wilson, A. W. Czarnik, *Combinatorial Chemistry, Synthesis and Application*, Wiley, New York, **1997**.

[3] a) S. Itsuno, Y. Sakurai, K. Ito, T. Maruyama, S. Nakahama, J. M. J. Fréchet, *J. Org. Chem.* **1990**, *55*, 304–310; b) K. Kamahori, S. Tada, K. Ito, S. Itsuno, *Tetrahedron: Asymmetry* **1995**, *6*, 2547–2555; c) S. Itsuno, K. Kamahori, K. Watanabe, K. Ito, *Macromol. Symp.* **1996**, *105*, 155–159; d) A. Petri, D. Pini, S. Rapaccini, P. Salvadori, *Chirality* **1995**, *7*, 580–585; e) F. Minutolo, D. Pini, P. Salvadori, *Tetrahedron Lett.* **1996**, *37*, 3375–3378; f) A. Mandoli, D. Pini, S. Orlandi, F. Mazzini, P. Salvadori, *Tetrahedron: Asymmetry* **1998**, *9*, 1479–1482; g) K. Nozaki, Y. Itoi, F. Shibahara, E. Shirakawa, T. Ohta, H. Takaya, T. Hiyama, *J. Am. Chem. Soc.* **1998**, *120*, 4051–4052.

[4] R. Dahinden, A. K. Beck, D. Seebach in *Encyclopedia of Reagents for Organic Synthesis, Vol. 3* (Ed.: L. Paquette), Wiley, Chichester, **1995**, pp. 2167–2170, and references therein.

[5] a) D. Seebach, R. Marti, T. Hintermann, *Helv. Chim. Acta* **1996**, *79*, 1710–1740; b) P. J. Comina, A. K. Beck, D. Seebach, *Org. Proc. Res. Dev.* **1998**, *2*, 18–26; c) B. Altava, M. I. Burguete, B. Escuder, S. V. Luis, R. V. Salvador, J. M. Fraile, J. A. Mayoral, A. J. Royo, *J. Org. Chem.* **1997**, *62*, 3126–3134; d) J. Irurre, A. Fernandez-Serrat, F. Rosanas, *Chirality* **1997**, *9*, 191–197; e) J. Irurre, A. Fernandez-Serrat, M. Altayo, *Enantiomer* **1998**, *3*(2), 103–120.

[6] P. B. Rheiner, H. Sellner, D. Seebach, *Helv. Chim. Acta* **1997**, *80*, 2027–2032.

[7] The TADDOL core unit was employed as hexahydroxy derivative, which was etherified with the corresponding benzyl bromide.[6] For the copolymerization, see references [5a, b, 6].

[8] The polymers obtained with the previously used simple styryl TADDOL derivatives also showed such a decline.[5a, b]

[9] Although the curves in Figure 1c have been reproduced several times, we choose this careful phrasing: The measurements are difficult, mainly due to a strong dependance of the rate upon the Ti(OCHMe$_2$)$_4$ concentration. Also, the 0.5-mmol scale of these kinetic measurements gives rise to difficulties in correct addition of substrates and sampling.

Chelated Bisphosphites with a Calix[4]arene Backbone: New Ligands for Rhodium-Catalyzed Low-Pressure Hydroformylation with Controlled Regioselectivity

Rocco Paciello,* Lorenz Siggel, and Michael Röper*

Dedicated to Professor Dr. Hans-Jürgen Quadbeck-Seeger on the occasion of his 60th birthday

The rhodium-catalyzed low-pressure hydroformylation of olefins is, in terms of production volume, one of the most important technical applications of homogeneous catalysis.[1] Rhodium complexes with ligands such as triphenylphosphane lead to aldehydes and especially to their linear isomers in very high yields. Furthermore, they allow the synthesis to be performed under low-pressure conditions, which is advantageous during processing.[2] Industrial laboratories in particular are constantly searching for catalysts with improved properties. At the center of attention are chelating ligands such as bisphosphanes[3] and sterically hindered bisphosphites,[4] which provide active rhodium complexes of a defined structure in a predictable and controlled fashion.

We have been looking for polyols that can be readily prepared and that contain backbones with a defined con-

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