[6] Computer-controlled apparatus with mixing and pressure handling capabilities are known. They are based on the concept of operating of traditional laboratory "glassware" procedures in parallel at a miniature scale and function batchwise with throughput testing frequencies (TTFs) of 10–40 day^{-1}. Mechanical mixing is the bottleneck for further miniaturization. Some information is available at www.ttpmyriad.co.uk, www.argotech.com, www.peptide.com, and www.gilson.com.

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Macromolecular-Multisite Catalysts Obtained by Grafting Diaminoaryl Palladium(II) Complexes onto a Hyperbranched-Polytriallylsilane Support**

Christian Schlenk, Arjan W. Kleij, Holger Frey,* and Gerard van Koten*

At present, dendrimers[1] are widely investigated as supports for catalytically active transition metal fragments.[2] Carbosilane dendrimers[3] are well-suited for this purpose, because they are relatively inert to common organometallic reagents and their structures can be easily modified. The main advantage of this type of nanosized, macromolecular catalyst is their convenient removal from product streams as realized recently in a continuously operating membrane reactor.[4] However, the synthesis of dendrimers, that is monodisperse, well-defined molecules, involves expensive, labor-intensive multistep procedures that also limit the amount of available material. In contrast, hyperbranched polymers[5] can be prepared in a single-step, one-pot procedure, from AB_m type monomers. This greatly facilitates their synthesis and allows the production of large quantities of material. However, as a consequence of the uncontrolled synthesis of such polymers, materials with high polydispersity are obtained. Furthermore, the reactive sites introduced by functionalization will be distributed throughout the molecules.

Recently, we reported carbosilane molecules functionalized with NCN $[C_6H_3(CH_2NMe_2)_2\text{-}2,6]^-$) ligands[6, 7] which could then be selectively lithiated without any decomposition of the carbosilane backbone.[8] This lithiation enabled the subsequent incorporation of transition metals by means of transmetalation with suitable Group 8 metal salts.[2a, 8b] Herein, we present the synthesis of a hyperbranched carbosilane (HCS), its functionalization with NCN moieties, and the introduction of palladium(II) sites into the structure. Furthermore, we show that this system can be conveniently converted into an effective catalyst system that can compete with metallodendritic catalysts.

To obtain hyperbranched HCS supports, neat triallylsilane[9] was polymerized with platinum catalysis by polyaddition (Scheme 1).[10] To keep the isomerization of the double bonds to a minimum, the reaction temperature was kept low (40 °C). This, however, led to prolonged reaction times (4 d in the case of **1**). The internal to external double-bond ratio could not be suppressed below 7.6 %. The presence of internal double bonds was indicated in the ^{1}H NMR spectrum of the isolated HCS material which showed the presence of extra multiplets at $\delta = 6.09$ ($SiCH{=}C\mathit{H}\text{-}CH_3$) and 5.58 ($SiC\mathit{H}{=}CH\text{-}CH_3$). The polytriallylsilane (PTAS) **1**, was obtained as a translucent, viscous oil, soluble in solvents such as diethyl ether and chloroform. The molecular weight (size exclusion chromatography (SEC), polystyrene (PS) standards was 5500 $\mathrm{g\,mol^{-1}}$ which corresponds to an apparent degree of polymerization of 36 (that is 72 allyl groups per molecule). As expected for a bulk polymerization of an AB_m monomer, the molecular-weight distribution was broad ($M_w/M_n = 5.2$).[11] This polydispersity is also influenced by an intramolecular reaction, of the Si–H groups with allyl end groups. This side reaction consumes Si–H groups without enhancement of the molecular weight, resulting in the formation of core-type molecules.

Polymer **1** was hydrosilylated with $HSiMe_2Cl$ by platinum catalysis (Scheme 1) in neat $HSiMe_2Cl$ at ambient temperature. After removal of the excess $HSiMe_2Cl$, the functionalized polymer HCS-$SiMe_2Cl$ (**2**) was dissolved in diethyl ether. This solution was added to 3,5-bis[(dimethylamino)-methyl] phenyllithium (Li-NCN)[8a] at −78 °C in diethyl ether (Scheme 2). Hydrolysis followed by extraction gave the crude HCS-$SiMe_2$-NC(H)N product. This diaminoaryl-functional-

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[*] Prof. Dr. G. van Koten, A. W. Kleij
Debye Institute
Department of Metal-Mediated Synthesis
Utrecht University
Padualaan 8, 3584 CH, Utrecht (The Netherlands)
Fax: (+31) 30-252-3615
E-mail: g.vankoten@chem.uu.nl

PD Dr. H. Frey, C. Schlenk
Freiburger Materialforschungszentrum und Institut für
Makromolekulare Chemie
Albert-Ludwigs-Universität, Freiburg
Stefan-Meier-Strasse 21/31, 79104 Freiburg (Germany)
Fax: (+49) 761-203-6319;
E-mail: holfrey@fmf.uni-freiburg.de

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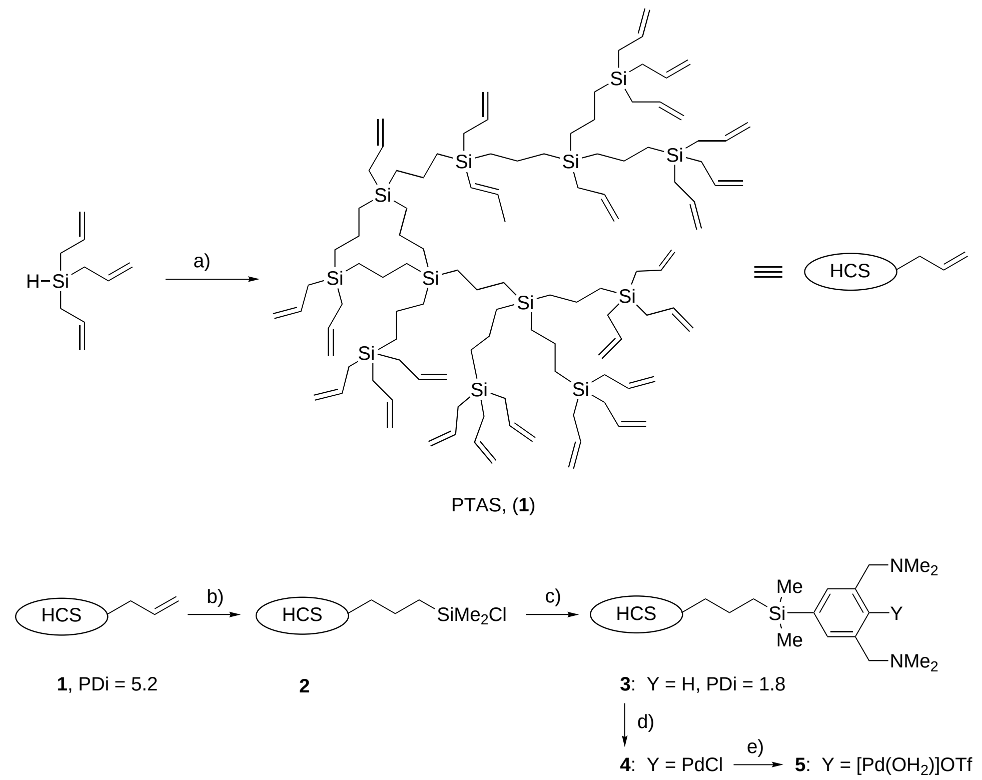
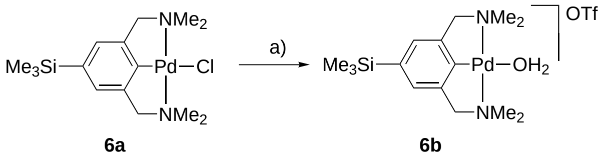


Scheme 1. Synthesis of the hyperbranched support **1** and its conversion into the (pre)catalytic hyperbranched Pd^{II} complex **5**. Reagents and Conditions: a) [(COD)PtCl$_2$], 40 °C, 4 d; b) excess HSiMe$_2$Cl, RT, [Pt(Bu$_4$N)$_2$PtCl$_6$], 12 h; c) excess Li-NCN, Et$_2$O, $-78\,^{\circ}C \rightarrow$ RT 16 h, *t*BuLi, pentane, dialysis; d) *t*BuLi, pentane, RT, 3 h; excess [PdCl$_2$(SMe$_2$)$_2$], THF, RT, 16 h; e) AgOTf, wet acetone, 16 h, RT, in the dark. PDi = polydispersity index.



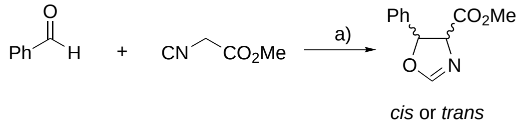
Scheme 2. Synthesis of the model compound **6b**. Reagents and conditions: a) AgOTf, wet acetone, RT, 5 min.

ized HCS polymer was purified by dialysis in diethyl ether with a benzoylated cellulose nanofiltration membrane with a cut off mass of 1000 g mol^{-1} to remove the excess NC(H)N ligand and the lower molecular weight fractions of the product. The polydispersity index dropped from 5.2 to 1.8 as monitored by SEC. This result shows that these polymers are good candidates for catalytic application in continuous membrane reactions.[4] The HCS-SiMe$_2$-NC(H)N material **3**, was obtained as clear yellow, viscous oil (72 %).

Lithiation[8] of **3** with an excess of *tert*-butyllithium in pentane at room temperature followed by transmetalation of HCS-SiMe$_2$-NCN-Li with an excess of [PdCl$_2$(SMe$_2$)$_2$] in THF gave the Pd^{II} complex HCS-SiMe$_2$-NCN-PdCl (**4**) (Scheme 1).[12] This reaction sequence illustrates one major advantage of the carbosilane backbone, that is the inertness to common organometallic reagents. Dialysis in CH$_2$Cl$_2$ with a membrane equivalent to that used for the purification of **3**, afforded **4** as a light brown solid in 71 % yield. The reaction was monitored by ^{1}H NMR spectroscopy and signals with the diagnostic shifts for the N(CH$_3$)$_2$ and CH$_2$N groups of the NCN ligand were observed.[11] The ^{1}H NMR spectrum showed signals that indicated the complete lithiation of all the NC(H)N groups in **3** and their quantitative conversion into NCN-PdCl groups. Subsequent treatment of **4** with AgOTf in wet acetone gave the cationic derivative [HCS-SiMe$_2$-NCN-Pd(OH$_2$)]OTf (**5**) (Scheme 1).

The mononuclear, cationic, precatalyst compound **6b** was prepared to model the catalytic activity of diaminoaryl palladium cations bound to a HCS support; **6b** was obtained by treatment of **6a**[8b] with AgOTf in wet acetone (Scheme 2 and Supporting Information). As the electronic environment of the metal center in model compound **6b** is similar to that of the catalytic sites distributed throughout the hyperbranched support, differences in catalytic performance of **6b** and the HCS catalysts give an indication of the influence of the HCS support on the accessibility of the Pd^{II} sites in these hyperbranched materials.

Polymer **5** was used as a soluble catalyst in the aldol condensation of benzaldehyde and methyl isocyanoacetate,[13] to give oxazolines (Scheme 3, Table 1, and Experimental Section). For comparison, model compound **6b** was used as a catalyst and both systems were compared with the uncata-



Scheme 3. Catalytic aldol condensation of benzaldehyde and methyl isocyanoacetate in the presence of **5** or **6b.** Reagents and conditions: a) 1 mol % **5** or **6b**, CH$_2$Cl$_2$, EtN(*i*Pr)$_2$, mesitylene, RT.

Table 1. Aldol condensation catalysis with **5** and **6b** using benzaldehyde and methyl isocyanoacetate as substrates.

Catalyst	mol %	*trans*/*cis*[a]	Yield [%][a]	TOF[b]	TTN/Pd site[a]
–	–	n.d.[c]	< 5	–	–
6b	0.99	1.88	99	37	100
5	0.79[d]	2.00	> 5	19[d]	78[d]

[a] After 24 h obtained by specific signal integration using ^{1}H NMR spectroscopy and mesitylene as an internal standard (duplo experiment); TTN = total turnover number. [b] Turnover frequency per Pd center per hour; during the first hour. [c] Not determined. [d] Corrected values, see ref. [12].

lyzed reaction. Table 1 shows that **5** is indeed an active catalyst for this reaction. Although the initial activity of **5** expressed in TOF per Pd site per h is somewhat lower than that of **6b**, the total turnover number (TTN)/Pd site for both **6b** and **5** are similar.

In summary, we have established a general route to nanosize, hyperbranched-polycarbosilane compounds that are functionalized with aryldiamine metal complexes using a lithiation/transmetalation procedure. The Pd^{II} centers in the soluble, macromolecular catalyst **5** function as independent catalytic sites in a standard aldol condensation reaction and their activity is similar to that of the single-site Pd catalyst **6b**. To our knowledge, this is the first example of the use of hyperbranched polymers as soluble macromolecular supports for homogeneous catalysis. Moreover, the catalyst support properties of hyperbranched polymers are very similar to those of analogous dendrimers; thus, structural perfection is not always required. Purification of the polymers **3** and **4** by means of dialysis shows that **5** is suitable for continuous membrane applications.

Experimental Section

Standard protocol for the catalytic aldol condensation reaction: 1 mol% of Pd catalyst was added to a mixture of benzaldehyde (2.4 mmol), methyl isocyanoacetate (1.6 mmol), mesitylene (1.6 mmol, internal standard), and $EtN(iPr)_2$ (10 mol%) in CH_2Cl_2 (10 mL). Samples were taken from the reaction mixture at regular time intervals, after careful removal of the solvent ^1H NMR spectra of these samples were recorded.

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Effective Gelation of Water Using a Series of Bis-urea Dicarboxylic Acids[**]

Lara A. Estroff and Andrew D. Hamilton[*]

A wide range of small organic molecules has been found, either through design or serendipity, to gel a variety of organic solvents.[1] The property of gelation is thought to arise from the self-assembly of these small molecules into fibers, which, like polymer gels, become entangled and trap solvent.[2] The formation of fibers requires a stabilizing intermolecular interaction and represents a balance between the tendency of the molecules to dissolve or to aggregate in a given solvent.

Organogelators often have hydrogen-bond donors and acceptors that promote aggregation and subsequent fiber formation. The attachment of long alkyl chains onto the hydrogen-bonded core enhances its solubility in organic solvents but also promotes association among the fibers, through van der Waals forces, and eventual gel formation. One effective class of organogelators exploits bis-urea derivatives to form a central, hydrogen-bonded stack to which long chain alkyl groups are attached. We[3] and others have shown that bis-ureas such as **1** are able to gel a variety of nonpolar organic solvents (including supercritical carbon dioxide)[3d] at concentrations less than 4 wt%. Recent crystal structures of these derivatives[3b,c] have confirmed the importance of

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[*] Dr. A. D. Hamilton, L. A. Estroff
Department of Chemistry
Yale University
P.O. Box 208107, New Haven, CT 06520-8107 (USA)
Fax: (+1) 203-432-3221
E-mail: andrew.hamilton@yale.edu

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