

Single-Site Catalysts on a Cylindrical Support beyond Nanosize

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Summary: Dendronized polymers (DenPol's) up to generation 3 were equipped with NCN–palladium and –platinum pincer complexes at their peripheries, using active ester chemistry. The palladium compounds catalyze the aldol condensation of benzaldehyde with methyl isocyanacetate and show a generation-independent activity.

Encouraged by the intriguing properties of a number of highly interesting tree-like macromolecules (i.e., dendrimers),¹ chemists have commenced constructing more complex materials, which, for example, combine dendritic and polymeric segments.² One of these new classes of macromolecules is dendronized polymers (DenPol's).³ These rather large molecules (up to the 0.5 μm regime)⁴ possess a high degree of structural rigidity due to steric congestion around the linear polymeric core. This property could render them ideal scaffolds for the immobilization of other functionalized molecules, yielding structurally well-defined materials.³ One type of functionalization is the selective introduction of a controlled number of catalytic sites at the periphery of the DenPol's. As their successful construction could represent a new step, one that is beyond nanosize, in the quest to close the gap between homogeneous and heterogeneous catalysis, we set out to immobilize NCN–metallopincer⁵ units on DenPol surfaces. In this communication, we report the synthesis and catalytic

performance of these new dendritic catalytic materials containing up to 3400 metal sites per single DenPol molecule.

Dendronized polymers of generations 1 (**PG1**), 2 (**PG2**), and 3 (**PG3**)⁴ were equipped with NCN–palladium(II) bromide and –platinum(II) chloride units employing the attach-to approach (Scheme 1 illustrates the G2 routes),^{3,6} using the respective activated pincer molecules **1PdBr** and **1PtCl**.⁷ In dichloromethane the resulting **PG n MX** ($n = 1–3$; M = Pd, X = Br; M = Pt, X = Cl) materials swell to gel-like particles, which precipitate when stirring is stopped. The efficiencies of the coupling reactions were determined by treating the remaining, nonreacted amine groups of the respective DenPol's with Sanger's reagent (2,4-dinitrofluorobenzene) and measuring the UV absorbance (see refs 4b,c for more details). Via this method, the free amine content of **PG n MX** could be assessed to be on the order of 7–9%. Information from ¹H NMR integrations provided further support for the proposed high coverages. These facts imply that **PG1MX**, **PG2MX**, and **PG3MX** ($P_n = 460$, PDI = 1.8)^{4b} were equipped with an average number of about 850 ($M_n = 550\,000$ (**PG1PdBr**), 590 000 (**PG1PtCl**)), 1700 ($M_n = 1\,150\,000$ (**PG2PdBr**), 1 230 000 (**PG2PtCl**)), and 3400 ($M_n = 2\,300\,000$ (**PG3PdBr**), 2 460 000 (**PG3PtCl**)) metal sites per single molecule, respectively. These architectures were further analyzed by means of ¹H and ¹³C NMR spectroscopy and elemental analysis (see the Supporting Information). For example, ¹H NMR spectroscopy on **PG n PdBr** clearly showed new, broad resonances (with respect to the parent **PG n**) centered at δ 2.8, 3.9, and 7.2 ppm, which are in good agreement with the corresponding (sharp) resonances observed for monoamide **2** (*p*-propylamido-NCN–PdBr, δ 2.87, 4.00, and 7.19 ppm). The structural integrity of **PG n PtCl** was furthermore indicated by the ability of these dendronized polymers to reversibly bind SO₂ (visualized by a dramatic color change from colorless to orange), which

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(6) The platinum compounds were initially prepared because of their robustness and in order to optimize the coupling conditions. The palladium analogues, however, are of interest from a catalytic point of view. Experimental details for the syntheses of **PG1PdBr**, **PG2PdBr**, **PG3PdBr**, **PG1PtCl**, **PG2PtCl**, and **PG3PtCl** as well as their full characterization data are given in the Supporting Information.

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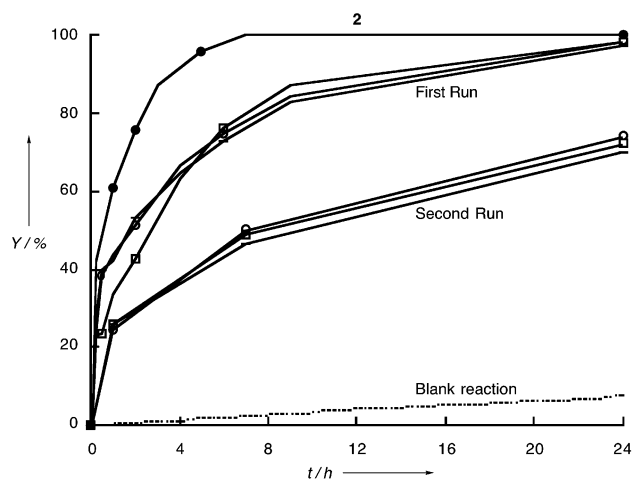


Figure 1. Yield of the oxazoline products Y vs time in the PG_nPdBr -catalyzed reaction of benzaldehyde with methyl isocyanoacetate (\square , PG1PdBr ; \circ , PG2PdBr ; $-$, PG3PdBr) in comparison with the activity of complex **2** and of the blank reaction. In all catalytic runs the concentration of palladium was kept constant (2.5 mol %), in accordance with elemental analyses and coverage measurements (UV).

Table 1. Catalytic and Kinetic Data for **2 and the Palladium-Coated Dendronized Polymers in the Aldol Condensation of Benzaldehyde with Methyl Isocyanoacetate^a**

catalyst	time/h	conversion $Y/\%$ ^b	TOF ^c
2	7	100	66
PG1PdBr	24	98	37
PG2PdBr	24	99	38
PG3PdBr	24	98	40

^a In all catalytic runs the concentration of palladium was kept constant (2.5 mol %), in accordance with elemental analyses and coverage measurements (UV). ^b The combined yields of cis and trans oxazoline product were >99%, and the amount of trans product formed during each reaction was approximately 70%. ^c Per palladium center per hour; based on conversion after 15 min.

may be deduced from the fact that, generally, when active sites are located in a dendritic interior, a generation-dependent activity is found.¹² After the first cata-

lytic run, the palladium-coated DenPol's were precipitated from the reaction mixture with diethyl ether and subsequently quantitatively collected by means of centrifugation. Using these recycled materials as catalysts under the exact same conditions in a second run (Figure 1) resulted in lower activities. However, the relative catalytic activity of all recycled palladium-decorated DenPol's was again equal.

In summary, we have described the synthesis of a new type of polymer-supported catalyst¹³ beyond nanosize. Predesigned metallopincer units are located at the periphery of the macromolecular structures, owing to the bulkiness of the dendronized polymer supports. Thus, they combine well-defined, accessible active sites with a high absolute amount of active sites per single molecule. Because of the diversity of metals which can be accommodated by pincer-type ligands,⁵ further elaboration of the catalytic properties of these DenPol's is now feasible.

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Supporting Information Available: Text giving experimental details for the syntheses of all PG_nMX species as well as their full characterization data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(11) This contrasts with the behavior of the end groups of regular dendrimers, which have a more globular, three-dimensional (and thus larger) space at their disposal, whereas the DenPol end groups have one dimension less (namely a two-dimensional disklike space); cf.: Karakaya, B.; Claussen, W.; Gessler, K.; Saenger, W.; Schlüter, A. D. *J. Am. Chem. Soc.* **1997**, *119*, 3296–3301.

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