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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 isocyanoacetate 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−metallopincer[5] 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 ^{1}H 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 ^{1}H and ^{13}C NMR spectroscopy and elemental analysis (see the Supporting Information). For example, ^{1}H 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 SO_2 (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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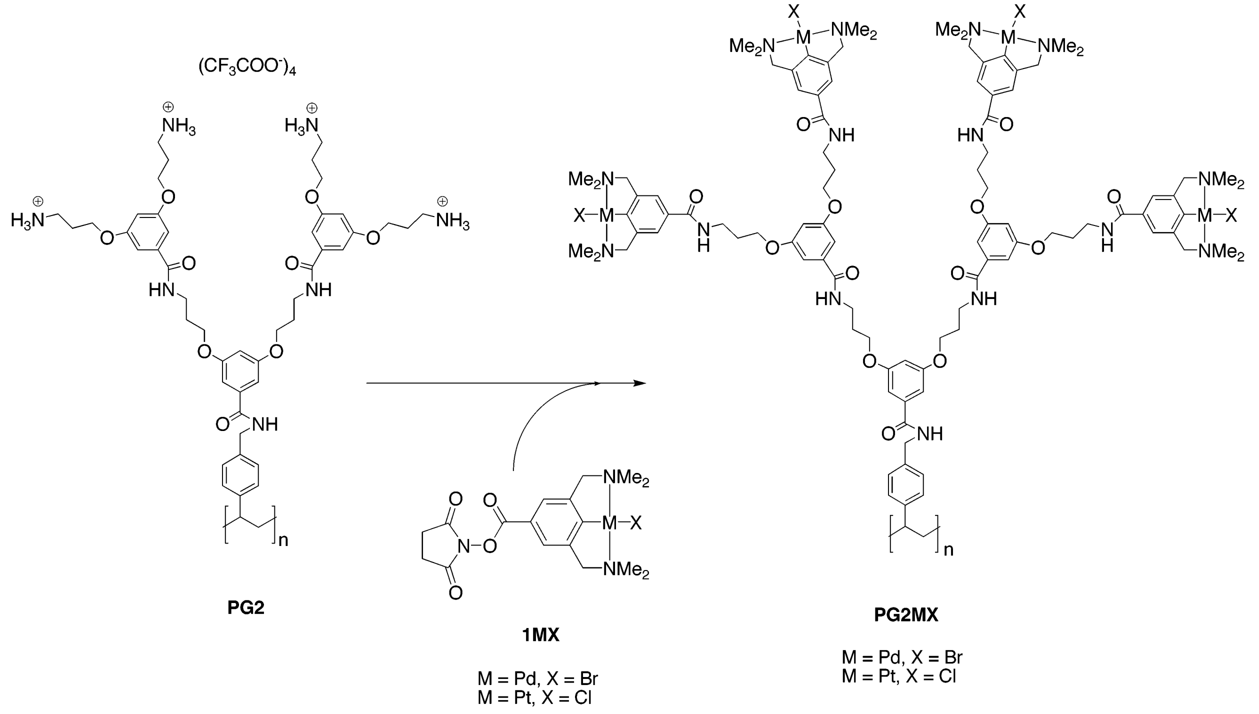
Scheme 1. Synthetic Route to Metallopincer-Decorated DenPol's PG*n*MX (G2 Examples)



PG2

1MX

M = Pd, X = Br
M = Pt, X = Cl

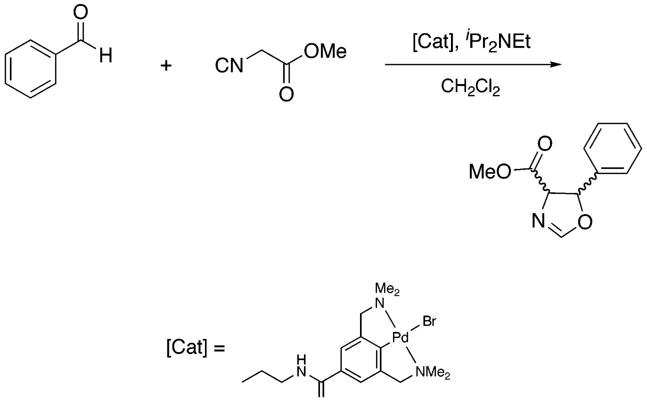
PG2MX

M = Pd, X = Br
M = Pt, X = Cl

proved retention of the full integrity of the NCN−Pt halide moieties in the isolated dendronized materials.[8]

The palladium-containing DenPol's **PG1PdBr**, **PG2PdBr**, and **PG3PdBr** were subsequently applied in the aldol condensation reaction of benzaldehyde with methyl isocyanoacetate in the presence of Hünig's base (see Scheme 2).[9] The catalytic activities of these materials were compared with those of the homogeneous reference compound **2** (*p*-propylamido-NCN−PdBr). From Figure 1 and Table 1 it is evident that the palladium-coated DenPol's are less active than their homogeneous counterpart **2**. This is probably caused by the solubility properties of **PG*n*PdBr** in the reaction medium, leading to a catalytic process at the solid/liquid interface. The most striking observation, however, is that all DenPol catalysts exhibit approximately the same activity per Pd site in the investigated reaction. Apparently, the relative number of active Pd sites is constant in each case and thus is independent of the dendron generation. This can be explained by the fact either that the active sites do not interfere with each other or that the generation of the dendritic wedges is not yet high enough for (a negative) interference to occur.[10] Furthermore, these results suggest that the rather bulky NCN−palladium(II) bromide moieties are forced outward by steric repulsions of the dendritic wedges (decreased back-folding) and finally reside on the polymer surface, making them equally accessible to substrate molecules.[11] Further indirect confirmation of this hypothesis

Scheme 2. Schematic Representation of the Aldol Condensation Reaction of Benzaldehyde with Methyl Isocyanoacetate



2

PG1PdBr

PG2PdBr

PG3PdBr

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[8] The integrity of both the NCN−Pt bond and the Pt−halide bond are a prerequisite for reversible SO_2 binding to occur: (a) Terheijden, J.; van Koten, G.; Mul, W. P.; Stufkens, D. J.; Muller, F.; Stam, C. H. *Organometallics* **1986**, *5*, 519−525. (b) Albrecht, M.; Gossage, R. A.; Frey, U.; Ehlers, A. W.; Baerends, E. J.; Merbach, A. E.; van Koten, G. *Inorg. Chem.* **2001**, *40*, 850−855. This SO_2-d^8 metal binding and the resulting induced coloration are specific for the NCN−platinum halide and −nickel halide compounds.

[9] Upon treatment of **PG*n*PdBr** with a silver-based dehalogenating agent, the silver halide formed could not be separated from the dehalogenated product. Recently, however, we discovered that NCN−palladium halide complexes catalyze this aldol condensation reaction, albeit with lower initial rates than for their "activated" cationic analogues. Actually, one molecule of methyl isocyanoacetate inserts into the palladium−carbon bond and a second one displaces one amino ligand. (cf.: Zografidis, A.; Polborn, K.; Beck, W.; Markies, B.; van Koten, G. *Z. Naturforsch.* **1994**, *49b*, 1494−1498). This insertion reaction may furthermore account for the drop in catalytic activity during the second run, due to a decreased stability of the organometallic moiety with a C,N-bidentate coordination geometry with respect to that of one with a N,C,N′-tridentate coordination geometry. Cf.: Mehendale, N.; Klein Gebbink, R. J. M.; van Koten, G. Manuscript in preparation.

[10] Negative effects of active site proximity have earlier been observed by us for dendritic catalysts derived from a single-site homogeneous catalyst: (a) Kleij, A. W.; Gossage, R. A.; Jastrzebski, J. T. B. H.; Boersma, J.; van Koten, G. *Angew. Chem., Int. Ed.* **2000**, *39*, 176−178. (b) Kleij, A. W.; Gossage, R. A.; Klein Gebbink, R. J. M.; Brinkmann, N.; Reijerse, E. J.; Lutz, M.; Spek, A. L.; van Koten, G. *J. Am. Chem. Soc.* **2000**, *122*, 12112−12124.

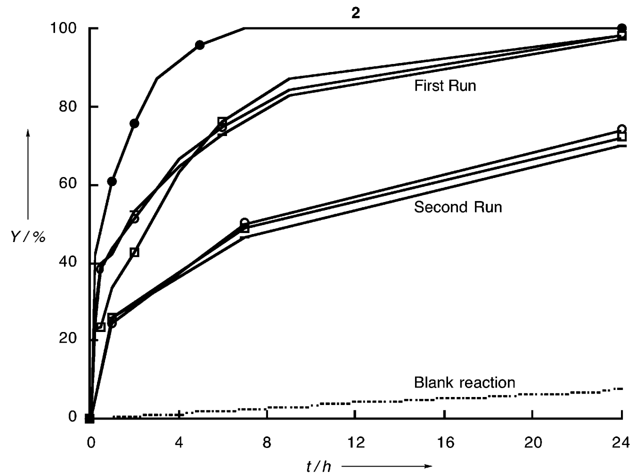

Figure 1. Yield of the oxazoline products Y vs time in the **PG*n*PdBr**-catalyzed reaction of benzaldehyde with methyl isocyanoacetate (□, **PG1PdBr**; ○, **PG2PdBr**, -, **PG3PdBr**) in comparison with the activity of complex **2** and of the blank reaction. In all catalytic runs the concentration 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 catalytic 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 catalyst[13] 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*n*MX** 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.

(12) For a review on dendrimer-encapsulated catalysts, see: Twyman, L. J.; King, A. S. H.; Martin, I. K.; *Chem. Soc. Rev.* **2002**, *31*, 69−82.

(13) For very recent, comprehensive reviews on "conventional" polymer- and dendrimer-supported catalysts, see: Recoverable Catalysts and Reagents. *Chem. Rev.* **2002**, *102* (Gladysz, J. A., Ed.).