

Recyclable Catalysts

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multi-chain nano-aggregates, SCNPs consist of only a single polymer chain, which is crosslinked via intramolecular

bonds.^[5-7] In the past, bioinspired SCNPs have been typically

synthesized via hydrogen- or covalent bonding in order to mimic biomacromolecules.^[8,9] More recently, additional

approaches employ external linker molecules, for instance

metal complexes, to induce the chain collapse via dynamic

bonding.^[10-13] While metal complexes, in the first place,

operate as triggers for the chain-collapse, their embedding

into the SCNP-structure additionally allows them to function,

for example, as catalytic centers.^[14-17] At present, only little

research has been carried out to exploit SCNP systems for

advanced catalysis.^[18] The advantages of SCNP systems in comparison to established catalysts are yet to be fully

established. In a recent study, Lemcoff et al. described the complexation of ROMP-derived polycycloocta-1,5-diene

(pCOD) with Ir- and Rh-complexes, which were successfully

applied in bimetallic cross-coupling reactions,^[15] whereas

Pomposo and co-workers employed Cu^{II}-SCNPs for the selective oxidative coupling of terminal alkynes.^[16] Further,

our team demonstrated the formation of SCNPs via Pd^{II} ions

and applied them as catalyst in a Sonogashira coupling.^[17] Nevertheless, the most intrinsic disadvantage in homogene-

Platinum(II)-Crosslinked Single-Chain Nanoparticles: An Approach towards Recyclable Homogeneous Catalysts

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Abstract: We introduce the synthesis and in-depth characterization of platinum(II)-crosslinked single-chain nanoparticles $(Pt^{II}$ -SCNPs) to demonstrate their application as a recyclable homogeneous catalyst. Specifically, a linear precursor copolymer of styrene and 4-(diphenylphosphino)styrene was synthesized via nitroxide-mediated polymerization. The triarylphosphine ligand moieties along the backbone allowed for the intramolecular crosslinking of single chains via the addition of $[Pt(1,5-cvclooctadiene)Cl_{2}]$ in dilute solution. The successful formation of well-defined Pt^{II}-SCNPs was evidenced by size exclusion chromatography, dynamic light scattering, nuclear magnetic resonance (¹H, ³¹P(¹H), ¹⁹⁵Pt), and diffusion-ordered spectroscopy. Finally, the activity of the Pt^{II}-SCNPs as homogeneous, yet recyclable catalyst was successfully demonstrated using the example of the amination of allyl alcohol.

n recent years, single-chain nanoparticles (SCNPs) have emerged as versatile nanostructures based on their outstanding characteristics combined with an array of applications in for example, information storage, catalysis, or drug delivery systems, since their properties can be readily varied and adapted to finely selected conditions.^[1-4] In comparison to

		ous catalysis the separation of the catalysts from the reaction			
[*]	N. D. Knöfel, ^[+] Prof. Dr. P. W. Roesky	mixture, has only been studied to a certain extent by applying			
	Institute for Inorganic Chemistry Karlsruher Institute of Technology (KIT)	SCNP chemistry. To date, organometallic complexes are still			
	Engesserstrasse 15 76131 Karlsruhe (Germany)	the most effective homogeneous catalysts for a wide range of			
	E-mail: roesky@kit.edu	chemical reactions. ^[19,20] However, their separation from the			
	H. Rothfuss. ^[+] Prof. Dr. C. Barner-Kowollik	reaction mixture is a highly challenging task, often demanding			
	Institut für Technische Chemie und Polymerchemie	extensive purification methods and sometimes the catalyst			
	Karlsruhe Institute of Technology (KIT)	simply remains in the final product. Heterogeneous catalysts			
	Engesserstrasse 18, 76131 Karlsruhe (Germany)	allow for simple separation, yet often suffer from lower			
	and	catalytic activity and require harsher reaction conditions. ^[21]			
	Institute for Biological Interfaces, Karlsruhe Institute of Technology	We herein introduce Pt ^{II} -SCNPs that are able to bridge the			
		gap between homogeneous activity and heterogeneous recy-			
	(Germany)	clability. Pt ^{II} ions are implemented, since they are very			
	and	efficient homogeneous catalysts for numerous transforma-			
	School of Chemistry, Physics and Mechanical Engineering, Queens-	tions. ^[22-24] Moreover, the NMR active ¹⁹⁵ Pt isotope offers the			
	land University of Technology (QUT), 2 George Street, Brisbane, QLD	possibility for in-depth solution studies. ^[25] We demonstrate			
	4001, (Australia)	that our current system allows for post-catalytic isolation and			
	E-mail: christopher.barner-kowollik@kit.edu	reuse of the Pt ^{II} -SCNPs, an important advantage given the			
	christopher.barnerkowollik@qut.edu.au	high cost and toxicity of Pt complexes (Scheme 1).			
	Dr. J. Willenbacher	As basis for the single-chain nanoparticles, a linear			
	Barbara	precursor copolymer was synthesized via nitroxide-mediated			
	Santa Barbara, CA 93106 (USA)	polymerization (NMP; Figure 1). Following the "repeat unit			
[+]	These authors contributed equally to this work	approach", ^[26,27] the monomers styrene and 4-(diphenylphos-			
. J	Supporting information and the ORCID identification number(s) for	phino)styrene were statistically copolymerized, incorporating			
	the author(s) of this article can be found under:	the functional units directly into the polymer chain (Fig-			
	http://dx.doi.org/10.1002/anie.201700718.	ure 1A). Phosphine moieties were introduced for their			

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Scheme 1. Illustration of a single-polymer-chain collapse into a nanoparticle via addition of the metal complex [Pt(cod)Cl₂]. The nanoparticles are further employed as homogeneous recyclable catalysts for the amination of allyl alcohol.

capability of forming stable 2:1 complexes via dynamic bonding with Pt^{II} ions. From a series of copolymers in different ratios and chain lengths (Table S2 in the Supporting Information), copolymer P1 was selected as the most suitable for SCNP chemistry based on chain length, polydispersity, and functional group distribution. The copolymer composition was determined via ³¹P{¹H} NMR inlet measurements with [Pd(PPh₃)₂Cl₂] as a reference substance (Figure S19) and for P1 resulted in 5 mol% of phosphine units. Size exclusion chromatography (SEC) analysis [RI, THF] of P1 indicated an $M_{\rm p}$ close to 40600 g mol⁻¹ and a narrow distribution with a dispersity index of $D \approx 1.15$. The intramolecular collapse of copolymer P1 into SCNPs was induced by addition of the platinum precursor complex $[Pt(cod)Cl_2]$, (COD = cyclooctadiene). In this case, COD can readily be substituted by two phosphine ligands. The folding of the copolymer P1 into welldefined SCNPs was initially confirmed by SEC analysis. In comparison to the copolymer **P1**, the SEC trace for the Pt^{II}-SCNPs is completely shifted towards longer retention times (Figure 2A), indicating a smaller hydrodynamic radius and thus pointing to the exclusive formation of SCNPs ($D \approx 1.22$) without any intermolecular side reactions. In addition, the decrease of the particles' mean hydrodynamic radius was confirmed by diffusion ordered spectroscopy (DOSY). The mean hydrodynamic radius of **P1** resulted in $R_{h,DOSY} = 7.4$ nm, while a radius of $R_{h,DOSY} = 4.9$ nm was determined for the Pt^{II}-SCNPs (Table S1). Furthermore, the transition of the linear copolymer into a more compact structure was demonstrated by dynamic light scattering (DLS). Figure 2B shows the number-weighted size distributions of **P1** and the Pt^{II}-SCNPs. For the copolymer, a mean hydrodynamic diameter of 15.2 nm ($R_{h,DLS} = 7.60$ nm) was obtained, whereas 8.50 nm $(R_{h,DLS} = 4.25 \text{ nm})$ was estimated for the Pt^{II}-SCNPs. Thus, the



Figure 1. A) Synthesis of copolymer **P1** via NMP of styrene and 4-(diphenylphosphino)styrene. The subsequent addition of [Pt(cod)Cl₂] results in SCNP formation. B) The complete complexation of the phosphine units in the polymer to platinum(II) ions is confirmed by ³¹P{¹H} NMR spectroscopy. The resonance of free phosphine, apparent in the spectrum of **P1** (top), is replaced by new characteristic resonances for platinum complexed phosphine species in Pt^{II}-SCNPs (bottom).

decrease in the hydrodynamic radius, determined by DOSY and DLS measurements, are in excellent agreement. As

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Figure 2. The decrease of the hydrodynamic radius for the SCNPs in comparison to copolymer **P1** is shown by A) SEC [RI, THF] and B) DLS. C) The *cis*- and *trans*-configuration of the phosphine units at the platinum centers is further evidenced via ¹⁹⁵Pt NMR spectroscopy.

depicted in Figure 1, the complete complexation of the phosphine units in **P1** to platinum was confirmed by ³¹P{¹H} NMR spectroscopy, since no resonance for free phosphine ($\delta = -6.22$ ppm) is detected in the spectrum of the Pt^{II}-SCNPs, instead a new set of resonances appears downfield ($\delta \approx 0.30$ ppm). The most intense resonance at $\delta = 13.4$ ppm and the corresponding ¹⁹⁵Pt satellites (d, ¹J_{P-Pt} = 3706 Hz) can be assigned to a square-planar coordinated ion with two triarylphosphine moieties in *cis*-configuration. The data is in close agreement with the complex *cis*-[Pt(PPh₃)₂Cl₂] ($\delta = 14.3$ ppm; ¹J_{P-Pt} = 3673 Hz).^[28] A less-intense signal at $\delta = 19.5$ ppm can be assigned to the *trans*-coordinated phosphine-platinum linker unit. Another resonance at $\delta = 29.1$ ppm is assigned to a phosphine oxide species, which is

already present in the unfolded chain. Within the boundaries of NMR spectroscopy, a *cis/trans*-configuration ratio of 9:1 of the two phosphine ligands is assumed for the Pt^{II}-SCNPs.^[29] The preference of a *cis*-configuration in the folding unit is presumably due to the predetermined coordination geometry of the *cis*-configured precursor [Pt(cod)Cl₂]. The ³¹P{¹H} NMR data (Figure 2 C) were further confirmed by ¹⁹⁵Pt NMR spectroscopy. The main resonance at $\delta = -4413$ ppm (t, ¹J_{Pt}- $_{P} = 3745$ Hz), can be assigned to the *cis*-coordinated platinum moiety. Another less-intense resonance at $\delta = -4023$ ppm (t, ¹J_{PtP} = 2621 Hz) is associated with a *trans*-coordinated platinum species.

Having synthesized Pt^{II}-SCNPs, we investigated their activity as homogeneous, yet reusable catalyst in the amination of allyl alcohol (Figure 3).^[30] In comparison to the established monomeric complex cis-[Pt(PPh₃)₂Cl₂],^[24] we used the Pt^{II}-SCNPs as a catalyst. Various aniline derivatives were employed as starting materials. The conversions and selectivity of the reactions were determined by ¹H NMR spectroscopy and are collated in Table 1. With aniline (1a), the allyl alcohol was converted nearly quantitatively within 24 h. The major product was the allyl-substituted amine 1b (ca. 91%), while the di-substituted side-product 1c was only formed to a small percentage (ca. 4%). Using the halidesubstituted aniline derivatives 3-chloroaniline, 3-fluoroaniline, and 4-chloroaniline (2a-4a), the conversion was still high (91-98%) with nearly identical yields for the corresponding products 2b-4b (79-86%). Employing 2,6-dimethylaniline (5a), the conversion of the allyl alcohol, as well as the yield of **5b**, decreased significantly (ca. 35%), a result of steric hindrance. To quantify the catalytic activity of the Pt^{II}-SCNPs, analogous reactions were carried out with the molecular platinum complex cis-[Pt(PPh₃)₂Cl₂] (Figure S10-S14). Although the metals are anchored to a polymer support, the activity and selectivity of the Pt^{II}-SCNPs are similar to those observed for cis-[Pt(PPh₃)₂Cl₂], which showed an allyl alcohol conversion of 90-97% for 1a-4a and yields of 79-85% for the corresponding products **1b-4b** (Table 1). Hence, the polymeric system still allows for ready access of the substrates to the catalytic platinum centers. Slightly higher conversions were achieved by the addition of SnCl₂ as a Lewis acid co-catalyst (Figure S29).

The applied reaction conditions not only enabled high conversion rates, but also ensured the ability to quantitatively recover the Pt^{II}-SCNPs after catalysis by applying dialysis in methanol. To determine the post-catalytic Pt^{II}-SCNP structure, further SEC and ³¹P{¹H} NMR measurements were carried out. The SEC traces of the nanoparticles after their application as catalyst match closely with the traces of the original Pt^{II}-SCNPs, indicating a still folded structure (Figure 3). In repeated measurements a certain degree of additional compactation of the recycled Pt^{II}-SCNPs was detected by SEC analysis. The corresponding ³¹P{¹H} NMR spectrum still points to the quantitative coordination of the phosphine ligands to the platinum ions, since no resonance for free phosphine moieties is detected (Figure S17). Interestingly, the Pt^{II}-SCNPs show an intense resonance at $\delta =$ 17.9 ppm, most likely associated with *trans*-coordinated Pt^{II}phosphine units. The change in geometry is presumably

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Figure 3. Top: Catalytic cycle of the amination of allyl alcohol with Pt^{II}-SCNPs as reusable homogeneous catalyst. Bottom: The SEC [RI, DMAc] analysis of the SCNPs after catalysis demonstrates their folded because the SEC traces of the used and unused SCNPs overlap.

related to the high temperature during catalysis, which allows a cis/trans-isomerization of the folding unit. Thus, explaining the slightly altered SEC traces and the different solubility behavior of the SCNPs after catalysis. The SEC analysis, combined with the $^{31}\text{P}\{^{1}\text{H}\}$ NMR spectroscopy data, reveal the still folded state of the SCNPs after catalysis. Independently, freshly synthesized platinum(II) nanoparticles, which are predominantly cis-configured, were heated to 100 °C and thus transformed mainly to a trans-geometry (Figure S18). These particles show nearly the same catalytic activity as the cisisomer (Figure S24). The recyclability of the recovered Pt^{II}-SCNPs was investigated in a second amination cycle of allyl alcohol with aniline (1a). With an allyl alcohol conversion of approximately 70%, the SCNPs retain their high catalytic activity (Figure S15), thus confirming them to be a recyclable homogeneous catalyst, obtaining high conversions while applying only 0.24 mol % of catalyst.

In summary, we introduce the synthesis and in-depth characterization of Pt^{II}-SCNPs, which was confirmed by SEC, NMR spectroscopy (¹H, ³¹P{¹H}, ¹⁹⁵Pt), DLS, and DOSY measurements. Furthermore, the Pt^{II}-SCNPs were found to be active homogeneous catalysts for the amination of allyl

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Table 1: Amination of allyl alcohol, catalyzed by Pt^{II} SCNPs and *cis*-[Pt(PPh₃)₂Cl₂].^[a]

Subst. ^[b]	Catalyst	Conv. [%] ^[c]	Product, yield [%] ^[c]		Side produ yield [%] ^[c]	ıct,
NH ₂	Pt-SCNPs $[Pt(PPh_3)_2Cl_2]$	99 97		91 85		3.8 3.2
NH ₂ Cl	Pt-SCNPs [Pt(PPh ₃) ₂ Cl ₂]	96 92	NH CI 2b	86 79		2.8 2.4
NH ₂ F	Pt-SCNPs [Pt(PPh ₃) ₂ Cl ₂]	98 90	NH F 3b	79 82	N F 3c	3.3 2.6
NH ₂ CI	Pt-SCNPs [Pt(PPh ₃) ₂ Cl ₂]	91 96		79 84		2.5 3.0
NH ₂	Pt-SCNPs $[Pt(PPh_3)_2Cl_2]$	35 34	ZH ZH	32 22		-
5a			5h		50	

[a] Conditions: 0.24 mol% catalyst, SnCl₂ (0.96 mol%), C₆D₆, 24 h, 100°C, molecular sieves (3 Å). [b] Aniline derivatives were used in excess (2 equiv). [c] Calculated by ¹H NMR spectroscopy with ferrocene as internal standard.

alcohol. In contrast to many heterogenized molecular catalysts, our system is as active and as selective as the homogeneous reference catalyst. We show—to our knowledge for the first time—the recovery of a Pt^{II}-SCNP system, which retains its folded structure and remains catalytically active after being employed as catalyst.

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Conflict of interest

The authors declare no conflict of interest.

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- E. B. Berda, E. J. Foster, E. W. Meijer, *Macromolecules* 2010, 43, 1430-1437.
- [2] A. M. Hanlon, C. K. Lyon, E. B. Berda, *Macromolecules* 2016, 49, 2-14.
- [3] S. Mavila, O. Eivgi, I. Berkovich, N. G. Lemcoff, *Chem. Rev.* 2016, 116, 878–961.
- [4] O. Altintas, C. Barner-Kowollik, Macromol. Rapid Commun. 2016, 37, 29–46.
- [5] E. Harth, B. V. Horn, V. Y. Lee, D. S. Germack, C. P. Gonzales, R. D. Miller, C. J. Hawker, J. Am. Chem. Soc. 2002, 124, 8653– 8660.
- [6] C. K. Lyon, A. Prasher, A. M. Hanlon, B. T. Tuten, C. A. Tooley, P. G. Frank, E. B. Berda, *Polym. Chem.* 2015, 6, 181–197.
- [7] B. S. Murray, D. A. Fulton, *Macromolecules* **2011**, *44*, 7242–7252.
- [8] A. Latorre-Sánchez, J. A. Pomposo, Polym. Int. 2016, 65, 855– 860.
- [9] I. Manners, Synthetic Metal-Containing Polymers, Wiley-VCH, Weinheim, 2004.
- [10] F. Wang, H. Pu, M. Jin, D. Wan, *Macromol. Rapid Commun.* 2016, 37, 330-336.
- [11] L. Greb, H. Mutlu, C. Barner-Kowollik, J.-M. Lehn, J. Am. Chem. Soc. 2016, 138, 1142–1145.
- [12] I. Berkovich, S. Mavila, O. Iliashevsky, S. Kozuch, N. G. Lemcoff, *Chem. Sci.* 2016, 7, 1773–1778.
- [13] S. Mavila, C. E. Diesendruck, S. Linde, L. Amir, R. Shikler, N. G. Lemcoff, Angew. Chem. Int. Ed. 2013, 52, 5767–5770; Angew. Chem. 2013, 125, 5879–5882.
- [14] T. Terashima, T. Mes, T. F. A. De Greef, M. A. J. Gillissen, P. Besenius, A. R. A. Palmans, E. W. Meijer, J. Am. Chem. Soc. 2011, 133, 4742–4745.

- [15] S. Mavila, I. Rozenberg, N. G. Lemcoff, Chem. Sci. 2014, 5, 4196–4203.
- [16] A. Sanchez-Sanchez, A. Arbe, J. Colmenero, J. A. Pomposo, ACS Macro Lett. 2014, 3, 439–443.
- [17] J. Willenbacher, O. Altintas, V. Trouillet, N. Knofel, M. J. Monteiro, P. W. Roesky, C. Barner-Kowollik, *Polym. Chem.* 2015, 6, 4358-4365.
- [18] Y. Bai, X. Feng, H. Xing, Y. Xu, B. K. Kim, N. Baig, T. Zhou, A. A. Gewirth, Y. Lu, E. Oldfield, S. C. Zimmerman, J. Am. Chem. Soc. 2016, 138, 11077-11080.
- [19] G. Duca, Homogeneous Catalysis with Metal Complexes: Fundamentals and Applications, Springer, Heidelberg, 2012.
- [20] G. J. P. Britovsek, Angew. Chem. Int. Ed. 2012, 51, 1518–1518; Angew. Chem. 2012, 124, 1548–1548.
- [21] Z. Ma, F. Zaera, Encyclopedia of Inorganic Chemistry, Wiley, Hoboken, 2006.
- [22] J. C. Bailar, H. Itatani, J. Am. Chem. Soc. 1967, 89, 1592-1599.
- [23] A. J. Chalk, J. F. Harrod, J. Am. Chem. Soc. 1965, 87, 16-21.
- [24] Y. Tsuji, R. Takeuchi, H. Ogawa, Y. Watanabe, *Chem. Lett.* 1986, 15, 293–294.
- [25] J. R. L. Priqueler, I. S. Butler, F. D. Rochon, *Appl. Spectrosc. Rev.* 2006, 41, 185–226.
- [26] O. Altintas, P. Krolla-Sidenstein, H. Gliemann, C. Barner-Kowollik, *Macromolecules* 2014, 47, 5877 – 5888.
- [27] J. Willenbacher, B. V. K. J. Schmidt, D. Schulze-Suenninghausen, O. Altintas, B. Luy, G. Delaittre, C. Barner-Kowollik, *Chem. Commun.* 2014, *50*, 7056–7059.
- [28] L. Bemi, H. C. Clark, J. A. Davies, C. A. Fyfe, R. E. Wasylishen, J. Am. Chem. Soc. 1982, 104, 438-445.
- [29] J. Huheey, E. Keiter, R. Keiter, R. Steudel, F. Breher, M. Finze, D. Johrendt, M. Kaupp, H. J. Lunk, U. Radius, *Anorganische Chemie: Prinzipien von Struktur und Reaktivität*, deGruyter, Berlin, 2014.
- [30] S. Bähn, S. Imm, L. Neubert, M. Zhang, H. Neumann, M. Beller, *ChemCatChem* 2011, *3*, 1853–1864.

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Recyclable Catalysts

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Platinum(II)-Crosslinked Single-Chain Nanoparticles: An Approach towards Recyclable Homogeneous Catalysts



Keeping in shape: Recyclable metal-containing single-chain nanoparticles (SCNPs) retain their form and function when used in homogeneous catalysis, paving the way as a new class of advanced catalytic systems. The novel platinum(II)-SCNP catalyst thus combines the advantages of homogeneous activity with heterogeneous recyclability.

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