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Organometallic Nanoparticles

Polycyclooctadiene Complexes of Rhodium(I): Direct Access to Organometallic Nanoparticles[**]

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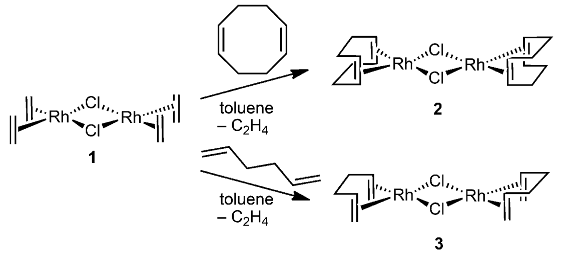
The search for new materials with novel properties continues to be a main driving force in materials science. For example, organic nanoparticles have recently emerged as valuable compounds for various applications.[1] Some of the proposed uses for organic nanoparticles are as vehicles for controlled release of small molecules, the encapsulation of fluorescent markers, and the change of physical properties of materials.[2] One of the methods to generate organic nanoparticles is the intramolecular cross-linking of dendrimers or polymers,[3] which is usually achieved by the formation of a covalent bond between pendant functional groups on the polymer chain. Alternatively, coordination chemistry can be used for the well-defined intramolecular cross-linking of polymers, but this method is not widespread. This latter method has the advantage to intrinsically introduce a metal to the organic nanoparticle lattice. In this context, metal-containing polymers have become quite popular during the past few decades.[4] The appeal of these hybrid compounds is attributed to their ability to impart some of the physical and functional properties of both the polymer and the incorporated metal to the material that is obtained. In this way, the advantage of facile fabrication of organic polymers can be combined with the magnetic, electronic, optical, and catalytic potential of metals. Thus, novel compounds such as conductive and semiconductive materials for electroluminescence, photovoltaics, electrocatalysis, and nanotechnological applications may be devised.[5] The most common synthetic methodologies to incorporate a metal to a polymer are either the use of metal-containing monomers or the coordination of the metal to a pre-existing polymer chain that contains suitable ligands. As an example of the first approach, Gladysz and co-workers recently reported the synthesis of π-bound iridium complexes of polyacetylene through the ring-opening metathesis polymerization of $[(\eta^5\text{-}C_5H_5)Ir(\eta^4\text{-}C_6H_6)]$ by using Schrock- and Grubbs-type initiators.[6] The metallopolymer thus obtained consisted of *cis*-butadiene moieties bound to cyclopentadienyl–iridium complexes. Examples based on the latter strategy were reported by the groups of Wang and Manners. In the first case, stable metal-containing micelles were prepared through coordination of metal ions to a terdentate-ligand-grafted PVP block of poly(4-vinylpyridine)-*b*-poly(ethyleneoxide).[7a] In the second case, reversible cross-linking by Pt–olefin coordination of polyisoprene-poly(ferrocenyldimethylsilane) micelles was shown.[7b] Herein, we report a very convenient and straightforward synthetic route to well-defined metal-containing polymeric nanoparticles of ROMP-derived poly(1,5-cyclooctadiene) (poly(COD)) that is intramolecularly cross-linked by π-bound rhodium(I) fragments, and study their physical properties.

The traditional procedure for the preparation of Rh^I/diene complexes such as **2** involves treatment of $RhCl_3{\cdot}H_2O$ with 1,5-cyclooctadiene in hot, deoxygenated aqueous ethanol in the presence of sodium carbonate.[8] However, this procedure would not be suitable for the preparation of organometallic complexes of poly(COD), chiefly due to the poor solubility of poly(COD) in polar solvents. Thus, an alternative route starting from the commercially available chlorobis(ethylene)rhodium(I) dimer (**1**), which possesses two labile ethylene molecules that are coordinated to the rhodium metal, was developed.

In order to obtain a mechanistic understanding of the exchange process, we first attempted a simple ligand-exchange reaction of complex **1** with 1,5-cyclooctadiene (COD) and 1,5-hexadiene (Scheme 1). Mixing of COD and **1** in toluene afforded the expected chloro(1,5-cyclooctadiene)rhodium(I) dimer (**2**) through the smooth exchange of ethylene with COD moieties in just one hour at room temperature. An upfield shift of the proton signal from $\delta = 5.53$ ppm to $\delta = 4.23$ ppm in the ^1H NMR spectrum could be readily observed, confirming the formation of **2** (see the



Scheme 1. Reaction of **1** with COD and 1,5-hexadiene.

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Supporting Information). Moreover, the observed signals at $\delta = 5.24$ and 122.9 ppm in ^{1}H and ^{13}C NMR spectra, respectively, indicate the liberation of the ethylene molecules (Scheme 1).

Similarly, the reaction of 1,5-hexadiene with **1** under the same reaction conditions readily afforded compound **3** through ethylene exchange. Once again, ^{1}H NMR spectroscopy confirmed the formation of the product. New signals were observed at 4.52 and 3.42 ppm (for **3**), and at 5.25 ppm (of liberated ethylene). In contrast to the aforementioned traditional protocol, this exchange methodology offers several advantages. On the one hand, the reaction can be carried out in a good polymer solvent (interactions between polymer and solvent are energetically favorable), and on the other hand, the reaction occurs at room temperature and under mild conditions and causes no damage to the polymer backbone. Furthermore, the only side product obtained during the ligand exchange is ethylene, which is readily removed by simple evaporation.

Having shown that our model diene monomer promptly exchanged ethylene in **1**, we set out to extend this methodology to poly(COD), a polymer that bears 1,5-diene units.[9] To our satisfaction, poly(COD) ($M_n = 25\,000$ g mol^{-1}, PDI = 1.34) quickly reacted with **1** (10 mol% relative to original COD content) in THF at room temperature to afford polymer-bound complex **4** (Scheme 2).

Formation of **4** in [D$_8$]THF was supported by the appearance of a broad resonance around $\delta = 4.38$ ppm, corresponding to the olefin protons bound to the rhodium metal center (see the Supporting Information). Assuming that complexation in dilute solutions occurs through binding of rhodium to 1,5-hexadiene units in the same polymer chain, the resulting polymer complex should exhibit a concomitant shrinkage in hydrodynamic radius compared to the parent polymer chain, because of intramolecular cross-linking.[2c,10–11] Indeed, a decrease in size was observed both by dynamic light scattering (DLS) and size-exclusion chromatography (SEC) analyses (Figure 1).

As a control experiment, polycyclooctene (poly(COE); $M_n = 35\,600$ g mol^{-1}; PDI = 1.34), which lacks the chelating 1,5-diene fragments, was also tested as a π-rich polymer backbone. Notably, reaction of poly(COE) with **1** under the reaction conditions previously described, did not show any reduction in the hydrodynamic radius of the polymer; quite the opposite, a slight increase in size was observed, most likely because of some intermolecular cross-linking (Supporting Information).

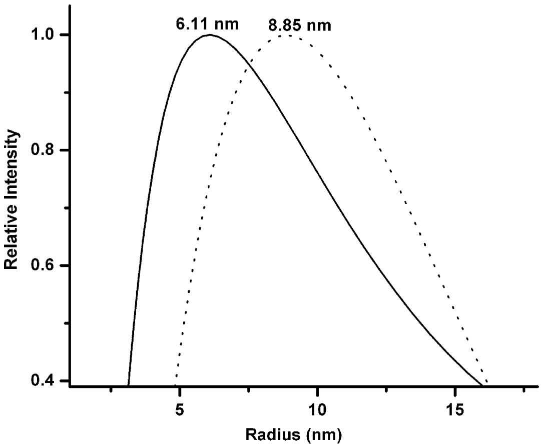
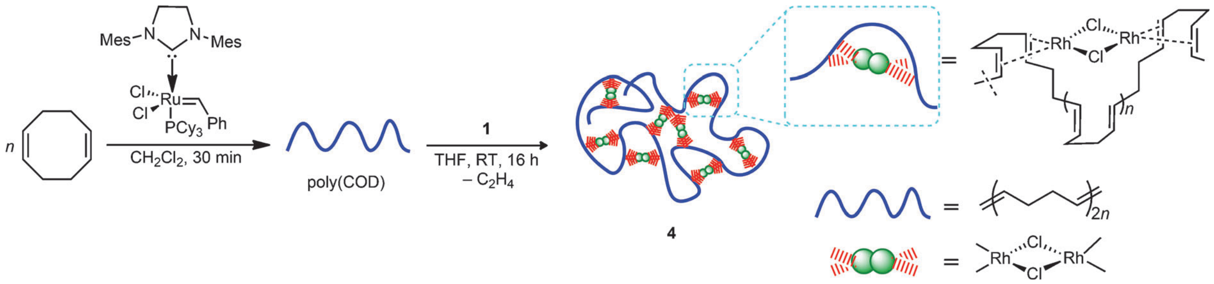


Figure 1. DLS study of poly(COD) (dotted line) and complex **4**, which contains 10 mol% rhodium (solid line).

Having secured a straightforward procedure to prepare the organorhodium constructs, we turned our attention toward studying the influence of varying the rhodium(I) content on the polymer chain. Thus, 1–10 mol% metal complex with respect to the 1,5-diene moieties in the polymer chain was added. To avoid precipitation as a result of intermolecular cross-linking of the polymer chains, the concentration of the polymer was kept very low ($\approx 10^{-5}$ M) and metal content was kept below 10 mol%, as detailed above. Notably, upon increasing the content of rhodium from 1–10 mol% with respect to the diene units, a systematic decrease in the hydrodynamic radius from 9.3 nm to 7.3 nm was observed, clearly indicating intramolecular complexation through chelation of 1,5-diene units (Table 1). The tunability of the polymer size by addition of rhodium is shown in Figure 2. Because of the well-defined size and composition of the resulting particles, we call these novel polymers organometallic nanoparticles.

Transmission electron microscopy (TEM) analysis was carried out as additional characterization of the organometallic nanoparticles. Figure 3 shows spherical particles of about 20 nm in diameter, which nicely correlates with the results obtained by DLS and triple-detector SEC.

Having shown the ease of their synthesis, we turned our attention to study some of the potential properties and catalytic uses of these new compounds. Thus, we tested the reactivity of **4** by mixing the organometallic nanoparticle with 2-(diphenylphosphino) benzaldehyde (PCHO) to determine



Scheme 2. Synthetic route toward **4**.

Table 1: SEC and DLS measurements of **4** with varying rhodium content.

Entry	Rh^{I} [mol%][a]	M_n[b] [$\times 10^4$ g mol^{-1}]	PDI[b]	R_g[c] [nm]
1	0	3.00	1.27	9.3
2	1	3.09	1.23	8.9
3	2	3.14	1.26	8.5
4	5	3.21	1.22	8.1
5	10	3.94	1.16	7.4

Conditions: Solvent = THF, t = 16 h, T = 35 °C, $Rh^{I} = [RhCl(C_2H_4)_2]_2$. [a] Relative to the original COD content. [b] M_n and PDI of the polymer, determined by triple-detector SEC in THF. [c] R_g determined by DLS in THF.

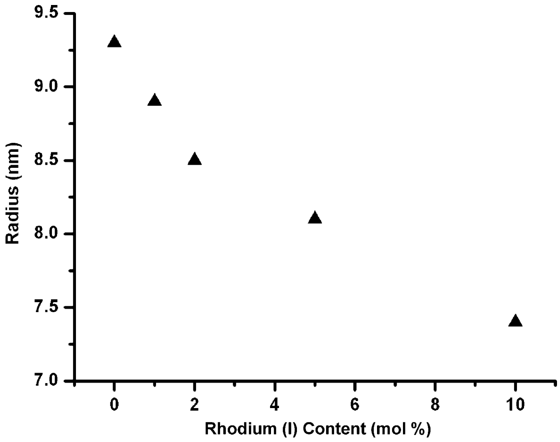


Figure 2. Effect of the rhodium(I) content on the radius of gyration (R_g) of **4**.

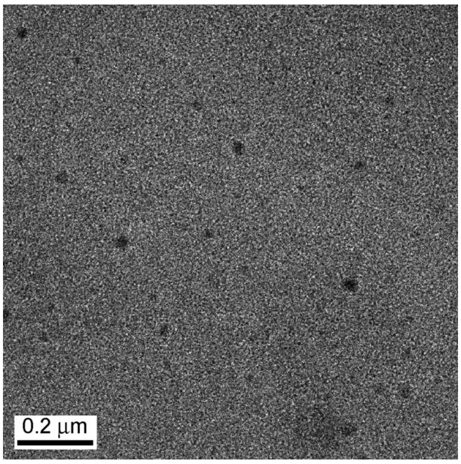
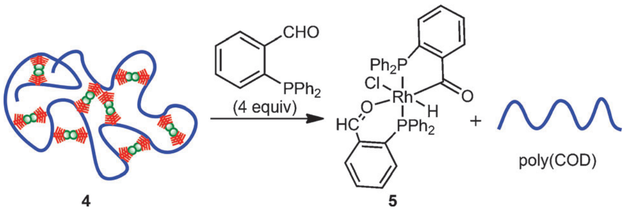


Figure 3. TEM image of **4**.

whether the corresponding acyl hydride derivative could be obtained through oxidative addition of PCHO to the metal, effectively dissociating the poly(COD) ligand (Scheme 3).[12–14] Therefore, a solution of **4** in [D_8]THF was treated with PCHO and monitored by ^{1}H NMR spectroscopy at 273 K.

The treatment caused the signal at $\delta = 4.52$ ppm, corresponding to protons of the olefins that were bound to rhodium, to completely disappear, and a new signal to appear at −13.8 ppm, corresponding to the rhodium-bound hydride. Furthermore, DLS analysis of the expelled poly(COD) showed that once rhodium is removed, the polymer returned exactly to its original size (9.3 nm).



Scheme 3. Reaction of **4** with PCHO resulting in the formation of **5** and metal-free poly(COD).

To determine the electronic properties of the hybrid, a conductivity study of the polymeric nanoparticle **4** was carried out in an interdigitated structure that consisted of a patterned gold contact on top of a Si/SiO_2 substrate using photolithography techniques. The conductivity measurements showed no current for the substrate without polymer and for the substrate that was spin-coated with poly(COD) (Figure 4, dotted curve). However, an exponential dependence of the current on the applied bias was clearly observed for the sample that was spin-coated with **4** (Figure 4, solid curve). Although the conductivity values were not very high, the introduction of the metal significantly changed the electronic behavior of the polymer and presents a very simple procedure to manipulate the properties of the material.

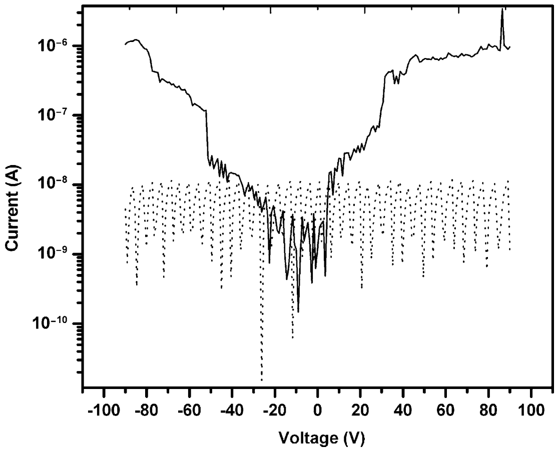


Figure 4. Logarithmic plot of the current versus voltage obtained for poly(COD) (dotted curve) and complex **4** (10 mol% Rh^{I}) (solid curve) spin-coated on Si/SiO_2 substrate.

In summary, a convenient synthesis of π-bound rhodium organometallic complexes was accomplished by the reaction of ROMP-derived poly(COD) and **1** in dilute solutions. The hydrodynamic radius of the polymer hybrid was found to be accurately controlled by the amount of added rhodium as a result of 1,5-diene units that fold through binding with the metal, actually generating a well-defined organometallic nanoparticle. Removal of the metal by reaction with a phosphine aldehyde derivative regenerated the size of the parent polymer, suggesting that the reactivity of the imbedded metal remains intact and can be catalytically active for further reactions. Finally, studies determined that the conductivity properties of rhodium(I) organometallic nanoparticles are significantly altered compared to those of the parent polycyclooctadiene. This initial proof of principle compels us to expand and generalize our studies toward the use of other metals, such as Ir, Ni, Pd, Pt, and Ru, to study the effect of the use of copolymers and to analyze in depth the catalytic potential and mechanism involved in these novel molecules.

Experimental Section

General procedure for the preparation of rhodium(I) organometallic nanoparticles (**4**): In a glove box, poly(COD) (10.0 mg, 0.26 μmol; $M_n = 30\,000$ g mol^{-1}, PDI = 1.27) was dissolved in dry THF (10 mL). A solution of **1** (1.80 mg, 4.62 μmol) in dry THF (1 mL) was added dropwise to the solution of poly(COD) over 30 min. The mixture was stirred at ambient temperature for 16 h to afford complex **4**.

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[1] a) R. Brayneret al. in *Nanomaterials: A Danger or a Promise?*, Springer, London, **2013**; b) T. Asahi, T. Sugiyama, H. Masuhara, *Acc. Chem. Res.* **2008**, *41*, 1790–1798, and references therein.

[2] a) S. Haam et al., *Angew. Chem.* **2011**, *123*, 461–464; *Angew. Chem. Int. Ed.* **2011**, *50*, 441–444; b) A. Kaeser, A. P. H. J. Schenning, *Adv. Mater.* **2010**, *22*, 2985–2997; c) M. K. Aiertza, I. Odriozola, G. Cabañero, H.-J. Grande, I. Loinaz, *Cell. Mol. Life Sci.* **2012**, *69*, 337–346; d) M. Elsabahy, K. L. Wooley, *J. Polym. Sci. Part A* **2012**, *50*, 1869–1880; e) J. Rao, A. D. Andrasi, H. Yao, *Curr. Opin. Biotechnol.* **2007**, *18*, 17–25; f) M. J. Ruedas-Rama, J. D. Walters, A. Orte, E. A. H. Hall, *Anal. Chim. Acta* **2012**, *751*, 1–23; g) M. A. Mackay, T. T. Dao, A. Tuteja, D. L. Ho, B. V. Horn, H. C. Kim, C. J. Hawker, *Nat. Mater.* **2003**, *2*, 762–766.

[3] a) S. K. Yang, S. C. Zimmerman, *Adv. Funct. Mater.* **2012**, *22*, 3023–3028; b) A. E. Cherian, F. C. Sun, S. S. Sheiko, G. W. Coates, *J. Am. Chem. Soc.* **2007**, *129*, 11350–11351; c) L. M. Van Renterghem, M. Lammens, B. Dervaux, P. Viville, R. Lazzaroni, F. E. Du Prez, *J. Am. Chem. Soc.* **2008**, *130*, 10802–10811; d) C. J. Hawker, K. L. Wooley, *Science* **2005**, *309*, 1200–1205; e) D. Mecerreyes, V. Lee, C. J. Hawker, J. L. Hedrick, A. Wursch, W. Volksen, T. Magbitang, E. Huang, R. D. Miller, *Adv. Mater.* **2001**, *13*, 204–208; f) J. B. Beil, S. C. Zimmerman, *Macromolecules* **2004**, *37*, 778–787; g) X. Jiang, H. Pu, P. Wang, *Polymer* **2011**, *52*, 3597–3602; h) P. Wang, H. Pu, M. Jin, *J. Polym. Sci. Part A* **2011**, *49*, 5133–5141.

[4] a) I. Manners, *Science* **2001**, *294*, 1664–1666; b) R. D. Archer in *Inorganic and Organometallic Polymers*, Wiley-VCH, Weinheim, **2001**; c) A. S. Abd-El-Aziz, I. Manners in *Frontiers in Transition Metal-Containing Polymers*, Wiley-Interscience, New York, **2007**; d) A. S. Abd-El-Aziz, *Macromol. Rapid Commun.* **2002**, *23*, 995–1031; e) P. Nguyen, P. Gomez-Elipe, I. Manners, *Chem. Rev.* **1999**, *99*, 1515–1548; f) G. R. Newkome, E. He, C. N. Moorefield, *Chem. Rev.* **1999**, *99*, 1689–1746.

[5] a) G. R. Whittell, I. Manners, *Adv. Mater.* **2007**, *19*, 3439–3468; b) B. J. Holliday, T. M. Swager, *Chem. Commun.* **2005**, 23–26; c) B. J. Holliday, T. B. Stanford, T. M. Swager, *Chem. Mater.* **2006**, *18*, 5649–5651; d) J. R. Sheats, H. Antoniadis, M. Hueschen, W. Leonard, J. Miller, R. Moon, D. Roitman, A. Stocking, *Science* **1996**, *273*, 884; e) D. Knapton, S. J. Rowan, C. Weder, *Macromolecules* **2006**, *39*, 651–657; f) J. S. Wilson, A. S. Dhoot, A. J. A. B. Seeley, M. S. Khan, A. Köhler, R. H. Friend, *Nature* **2001**, *413*, 828; g) A. Köhler, H. F. Wittmann, R. H. Friend, M. S. Khan, J. Lewis, *Synth. Met.* **1996**, *77*, 147–150; h) D. J. Caruana, A. Heller, *J. Am. Chem. Soc.* **1999**, *121*, 769–774; i) X. S. Wang, R. McHale, *Macromol. Rapid Commun.* **2010**, *31*, 331–350; j) F. Bossé, P. Das, L. A. Belfiore, *Macromolecules* **1995**, *28*, 6993–7004.

[6] P. D. Zeits, T. Fiedler, J. A. Gladysz, *Chem. Commun.* **2012**, *48*, 7925–7927.

[7] a) J. Wang, M. A. Cohen Stuart, A. T. M. Marcelis, M. Colomb-Delsuc, S. Otto, J. van der Gucht, *Macromolecules* **2012**, *45*, 7179–7985; b) P. A. Rupar, G. Cambridge, M. A. Winnik, I. Manners, *J. Am. Chem. Soc.* **2011**, *133*, 16947–16957.

[8] G. Giordano, R. H. Crabtree, *Inorg. Synth.* **1990**, *28*, 88.

[9] W. Bielawski, R. H. Grubbs, *Macromolecules* **2001**, *34*, 8838–8840.

[10] N. G. Lemcoff, T. A. Spurlin, A. A. Gewirth, S. C. Zimmerman, J. B. Beil, S. L. Elmer, G. Vandeveer, *J. Am. Chem. Soc.* **2004**, *126*, 11420–11421.

[11] J. B. Beil, N. G. Lemcoff, S. C. Zimmerman, *J. Am. Chem. Soc.* **2004**, *126*, 13576–13577.

[12] R. El Mail, M. A. Garralda, R. Hernández, L. Ibarlucea, *J. Organomet. Chem.* **2002**, *648*, 149–154.

[13] C. Bianchini, A. Meli, M. Peruzzini, J. A. Ramirez, A. Vacca, F. Vizza, F. Zanobini, *Organometallics* **1989**, *8*, 337–345.

[14] C. Bianchini, A. Meli, M. Peruzzini, A. Vacca, F. Zanobini, *Organometallics* **1989**, *6*, 2453–2455.