DOI: 10.1002/anie.200703294

Supramolecular Catalysts

Templated Encapsulation of Pyridyl-Bian Palladium Complexes: Tunable Catalysts for CO/4-*tert*-Butylstyrene Copolymerization**

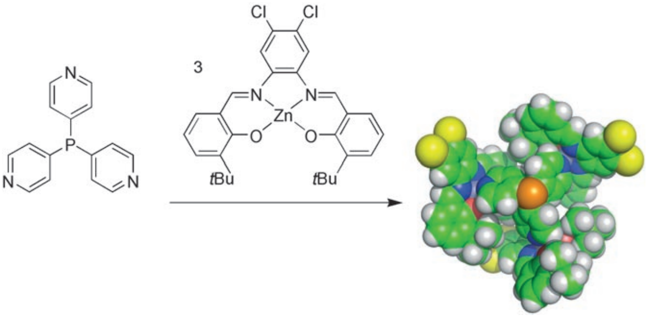
*Jitte Flapper and Joost N. H. Reek**

Dedicated to Professor David N. Reinhoudt on the occasion of his 65th birthday

The properties of transition-metal catalysts are largely dominated by the direct environment around the metal center, and traditionally the steric environment has been adjusted by ligands that are coordinated to the metal center. Enzymes create a suitable cavity around an active site to provide the required steric and electronic environment. This has inspired scientists to create nanosized capsules to facilitate stochiometric and catalytic transformations in synthetic cavities, resulting in unique conversions.[1,2]

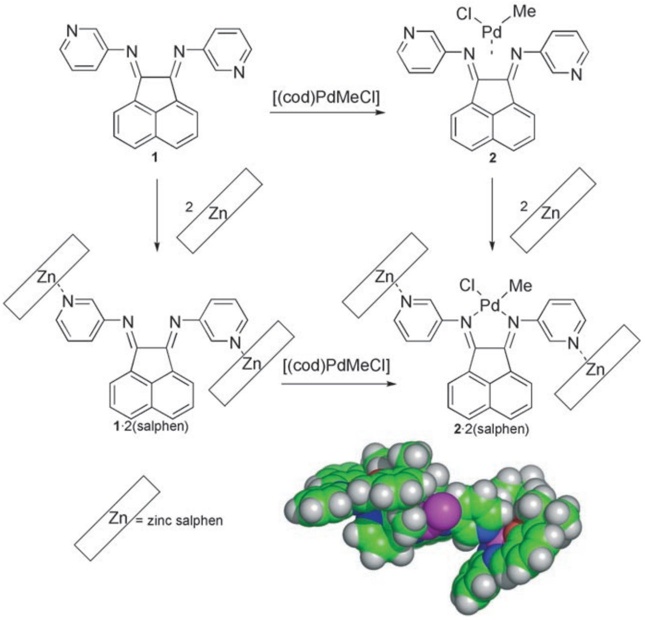
We have been particularly interested in the encapsulation of transition-metal complexes and the effect on the catalytic performance, and we therefore developed a template-ligand-assisted approach as a new strategy to make such complexes generally accessible.[3–7] For example, trispyridylphosphine templates and rhodium complexes thereof can be encapsulated by three zinc(II) porphyrin units through nitrogen–zinc coordination. Rhodium encapsulation results in a remarkable change in catalyst selectivity; in the hydroformylation of 1-octene,[3,4] mainly branched aldehydes are formed; for internal octenes, such as 3-octene, regioselective reactions were also accomplished.[7] The approach was extended to templated ligand assemblies based on zinc(II) salphen complexes (salphen = *N*,*N*′-bis(salicylidene)-*o*-phenylenediamine dianion), which are more accessible building blocks and easier to vary structurally.[5] Scheme 1 shows an example of the efficient ligand encapsulation by zinc(II) salphen complexes and also displays the solid-state structure of the three-to-one assembly that was also shown to exist in solution.[6]

So far, templated encapsulation has been based on the complementary use of donor atoms; zinc has a low affinity for phosphine ligands, and the monopyridyl ligands have lower affinity for the catalytically active metals used to date. Herein, we demonstrate that similar assemblies can be based on template ligands that only have nitrogen donor atoms, in which case selective coordination is based on steric differences. The palladium complexes thus obtained are active in the CO/4-*tert*-butylstyrene copolymerization, and the activity and selectivity strongly depend on the building blocks used for the ligand assembly.



Scheme 1. Formation of a three-to-one assembly as a typical example of the template-ligand approach to encapsulation. The structure depicts the three-to-one assembly; P orange, Zn light blue, O red, N blue, Cl yellow, C green, H gray.

With the 3-pyridyl-bian ligand (*m*Py-bian (**1**), see Scheme 2), encapsulation[8] takes place through the pyridyl groups, whereas in the presence of zinc(II) salphen building blocks, palladium complexes are coordinated to the bis-imine



Scheme 2. Formation of an encapsulated neutral palladium complex and the PM3-TM optimized structure of the assembly with salphen **C** from Scheme 4; Pd, Zn, Cl all purple, O red, N blue, C green, H gray.

---

[*] J. Flapper, Prof. Dr. J. N. H. Reek
Homogeneous and Supramolecular Catalysis
van 't Hoff Institute for Molecular Sciences
Universiteit van Amsterdam
Nieuwe Achtergracht 166, 1018WV Amsterdam (The Netherlands)
Fax: (+31) 20-5255604
E-mail: reek@science.uva.nl
Homepage: http://www.science.uva.nl/research/imc/HomKat/

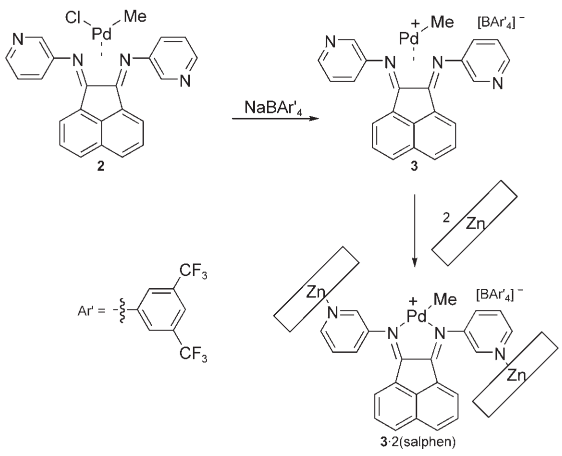
[**] This work was financially supported by NWO (VICI-grant to J.N.H.R.). bian = bis(arylimino)acenaphthene.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

site. It was anticipated that coordination of the zinc(II) salphen unit to the imine nitrogen atom would not be possible for steric reasons. Indeed, control experiments show that the Ph-bian ligand does not coordinate to zinc(II) salphen complexes. Furthermore, Job-plot analysis showed that the *m*Py-bian ligand is encapsulated by two zinc(II) salphen units.[9] Coordination of these building blocks can therefore only take place at the pyridyl nitrogen atom. In contrast, we expected that the palladium precursor would have a preference for the bis-imine ligand because of the chelate effect. Indeed, when [(cod)PdMeCl] was added to a solution of the *m*Py-bian ligand encapsulated by two zinc(II) salphen building blocks, the corresponding palladium complex was quantitatively formed (Scheme 2). Interestingly, the same reaction in the absence of zinc(II) salphen building blocks resulted in the formation of a mixture of complexes, thus indicating that in this experiment the pyridyl groups are also coordinated to palladium centers. Upon addition of two equivalents of zinc(II) salphen to a solution of this mixture, the expected complex formed, with the salphen units coordinated to the pyridyl groups and the {PdMeCl} moiety to the bis-imine ligand. The current experiments imply that the complexes are formed under thermodynamically controlled conditions. By applying different zinc(II) salphen building blocks, different encapsulated palladium complexes can be obtained.

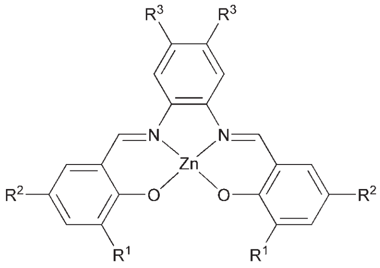
Palladium complexes of bian ligands are well-studied[10] and have been used as catalysts in ethene homopolymerization[11] and CO/4-methylstyrene copolymerization.[12,13] Alternating copolymerization of CO and olefins provides polymers with interesting properties.[14–17] Copolymers that are almost completely isotactic were obtained from CO and propene[18] and from CO and alkylstyrene;[19] for the latter reaction, very high degrees of syndiotacticity could also be achieved.[20] If 4-*tert*-butylstyrene (TBS) is used, a soluble polymer is obtained. The molecular weight and stereoregularity of this polymer can be steered by the ligands applied.[19,21–24] The selectivity of the catalyst strongly depends on the steric properties of the ligands. We therefore evaluated the encapsulated bian palladium complexes in the copolymerization of CO and TBS, since the steric demand can be delicately changed by altering the building blocks used for the assembly. As this reaction requires cationic palladium complexes, the chloride was abstracted from [(*m*Py-bian)PdMeCl] using NaBAr′$_4$ [Ar′ = 3,5-$C_6H_3(CF_3)_2$]. Again, a mixture of complexes was obtained with a 1:1 stochiometry of *m*Py-bian and {PdMe}$^+$[BAr′$_4$]$^-$, which was likely the result of pyridyl coordination to the vacant site of palladium. Similar to the neutral palladium(methyl)chloride complex, this mixture gave the expected species upon addition of two equivalents of zinc(II) salphen, which efficiently blocked the pyridyl groups (Scheme 3). The cationic complex in [(*m*Py-bian)PdMe]-[BAr′$_4$] proved to be a good precursor for the formation of well-defined encapsulated complexes, which simplified the preparation of a series of such complexes.

In a typical catalysis experiment, the cationic palladium complex was mixed with two equivalents of one of the zinc salphen building blocks (**A**–**D**, Scheme 4) in a mixture of dichloromethane and TBS and subsequently stirred under CO pressure for 16 h. The activity of the catalyst and the molecular weight, polydispersity, and stereoregularity of the obtained copolymer (CP) were evaluated and are displayed in Table 1. For comparison, complex [(Ph-bian)PdMe(MeCN)]-[BAr′$_4$]$^-$ (**4**), which lacks sites for zinc salphen coordination, was synthesized[9] and studied under the same conditions.



Scheme 3. Formation of an encapsulated cationic palladium complex.

	R¹	R²	R³
A	*t*Bu	H	Cl
B	*t*Bu	*t*Bu	Cl
C	*t*Bu	H	H
D	*t*Bu	*t*Bu	H



Scheme 4. Zinc salphen units used in the copolymerization study.

Table 1: CO/TBS copolymerization catalyzed by various catalyst assemblies.[a]

entry	Pd complex	Zn salphen (equiv)	Activity [$g_{CP}\,g_{Pd}^{-1}$]	M_w [g mol^{-1}][b] (M_w/M_n)	Stereoregularity[c] % ll[d]	% ul, lu[d]	% uu[d]
1	**3**	**A** (2.0)	98	44×10^3 (1.9)	2	27	71
2	**3**	**B** (2.0)	184	58×10^3 (1.9)	<1	21	79
3	**3**	**C** (2.0)	259	118×10^3 (2.9)	<1	15	85
4	**3**	**D** (2.0)	411	104×10^3 (2.2)	<1	13	87
5	**3**	**D** (1.0)	167	34×10^3 (1.6)	2	28	70
6	**3**	– (0)	0	–	–	–	–
7	**4**	– (0)	284	35×10^3 (1.2)	18	57	25
8	**4**	**D** (2.0)	92	18×10^3 (1.4)	17	56	27

[a] Reaction conditions: 12.5 μmol Pd complex, 1.0 mL (5.5 mmol) TBS, 1.5 mL CH_2Cl_2, 10 bar CO, 25 °C, 16 h. [b] Determined by size-exclusion chromatography relative to polystyrene standards. [c] Determined by ^{13}C NMR spectroscopy. [d] l = like, u = unlike; this notation refers to a triad of two chiral centers with the same (l) or opposite (u) stereochemistry in the CP.

From ligand **3** and building blocks **A**–**D**, four assembled active catalysts for the CO/TBS copolymerization are formed that give very different results (Table 1, entries 1–4). Activities vary between 98 and 411 $g_{CP}\,g_{Pd}^{-1}$ depending on the structure of the salphen building block. This maximum activity is much higher than that of parent complex **4**, which showed an activity of 284 $g_{CP}\,g_{Pd}^{-1}$ (Table 1, entry 7). Addition of zinc(II) salphen to this catalyst gave a lower activity (Table 1, entry 8), which we currently cannot explain. Interestingly, the supramolecular catalysts **3·A**$_2$–**3·D**$_2$ all provide much more selective catalysts, thus leading to highly stereoregular polymers, as is clear from the ^{1}H and ^{31}C NMR spectra.[9] Whereas **4** gives rise to atactic copolymers, the supramolecular catalysts provide syndiotactic copolymers. The highest degree of syndiotacticity is displayed by complex **3·D**$_2$ with a maximum percentage of uu triads of 87 %, which places **3·D**$_2$ among the most selective catalysts known to date. Moreover, the molecular weight of the copolymer can be tuned by small changes to the salphen building blocks and is much higher than the molecular weight of the polymer produced by the parent complex **4**. The copolymer produced by **4** has an average molecular weight of 35×10^3 g mol^{-1}, and that of the copolymer formed by the supramolecular catalysts varies between 44×10^3 (**3·A**$_2$) and 118×10^3 g mol^{-1} (**3·C**$_2$). For the activity of complex **3**, the coordination of salphen building blocks is crucial. Complex **3** is completely inactive in the absence of salphen ligands (Table 1, entry 6), and the activity is much lower if only one equivalent of salphen is present (Table 1, entry 5).

In conclusion, we have developed a supramolecular ligand approach, based on the new ligand 3-pyridyl-bian (*m*Py-bian), for the preparation of palladium catalysts for the CO/TBS copolymerization. The catalytic activity of the complex and the molecular weight of the copolymer obtained can be tuned by altering the properties of the zinc salphen units used to assemble the catalyst. The catalyst activity and copolymer stereoregularity are amongst the best reported for CO/TBS copolymerization under similar conditons (no use of trifluoroethanol,[25] room temperature), and the molecular weight of the copolymer produced under these conditions by **3·C**$_2$ (118×10^3 g mol^{-1}) is the highest reported to date.[14,15]

Received: July 23, 2007

Keywords: homogeneous catalysis · palladium · polymerization · self-assembly · supramolecular catalysis

---

[1] M. D. Pluth, R. G. Bergman, K. N. Raymond, *Science* **2007**, *316*, 85.

[2] M. Yoshizawa, M. Tamura, M. Fujita, *Science* **2006**, *312*, 251.

[3] V. F. Slagt, J. N. H. Reek, P. C. J. Kamer, P. W. N. M. Van Leeuwen, *Angew. Chem.* **2001**, *113*, 4401; *Angew. Chem. Int. Ed.* **2001**, *40*, 4271.

[4] V. F. Slagt, P. C. J. Kamer, P. W. N. M. Van Leeuwen, J. N. H. Reek, *J. Am. Chem. Soc.* **2004**, *126*, 1526.

[5] A. W. Kleij, M. Lutz, A. L. Spek, P. W. N. M. van Leeuwen, J. N. H. Reek, *Chem. Commun.* **2005**, 3661.

[6] A. W. Kleij, J. N. H. Reek, *Chem. Eur. J.* **2006**, *12*, 4218.

[7] M. Kuil, T. Soltner, P. W. N. M. Van Leeuwen, J. N. H. Reek, *J. Am. Chem. Soc.* **2006**, *128*, 11344.

[8] We have shown that the extent of encapsulation of the catalyst depends strongly on the template ligand and on the other building blocks used (see reference [6]). In the current example, it is clear from the modeled structure that a rather open capsule is formed.

[9] See the Supporting Information.

[10] R. van Asselt, C. J. Elsevier, W. J. J. Smeets, A. L. Spek, R. Benedix, *Recl. Trav. Chim. Pays-Bas* **1994**, *113*, 88.

[11] S. D. Ittel, L. K. Johnson, M. Brookhart, *Chem. Rev.* **2000**, *100*, 1169.

[12] B. Binotti, G. Bellachioma, G. Cardaci, C. Carfagna, C. Zuccaccia, A. Macchioni, *Chem. Eur. J.* **2007**, *13*, 1570.

[13] B. Binotti, C. Carfagna, C. Zuccaccia, A. Macchioni, *Chem. Commun.* **2005**, 92.

[14] J. Durand, B. Milani, *Coord. Chem. Rev.* **2006**, *250*, 542.

[15] E. J. Garcia Suárez, C. Godard, A. Ruiz, C. Claver, *Eur. J. Inorg. Chem.* **2007**, 2582.

[16] K. Nakano, N. Kosaka, T. Hiyama, K. Nozaki, *Dalton Trans.* **2003**, 4039.

[17] C. Bianchini, A. Meli, *Coord. Chem. Rev.* **2002**, *225*, 35.

[18] K. Nozaki, N. Sato, H. Takaya, *J. Am. Chem. Soc.* **1995**, *117*, 9911.

[19] M. Brookhart, M. I. Wagner, G. G. A. Balavoine, H. A. Haddou, *J. Am. Chem. Soc.* **1994**, *116*, 3641.

[20] C. Carfagna, G. Gatti, D. Martini, C. Pettinari, *Organometallics* **2001**, *20*, 2175.

[21] M. Brookhart, F. C. Rix, J. M. DeSimone, J. C. Barborak, *J. Am. Chem. Soc.* **1992**, *114*, 5894.

[22] M. T. Reetz, G. Haderlein, K. Angermund, *J. Am. Chem. Soc.* **2000**, *122*, 996.

[23] A. Bastero, C. Claver, A. Ruiz, S. Castillon, E. Daura, C. Bo, E. Zangrando, *Chem. Eur. J.* **2004**, *10*, 3747.

[24] J. M. Benito, E. de Jesus, F. J. de La Mata, J. C. Flores, R. Gomez, *Organometallics* **2006**, *25*, 3045.

[25] A. Scarel, J. Durand, D. Franchi, E. Zangrando, G. Mestroni, B. Milani, S. Gladiali, C. Carfagna, B. Binotti, S. Bronco, T. Gragnoli, *J. Organomet. Chem.* **2005**, *690*, 2106.