

Homo- and Hetero-bimetallic Flexibly Linked Dinuclear Salphen Complexes

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Dedicated to Professor Wolfgang Beck on the occasion of his 80th birthday

A modification of the previously developed synthetic approach towards dinuclear flexibly linked salphen complexes is successfully utilized for the preparation of heterodinuclear salphen dimers. A dinuclear salphen species with Pd(II) and Cr(III) centers bears a stronger structural resemblance to the related bis-Cr(III) compound than the corresponding mononuclear Cr(III) salphen complex. Therefore, it was considered as a more useful model for the comparison with the homobinuclear Cr(III) complex regarding the catalytic activity in the ring-opening polymerization of β -butyrolactone, for which a bimetallic catalytic mechanism seems to operate. The polymerization results again have shown a higher activity of the homobinuclear Cr(III) complex.

Key words: Ring-opening Polymerization, β -Butyrolactone, Catalysis, Heterobimetallic Complexes

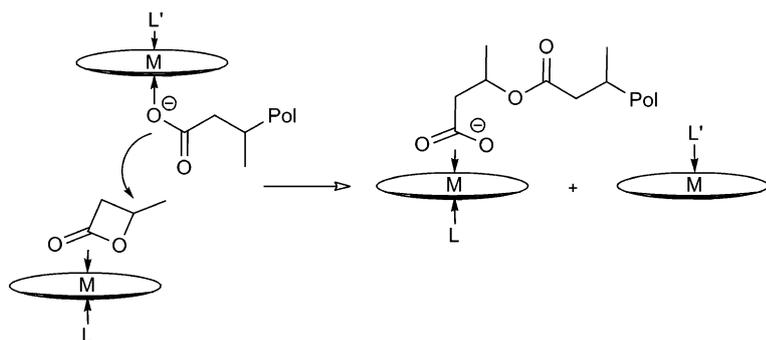
Introduction

Ring-opening polymerization (ROP) of β -butyrolactone (β -BL) to produce poly(3-hydroxybutyrate) (PHB) has long been considered as a promising alternative to the biological synthesis of this biodegradable material. Successful results in this respect have been achieved using various catalytic systems including those based on phenolate complexes of lanthanides and group III metals [1], zinc complexes of β -diiminates [2], chromium complexes of salphens [3], *etc.* In some cases, stereoregularly enriched PHBs could be obtained from racemic β -BL upon utilization of certain achiral catalysts [4], whereas their structurally most closely analogous complexes do not necessarily exhibit stereocontrol during the polymerization. This is especially inherent to the chromium(III) salphen complexes, which can even switch the stereoregularity of produced PHB from isotactically enriched (bulk polymerization) to syndiotactically enriched (in the presence of solvent, such as chlorobenzene) [5]. The substituents at the phenylene ring or at the phenolate moieties of the salphen ligand have also been shown to influence the tacticity of PHB in bulk polymerization of β -BL,

resulting either in isotactically enriched or completely atactic polymer.

All these observations together with DFT calculations strongly support a bimetallic catalytic mechanism of the ROP of butyrolactone, according to which the polymer chain growth takes place by way of nucleophilic attack of a metal-coordinated carboxylato chain end onto the activated monomer at another metal center, as shown in Scheme 1 [3]. Upon the appropriate spatial orientation of the two complexes the conditions for stereocontrolled β -BL ring opening can be realized.

In order to verify the occurrence of bimetallic catalysis in ROP of β -BL in the presence of chromium salphen complexes, we have recently synthesized a series of mono- and dinuclear chromium salphens, where the chromium centers were considered to have the same electronic environment [6]. With the chromium to β -BL loading of 0.1 mol-%, the dinuclear complexes have shown approximately 5 times higher activity than the mononuclear one. This was attributed to the effect of a higher local concentration of chromium centers in dinuclear complexes, thus testifying to the involvement of bimetallic processes in the studied ring-opening polymerization.



Scheme 1. Possible path for the ROP of β -BL in the presence of Cr-salphen.

Despite the similarity of the compared complexes in terms of electronic properties of the central metal, still there can be some difference in solution behavior of monomeric and dimeric complexes due to the distinct bulk structure (difference in molecular weight, dipole moment, number of functional centers per molecule, *etc.*). Thus, the solubility and aggregation tendency of these catalytic systems due to specific as well as van der Waals interactions between catalyst molecules can be distinct, which may be reflected in the catalytic activity, as was noticed for example in the experiments on copolymerization of propylene oxide and carbon dioxide [7]. In this respect, a comparison of the polymerization activity of two dinuclear systems, one bearing two active metal centers and the other bearing active and inactive metal centers, would be more reasonable.

Here we report on the synthesis and β -BL polymerization activity of a heterometallic Cr/Pd catalyst, which resembles structurally the previously reported bis-chromium salphen system, but possesses only one ROP-active center.

Results and Discussion

The previously described synthetic approach towards dinuclear salphen systems can be modified to afford heterodimetallic complexes (Scheme 2).

The resorcine-functionalized product **1** is a versatile precursor for modular design of di-salphen, where the length of the spacer and the nature of the metal centers can be easily varied. To afford the heterobimetallic systems, the alkylation of **1** with excess α,ω -dibromoalkanes has to be carried out first. For example, reaction with *ca.* 20 equivalents of 1,3-dibromopropane allowed to isolate 69% of the 3-bromopropyl-functionalized salphen **4** in 92% purity without chromatographic purification. The main impu-

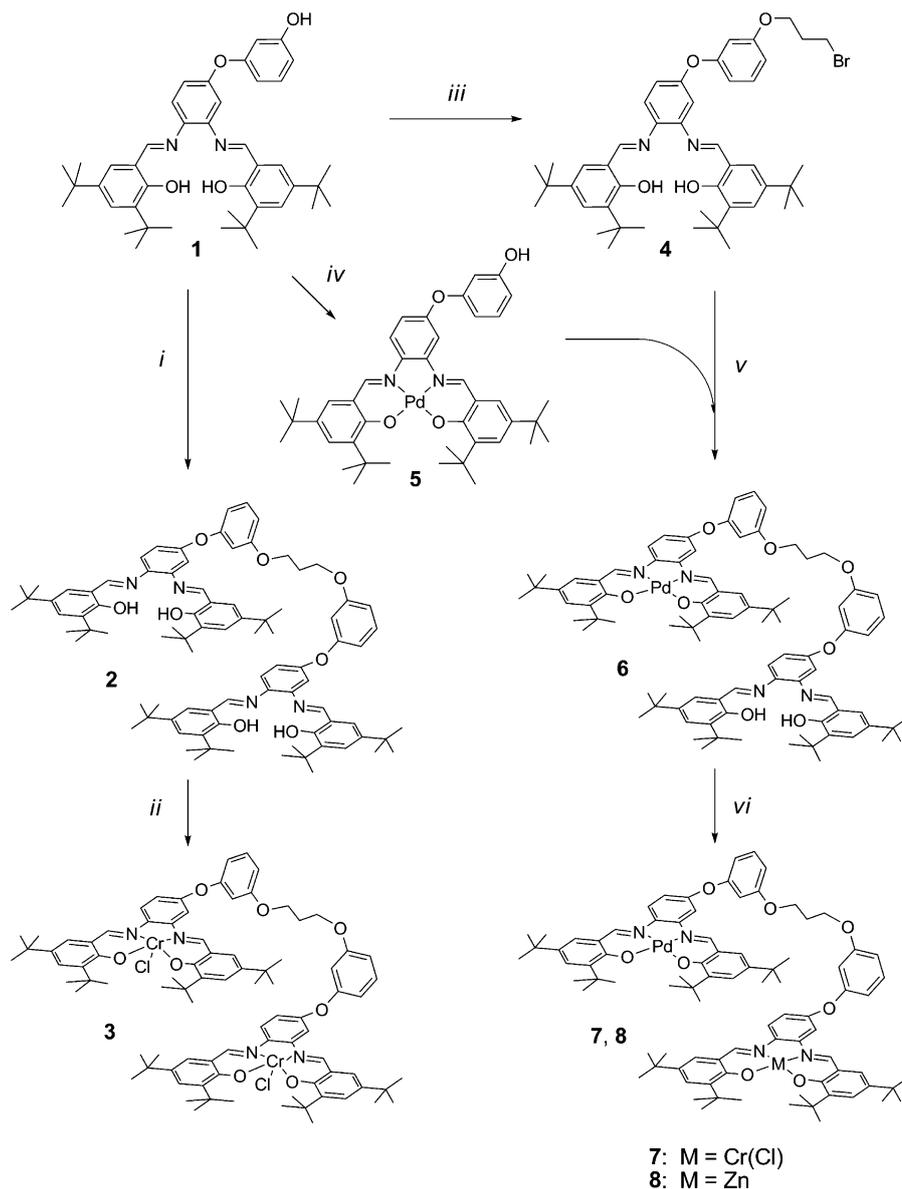
rity in this product was a dehydrobrominated derivative of **4**.

Compound **4** can be subsequently coupled with a metal complex of **1** possessing enough stability under the conditions of the coupling reaction. For example, the Zn complex proved to be unsuitable due to scrambling. That is, the signals of metal-free di-salphen molecules together with mono- and dimetalated species were detected by ESI mass spectral analysis of such a reaction mixture. This cannot be attributed to an artifact of the ESI measurement, since according to our experience a demetallation of Zn-salphen complexes is usually not observed under ESI conditions.

In contrast, palladium(II) forms a very stable complex with salphen **1**, which therefore can be applied in the coupling reaction. Furthermore, this complex is coordinatively saturated, which makes it inactive in catalysis. In this respect, the heteronuclear Cr/Pd species would be ideal for the comparison with the previously reported homodinuclear Cr-salphen species [6].

The reaction of equimolar amounts of **4** and **5** provided a di-salphen species **6** with one coordinated Pd ion. Simple precipitation of this compound from acetonitrile yielded the product in *ca.* 90% purity as estimated by ^1H NMR spectroscopy. High purity was achieved by column chromatography. The ^1H NMR spectrum of **6** represents a superposition of signals of **4** and **5** in the aromatic region as well as in the region of the *t*-Bu proton signals, indicating high conformational flexibility of **6** in CD_2Cl_2 solution (Fig. 1).

Representative is the disappearance of $-\text{OH}$ (resorcine) and of $-\text{CH}_2\text{-Br}$ resonances in the spectrum of **6**. This complex could be easily metallated further, as shown by its reactions with CrCl_2 or with $\text{Zn}(\text{OAc})_2$ to give the heterodinuclear complexes **7** and **8**, respectively. The first reaction was performed on a preparative scale, whereas the second one was only a quali-



Scheme 2. Synthesis of difunctional salphen ligands: *i* 0.5 equiv. 1,3-dibromopropane, Cs_2CO_3 in acetonitrile; *ii* CrCl_2 in THF, lutidine, air; *iii* 20 equiv. 1,3-dibromopropane, Cs_2CO_3 in acetonitrile; *iv* $\text{Pd}(\text{OAc})_2$, DMF; *v* Cs_2CO_3 in acetonitrile; *vi* CrCl_2 in THF, lutidine, air (**7**) or $\text{Zn}(\text{OAc})_2$ in DMF (**8**).

tative test. The recorded ESI-MS spectra of the complexes display neither signs of metal scrambling or substitution, nor of incompletely metallated products (Fig. 2).

We believe that salphen building units like **1** and **4** can also be utilized for grafting reactions as well as for the construction of various homogeneous and

heterogeneous multicomponent systems. Nevertheless, the main object pursued in the present work was to investigate the effect of heterodinuclear salphen complexes on the catalytic performance in the synthesis of PHB.

Thus, polymerization of β -BL in the presence of complexes **3** and **7** was compared under equal con-

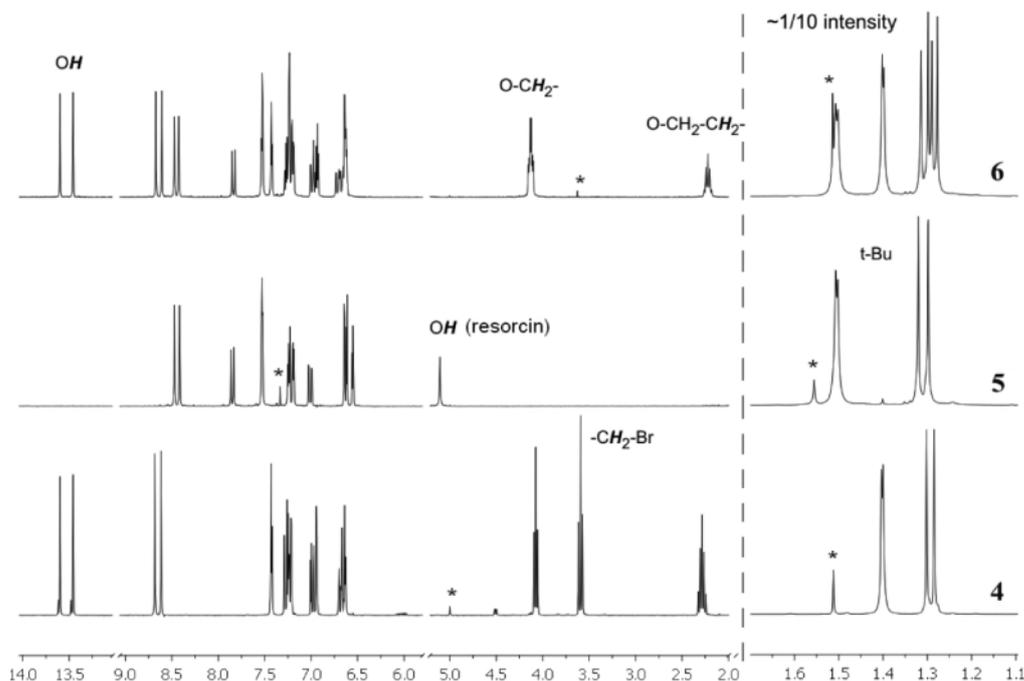


Fig. 1. Comparison of ^1H NMR spectra (CD_2Cl_2) of monomeric precursors **4** and **5** and their condensation product **6**. The spectra are cut for better visualization. Signals originating from solvent or impurities are marked with asterisks. In the spectrum of **4** the low-intensity low-field-shifted satellites of the signals of the inner OH groups are due to the marginal deuterium exchange.

ditions (100°C). In order to minimize an error in the results, the polymerization was performed simultaneously for both systems using the same lactone batch as well as the same heating device. The ratio of chromium centers to β -BL was also practically the same for both experiments (1 : 631 for **3** and 1 : 623 for **7**). The progress of the reaction was monitored by ^1H NMR measurements of aliquots, as shown in Fig. 3. The reaction seems to accelerate with time up to a certain time, after which a typical dependency for a zero order reaction for lactone is observed. The acceleration effect found for the reaction cannot be unambiguously ascribed yet. The plots of conversion *versus* reaction time can be very reliably approximated by polynomial functions of third order. This allows an easy determination of the reaction rate at any time of the reaction. The ratio of reaction rates for complexes **3** and **7** at β -BL conversions of 0%, 20% and 40% has been determined to be 1.88, 1.92 and 2.04, respectively.

Previously we have reported on β -BL polymerization with the dinuclear complex **3** at a Cr to β -BL

ratio of 1 to 1000 [6]. In the experiment with a ratio of 1 to 631, complex **3** afforded nearly twice the conversion than with a 1 : 1000 ratio to β -BL: The yields of PHB after 5 hours of reaction were 67% and 35%, respectively, which is in a good agreement with the expectations. However, the difference in activity (per chromium center) between complexes **3** and **7** is not that drastic as the difference between productivities of the di- and mononuclear chromium salphen described before [6].

It is doubtful that the palladium center in a salphen can participate in the cooperative polymerization mechanism. In this respect, the higher activity of the heterodinuclear Pd/Cr complex compared to the mononuclear Cr complex can rather be attributed to the presence of a covalently linked Pd-salphen unit which causes an enhanced intermolecular interaction between two Pd/Cr molecules, *e. g.* by π stacking (dimerization or even a higher degree of aggregation). Indeed, the planar Pd-salphen unit is unpolar and may have a tendency to aggregate in a polar solvent like β -BL. This would lead to an increased local concentration of Cr centers

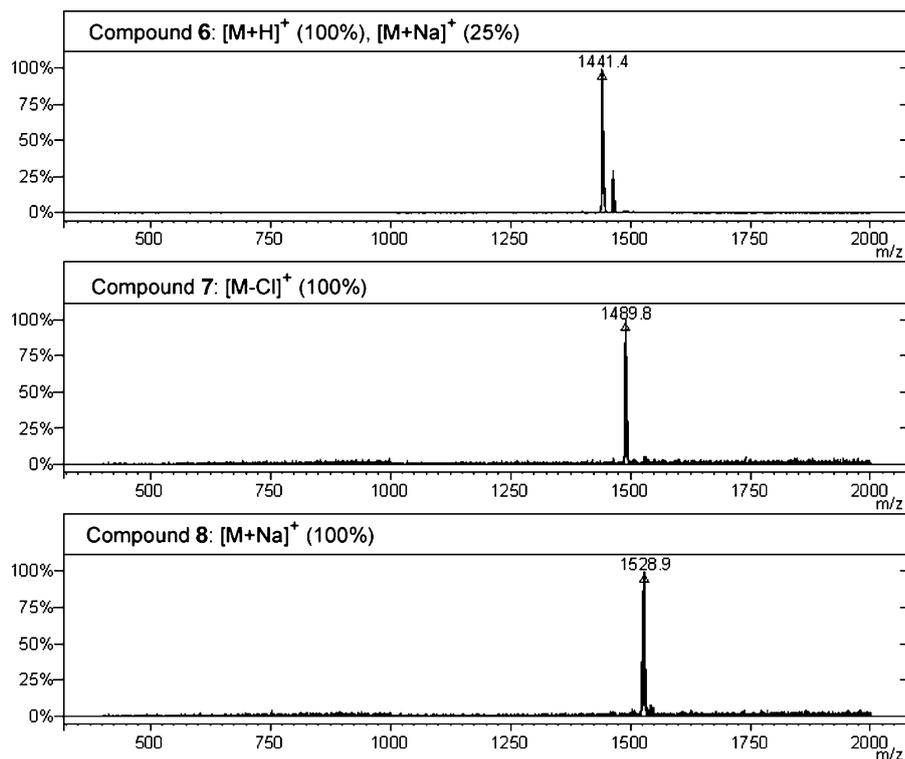


Fig. 2. ESI-MS spectra of **6**, **7** and **8**.

and explain a relatively high activity of the Pd/Cr complex. It is, however, interesting to note that the average molecular weights of polymers obtained with catalysts **3** and **7** at nearly the same conversion differ by approximately a factor of 2. That is, catalyst **3** gave

PHB with M_w of 24.5 kg mol^{-1} and a PDI of 2.2 at 36% conversion, whereas PHB obtained with **7** had M_w of 13 kg mol^{-1} and a PDI of 3.5 at 45% conversion. ^1H NMR analysis proved that PHB formed with **7** has a higher content of crotonic ester end groups compared to PHB obtained with **3**, which is a consequence of the thermal degradation of PHB due to a longer reaction time at 100°C [8]. Indeed, catalyst **7** requires nearly the double time to reach the same conversion of β -BL as compared to catalyst **3**, during which the degradation proceeds with the rate proportional to the polymer concentration.

In conclusion, by synthesizing heterodinuclear bis-salphens we have demonstrated the versatility of the earlier developed approach towards dinuclear salphen complexes. Comparison of two dinuclear species, namely one bearing Pd and Cr centers and another possessing two Cr centers, has been performed on the ground of their activity in the ring-opening polymerization of β -butyrolactone. The bis-chromium species was found to be more active than its Pd/Cr analog, thus once again underlining the role of a cooperative bimetallic mechanism in the studied reaction.

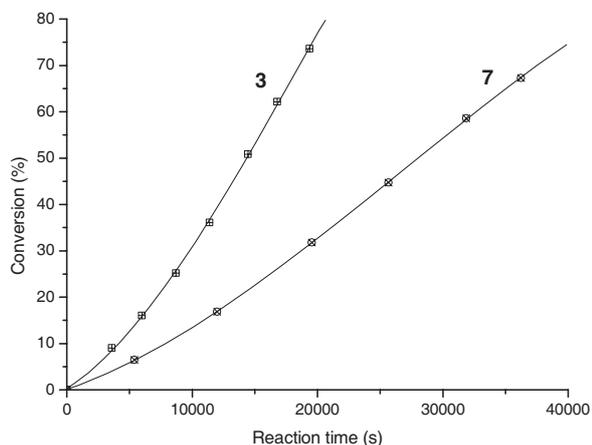


Fig. 3. Plots of conversion *versus* reaction time for catalysts **3** and **7** in ROP of β -BL.

Experimental Part

Starting materials and solvents were purchased from commercial sources and were used as received, unless mentioned otherwise. Bis-1,2-(3,5-bis-*tert*-butylsalicylaldimino)-4-(3-hydroxyphenoxy)-benzene **1**, the difunctional ligand **2** and its bis-chromium complex **3** were prepared as described previously [6].

Instrumentation

FT-NMR: Bruker ARX 300 MHz ^1H , 75 MHz ^{13}C . FT-IR: Bruker Vertex 70 with Bruker Platinum ATR-unit. ESI-MS: Varian LC-MS 500 (50–2000 Da). GPC: Varian GPC-50 (chloroform with 0.1% Bu_4NBF_4 , polystyrene narrow standard calibration, Varian Olexis column set 600 mm). Elemental analysis: EA Euro 3000 (Kehatech), Elementar Vario EL. EDX analysis: Tabletop SEM Hitachi TM 1000 equipped with Oxford Instruments detector.

Synthesis

Palladium complex of **1** (compound **5**)

150 mg (0.23 mmol) of **1** and 65 mg (0.29 mmol) of $\text{Pd}(\text{OAc})_2$ in 4 mL DMF were stirred at room temperature for 6 h. The product was precipitated by addition of water, centrifuged and passed through a short silica column with dichloromethane. Yield after drying 158 mg (90%). – ^1H NMR (CD_2Cl_2): δ = 1.30 (s, 9H), 1.32 (s, 9H), 1.50 (2s, 18H), 5.11 (s, 1H), 6.55 (t, 1H), 6.61–6.65 (dd, 2H), 6.99–7.03 (dd, 1H), 7.19–7.25 (m, 3H), 7.53 (m, 3H), 7.84 (d, 1H), 8.42 (s, 1H), 8.47 (s, 1H). – FT-IR (ATR): ν = 2951 s, 2904 m, 2866 m, 1578 s, 1546 vw, 1517 s, 1483 s, 1461 s, 1416 s, 1384 s, 1357 s, 1332 m, 1266 s, 1237 m, 1186 w, 1164 vs, 1128 vs, 1098 m, 1025 w, 986 m, 950 w, 933 m, 914 w, 887 w, 861 w, 840 m, 803 w, 784 m, 749 w, 682 m, 634 m, cm^{-1} . – MS ((+)-ESI; isopropanol): m/z (%) = 1528 (100), $[\text{2M}+\text{Na}]^+$, 775 (40), $[\text{M}+\text{Na}]^+$, 753 (20), $[\text{M}+\text{H}]^+$. – Analysis for $\text{C}_{42}\text{H}_{50}\text{N}_2\text{O}_4\text{Pd}$: calcd. C 66.97, H 6.69, N 3.72; found C 66.92, H 6.89, N 3.38.

Bis-1,2-(3,5-bis-*tert*-butylsalicylaldimino)-4-(3-(3-bromo-1-propyloxy)phenoxy)-benzene (**4**)

Compound **1** (1 g, 1.54 mmol) and Cs_2CO_3 (0.4 g, 1.2 mmol) in 10 mL acetonitrile were stirred at 60 °C for 30 min, followed by addition of 1,3-dibromopropane (6.2 g, 30.8 mmol). After 1 h the reaction mixture was cooled, water was added, and the mixture was vigorously stirred and centrifuged. The water phase was decanted, and the residue was washed with small portions of methanol, followed by re-precipitation from a minimal quantity of hot acetonitrile. Yield ca. 0.8 g (69%) of > 92% pure (^1H NMR) product. – ^1H NMR (CD_2Cl_2): δ = 1.28 (s, 9H), 1.30 (s, 9H), 1.40 (2s, 18H), 2.28 (p, 2H), 3.59 (t, 2H), 4.07 (t, 2H), 6.62–6.70 (m, 3H), 6.94–7.01 (m, 2H), 7.21–7.29 (m, 4H), 7.43 (t, 2H),

8.62 (s, 1H), 8.68 (s, 1H), 13.46 (s, 1H), 13.60 (s, 1H). – MS ((+)-ESI; isopropanol): m/z (%) = 790 (100), $[\text{M}+\text{Na}]^+$, 768 (10), $[\text{M}+\text{H}]^+$. – Analysis for $\text{C}_{45}\text{H}_{57}\text{BrN}_2\text{O}_4$: calcd. C 70.21, H 7.46, N 3.64; found C 70.47, H 7.57, N 3.77.

Mono-palladium complex **6** of the difunctional ligand **2**

100 mg (0.133 mmol) of complex **5**, 120 mg (ca. 0.143 mmol) of 92% pure compound **4** and 29 mg (0.089 mmol) Cs_2CO_3 were stirred at 80 °C in 2 mL acetonitrile for 2 h. The formed precipitate was separated by decantation, and 20 mg of **4** together with 20 mg of Cs_2CO_3 were added to the residual solution. This was heated with stirring for additional 3 h, followed by decantation of the formed precipitate. The precipitates were combined and re-precipitated from acetonitrile by heating up to 80 °C and cooling down, giving 130 mg of 90% pure (^1H NMR) compound **7**. All the residual solutions were also combined, evaporated to dryness and exposed to column chromatography on silica gel using a pentane / dichloromethane mixture with gradient. By this procedure additional 33 mg of relatively pure compound **6** was isolated. Finally, overall product **6** was chromatographed to give 126 mg (66%) of ^1H NMR-pure **6**. It has to be noticed that chromatography causes a partial irreversible adsorption / decomposition of the product on silica gel according to the residual coloring of the phase. – ^1H NMR (CD_2Cl_2): δ = 1.28–1.31 (4s, 36H), 1.40 (2s, 18H), 1.50 (2s, 18H), 2.22 (p, 2H), 4.10–4.15 (m, 4H), 6.62–6.74 (m, 6H), 6.92–7.01 (m, 3H), 7.18–7.29 (m, 7H), 7.43 (t, 2H), 7.52–7.54 (m, 3H), 7.83 (d, 1H), 8.43 (s, 1H), 8.47 (s, 1H), 8.61 (s, 1H), 8.67 (s, 1H), 13.46 (s, 1H), 13.60 (s, 1H). – FT-IR (ATR): ν = 2952 s, 2905 m, 2868 m, 1611 sh, 1579 s, 1518 s, 1483 s, 1467 s, 1439 m, 1417 s, 1387 m, 1360 s, 1331 w, 1268 s, 1250 m, 1166 vs, 1131 vs, 1100 w, 1058 w, 1026 w, 986 w, 932 w, 915 w, 858 m, 841 m, 805 w, 785 m, 772 m, 729 w, 684 m, 643 w, 635 w, cm^{-1} . – MS ((+)-ESI; isopropanol): m/z (%) = 1441 (100), $[\text{M}+\text{H}]^+$, 1463 (25), $[\text{M}+\text{Na}]^+$. – Analysis for $\text{C}_{87}\text{H}_{106}\text{N}_4\text{O}_8\text{Pd}$: calcd. C 72.45, H 7.41, N 3.88; found C 72.06, H 7.43, N 3.78.

Heterodinuclear palladium/chromium complex **7** of the dimeric ligand **2**

The complex was prepared by a quantitative reaction of **6** with CrCl_2 as described previously [6]. – FT-IR (ATR): ν = 2952 s, 2904 m, 2867 m, 1578 br. s, 1520 s, 1484 s, 1462 s, 1418 s, 1384 s, 1358 s, 1330 m, 1261 br. s, 1166 vs, 1130 vs, 1099 w, 1058 w, 998 w, 955 w, 931 w, 915 w, 841 s, 808 w, 784 s, 749 m, 684 m, 635 m, cm^{-1} . – MS ((+)-ESI; isopropanol): m/z (%) = 1490 (100), $[\text{M}-\text{Cl}]^+$. – EDX analysis for the Cr/Cl/Pd ratio: 1.00 : 0.99 : 1.06. – Analysis for $\text{C}_{87}\text{H}_{104}\text{N}_4\text{O}_8\text{ClCrPd}$: calcd. C 68.40, H 6.86, N 3.67; for $\text{C}_{87}\text{H}_{104}\text{N}_4\text{O}_8\text{ClCrPd}\cdot\text{H}_2\text{O}$: calcd. C 67.60, H 6.91, N 3.62;

for $C_{87}H_{104}N_4O_8ClCrPd \cdot THF$: calcd. C 68.32, H 7.06, N 3.50; found C 67.94, H 7.42, N 3.43.

Polymerization of β -butyrolactone

Two small baked out flasks equipped with magnetic stirrer were charged with 27.8 mg of **3** and 28.5 mg of **7**, respec-

tively. Purified β -butyrolactone (vacuum distillation from CaH_2) was added subsequently (2 mL for compound **3** and 1 mL for compound **7**), both flasks were tightly closed and immersed into the preheated oil bath (100 °C). During the course of the reaction, small aliquots were quickly taken for analysis. All manipulations were performed under air.

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