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Synthesis of Bis(phosphane) Palladium and Rhodium Complexes on a Polyethylene Oxide Grafted Polystyrene Matrix (TentaGel) and the Catalytic Behavior of the Rhodium Complexes

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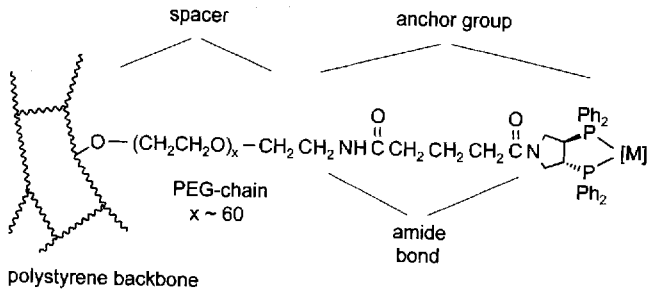
A new polymer-attached rhodium catalyst on a polyethylene oxide-grafted styrene matrix (TentaGel) is described. The corresponding anchor molecules were prepared by starting from different Boc-protected chiral pyrrolidinebis(phosphane)Pd complexes. The crystal structure of [3*R*,4*R*)-*N*-(4-carboxybutanoyl)-3,4-bis(diphenylphosphanyl)pyrrolidine-*P*,*P'*]-diiodopalladium (**1c**) was determined. The formation of an amide bond between TentaGel and anchor molecules resulted in polymer-bound Pd bisphosphane complexes. Decomplexation of the Pd with cyanide and reaction of the free polymeric ligand with $[Rh(COD)_2]BF_4$ led to the active hydrogenation catalyst. The influence of different solvents on the swelling volume and the catalytic behavior was tested. The polymer-bound rhodium complex [(3*R*,4*R*)-*N*-(1,5-dioxo-5-TentaGel-amino-pentyl)-3,4-bis(diphenylphosphanyl)pyrrolidine*P*,*P'*] (1,5-cyclooctadiene)rhodium tetrafluoroborate (**7**) has about the same catalytic activity and enantioselectivity as the homogeneous complex [(3*R*,4*R*)-*N*-(*tert*-butoxycarbonyl)-3,4-bis(diphenylphosphanyl)pyrrolidine-*P*,*P'*] (1,5-cyclooctadiene)rhodium tetrafluoroborate (**9**) in the same solvent mixture. It is possible to reuse **7** once, then it abruptly loses activity. This behavior remains to be clarified.

The main advantage of a homogeneous catalyst compared to a heterogeneous catalyst is its higher selectivity (in our case high *ee*). The main advantage of a heterogeneous catalyst is the simple separation of the catalyst from the product. Since the introduction of homogeneous rhodium phosphane complexes for enantioselective catalysis[1] many attempts have been made to immobilize chiral bis(phosphane) complexes on polymer matrices[2]. In these attempts many difficulties arose, which resulted in reduced activity, stability and selectivity of the polymer-bound catalyst. Often leaching effects are mentioned in the literature[3]. Stille[4] reported on some results on hydroxyethylacrylate polymers containing diphosphanes as ligand, which were useful catalysts. In this paper we describe the synthesis of chiral bis(phosphane)palladium and -rhodium complexes bound to a polymer matrix (TentaGel)[5]. With this catalyst we tried to combine the advantages of both homogeneous and heterogeneous catalysts.

The starting material TentaGel (**4**) is composed of crosslinked polystyrene beads (30% per weight) and polyethylene glycol chains of about 3000 Dalton grafted with one end onto the polystyrene. The other end carries a primary amino group. This results in a homogeneous distribution of about 0.2 mmol/g primary amino functions over the polymer. The PEG-PS beads are stable at pressures up to 200 bar. According to NMR investigations the mobility of the free PEG chain end in TentaGel is about the same as that of a PEG chain end in solution[5]. In all cases BET measurements of the dry polymers **4** and **5** showed only a very small surface. The dry polymers have no accessible pores. The polymer beads show high swelling factors in all solvents which dissolve PEG. The swollen beads are easily accessible to solute molecules. We suggest to call such systems "interphases". In our definition of interphases we mean penetration of a stationary (e.g. immobilized polymer phase) and a mobile phase (solvent) in molecular dimensions without formation of a homogeneous mixture[6].

Scheme 1. View of one tentacle of TentaGel with anchor group and metal complex



[M]: PdI_2 (**5**), ./. (**6**), $Rh(COD)BF_4$ (**7**)

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Scheme 2. Synthesis of coupling precursor molecules **1c–3c**

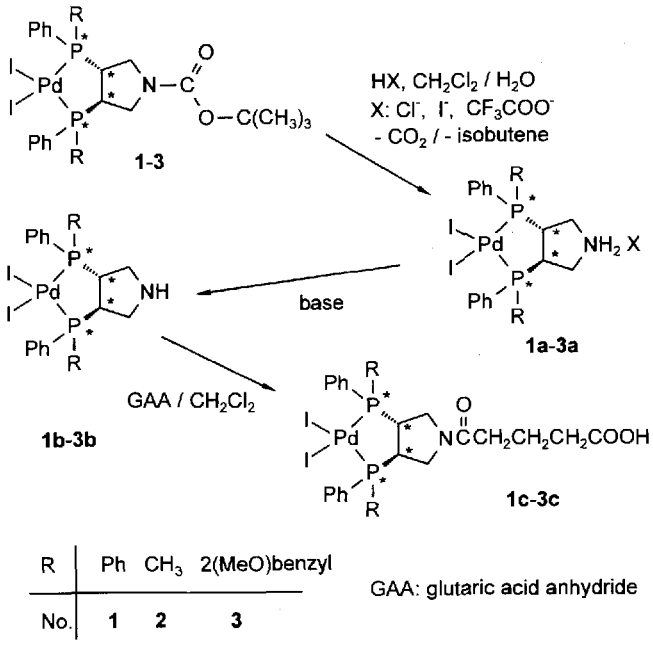
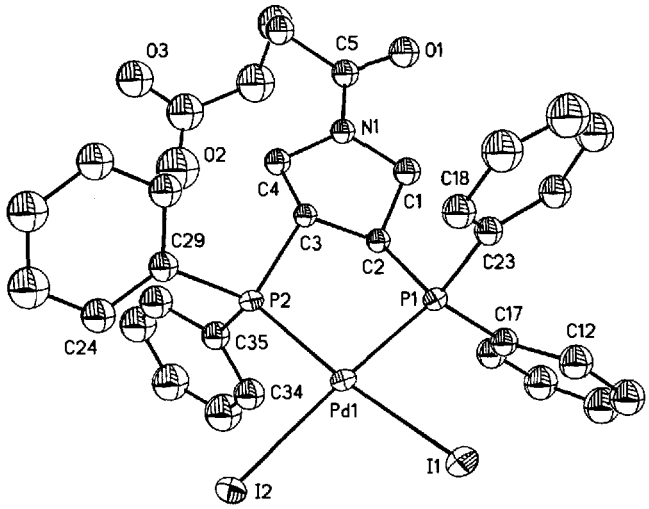


Figure 1. Molecular structure of **1c**. Selected data [pm, °]: Pd1–I1 263.1(1), Pd1–I2 263.4(1), Pd1–P1 227.3(3), Pd1–P2 227.6(3), P1–C2 186(1), P1–C17 177(1), P1–C23 118(1), P2–C3 184(1), P2–C29 185(2), P2–C35 179(1), C2–C3 155(2); P1–Pd1–P2 88.5(1), I1–Pd1–I2 93.0(1), I1–Pd1–P2 171.2(1), I2–Pd1–P1 170.2(1); P1–C2–C3–P2 –59(1)

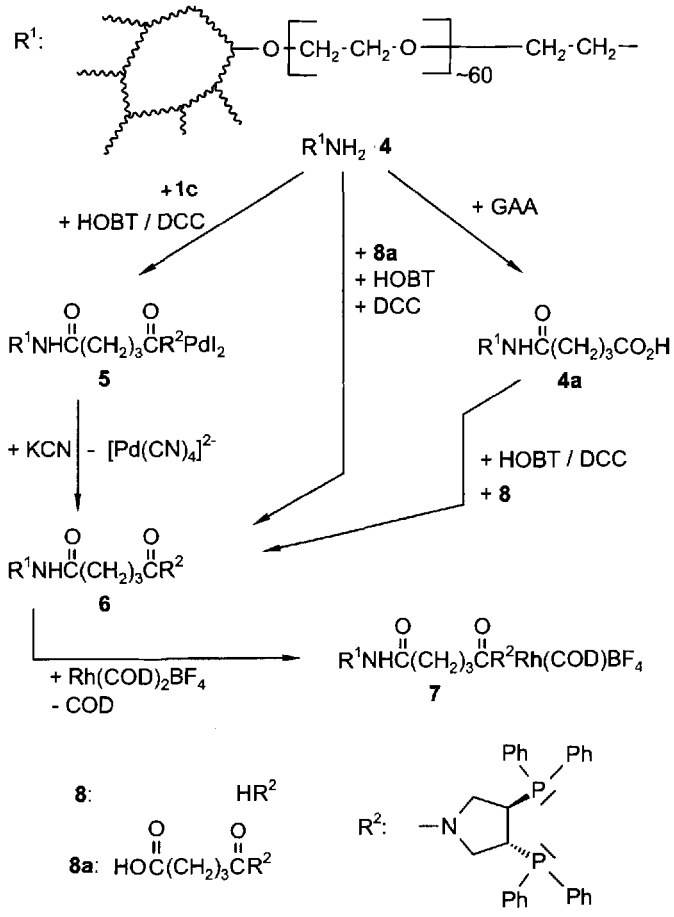


Synthesis

Chiral palladium complexes with a terminal carboxy group were synthesized according to Scheme 2 in high overall yield. Using ^{31}P-NMR spectroscopy we did not find any isomerization at the chiral phosphorus atoms or ligand exchange at the palladium atom, although we used strong acids such as HCl or CF_3COOH to cleave the Boc group from the palladium complexes. Cleaving with HCl proceeded slowly (two-phase system HCl/CH_2Cl_2) whereas the reaction with CF_3COOH was very fast at 0 °C. Cleavage of the methoxy groups from the aryl systems of **3** was not observed. In the case of HI as cleaving agent we obtained byproducts in yields up to 20%. The resulting salts **1a–3a** are poorly soluble in organic solvents. Treatment with bases in CH_2Cl_2/water led to the free amines **1b–3b**. Reaction with glutaric acid anhydride gave **1c–3c** in quantitative yield. Figure 1 shows the X-ray structure of **1c**. The complexes **1c–3c** are useful synthons for polymer-bound catalysts.

As indicated in Scheme 3 we applied three different routes to the preparation of the polymer-anchored catalyst. In path A the terminal amino group of the polymer TentaGel (**4**) is bound to the carboxy group of **1c** in a peptide-like coupling reaction[5]. We used 1-hydroxybenzotriazole (HOBT) and dicyclohexylcarbodiimide (DCC) as coupling agents. Cleavage of PdI_2 with potassium cyanide gave the polymer-bound ligand **6**, and reaction with $[Rh(COD)_2]BF_4$ led to the immobilized rhodium bis(phosphane) complex **7** which is used as enantioselective hydrogenation catalyst. In path B the uncomplexed carboxy bis(phosphane) **8a**[7] is coupled with TentaGel (**4**) to give **6** followed by treatment with $[Rh(COD)_2]BF_4$. In path C the carboxy-TentaGel **4a** is coupled with the secondary amino group of the bis(phosphane) **8**[7]. This reaction is slow and does not go to completion. All coupling steps were checked by the Kaiser test[8] to confirm that the reaction was complete.

Scheme 3. Three different synthetic routes to the polymeric catalyst **7**. HOBT: 1-hydroxybenzotriazole, DCC: dicyclohexylcarbodiimide, GAA: glutaric acid anhydride



Physical Behavior

We estimated the swelling volume of the TentaGel bis-(phosphane) palladium complex **5** with different solvents. Our results differ from the results of Bayer performed with the free resin[5]. The palladium complex **5** does not swell as readily as the free TentaGel in nearly all solvents we used. In the same solvents we carried out $^{31}P\{^1H\}$-NMR investigations (Table 1) of the swollen polymer-bound complex **5**. We determined the ratio of the integral of the ^{31}P-NMR signal of **5** to that of an external standard. Provided that the relaxation time of the ^{31}P signal is of the same order of magnitude in all solvents used, this ratio is a measure of the mobility of the P atoms. The $^{31}P\{^1H\}$-NMR data indicate the same order of solvents as in the swelling experiments.

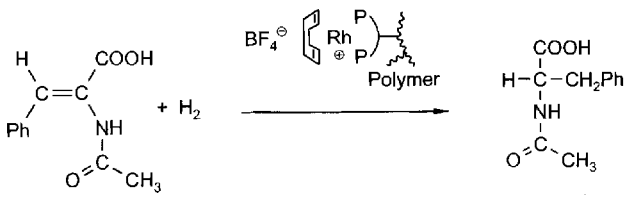
Table 1. $^{31}P\{^1H\}$-NMR integral data of the polymeric complex **5**. The complex was swollen in the solvent for 1 h and measured against an external standard. The integral relative to the standard was normalized on CH_2Cl_2 as 100%

Solvent	I standard	I peak	I_P/I_S	%	Scans	Temp.
acetonitrile	2.97	31.74	10.69	128	710	25°C
CH_2Cl_2	3.65	30.46	8.35	100	700	25°C
benzene/MeOH (1:1)	4.76	24.84	5.22	62	700	25°C
toluene/MeOH (1:1)	4.37	20.33	4.65	56	300	25°C
acetophenone	3.97	15.95	4.02	48	748	25°C
$CHCl_3$	8.30	32.58	3.93	47	708	-30°C
benzene	17.15	46.11	2.69	32	710	25°C
CH_2Cl_2	5.12	5.81	1.13	14	705	-30°C
DMF	7.51	0.91	0.12	1	709	25°C
MeOH	7.91	0	0	0	703	-30°C
acetone	8.76	0	0	0	741	-30°C
THF	7.62	0	0	0	703	-30°C
EtOH	6.50	0	0	0	705	-30°C
toluene	5.19	0	0	0	736	-30°C
Et_2O	5.17	0	0	0	703	-30°C
H_2O	26.23	0	0	0	711	-30°C
toluene/MeOH (1:1)	5.46	0	0	0	709	-30°C

We obtained the best swelling of the polymer palladium complex **5** and the highest mobility of the phosphorus atoms in halogenated solvents like CH_2Cl_2 and $CHCl_3$ or in dipolar aprotic solvents (DMF, acetonitrile). These solvents are not optimal for catalytic hydrogenation. With alcohols, the optimal solvents for enantioselective hydrogenation, the solvation of the Pd complexes is not very effective. However, mixtures of toluene and methanol show a good solvation of the Pd complex **5**. One may speculate that toluene solvates the polystyrene part of the polymer and methanol the polyoxyethylene part.

In this context it should be mentioned that the chemical and kinetic behavior of polystyrene-PEG beads also depends on the chain length of PEG[9]. Moreover, the mobility of the polymers depends on the temperature. The sharp $^{31}P\{^1H\}$-NMR signal of the toluene/methanol mixture at 25°C becomes very broad (not detectable) at −30°C; at this temperature the polymer is not swollen. ^{31}P-NMR CP/MAS measurements of the unswollen ligand-containing polymers showed nearly the same chemical shifts as the unimmobilized complexes or ligands.

Scheme 4. Catalytic hydrogenation reaction with polymeric rhodium complex



Catalysis

We compared the homogeneous catalyst [(3*R*,4*R*)-*N*-(*tert*-butoxycarbonyl)-3,4-bis(diphenylphosphanyl)pyrrolidine-*P*,*P*'] (1,5-cyclooctadiene)rhodium tetrafluoroborate (**9**)[7] and the analogous polymer-fixed rhodium complex **7**. As standard substrate α-(acetylamino)cinnamic acid (AAZ) was used. An autoclave was used as batch reactor. The autoclave was shaken with constant speed. Rapid stirring should be avoided, because stirring causes mechanical breakdown of the polymer particles. For evaluation of the kinetic date we used the interpretation by Halpern[10] and Brown[11]. Table 2 compiles the results of the hydrogenation experiments.

Table 2. Hydrogenation results. Reaction temperature 25°C, catalyst content 10 μmol, molar substrate-to-catalyst. If not stated otherwise, the reaction mixture was shaken, the turnover numbers are given after 50% substrate consumption. AAZ: α-(acetylamino)-cinnamic acid

Nr.	catalyst	substrate	sub./cat.	solvent	p [bar]	t [min]	TO [1/s]	ee [%]
1	TentaGel	-	-	50 ml MeOH	8	-	-	-
2	TentaGel	AAZ	-	50 ml MeOH	8	-	-	-
3	5	AAZ	600	25 ml MeOH	8	>2000	-	-
4[a]	9	AAZ	600	25 ml MeOH	8	170	0.075	96.6 S
5	9	AAZ	500	25 ml MeOH	8	110	0.088	96.6 S
6	9	AAZ	600	25 ml MeOH	8	150	0.090	96.5 S
7	7	AAZ	600	25 ml MeOH	8	>2000	-	-
8	7 + $AgBF_4$	AAZ	600	25 ml MeOH	8	>2000	-	-
9	7	AAZ	200	25 ml MeOH	8	>2000	-[b]	-
10	7	AAZ	200	25 ml MeOH + 4% benzene	8	>2000	-	-
11	7	AAZ	200	25 ml EtOH	8	1440	< 0.005	89.6 S
12[c]	7	AAZ	200	25 ml EtOH	8	>2000	-	-
13	7	AAZ	200	25 ml benzene :MeOH = 1:1	8	200	0.033	96.1 S
14[c]	7	AAZ	100	25 ml benzene :MeOH = 1:1	8	110	0.023	97.2 S
15[d]	7	AAZ	100	25 ml benzene :MeOH = 1:1	8	>2000	-	-
16	9	AAZ	500	25 ml benzene : MeOH = 1:1	8	360	0.042	97.4 S

[a] Solution was stirred. – [b] 0.5 mmol turnover after 4 d. – [c] Catalyst reused first time. – [d] Catalyst reused second time.

The first three entries demonstrate that neither the palladium species **5** nor TentaGel are catalytically active (No. 1, 2, 3). With the homogeneous reference catalyst **9**, stirred solutions (No. 4) react about as fast as shaked ones (No. 5,

6). Hydrogenation attempts in methanol with a low amount of the polymer catalyst **7** gave no measurable reaction (No. 7), even if $AgBF_4$ (No. 8) was added[12]. With an increased catalyst-to-substrate ratio a trace of product was detected after a reaction time of four days (No. 9). Also the addition of a small amount of benzene did not lead to better results (No. 10). If ethanol was used as solvent, a slow hydrogenation of AAZ was observed. After the reaction was finished, the *ee* of the product was only 89%. An attempt to reuse the catalyst failed (No. 12), the catalytic activity was too low. The use of a mixture of benzene/methanol (1:1) gave good results (No. 13). The polymeric catalyst **7** afforded two turnovers per minute and 96% *ee*. The homogeneous catalyst **9** furnished comparable results in the same solvent mixture (No. 16). When the polymer-bound catalyst **7** was reused after one hydrogenation sequence, the activity of the catalyst **7** was reduced slightly while the *ee* of the product remained constant (No. 13, 14). An attempt to reuse the catalyst again failed (No. 15). The loss in activity after the first reuse has not yet been clarified. With AAS there is no Rh detectable in the product solution from the reactor. According to ^{31}P-CP/MAS NMR measurements the catalyst **7** contained uncoordinated phosphane before hydrogenation. After the hydrogenations the signal of uncoordinated phosphane had disappeared. The NMR spectrum of the polymer exhibits broad signals. We cannot decide, if phosphane oxide has formed or if chelation with Rh has occurred.

We could demonstrate that Rh complexes on TentaGel polymers are catalytically equally active and selective as in homogeneous solution. But the type of the polymer restricts the range of usable solvents. We are now attempting to extend the range of solvents to be used and to enhance the life span of the catalyst.

We are grateful to the *Deutsche Forschungsgemeinschaft* and the *Fonds der Chemischen Industrie* for financial support, to *Rapp Polymere* for a sample of TentaGel.

Experimental

Elementary analyses: Carlo Erba, Modell 1106 with IBM-PC and Software Eager 1.1. – MS: Finnigan TSQ 70 (nitrobenzyl alcohol, 70 eV, 30°C, FAB), Finnigan MAT 711A (CH_2Cl_2, Ion-source temp. 35°C, heater 0–50 mA, voltage 2 kV, acceleration voltage 8 kV, FD). – IR: Bruker IFS 48 with computer Aspekt 1000. – ^{1}H NMR: Bruker AC 250 and Bruker WM 400 (250.13 and 400.13 MHz), internal standard TMS. – ^{13}C{^{1}H} NMR: Bruker AC 250 and Bruker WM 400, internal standard TMS. – ^{31}P{^{1}H} NMR: Bruker WP 80, Bruker AC 80 and Bruker DRX 250 (32.39, 32.44, und 101.25 MHz); measurements at 25°C: external standard 85% H_3PO_4 in D_2O, measurements at −30°C: external standard 1% H_3PO_4 in acetone; a polymeric sample was swollen for one hour before each NMR measurement, and subsequently all solvent was evaporated during 1 h. – Solid-state NMR: Bruker MSL 200, wide-bore magnet (4.7 T) or Bruker AMX 300, wide-bore magnet (7.05 T), magic-angle spinning (MAS) at a rotational frequency of 4 KHz at 297 K; frequencies and standards: ^{31}P, 81 or 121.49 MHz ($NH_4H_2PO_4$), ^{13}C, 50.325 MHz [TMS, signal of the carbonyl group of glycine (δ = 170.09) as second standard]. – GC: Chrompack, model 438 A, FID (250°C), Permabond L-Chirasil Val® (50 m, 0.25 mm i.d., Macherey-Nagel) 175°C isotherm, 1.4 bar H_2 pressure, split injector 250°C, integration software Fa. Kontron, Data System 450-MT2, V1.02. – BET isotherms: Gemini 2370, Micromeritics GmbH.

Ultrahigh purity grade hydrogen (Messer Griesheim) was used without further purification. All solvents were dried by standard methods, purified by distillation and kept under argon. All manipulations were carried out under dry argon with standard Schlenk technique. $[Rh(COD)_2]BF_4$[13], [(3*R*,4*R*)-*N*-(*tert*-butoxycarbonyl)-3,4-bis(diphenylphosphanyl)pyrrolidine-*P*,*P*']diiodopalladium (**1**)[14], [(P*R*,3*R*,4*R*,P'*S*)-*N*-(*tert*-butoxycarbonyl)-3,4-bis(methylphenylphosphanyl)pyrrolidine-*P*,*P*']diiodopalladium (**2**)[15], [(P*S*,3*R*,4*R*,P'*S*)-*N*-(*tert*-butoxycarbonyl)-3,4-bis[(2-methoxybenzyl)phenylphosphanyl]pyrrolidine-*P*,*P*']diiodopalladium (**3**)[16], (3*R*,4*R*)-3,4-bis(diphenylphosphanyl)pyrrolidine hydrochloride (**8**)[7], (3*R*,4*R*)-3,4-bis(diphenylphosphanyl)-*N*-(4-carboxybutanoyl)pyrrolidine (**8a**)[7], [(3*R*,4*R*)-*N*-(*tert*-butoxycarbonyl)-3,4-bis(diphenylphosphanyl)pyrrolidine-*P*,*P*'] (1,5-cyclooctadiene)rhodium tetrafluoroborate (**9**)[7] were prepared by literature methods. TentaGel (**4**) was a gift from Rapp Polymers[5]. Iodide was titrated with potassium thiosulfate[17]. All coupling reactions were checked with the ninhydrine test (Kaiser test)[8]. Palladium or rhodium samples did not interfere with the test.

Determination of Free Amino Groups: 1051 mg of dry TentaGel was treated with 10 ml of 1 N HCl. After the mixture had been kept overnight, the polymer was filtered off and dried until the mass remained constant (2 d). Then 10 ml of 0.5 N NaOH was added, and the polymer was shaken for several hours, filtered off and washed with water. The filtrate and the washing were combined in a measuring flask, and the chloride was titrated[18]. We found 0.12 mmol of amino groups.

Hydrogenations: We used stainless steel reactors with temperature and pressure control. The temperature and pressure data were continuously monitored by a PC. Mixing of the solution with hydrogen was performed by magnetic stirring or mechanical agitation as indicated in Table 2. The polymer catalyst was placed in the autoclave by using Schlenck technique. After the autoclave had been closed, it was evacuated, and the substrate solution was introduced. Then the vessel was pressurized with hydrogen. For all hydrogenations we determined the turnover of the catalyst, depending on reaction time and substrate consumption. The turnover values compiled in Table 2 refer to 50% substrate conversion. These values are not very much below the maximum. After the reaction was finished, the solution was forced out by means of a steel capillary by using excess hydrogen pressure. The polymeric catalyst was retained by a filter in the lid of the autoclave and could be reused after refilling of the autoclave. The solvent was removed, the residue dissolved in 25 ml of methanol, and to the solution 25 ml of a mixture of 1.4 ml of acetyl chloride and 100 ml of methanol was added. After stirring of the mixture overnight, all solvents were removed, and the yellow oil was taken up in ethyl acetate. This solution was passed through a short silica gel column (eluent: *tert*-butyl methyl ether). The obtained colorless eluate after dilution was directly used for GC analysis.

Palladium Complexes **1c–3c**

Boc Deprotection with HCl or HI: The Boc-protected complex (**1–3**) was dissolved in CH_2Cl_2, the solution cooled to 0°C and treated with concd. acid (HCl, HI). A precipitate formed. After stirring for 12 h, all solvents were removed and $CH_2Cl_2/H_2O/K_2CO_3$ was added to the residue. The mixture was stirred until all solid had dissolved. The CH_2Cl_2 phase was filtered through $MgSO_4$, which was washed three times with CH_2Cl_2. The combined filtrate and washings were concentrated to half the volume, then glutaric acid anhydride (1 to 5-fold excess) was added and the solution stirred overnight. After washing with water, the CH_2Cl_2 phase was filtered again through

$MgSO_4$. Addition of diethyl ether to the CH_2Cl_2 phase yielded yellow crystals which were separated by filtration.

Deprotection of Boc with CF_3COOH: Trifluoroacetic acid was cooled to 0°C, the palladium complex (**1**–**3**) was added, and the red-orange solution was stirred for 30 min. The solvent was removed, and the red-brown residue was stirred in a $H_2O/CH_2Cl_2/K_2CO_3$ mixture for 10 min. The CH_2Cl_2 phase was separated and filtered through $MgSO_4$. Evaporation of the solvent from the filtrate gave a yellow-orange powder in quantitative yield, which was dissolved in CH_2Cl_2. The solution was treated with glutaric acid anhydride as above.

[(3R,4R)-N-(4-Carboxybutanoyl)-3,4-bis(diphenylphosphanyl)pyrrolidine-P,P']diiodopalladium (**1c**): *Compound* **1a** (HI salt): 5.063 g (5.62 mmol) of **1** and 10 ml of HI (75 mmol) were allowed to react as described above. – IR (THF): $\tilde{\nu}$ = 1435 cm^{-1} (P-phenyl). – ^{31}P NMR (CH_2Cl_2): δ = 27.0 (s).

1a (HCl salt): 1.632 g (1.81 mmol) of **1** and 5 ml of 12 N HCl were allowed to react as described above. – IR (THF): $\tilde{\nu}$ = 1435 cm^{-1} (P-phenyl). – ^{31}P NMR (methanol/CH_2Cl_2): δ = 31.2 (s). – MS (FD), *m/z* (%): 837 (10) [M^+], 798 (100) [M^+ – HCl], 673 (15) [M^+ – HCl – I]. Very poorly soluble in CH_2Cl_2, acetone, water; soluble in methanol. – $C_{28}H_{28}ClI_2NP_2Pd$ (836.2): calcd. C 40.22, H 3.38, Cl 4.24, N 1.68; found C 40.79, H 3.45, Cl 4.46, N 1.68.

1b [from **1a** (HI salt)]: – ^{31}P NMR (CH_2Cl_2): δ = 24.8 (s). – ^{31}P NMR (acetone): δ = 26.1 (s).

1c: 3.2 g (28.1 mmol) of glutaric acid anhydride and **1b** were allowed to react as described above; yield: 4.1 g (80%, based on **1**); red crystals. Slightly soluble in diethyl ether, ethanol, better in CH_2Cl_2, acetone, 1,2-dichloroethane, $CHCl_3$. Some by-products were found in the mother liquor of the diethyl ether precipitate. – TLC: SiO_2/Al, (CH_2Cl_2/methanol, 10:1), R_f = 0.28. – IR (THF): $\tilde{\nu}$ = 1730 cm^{-1} (COOH), 1643 (CO-amide), 1434 (P-phenyl). – ^1H NMR ([D_6]DMSO): δ = 7.5–7.9 (m, 20H, Ph), 2.9–3.6 (m, 6H, pyr.), 1.5–2.1 (m, 6H, glutaryl). – ^1H NMR ($CDCl_3$): δ = 7.4–7.9 (m, 20H, Ph), 3.7 (m, 1H, pyr.), 3.5 (m, 1H, pyr.), 2.6–3.2 (m, 4H, pyr.), 2.2 (t, 2H, $^3J_{HH}$ = 6.8 Hz, CH_2CH_2COOH), 1.9–2.1 (m, 2H, CH_2CH_2COOH), 1.7 (t, 2H, $^3J_{HH}$ = 7 Hz, $CH_2CH_2CH_2COOH$). – ^{13}C CP/MAS NMR (ν_{Rot} = 3.2 kHz): δ = 172.8, (s, 2 CO), 129.1 (s, Ph), 43.5 (s, N–C-pyr. and P–C-pyr.), 33.2 [s, CCO(O)N and *C*COOH], 20.2 (s, $CH_2CH_2CH_2$). – $^{13}C\{^1H\}$ NMR ([D_6]DMSO): δ = 174.2 (s, COOH), 170.7 (s, CON), [136.5 (s), 131.9–133.3 (m), 128.4–128.9 (m), 125.3 (m) (Ph)], 42.8–45.7 (m, N–C-pyr.), 38.4–38.9 (m, P–C-pyr.), 32.8 (s, *C*COOH), 32.2 (s, *C*CON), 19.5 (s, CH_2CHCH_2). – ^{31}P CP/MAS NMR (ν_{Rot} = 3.225 kHz): δ = 38.5 (s, 31.3 Hz line broadening). – ^{31}P NMR ($CHCl_3$): δ_1 = 31.4, δ_2 = 30.8, (AB, $^3J_{PP}$ = 19.8 Hz). – ^{31}P NMR (CH_2Cl_2): 30.5 (s). – MS (FD), *m/z* (%): 914.9 (10) [M^+ + 1], 1699.1 (100) [2 M – I]$^+$, 798.6 (100) [M^+ – glutaryl]. – MS (FAB); *m/z* (%): 912.8 [M^+ – 1], 786 [M^+ – I], 659.1 [M^+ – 2 I]. – $C_{33}H_{33}I_2NO_3P_2Pd$ (913.4): calcd. C 43.38, H 3.64, I 27.78, N 1.53; found C 43.14, H 3.76, I 27.94, N 1.55.

[(PR,3R,4R,P'S)-N-(4-Carboxybutanoyl)-3,4-bis(methylphenylphosphanyl)pyrrolidine-P,P']diiodopalladium (**2c**): *Compound* **2a**: 402 mg (0.596 mmol) of **2** and 20 ml of a HI solution (57%) were allowed to react as described above. The resulting salt **2a** is poorly soluble in organic solvents. – ^1H NMR ([D_7]DMF): δ = 7.6–8.0 (m, 10H, Ph), 4.0–2.9 (m, 6H, pyr.), 2.3–1.6 (m, 6H, glutaryl). – ^{31}P NMR (CH_2Cl_2): δ_1 = 27.7, δ_2 = 22.6, (AB-1, $^3J_{PP}$ = 27.4 Hz), δ_1 = 27.5, δ_2 = 23.1 (AB-2, $^3J_{PP}$ = 27.4 Hz). – MS (FAB), *m/z* (%): 675.3 (5) [M^+ – I], 547.9 (10) [M^+ – 2 I], 460.4 (25) [M^+ – 3 I].

2b: From **2a** as described above; amine **2b** is only poorly soluble. – ^{31}P NMR (acetone): δ = 25.9–27.7 (br. m), 29.7–31.2 (br. m). – ^{31}P NMR (CH_2Cl_2): δ_1 = 28.1, δ_2 = 23.0 (AB, $^3J_{PP}$ = 27.4 Hz). – MS (FD), *m/z* (%): 675.1 (30) [M^+], 547.9 (70) [M^+ – I].

2c: From **2b** and 340 mg (2.98 mmol) of glutaric acid anhydride, yield 470 mg (100%). – ^1H NMR ([D_6]acetone): δ = 8.1–7.5 (m, 10H, Ph), 4.0–2.8 (m, 6H, pyr.), 2.2–2.0 (m, 4H, glutaryl), 1.76–1.70 (m, 2H, glutaryl). – ^{31}P NMR (CH_2Cl_2): δ_1 = 27.2, δ_2 = 21.7 (AB-1, $^3J_{PP}$ = 27.4 Hz), δ_1 = 26.9, δ_2 = 22.9 (AB-2, $^3J_{PP}$ = 27.4 Hz). – MS (FAB), *m/z* (%): 677.9 (90) [M^+ – glutaryl], 663.9 (90) [M^+ – I].

{(PS,3R,4R,P'S)-N-(4-Carboxybutanoyl)-3,4-bis[(2-methoxybenzyl)phenylphosphanyl]pyrrolidine-P,P'}diiodopalladium (**3c**): *Compound* **3a** (CF_3COOH salt): From 200 mg (0.202 mmol) of **3** and 5 ml of CF_3COOH as described above. – IR (KBr): $\tilde{\nu}$ = 1423 cm^{-1} (P-phenyl), 1263 (OMe). – ^{31}P NMR (CF_3COOH): δ = 31.6 (s). – ^1H NMR ($CDCl_3$): δ = 11.06 (s, 1H, COOH), 8.2 (d, 2H, benzyl), 6.9–7.6 (m, 16H, P-phenyl, benzyl), 4.5–2.6 (m, 4H, pyr.), 3.8 (s, 6H, OMe).

3b: 0.1 g (0.1 mmol) of **3** was allowed to react with HCl for 4 d as described above. Treatment with Na_2CO_3 afforded **3b**, yield 89 mg (100%); or from **3a** (CF_3COOH salt) in quantitative yield. – IR (KBr): $\tilde{\nu}$ = 1434 cm^{-1} (P-phenyl), 1243 (OMe). – ^1H NMR ([D_6]acetone): δ = 8.3–8.4 (m, 2H, benzyl), 6.7–7.3 (m, 16H, benzyl, P-phenyl), 4.0–4.5 (m, 4H, CH_2-benzyl), 3.7 (s, 6H, OMe), 3.6–1.5 (m, 6H, pyr.). – ^{31}P NMR (CH_2Cl_2): 30.6 (s). – MS (FD), *m/z* (%): 887.9 (5) [M^+], 760.1 (40) [M^+ – I], 632.2 (5) [M^+ – 2 I].

3c: From **3b** and 50 mg (0.438 mmol) of glutaric acid anhydride. – ^1H NMR ([D_6]DMSO): δ = 8.2 (br. s, 2H, benzyl), 7.7–7.2 (m, 16H, benzyl, P-phenyl), 4.5–3.7 (m, 16H, CH_2-benzyl, OMe, pyr.), 2.5–1.2 (m, 6H, glutaryl). – ^1H NMR ([D_6]acetone): δ = 8.42 (pseudo t, 2H, benzyl), 7.0–7.5 (m, 16H, benzyl, P-phenyl), 4.6–4.2, (m, 4H, pyr.), 3.8 (s, 3H, OMe), 3.7 (s, 3H, OMe), 2.8–2.5 (m, 2H, pyr.), 2.3 (t, 2H, $^3J_{HH}$ = 7.3 Hz, glutaryl), 2.0 (p, 2H, $^3J_{HH}$ = 7.3 Hz, glutaryl), 1.8 (t, 2H, $^3J_{HH}$ = 7.2 Hz, glutaryl). – $^{13}C\{^1H\}$ NMR ([D_6]acetone): δ = 174.2 (s, CON), 158.7 (s, COOH), [135.2 (d, J_{PC} = 10 Hz), 133.0 (s), 130.4 (s), 129.5 (d, J_{PC} = 10. Hz), 129.3 (s), 121.8 (s), 112.2 (s), 112.3 (s, aryl-C)], 55.9 (s, OMe), 55.7 (s, OMe), 46.5–44.7 (m, C-pyr.), 33.2 (s, CH_2CON), 33.1 (s, CH_2COOH), 26.7 (m, PCH_2), 20.4 (s, $CH_2CH_2CH_2$). – ^{31}P NMR (CH_2Cl_2): δ_1 = 38.9, δ_2 = 38.0, (AB, $^3J_{PP}$ = 32 Hz). – MS (FD), *m/z* (%): 873.8 (70) [M^+ – I, 758.5 (100) [M^+ – I – glutaryl].

Immobilisation of Catalysts

1c *on TentaGel* (**5**): A solution of 135 mg (1 mmol) of 1-hydroxybenzotriazole (HOBT) in 10 ml of DMF, 908 mg (0.99 mmol) of **1c** and a solution of 206 mg (1 mmol) of dicyclohexylcarbodiimide (DCC) in 5 ml of DMF was stirred for 15 min at 40°C and then for 45 min at 22°C. Subsequently, the solution was cooled to 0°C. After 15 min the solution was filtered to remove the urea. To the clear solution 1 g of TentaGel (0.2 mmol/g NH_2 groups) was added, and the mixture was shaken for several hours until the Kaiser test was negative (2–6 h). After filtration, washing three times with 10 ml of DMF, 10 ml of toluene, and 10 ml of Et_2O each the crude product was dried. Yield 1110 mg. – IR (KBr): $\tilde{\nu}$ = 3025–2922 cm^{-1} (br., polystyrene matrix), 1653 (st., CO-amide), 1489–1242 (br., polystyrene matrix), 1105 (br., C–O–C). – ^1H NMR (C_6D_6): δ = 7.69–7.15 (m, P-phenyl and phenyl), 3.4 (s, PEG chain), 2.9 (s, glutaryl), 1.5–2.5 (m, glutaryl and CH_2CH-polystyrene matrix). – $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 174.2 (s, CON-pyr.), 170.3 (s, CON-TentaGel), [136.5 (s), 132.4 (s), 131.0 (s), 128.3 (m) (P-phenyl)], 120–127, (m, polystyrene and C_6D_6), 70.9 (s, PEG), 40.0–45.9 (m, P–C-pyr.), 38.4 (m, N–C-pyr.), 34.0 (s, *C*CON-TentaGel), 32.3 (s, *C*CON-pyr.), 19.82 (s, $CH_2CH_2CH_2$). – ^{13}C CP/MAS NMR (ν_{Rot} = 3.36 kHz): δ = 170.9 (s, 2 CO), 145.4 (s, P-phenyl), 128.0 (s, polystyrene), 71.0 (s, PEG); 39.8 (s, glutaryl). – ^{31}P NMR (C_6H_6): δ = 29.7 (s). – ^{31}P CP/MAS (ν_{Rot} = 3.394 (kHz): δ = 31.4 (s).

(3R,4R)-N-[1,5-Dioxo-5-(TentaGel-N-)pentyl]-3,4-bis(diphenylphosphanyl)pyrrolidine (**6**): *Method A:* 380 mg (0.065 mmol) of palladium complex **5** was treated with a solution of 25.3 mg (0.39 mmol) of KCN in 50 ml of water. The suspension was shaken for 12 h. The polymer was filtered off and washed three times with 20 ml of water. Shaking of the polymer three times for 30 min with water afforded the crude product. The last washing was tested with $AgNO_3$ for absence of CN^-. The crude product was washed with THF and diethyl ether and dried until the weight remained constant. The nearly white polymer contained some red beads which were detectable under a microscope. Yield nearly quantitative. – IR (KBr): $\tilde{\nu}$ = 2880 cm^{-1} (br., polystyrene matrix), 1669, 1653 (m, CO-amide), 1494 (br., polystyrene matrix), 1103 (br., C–O–C). – ^1H NMR (C_6D_6: δ = 6.9–7.6 (m, P-phenyl and polystyrene), 3.5 (s, PEG), 2.8 (s, glutaryl), 2.2 (s, glutaryl and CH_2-polystyrene matrix), 1.7 (s, CH-polystyrene matrix and glutaryl signals). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 172.6 (s, CON-TentaGel), 171.0 (s, CON-pyr.); 135.9–135.5 (m, P-phenyl), 133.6–133.4 (m, P-phenyl), 129.5–128.7 (m, P-phenyl and Ph-polystyrene matrix), 70.6 (s, PEG), 69.8 [s, PEG–O–CH_2–CH_2–NC(O)], 48.7–48.0 (m, CH-polystyrene matrix), 40.3 (m, C–P-pyr.), 39.1 (s, C–N-pyr.), 39.0 (m, CH_2-polystyrene matrix), 37.2 (m, PEG–O–CH_2–CH_2–NC(O)), 35.4 (s, *C*CON-TentaGel), 33.4 (s, *C*CON-pyr.), 20.7 (s, $CH_2CH_2CH_2$). – ^{31}P NMR [C_6D_6 (10%)/CH_2Cl_2]: δ = –17.8 (s).

Method B: 0.55 g (1 mmol) of **8a**, 135 mg (1 mmol) of HOBT and 206 mg (1 mmol) of DCC were allowed to react with 1 g (0.2 mmol) of TentaGel (**4**) as described above.

Method C: Glutaroyl-TentaGel (**4a**): 1079 mg (0.215 mmol NH_2 groups) of TentaGel and 73.6 mg (0.65 mmol) of glutaric acid anhydride were shaken in toluene until the ninhydrin test was negative (about 10 h). The polymer was filtered off, resuspended in 20 ml of toluene and the suspension shaken for 30 min. This procedure was repeated three times. Then the polymer was dried until the weight remained constant. – IR (KBr): $\tilde{\nu}$ = 3081–2797 cm^{-1} (br., COOH), 1734 (st., COOH), 1675 (CO-amide), 1105 (C–O–C). – ^1H NMR ($CDCl_3$): δ = 6.5–7.3 (s, P-phenyl), 3.4 (s, PEG).

Coupling of **4a** *with* **8** *Affording* **6**: 500 mg (0.1 mmol) of **4a**, 50.5 mg (0.26 mmol) of DCC, and 54 mg (0.4 mmol) of HOBT were dissolved in 50 ml of DMF, and the solution was shaken for 30 min, then 205 mg (0.4 mmol) of **8** was added. The suspension was heated at 50°C and shaken for 20 h. The solvent was removed, the polymer was washed with 20 ml of DMF, 20 ml of methanol, Et_2O (three times each) and dried in vacuo. The coupling reaction was not complete, about one third of **4a** remained unreacted. – ^{31}P NMR (toluene): δ = –16.1 (s).

{(3R,4R)-N-[1,5-Dioxo-5-(TentaGel-N-)pentyl]-3,4-bis(diphenylphosphanyl)pyrrolidine-P,P'} (1,5-cyclooctadiene)rhodium Tetrafluoroborate (**7**): A suspension of 270 mg of **6** in 30 ml of methanol was cooled to –30°C. Then 20 mg (0.05 mmol) of $[Rh(COD)_2]BF_4$ was added. Shaking for 6 h, warming to room temp., filtration and washing with methanol until the filtrate was colourless furnished a bright yellow complex. Drying until the weight remained constant afforded the product in quantitative yield. – $^{13}C\{^1H\}$ NMR (CH_2Cl_2/C_6D_6 (10%)): δ = 172.4 (s, CON-TentaGel), 171.4 (s, CON-pyr.), [136.8 (d, J_{PC} = 12 Hz), 132.9 (dd, J_{RhC} = 86, J_{PC} = 4 Hz), 130.8–131.1 (m), 126.2 (d, J_{PC} = 22 Hz, P-phenyl-C)], 120–140 (m, polystyrene matrix), 104.4 and 98.4 (s, COD-CH), 70.8 (s, PEG), 40.8–44.3 [m, PEG–O–CH_2–CH_2–NC(O) and P–C-pyr.], 39.2 (s, N–C-pyr.), 35.2 (s, *C*CON-TentaGel), 33.13 (s, *C*CON-pyr.), 32.17 and 28.51 (s, COD-CH_2), 20.7 (s, $CH_2CH_2CH_2$). – ^{31}P NMR [C_6D_6 (10%)/CH_2Cl_2]: δ_A = 33.25, δ_B = 28.65 (AB-part of ABX, $^3J_{PP}$ = 13.2, $^1J_{PRh}$ = 149 Hz). – ^{13}C CP/MAS NMR (ν_{Rot} = 3.36 kHz) HWB (Hz), before catalysis: δ = 171.8 (s, CO), 145.4 (s, P-phenyl, 400), 128.1 (s, Ph-polystyrene, 470), 70.7 (s, PEG, 240), 29.3–46.3 (m, glutaryl, 270), after catalysis: δ = 145.8 (s, P-phenyl, 490), 127.8 (s, P-polystyrene, 490), 70.6 (s, PEG, 245), 29.3–46.3 (m, glutaryl, 306). – ^{31}P CP/MAS (ν_{Rot} = 10 kHz) HWB (Hz), before catalysis: 34.6 (s, 908), –13.5 (s, 680), after catalysis: 35.0 (s, 770).

(3R,4R)-N-[1,5-Dioxo-5-(TentaGel-N-)-pentyl]-3,4-bis(diphenylphosphanyl)pyrrolidine Dioxide: A suspension of 200 mg (0.04 mmol) of **6** in a small amount of water was treated with 5 drops of a 30% H_2O_2 solution. Standing of the mixture for 2 h resulted in total oxidation to the white phosphane oxide. The product was separated by filtration, washed with water (three times) and then dried in vacuo until the weight remained constant. Yield 203 mg (100%). – ^1H NMR ($CDCl_3$): δ = 6.7–7.1 and 7.1–7.7 (m, very br., P-phenyl and phenyl-polystyrene), 3.5 (s, br., PEG chain), 2.0–1.3 (m, br., glutaryl and CH_2CH-polystyrene matrix). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 171.9 (s, CON-TentaGel), 169.0 (s, CON-pyr.), [131.2 (d, J_{PC} = 26 Hz), 131.0 (s), 129.7 (s), 127.9 (s) (P-phenyl-C)], 71.5 [m, POE–O–CH_2–CH_2–NHC(O)], 69.4 (s, PEG), 45.1–44.7 (m, C–P–pyr.), 40 (m, br., CH_2-polystyrene matrix), 37.9 (s, C–N-pyr.), 34.0 (s, CH_2CON-TentaGel), 31.7 (s, CH_2CON-pyr.), 19.8 (s, $CH_2CH_2CH_2$). – ^{31}P NMR (benzene/methanol, 1:1): δ = 36.7 (s). – ^{31}P CP/MAS (ν_{Rot} = 10 kHz, b) = 5 KHz, c) = 2.5 kHz), HWB (Hz): δ = a) 36.1 (s, <230), b) 36.2 (s, 230), c) 36.7 (s, 230).

X-Ray Structure Determination of **1c**: *Crystal Data:* $C_{33}H_{33}I_2NO_3P_2Pd \cdot 2\ CHCl_3$, M = 1151.5 g · mol^{-1}, a = 1220.1(2), pb = 1567.8(3), c = 2295.4(4) pm, Z = 4, $_{ber}$ = 1.702 gcm^{-3}, orthorhombic, $P2_12_12_1$ (No. 19). – *Data Collection:* Siemens P4, Mo-K_α (71.073 pm), graphite monochromator, crystal dimensions 0.2 × 0.4 × 0.5 mm^3, measuring temp. 173 K, omega scan, 2Θ = 4–50°, ±h, ±k, ±l, 24799 reflections measured, 7708 independent, 4558 observed reflections [$I > 2\sigma(I)$], μ = 2.298 mm^{-1}, no absorption correction applied. – *Structure Analysis and Refinement:* program SHELXL V5.03, solution with Patterson method, full matrix refinement, 219 parameters, F_o/parameter = 20.8, R = 0.068, $wR2$ = 0.166, GooF = 1.375. Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe, D-76344 Leopoldshafen-Eggenstein, Germany, on quoting the depository number CSD-404620, file-ID leipold2, formula $C_{35}H_{35}Cl_6I_2NO_3P_2Pd$.

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