Synthesis and Polymerization Performance of Pd^{II} Complexes of New 2-Hydroxyethyl-Substituted Diphosphane Ligands

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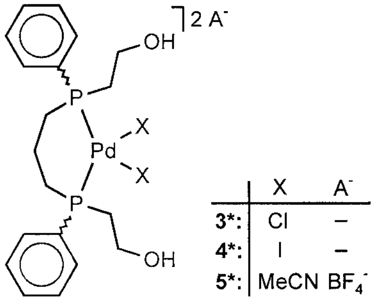
We have synthesized a new diphosphane ligand, 1,3-bis[(2-hydroxyethyl)(phenyl)phosphanyl]propane (**2***) (*: mixture of *meso-* and racemic diastereoisomers), and its corresponding neutral dichloro palladium(II) (**3***), diiodo palladium(II) (**4***), and dicationic diacetonitrile palladium(II) ditetrafluoroborate (**5***) complexes. Separation of the **4 *rac*** and **4 *meso*** diastereoisomers was achieved by column chromatography and subsequent crystallization. Assignments of the particular complex geometries of **3 *meso*** and **4 *rac*** were facilitated by single-crystal X-ray diffraction analysis. After activation with MAO, complex **3*** exhibits superior activity in the homopolymerization of 2-norbornene relative to that of the dichloro Pd^{II} derivative of 1,3-bis(diphenylphosphanyl)propane (dppp). Compound **5*** and the dppp-analogue possess similar catalytic potentials in ethylene/CO copolymerization experiments. Applying complex **5*** to propylene/CO copolymerization leads to highly regio- and predominantly stereoregular polyketone materials.

Introduction

Bridged bisphosphane ligands play an important role in homogeneous catalysis. The variety of tools available for tailoring their structures makes these ligands ideal platforms upon which to design selective, molecularly defined catalysts for small-molecule transformations and for polymerization reactions.[1] Until now, the functionalities that have been attached, such as oxygen-containing or fluorinated substituents, have been used primarily to impart particular steric and electronic properties to the ligands, as well as solubility properties of the complexes.[2] A novel approach for further developments is the introduction of suitable functional groups that help to open up selective reaction channels by reversible interactions with either the metal center, the incoming substrate, or the growing polymer chain. In this paper we report the synthesis and structural characterization of Pd^{II} complexes of a new bisphosphane ligand, which bears (2-hydroxyethyl)(phenyl)phosphane units (Scheme 1). We have performed 2-norbornene homopolymerizations, as well as ethylene/CO and propylene/CO copolymerization experiments, to investigate the catalytic potential of these novel complex structures.



Scheme 1. Novel hydroxy-functionalized bisphosphane Pd^{II} complexes

Results and Discussion

Ligand and Complex Synthesis

Nucleophilic attack of the dilithium diphosphide, which is accessible from 1,3-bis(phenylphosphanyl)propane (**1**) by deprotonation with 2 equiv. of *n*BuLi, on ethylene oxide[3] gave, after aqueous workup, the desired bisphosphane **2*** (Scheme 2). We obtained the ligand as a mixture of the racemic (*R*,*R*;*S*,*S*) and *meso* (*R*,*S*) components in a 1:1.3 ratio (^{31}P NMR: $\delta_{rac} = -32.50$, $\delta_{meso} = -32.64$ ppm).

Complexation of **2*** with $(COD)PdCl_2$ in CH_2Cl_2 gave the corresponding neutral dichloro palladium(II) complex (**3***) in the expected ratio of diastereoisomers (1:1.3, Scheme 3). Extraction of the mixture **3*** with DMSO and subsequent crystallization from $DMSO/CH_2Cl_2$ gave pure **3 *meso***. Replacement of the chloro ligands in **3*** by treat-

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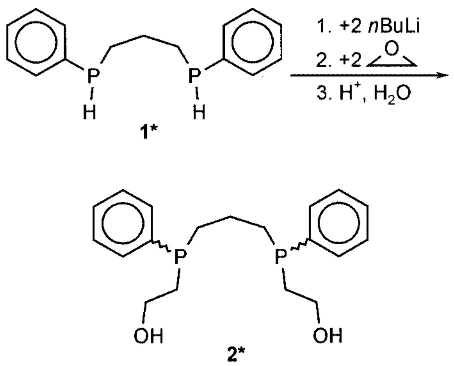
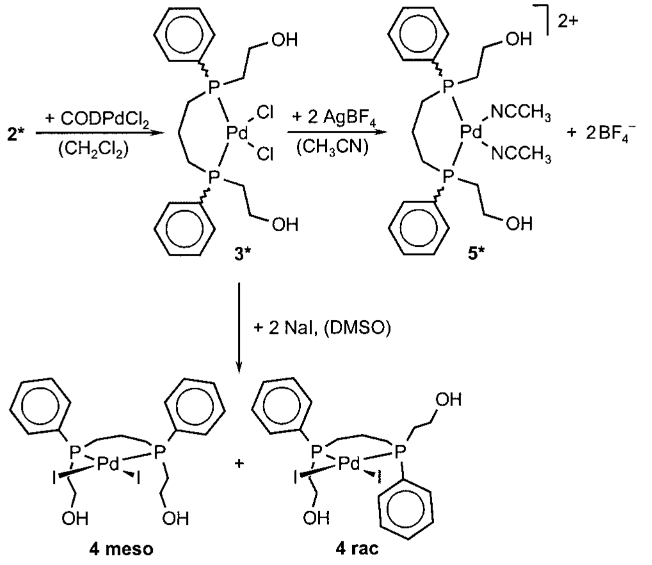


Scheme 2. Synthesis of 2-hydroxyethyl-substituted bisphosphane **2***



Scheme 3. Preparation of the neutral and dicationic Pd^{II} complexes of ligand **2***

ment with sodium iodide in DMSO affords the corresponding diiodo palladium(II) compounds **4***. Separation into pure racemic (**4** ***rac***) and *meso* fractions (**4** ***meso***) was performed by crystallization and subsequent chromatography over silica (CH_2Cl_2/acetone).[4] The dicationic complex **5*** was obtained from **3*** by halide abstraction using $AgBF_4$ in acetonitrile.

Single crystals of **3** ***meso*** (Figure 1, left) were grown from a DMSO extract of **3*** after treatment with CH_2Cl_2. Suitable crystals of **4** ***rac*** (Figure 1, right) were obtained by slow evaporation of the solvent from a CH_2Cl_2/acetone (1:1) solution. The coordination geometry around the Pd^{II} center is nearly square planar, as expected for palladium complexes of non-rigid diphosphanes. Both complexes show Pd−P and Pd−Hal bond lengths (Table 1) that resemble those of the symmetric [1,3-bis(diphenylphosphanyl)propane]$PdCl_2$ (Pd−P: 2.244(1)/2.249(2) Å; Pd−Cl: 2.351(1)/2.358(2) Å] and [1,2-bis(diphenylphosphanyl)ethane]PdI_2 (Pd−P: 2.2608(14)/2.2756(12) Å; Pd−I: 2.6649(8)/2.6446(10) Å] analogues.[5,6] The corresponding bond angles at the Pd centers of the complexes **3** ***meso*** and **4** ***rac*** are similar, i.e., they are independent of the nature of the chloro or iodo ligands, but the bond angle X−Pd−X is slightly enlarged in case of X = Cl [91.24(5)°] relative to X = I [90.46(2)°]. The orientation of the hydroxyethyl substituents is fixed in the solid state by intermolecular hydrogen bonding between neighboring complexes. Pairs of two

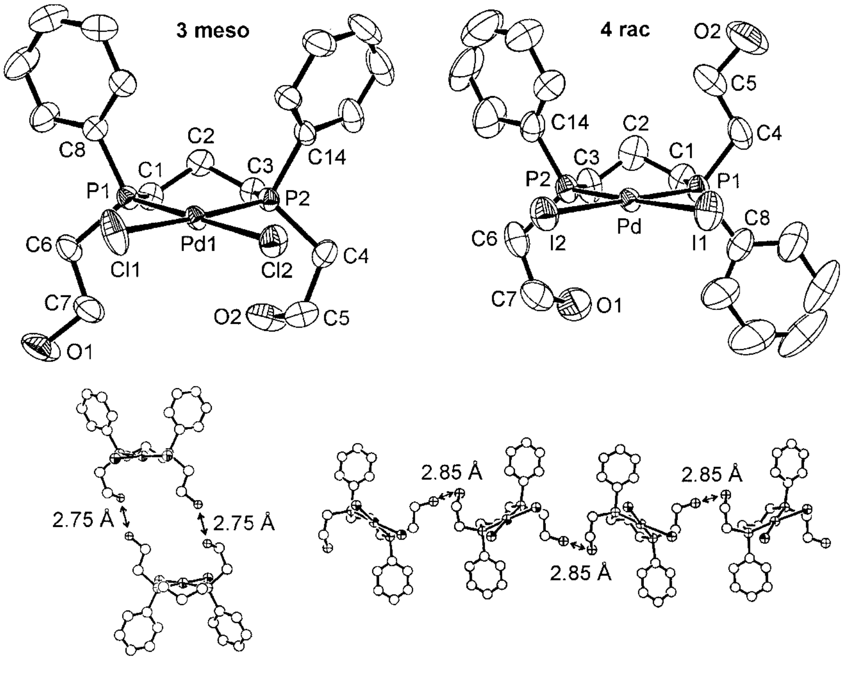


Figure 1. ORTEP plots of ***3 meso*** (left) and ***4 rac*** (right) complexes and arrangements of the complexes in the solid state; thermal ellipsoids are depicted at the 50% probability level; hydrogen atoms are omitted

Table 1. Selected bond lengths (Å) and angles (deg) for **3 *meso*** and **4 *rac***

3 *meso*		**4 *rac***	
Bond lengths			
Pd(1)−P(1)	2.243(1)	Pd−P(1)	2.268(2)
Pd(1)−P(2)	2.254(1)	Pd−P(2)	2.264(2)
Pd(1)−Cl(1)	2.354(1)	Pd−I(1)	2.661(1)
Pd(1)−Cl(2)	2.381(1)	Pd−I(2)	2.657(1)
P(1)−C(1)	1.815(5)	P(1)−C(1)	1.827(6)
P(1)−C(6)	1.827(5)	P(1)−C(4)	1.801(6)
P(1)−C(8)	1.805(5)	P(1)−C(8)	1.792(6)
P(2)−C(3)	1.825(5)	P(2)−C(3)	1.816(6)
P(2)−C(4)	1.832(5)	P(2)−C(6)	1.822(6)
P(2)−C(14)	1.817(5)	P(2)−C(14)	1.813(6)
Bond angles			
P(1)−Pd(1)−P(2)	94.54(4)	P(1)−Pd−P(2)	94.89(6)
Cl(1)−Pd(1)−Cl(2)	91.24(5)	I(1)−Pd−I(2)	90.46(2)
P(1)−Pd(1)−Cl(1)	87.25(5)	P(1)−Pd−I(1)	87.07(4)
P(1)−Pd(1)−Cl(2)	178.41(5)	P(1)−Pd−I(2)	177.47(4)
P(2)−Pd(1)−Cl(2)	86.94(4)	P(2)−Pd−I(2)	87.55(4)
P(2)−Pd(1)−Cl(1)	175.61(5)	P(2)−Pd−I(1)	177.08(4)

complex molecules are bridged by two hydrogen bonds in the unit cell of **3 *meso***. The intermolecular oxygen−oxygen distance is 2.754 Å. In **4 *rac***, one molecule is bridged by hydrogen bonding with two other complex units, which, thus, forms a linear polymeric chain. The intermolecular oxygen−oxygen distance in **4 *rac*** (2.853 Å) is slightly enlarged relative to that in **3 *meso***.

Homo- and Copolymerization Experiments

The use of bulky, substituted chelating ligands is a prerequisite for achieving polymeric products in late transition metal catalyzed ethylene polymerization reactions.[7] Therefore, we chose 2-norbornene to be the first monomer we applied to verify the homopolymerization capabilities of these new complexes. In addition, chain termination induced by β-hydride elimination is thermodynamically unfavorable when using this monomer.[8] The active complex species was obtained by treating the dichloropalladium(II) compound **3*** with MAO in toluene. As expected, polymerization of 2-norbornene resulted in a completely insoluble poly(norbornene) material[9] (Table 2). The monomer conversion is more than twice as high as that obtained when using the structurally related dichloro(dppp)palladium(II) complex, under analogous experimental conditions.

Table 2. Results of 2-norbornene and ethylene homopolymerization experiments using **3*** and the reference dpppPd^{II}Cl$_2$ after activation with MAO in toluene

Run[a]	Monomer	Catalyst	Al:Pd[b]	Yield[c]	Activity[d]
1	norbornene	**3***	500	0.5	180
2	norbornene	(dppp)PdCl$_2$	500	0.2	80
3	norbornene	**3***	1000	0.8	320
4	norbornene	(dppp)PdCl$_2$	1000	0.3	130

[a] Toluene (100 mL), catalyst (15 µmol), 2-norbornene (5 g), 25 °C, 10 min. [b] Ratio Al(MAO):Pd. [c] [g]. [d] [kg[mol(Pd)h]$^{-1}$].

The dicationic complex **5*** shows a satisfying activity in the alternating copolymerization of ethylene and carbon monoxide after activation with methanol; it is similar to the results obtained when using the standard polyketone catalyst [(dppp)Pd(NCCH$_3$)$_2$](BF$_4$)$_2$ (Table 3). In the propylene/CO copolymerization reaction, complex **5*** shows a completely different behavior than that of the dppp-ligated catalyst, which is known to produce regio-irregular polyketones.[10] In contrast, the propylene/CO material resulting from **5*** is brittle and insoluble in common solvents, which we attribute to a polyspiroketal chain structure. ^{13}C NMR spectroscopy investigations in [D$_2$]hexafluoro-2-propanol (HFIP) proved that the product has high regioregularity (head−tail sequences >97%; Figure 2). Interestingly, the methyl area is dominated by a single resonance,[11] which indicates a stereoregular, isotactic microstructure. This finding is supported by the relatively high melting transition temperature (T_m = 169 °C).[12]

One reason for the observed regioregular microstructure could be the alkyl substitution on the phosphorus moieties, which is known to produce regioregular polyketones.[13] We have no genuine explanation for the high stereoregularity of the propylene/CO copolymer material (PCO). The chiral cage, formed by the phenyl- and 2-hydroxyethyl P-substituents around the Pd^{II} center is not significantly pronounced to explain the isotacticity of the PCO product. One possible explanation is that the C_2-symmetric *rac*-catalyst species

Table 3. Ethylene/CO and propylene/CO copolymerization performance of **5*** in comparison to the related dpppPd^{II} complex

Run	Monomer	Catalyst	Amount[a]	Yield[b]	Activity[c]	M_w[d]	M_w/M_n	Regio[e]
5[f]	E/CO	**5***	20	1.3	21	–[g]	–[g]	–
6[f]	E/CO	dppp[h]	20	1.2	20	–[g]	–[g]	–
7[i]	P/CO	**5***	40	0.15	0.2	–[i]	–[i]	97
8[i]	P/CO	dppp[h]	20	1.3	3.4	65	1.8	56

[a] [µmol]. [b] [g]. [c] [kg[mol(Pd)h]$^{-1}$]. [d] [kg mol^{-1}]. Determined by GPC in CHCl$_3$. [e] Regioregularity (head−tail units) [%]. Determined by ^{13}C NMR spectroscopy in [D$_2$]HFIP and CDCl$_3$. [f] 100-mL Steel autoclave, CH$_2$Cl$_2$ (40 mL), MeOH (1 mL), ethylene (40 bar), CO (80 bar), 25 °C, 3 h. [g] Not determined. [h] (NCCH$_3$)$_2$(dppp)Pd(BF$_4$)$_2$. [i] 100-mL Steel autoclave, CH$_2$Cl$_2$ (40 mL), MeOH (run 7: 1 mL; run 8: 0.12 mL), propylene (saturated for 30 min), CO (60 bar), 25 °C, 19 h.

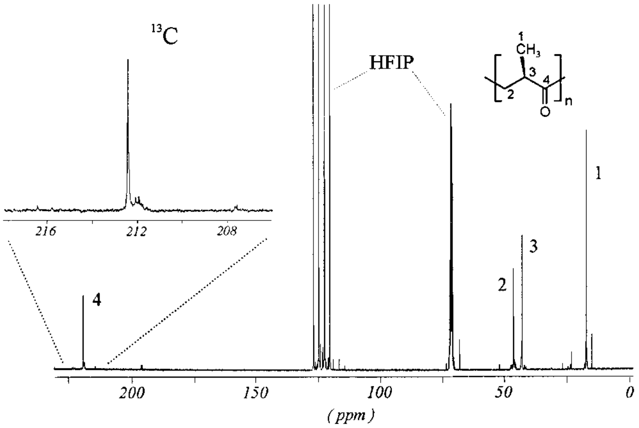


Figure 2. ^{13}C NMR spectrum ([D$_2$]HFIP) of a propylene/CO-copolymer resulting from the use of **5*** in methanol

has a higher activity than the *meso* complex and leads to the observed isotacticity through interaction of the 2-hydroxy ethyl substituents with the Pd^{II} dicationic metal center (O-coordination). This situation would afford the reversible formation of a chiral and stereorigid metallacycle that might lead to an effective enantiofacial differentiation of the incoming propylene monomer. A second explanation involves reversible interactions of the same OH groups with the coordinated acyl species after CO insertion. Further work toward gaining a deeper insight into these mechanisms is underway.

Conclusion

Our research on multifunctional chelating ligands resulted in the preparation of a 2-hydroxyethyl-substituted bisphosphane **2*** that is accessible by nucleophilic attack of the corresponding dilithium bisphosphide on ethylene oxide. The new ligand exists as a mixture of racemic and *meso* diastereoisomers in a 1:1.3 ratio. Separation of the diastereoisomeric compounds was performed by crystallization and column chromatography of the diiodo Pd^{II} complexes **4***. The neutral dichloro **3*** and the dicationic diacetonitrile Pd^{II} ditetrafluoroborate complexes **5*** are active for the homopolymerization of norbornene and CO/olefins, respectively. Interestingly, the application of complex **5*** affords isotactic propylene/CO copolymers. Elucidating the different polymerization behavior of the *rac* and *meso* isomers and studying the influence of the 2-hydroxyethyl P-substituents will be the subjects of further investigations.

Experimental Section

General: Reactions were performed under argon using standard Schlenk techniques. Solvents were dried by distillation from CaH_2 (dichloromethane) and $LiAlH_4$ (diethyl ether, *n*-pentane). Dry acetonitrile was received from Roth, deoxygenated in vacuo, and stored over molecular sieves (3 Å). H_2O was deoxygenated in vacuo and saturated with argon. 1,3-Bis(phenylphosphanyl)propane (**1**; Strem Chemicals), ethylene oxide (Fluka), $AgBF_4$ and (dppp)$PdCl_2$ (Aldrich), and 2-norbornene (Merck) were used as received. (COD)$PdCl_2$ [14] and $(CH_3CN)_2$(dppp)$Pd(BF_4)_2$ [15] were prepared according to literature procedures. ^{1}H, ^{13}C, ^{19}F, and ^{31}P NMR spectra were recorded on either a Bruker DRX 400 or an AMX 500 spectrometer. TMS was used as internal standard for the ^{1}H and ^{13}C spectra. ^{31}P NMR spectroscopic shifts were referenced to the external standard H_3PO_4 (85%). ^{19}F NMR spectra were calibrated to CCl_3F as the internal standard. Mass spectra were acquired using Varian MAT 711 and Finnigan TSQ 7000 instruments. X-Ray structural analyses were performed as described. MAO (in toluene) was supplied by WITCO. Ethylene (2.7), propylene (2.6), and carbon monoxide (2.0) were used without further purification as received from BASF.

1,3-Bis[(2-hydroxyethyl)(phenyl)phosphanyl]propane (2*): 1,3-Bis(phenylphosphanyl)propane (**1**) (11.3 g, 43.4 mmol) was dissolved in THF (400 mL) and cooled to −78 °C. Subsequently, 1.6 M *n*-butyllithium in hexane (53.4 mL, 86.8 mmol) was added to the mixture, which was warmed to room temperature overnight. The orange solution was then cooled to −18 °C and ethylene oxide (7.63 g, 174 mmol, 2 equiv.) was condensed into the reaction mixture. After stirring the resulting white suspension for 1 h at room temperature, all the solvents are removed in vacuo. The residue was hydrolyzed with water and deoxygenated 1 M hydrochloric acid was added, to pH 1, to protonate the bisphosphane. The aqueous solution was extracted with CH_2Cl_2 to remove impurities. Subsequently, after adding CH_2Cl_2 (100 mL) to the resulting acidic water phase, the mixture was adjusted to pH 7, to deprotonate the bisphosphane, by adding deoxygenated aqueous NaOH. The mixture was extracted with CH_2Cl_2 and the combined organic layers were dried over Na_2SO_4. Evaporation of the solvent in vacuo gave ligand **2*** as a colorless, highly viscous oil. Yield 12.2 g (82%). ^{1}H NMR ($CDCl_3$): $\delta = 7.47-7.39$ (m, 4 H, Ph), 7.33−7.25 (m, 6 H, Ph), 3.68−3.59 (m, 4 H, CH_2O), 2.30−2.15 (br. s, 2 H, OH), 2.01−1.88 (m, 4 H, PCH_2), 1.87−1.72 (m, 4 H, PCH_2, bridge), 1.52−1.39 (m, 2 H, CH_2, bridge) ppm. ^{13}C NMR ($CDCl_3$): $\delta =$ 137.7−137.4 (2 × d, *rac*/*meso*, *ipso* Ph), 132.4−132.1 (2 × d, *rac*/*meso*, *ortho* Ph), 128.9 (s, *para* Ph), 128.5−128.3 (2 × d, *rac*/*meso*, *meta* Ph), 60.0 (d, CH_2-OH), 32.0 (vt, *rac*/*meso*, PCH_2), 29.5 (vt, PCH_2, bridge), 22.4−22.1 (m, CH_2, bridge) ppm. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): $\delta = -32.50$ (s, *rac*), −32.64 (s, *meso*) ppm; ratio *rac*:*meso* = 1:1.3. IR (film): $\tilde{\nu} = 3344\ cm^{-1}$ (br., OH). MS (FD): *m*/*z* (%) = 348 (100) $[M]^+$, 303 (5) $[M - CH_2CH_2OH]^+$. $C_{19}H_{26}O_2P_2$ (348.4): calcd. C 65.51, H 7.52; found C 65.23, H 7.35.

Dichloro{1,3-Bis[(2-hydroxyethyl)(phenyl)phosphanyl]propane}-palladium(II) (3*): Ligand **2*** (9.42 g, 27.1 mmol) was dissolved in CH_2Cl_2 (50 mL) and then added to a solution of (COD)$PdCl_2$ (7.72 g, 27.1 mmol) in CH_2Cl_2 (450 mL). After stirring the mixture for 1 h, the precipitated product was separated. Washing with CH_2Cl_2 and pentane and then drying in vacuo gave complex **3*** as a yellow solid. Yield:13.5 g (95%). Extraction of compound **3*** with a small amount of DMSO, followed by crystallization from the DMSO extract by the addition of CH_2Cl_2, gave the pure *meso* complex (**3 *meso***) containing single-crystals suitable for X-ray diffraction analysis. ^{1}H NMR ([D$_6$]DMSO): $\delta = 8.00-7.91$ [m, 4H (*rac*) +4H (*meso*), Ph], 7.55−7.39 [m, 6H (*rac*) + 6H (*meso*), Ph], 5.10 (t, 2 H, *rac*, OH), 5.05 (t, 2 H, *meso*, OH), 4.08−3.85 [m, 4H (*rac*) + 4H (*meso*), CH_2O], 2.91−2.78 (m, 2 H, *rac*), 2.77−2.64 (m, 2 H, *meso*), 2.64−2.40 [m, 2H (*rac*) + 2H (*meso*)], 2.40−2.26 (m, 2 H, *meso*), 2.22−2.07 [m, 2H (*rac*) + 3H (*meso*)], 2.07−1.90 (m, 2 H, *rac*), 1.88−1.70 (m, 2 H, *rac*), 1.20−0.96 (m, 1 H, *meso*) ppm. $^{31}P\{^{1}H\}$ NMR ([D$_6$]DMSO): $\delta = 17.0$ (s, *rac*), 13.6 (s, *meso*) ppm;

ratio *rac*:*meso* = 1:1.3. IR (KI): $\tilde{\nu}$ = 3422 cm^{-1} (br., OH). MS (FAB): *m*/*z* (%) = 491 (76) $[M - Cl]^+$, 453 (100) $[M - 2Cl]^+$. $C_{19}H_{26}Cl_2O_2P_2Pd$ (525.7): calcd. C 43.41, H 4.99; found C 43.30, H 4.93.

{1,3-Bis[(2-hydroxyethyl)(phenyl)phosphanyl]propane}diiodopalladium(II) (4*) and Its Separation into 4 *meso* and 4 *rac*: The following procedure was performed using solvents as supplied without further purification. Complex **3*** (7.0 g, 13.3 mmol) was dissolved in DMSO (200 mL). After adding NaI (7.97 g, 53.2 mmol), the reaction mixture was stirred for 15 h at room temperature. The DMSO was separated from the crude product by successive extraction with ether and removal of the resulting DMSO-containing ether layers. Extracting of the resulting solid with CH_2Cl_2 and acetone, followed by crystallization, led to an enrichment of the two diastereoisomers in different product fractions. Complete separation and purification of the diastereoisomers was performed by chromatography over silica (CH_2Cl_2/acetone, 1:2) and subsequent crystallization.

{(P*S*,P′*S*)-1,3-Bis[(2-hydroxyethyl)(phenyl)phosphanyl]propane}diiodopalladium(II) and {(P*R*,P′*R*)-1,3-Bis[(2-hydroxyethyl)(phenyl)phosphanyl]propane}diiodopalladium(II) (4 *rac*): Yield: 2.8 g (30%). ^1H NMR ([D$_6$]DMSO): δ = 7.93−7.90 (m, 4 H, Ph), 7.51−7.42 (m, 6 H, Ph), 5.14 (t, br, 2 H, OH), 4.11−3.96 (m, 4 H, CH_2O), 3.14−2.84 (m, 4 H, PCH_2), 2.24−2.11 (m, 2 H, bridge), 2.00−1.72 (m, 4 H, bridge) ppm. $^{31}P\{^1H\}$ NMR ([D$_6$]DMSO): δ = 7.27 (s) ppm. IR (KI): $\tilde{\nu}$ = 3425 cm^{-1} (br., OH). MS (FAB): *m*/*z* (%) = 581 (100) $[M - I]^+$, 454 (10) $[M - 2I]^+$. $C_{19}H_{26}I_2O_2P_2Pd$ (708.6): calcd. C 32.21, H 3.70; found C 32.07, H 3.62.

{(P*S*,P′*R*)-1,3-Bis[(2-hydroxyethyl)(phenyl)phosphanyl]propane}diiodopalladium(II) (4 *meso*): Yield 2.1 g (23%). ^1H NMR ([D$_6$]DMSO): δ = 7.98−7.91 (m, 4 H, Ph), 7.50−7.42 (m, 6 H, Ph), 5.11 (t, br, 2 H, OH), 4.07−3.87 (m, 4 H, CH_2O), 3.08−2.82 (m, 4 H, PCH_2), 2.24−2.02 (m, 5 H, bridge), 1.22−1.00 (m, 1 H, bridge) ppm. $^{31}P\{^1H\}$ NMR ([D$_6$]DMSO): δ = 5.48 (s) ppm. IR (KI): $\tilde{\nu}$ = 3347 cm^{-1} (br., OH). MS (FAB): *m*/*z* (%) = 581 (100) $[M - I]^+$, 454 (7) $[M - 2I]^+$. $C_{19}H_{26}I_2O_2P_2Pd$ (708.6): calcd. C 32.21; H 3.70; found C 32.26; H 3.74.

Diacetonitrile{1,3-bis[(2-hydroxyethyl)(phenyl)phosphanyl]propane}palladium(II) Ditetrafluoroborate (5*): $AgBF_4$ (1.48 g, 7.62 mmol) was added to a suspension of **3*** (2.00 g, 3.81 mmol) in acetonitrile (80 mL). After stirring for 1 h, the reaction mixture was filtered and concentrated in vacuo. The concentrated solution was filtered again and then the complex was precipitated with ether. The solid was washed with diethyl ether and *n*-pentane and then dried in vacuo to give **5***. Yield 2.4 g (89%). ^1H NMR (CD_3OD): δ = 8.17−7.39 (m, 10 H, *meso*/*rac*, Ph), 4.26−3.92 (m, 2 H, *meso*/*rac*, CH_2), 3.78−3.61 (m, 2 H, *meso*/*rac*, CH_2), 3.19−2.15 and 1.64−1.45 (2 × m, 10 H, *meso*/*rac*, CH_2), 2.06 (CH_3CN) ppm. $^{19}F\{^1H\}$ NMR (CD_3OD): δ = −155.55 (s) ppm. $^{31}P\{^1H\}$ NMR (CD_3OD): δ = 44.30 (s, *rac*), 33.37 (s, *meso*) ppm; ratio *rac*:*meso* = 1:1.3. IR (KI): $\tilde{\nu}$ = 3481 (br., OH), 2325, 2297 (w, C≡N), 1076 (br., BF_4) cm^{-1}. MS (FAB): *m*/*z* (%) = 453 (100) $[M - 2CH_3CN,2BF_4]^+$.

2-Norbornene Polymerization Experiments: The corresponding dichloro Pd^{II} complex (15 µmol) was dissolved in toluene (final total volume including MAO: 100 mL), treated with MAO solution

Table 4. Summary of crystal data and structural refinement parameters for **3 *meso*** and **4 *rac***

	3 *meso*	**4 *rac***
Empirical formula	$C_{19}H_{26}Cl_2O_2P_2Pd$	$C_{19}H_{26}I_2O_2P_2Pd$
Molecular mass	525.64	708.54
Crystal color and shape	colorless prism	orange needle fragment
Crystal size (mm)	0.15 × 0.31 × 0.46	0.26 × 0.19 × 0.12
Crystal system	monoclinic	orthorhombic
Space group	*I*2/*a*	*Pbcn*
a (Å)	13.946(1)	18.322(4)
b (Å)	11.120(1)	18.947(3)
c (Å)	30.962(2)	15.425(2)
α (°)	90	90
β (°)	101.23(1)	90
γ (°)	90	90
V ($Å^3$)	4709.5(5)	5354.7(17)
Z	8	8
Calculated density [g/cm^3]	1.483	1.758
Absorption coefficient [mm^{-1}]	1.161	3.128
F(000)	2128	2704
θ range (°)	2.57−25.96	2.76−26.00
Index range	$-16 = h = 16$	$-22 = h = 22$
	$-13 = k = 13$	$-23 = k = 23$
	$-38 = l = 32$	$-18 = l = 18$
Reflections collected	13855	39740
Reflections unique	4538 [*R*(int) = 0.0267]	5109 [*R*(int) = 0.0825]
Goodness-of-fit on F^2	1.093	0.935
Final R_{int} [$I > 2\sigma(I)$]	$R1 = 0.0446$	$R1 = 0.0311$
	$wR2 = 0.1583$	$wR2 = 0.0660$
R_{int} (all data)	$R1 = 0.0497$	$R1 = 0.0644$
	$wR2 = 0.1650$	$wR2 = 0.0704$
Largest diff peak and hole (e/Å^3)	3.340 and −1.232	1.036 and −0.478

(Al:Pd = 1000), and stirred 2 min to form the active species. 2-Norbornene (5 g) was then added to the solution. The polymerization reaction was quenched after 10 min by pouring the mixture into a glass beaker containing MeOH (500 mL)/conc. hydrochloric acid (5 mL). Separation and drying in vacuo at 80 °C gave the polymer as a white powder.

Ethylene/CO Copolymerization Experiments: The corresponding dicationic diacetonitrile palladium(II) ditetrafluoroborate complex was dissolved in a mixture of CH_2Cl_2 (40 mL) and MeOH (1 mL). The activated catalyst solution was transferred into a 100-mL steel autoclave equipped with a magnetic stirring bar. After pressurizing with ethylene (40 bar) for 5 min, the reactor was charged with carbon monoxide at 80 bar. Following a polymerization time of 3 h, the remaining gases were vented off and the reaction mixture was poured into MeOH. The copolymer was isolated by filtration and then it was dried in vacuo at 60 °C.

Propylene/CO Copolymerization Experiments: The catalyst solution was prepared and transferred into the autoclave as described above for the ethylene/CO copolymerization experiments. The reactor was saturated with propene (30 min) and charged with carbon monoxide at 60 bar. The remaining gases were vented off after a reaction time of 19 h at 25 °C. The resulting reaction mixture was diluted with CH_2Cl_2 and stirred with water for 2 h. The organic phase was separated, the solvent evaporated in vacuo, and the copolymer dried in vacuo at 60 °C.

X-ray Crystallography of 3 *meso* and 4 *rac*: The crystals used in this study were mounted onto the ends of a glass fiber. X-Ray diffraction data were collected on a STOE IPDS unit (Imaging Plate Diffraction System) at 20 °C. Graphite-monochromatized Mo-K_α radiation ($\lambda = 0.71073$ Å) was used. Crystal data are listed in Table 4 together with refinement details. An absorption correction (analytical method) was applied. The structure of **3** ***meso*** was solved by direct methods using XMY93[16] and that of **4** ***rac*** by the Patterson method. The atomic coordinates and anisotropic thermal parameters of the non-hydrogen atoms were refined using the SHELXL-97 program[17] (full-matrix method on F^2 data). Hydrogen atoms, except those attached to oxygen atoms, were included at their calculated positions in the final refinement cycles. The riding model was used to locate the other hydrogen atoms.

CCDC-224744 (for **3** ***meso***) and -224402 (for **4** ***rac***) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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