Ligand-Dependent Diastereoselectivity in the Palladium-Catalyzed Copolymerization of Styrene with Carbon Monoxide

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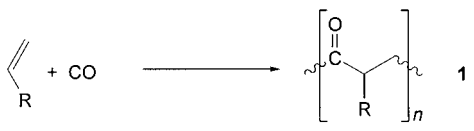
Dedicated to the memory of *Luigi M. Venanzi* in recognition of his significant contribution to transition metal chemistry

[(L^L′)Pd(H_2O)]($OTf)_2$ complexes, in which L^L′ is a chelate ligand containing the chiral 4-benzyl-4,5-dihydrooxazole moiety and either pyridin-2-yl or 2-(diphenylphosphino)phenyl substituents, catalyze the copolymerization of styrene with carbon monoxide with an isotactic or prevailingly syndiotactic microstructure, respectively. The chiroptical properties of the copolymers and model studies for carbon monoxide and olefin insertion on related Pd complexes suggest that the reason for the different stereochemistry of the copolymers is a site-selective coordination of the olefin in the intermediates containing the P∧N ligand; a lower regioselectivity in the coordination and a different coordination site lead to the different diastereoselectivity for the copolymer formation by the complex containing the N^N′-ligand.

Introduction. – The synthesis of alternating copolymers between CO and alk-1-enes (*Scheme 1*) is achieved through a variety of cationic Pd complexes modified by N or P ligands, in which the ligand is mostly chelate, *e.g.*, [(L^L′)Pd($S)_2$]X_2 (L = or ≠ L′, S = solvent) [1]. When styrene is the substrate, catalysis to the corresponding polyketone **1** (R = Ph) does not take place with catalytic systems modified by bidentate phosphorus ligands [2][3] and is efficient essentially only with chelate nitrogen (N^N) or hybrid nitrogen-phosphorus (P^N) ligands. Notable exceptions are represented by the phosphane–phosphite chelate system (*R*)-2-(diphenylphosphino)-1,1′-binaphthalen-2′-yl-(*S*)-1,1′-binaphthalen-2′-ylphosphite that shows, however, low productivity [4], and by a bidentate chiral diphosphine ligand, 1,4:3,6-dianhydro-2,5-dideoxy-2,5-bis(diphenylphosphino)-L-iditol, which cannot chelate [5]. Previous investigations showed that catalyst precursor **2** produces syndiotactic poly[1-oxo-2-phenylpropane-1,3-diyl] (**1**, R = Ph) (content of *u*-diads *ca.* 90%) [6][7], while systems containing various monosubstituted bi(dihydrooxazoles) related to **3** (R^1 = H) or bi(dihydrooxazoles) gave a prevailingly isotactic copolymer [8–10]. Surprisingly, whereas **4a** (and

Scheme 1



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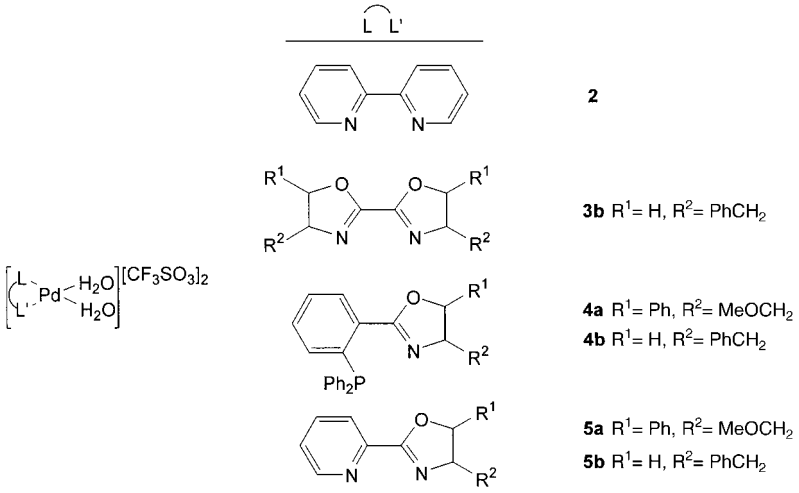
related dihydro(phosphino)oxazole-containing systems) gave a highly isotactic copolymerization (favored *l*-enchainment) [11], **5a** gave syndiotactic copolymers, with favored *u*-enchainment [8][12]. NMR Investigation of catalyst precursor **4a**, however, showed that the electrophilic metal center interacted with the ether substituent of the ligand [13].



To better define the factors involved in the phenomenon of enantioface discrimination during the copolymerization process, we synthesized the catalyst precursors **3b** and **5b**, and the previously studied **4b** and used them as catalyst precursors for the styrene–CO copolymerization. Some model studies are also presented.

Results and Discussion. – The optimum conditions for the copolymerization experiments (*Table 1*) with the three different catalyst precursors differ due to the different kinetic order with respect to CO. Whereas, with the catalysts precursors **5b** and **3b**, similar to **2** [14][15], the reaction rate decreases with increasing CO pressure, with **4b** the reverse is true [11]. In the case of **5b** and **3b**, the CO pressure was as low as 5 and 1.5 bar, respectively, during the copolymerization reaction, whereas reactions with **4b** were carried out under 320 bar CO pressure. The catalytic system **5b** showed a high

Table 1. *Copolymerization of Styrene and CO with* $[(L\hat{}L')Pd(H_2O)_2](OTf)_2$ **2**, **3b**–**5b** *as the Catalyst Precursor*[a])

Catalyst	p(CO) [bar]	Productivity [g/(g Pd·h)]	M_n [g·mol^{-1}]	$\Delta\varepsilon$ (280 nm) [l·mol^{-1}·cm^{-1}]
2	100	7.1	9600	–
3b	1.5	20	2200	– 7.5
4b	320	20	6600	– 10.3
5b	5	180	2300	– 1.7

[a]) Reaction conditions: 50 ml (435 mmol) of styrene, 10 ml of MeOH, 216 mg (2.0 mmol) of BQ, 0.1 mmol of catalyst precursor, 50°.

Table 2. *Influence of the Concentration of BQ on the Copolymerization of Styrene and CO with* **4b** *or* **5b** *as the Catalyst Precursor*[a])

Catalyst	BQ [mmol]	Reaction time [h]	Yield [g]	Productivity [g/(g Pd·h)]	M_n [g·mol^{-1}]
5b	4	7.6	14.39	182	5000
5b	2	5.4	10.36	181	5800
5b	1	3.7	7.27	185	6400
4b	4	40.5	6.24	14.6	4430
4b	2	41.5	5.74	13.1	4630
4b	1	45.5	6.79	14.2	4600

[a]) Reaction conditions: 50 ml (435 mmol) of styrene, 10 ml of MeOH, 0.1 mmol of catalyst precursor, 50°, p(CO) 5 bar for **5b** and 320 bar for **4b**.

productivity of 180 g/(g Pd·h). With **3b**, a considerably lower productivity of 20 g/(g Pd·h) was observed.

The polymer yield (turnover number) of **5b** is strongly influenced by the concentration of the oxidant used, namely 1,4-benzoquinone (BQ; *Table 2*).

However, the turnover frequency (productivity) of the catalysts is not affected, as shown by the rate of CO consumption (*Fig. 1*). The steady rate is followed in each case by a sudden cessation of gas uptake [16]. Larger amounts of BQ result in somewhat lower molecular weight [9]. In contrast, for the system modified by ligand **4b**, the CO consumption was constant and showed no sign of flattening during the given reaction time, independent of the quantity of benzoquinone used.

The addition of free ligand to the corresponding catalytic system **5b** also improves the stability of the catalyst [17]. The copolymers obtained with an additional amount of free ligand (*Table 3*) were white, indicating that the catalytic system was stable until the

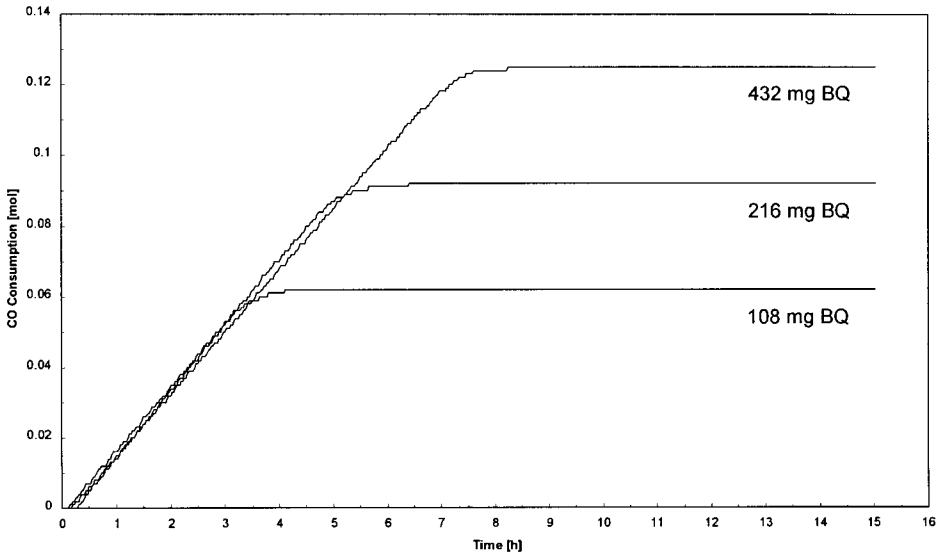


Fig. 1. *CO Consumption* vs. *time for the copolymerization reactions catalyzed by* **5b** *with different amounts of oxidant* (for the reaction conditions see *Table 2*)

Table 3. *Influence of Free Ligand* **5b** *During the Copolymerization of Styrene and CO Catalyzed by* [(**5b**)$Pd(H_2O)_2](OTf)_2$[a])

Molar ratio [ligand]/[Pd]	Reaction time [h]	Yield [g]	Productivity [g/(g Pd·h)]	M_n [g·mol^{-1}]
0	11	10.36	170	5600
1	13.5	17.30	228	6000
2	14.8	18.00	210	5900

[a]) Reaction conditions: 50 ml (435 mmol) of styrene, 10 ml of MeOH, 216 mg (2 mmol) of BQ, 0.05 mmol of catalyst precursor, 5 bar CO; 50°.

end of the reaction. The productivity of the systems also improved when 1 equiv. of the free ligand was added, but then decreased slightly upon addition of larger amounts.

The microstructure of the copolymers obtained was investigated by ^{13}C- and ^{1}H-NMR [7]. *Fig. 2* shows the *ipso*-C-atom region of the ^{13}C-NMR spectra for the copolymers synthesized with the catalyst precursors **3b**, **4b**, and **5b**. For the copolymer obtained with **4b**, the only signal observed was the one attributed to the *ll*-triad [7]. According to the sign of the molar ellipticity of the CD band (*Table 1*) this is the (*R*,*R*,*R*)-triad [10][11]. In the spectrum of the copolymer produced with **3b**, the same signal corresponding to the *ll*-triad (again the (*R*,*R*,*R*)-triad) prevails. However, the band is broader than in the previous case, and other weak signals are observed, indicating a less stereoregular structure. This is supported by the lower $\Delta\varepsilon$ value of the CD band. In the spectrum of the copolymer synthesized with **5b**, the most intense signal corresponds to the *uu*-triad; less intense signals of the *ul*- or *lu*-triad are also visible. The low molar ellipticity measured for this material is consistent with the presence of some *l*-diads. The same sign of the ellipticity of the CD band for the two copolymers indicates that the same enantioface of the styrene unit was prevailingly inserted into the polymer chain with all three ligands **3b** to **5b**.

As reported in [12][18], catalytic system **5a**, which contains the same chiral dihydrooxazoline moiety as **4a**, produces a prevailingly syndiotactic copolymer, in contrast to **4a**, which gives an isotactic copolymer. Similar results have now been obtained with catalyst precursors **4b** and **5b**, despite the absence on the dihydrooxazole moiety of a basic group capable of interactions with the electrophilic metal center. However, the productivity of **5b** is *ca.* six times higher than that of **5a**, showing that the ether substituent of the ligand **5a** can play a crucial role during the copolymerization reaction.

Table 4 summarizes the end-group analysis by ^{1}H-NMR for the copolymers produced with catalyst precursors **4b** and **5b** as a function of the concentration of BQ in the reaction mixture. Unsaturated end groups correspond to chain termination through β-H elimination. With catalyst **4b**, most chains, therefore, start by styrene insertion into a L_nPd-H intermediate [19], and a higher concentration of the oxidant has practically no influence on the species responsible for initiation. In contrast, with catalyst **5b**, most of the chains begin by styrene insertion into a $L_nPd-COOMe$ intermediate, the formation of which is promoted by a higher concentration of the oxidant [1]. A MALDI high-resolution mass spectrum of a copolymer obtained with this catalyst precursor under 20 bar CO enabled us to identify, in the low-mass range, the copolymer chains shown below [15][20].

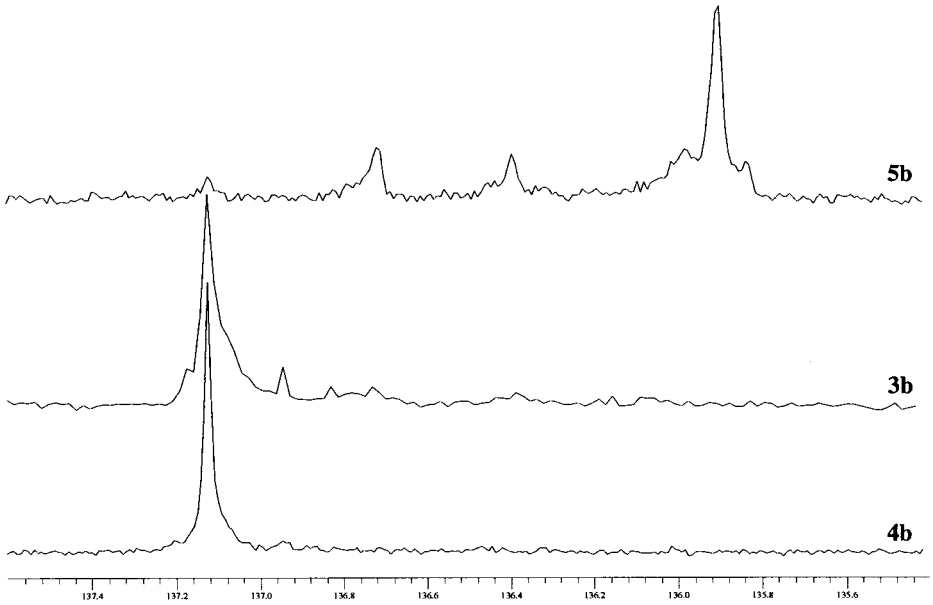
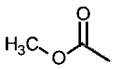
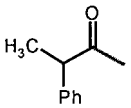
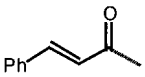
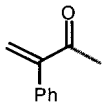
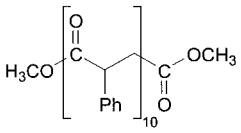
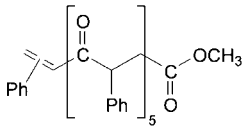
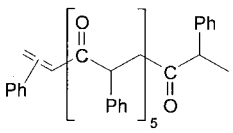


Fig. 2. *^{13}C-NMR Spectra of the* ipso-*C atom region of the copolymers produced with the Pd-catalyst precursors* **5b**, **3b**, *and* **4b**

Table 4. *Influence of the Amount of BQ on the Relative Concentration* (%) *of the End Groups in the Copolymers Produced with Catalyst Precursors* **5b** *and* **4b**[a])

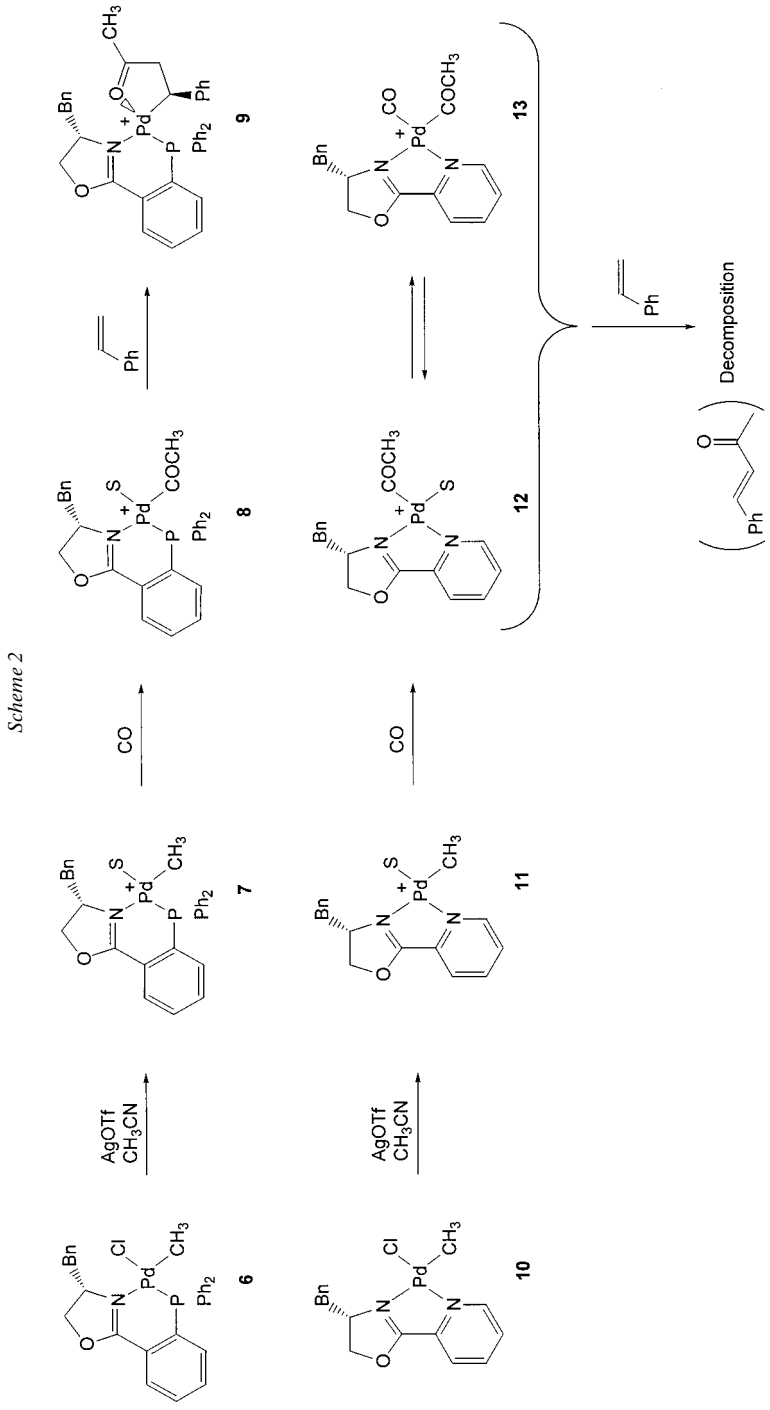
Catalyst	BQ [mmol]				
5b	4	51	19	25	5
5b	2	44	23	28	5
5b	1	40	25	29	6
4b	4	15	56	11	18
4b	2	15	51	11	23
4b	1	11	54	14	21

[a]) See *Table 2* for the reaction conditions.

To obtain more information about the factors involved in the copolymerization with **4b** and **5b**, we carried out NMR model studies for comonomer insertion with the two ligand systems. The results are summarized in *Scheme 2*.

Scheme 2

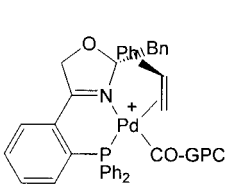


The chemistry of the system containing the P^N ligand is similar to the previously investigated dibenzophosphole homologue, even though the interpretation of the NMR spectrum was more difficult because of the fortuitous overlapping of the signals [18][21]. Starting with **6**, both the alkyl and the acyl derivatives, **7** and **8**, respectively, are regiospecifically formed, the alkyl and acyl groups being *trans* to the oxazoline N-ligand. Styrene insertion to give **9** is essentially regio- and diastereospecific.

The monocationic [PdMe(MeCN){N^N′}](OTf) (**11**) complex was analogously prepared by halogen abstraction from PdMeCl(N^N′) **10** with 1 equiv. of AgOTf (*Scheme 2*) [22][23]. The ^{1}H-NMR spectrum revealed the presence of a single regioisomer in solution. Difference-NOE spectroscopy of this complex established the *cis* relationship between the dihydrooxazole ring and the PdMe group [24]. Complex **11** reacts completely in *ca.* 4 h in a CH_2Cl_2 solution at $-78°$ with (either labelled or unlabelled) CO to give regioselective formation of the acetyl-solvento complex **12**, together with smaller amounts of a second species **13** associated with broad bands in the ^{1}H-NMR spectrum. The latter species is the only one observable after 14 h at $-78°$ but can be transformed slowly into **12** (*ca.* 1:1 molar ratio after 40 min) by bubbling Ar through the solution at $-78°$. Structural assignment is based on the presence of two CO resonances in the ^{13}C-NMR spectrum and on a NOE effect of the H–C(6) of pyridine with the signal in the region of the Ac resonances. Styrene does not react at $-78°$ with a mixture of **12** and **13** over a period of 24 h. Allowing the mixture to warm to room temperature leads to the formation of a complex mixture in which species similar to **9** could not be identified with certainty [25]. Under these conditions, decomposition takes place, as demonstrated by the formation of benzalacetone (=(*E*)-4-phenylbut-3-en-2-one) (22% yield with respect to styrene).

With **11** as the catalyst precursor for the copolymerization reaction of styrene with CO, lower (*ca.* 1/5) productivity with respect to **5b** was observed, but the microstructure of the produced polymer was the same.

Conclusions. – A site-selective coordination of the olefin (*trans* to P) and a secondary insertion of the incoming styrene units were assumed to take place for the catalytic system **4a** (and for similar phosphino-dihydrooxazole-modified catalysts) (see **14**) [11].



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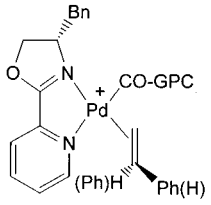

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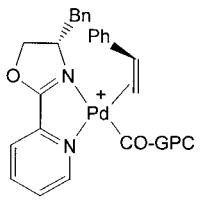

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The very high enantioface discrimination to produce the isotactic copolymers is caused by the steric interaction of the substituent on the dihydrooxazole ring and the Ph group of the olefin. Consequently, on the basis of the kinetically preferred formation of **12**, it seems reasonable to assume that, for the systems bearing dihydro(pyridinyl)-oxazole ligands, the olefin coordination takes place preferentially *cis* to the pyridine

moiety (*Scheme 5*, **15**). This intermediate, like the one modified by the bipyridine ligand, should cause olefin insertion to form mostly *u*-diads. In keeping with the formation of **13**, it is assumed that isomeric intermediate **16** plays also a role, thus causing the formation of some *l*-diads; enantioface discrimination in this intermediate is probably caused by the same steric factors as for intermediate **14**, leading to the same sign of the optical rotation of the produced copolymers.

Experimental Part

General. All reactions and manipulations were carried out in a purified Ar or N_2 atmosphere with *Schlenk* techniques or a glove box. The solvents used were of '*puriss p.a.*' quality (*Fluka*). Et_2O and THF were dried over Na/benzophenone prior to use. The fine chemicals were *Fluka* or *Aldrich* products and were used without further purification. $[PdCl_2(NCPh)_2]$ [26], $[PdMe_2(tmeda)]$ [22], and the ligands **5a**,**b** [27] and **4a**,**b** [28] were prepared according to literature procedures. Ligand **3b** was purchased from *Aldrich* and was used without further purification. The reaction of the ligands with $[PdCl_2(NCPh)_2]$ to $[PdCl_2(L\frown L')]$ followed by treatment with $AgCF_3SO_3$ to the corresponding $[(L\frown L')Pd(H_2O)_2](OTf)_2$ complexes was carried out according to procedures described in the literature for similar compounds [29]. The spectral data of the Pd derivatives of **4a**,**b** and **5a** were published elsewhere [12]. CD Spectra were recorded at r.t. on a *Jasco 600* polarimeter in $CDCl_3$/HFIP 10:1. NMR Spectra were recorded in $CDCl_3$/1,1,1,3,3,3-hexafluoro(2-$^2H_1$) propan-2-($^2H_1$)ol (HFIP) 10:1 as solvent and with TMS as the internal standard on a *Bruker DPX-200*, *DPX-300*, or *Avance-500*; chemical shifts δ [ppm] relative to TMS. Elemental analyses were carried out at the microelemental laboratory of the ETH Zürich.

*Synthesis of {(*S*)-4-Benzyl-4,5-dihydro-2-(pyridin-2-yl-*κ*N)oxazole-*κ*N}(dichloro)palladium(II)* 4.49 g (11.7 mmol) of $[PdCl_2(NCPh)_2]$ were dissolved in 280 ml of toluene and heated to 70°. To this soln. 2.93 g (12.3 mmol, 1.05 equiv.) of (*S*)-4-benzyl-4,5-dihydro-2-(pyridin-2-yl)oxazole dissolved in 120 ml of toluene was added dropwise through a funnel, and the mixture was stirred at 70° for 2 h. After cooling to r.t., 200 ml of freshly distilled Et_2O were added, and the yellow precipitate was filtered under Ar, washed with Et_2O (2 · 30 ml), and dried *in vacuo* to give the desired dichloropalladium complex as an orange-yellow powder (3.46 g, 8.3 mmol, 71%). ^{1}H-NMR: 3.05 (*dd*, ^2J = 13.8, ^3J = 8.1, 1 H, PhCH_2); 3.61 (*dd*, ^2J = 13.8, ^3J = 2.4, 1 H, PhCH_2); 4.74–4.93 (*m*, 2 H–C(5), H–C(4)); 7.19–7.41 (*m*, 6 arom. H); 7.62–7.74 (*m*, H–C(4) of Py); 8.09 (*dt*, ^2J = 7.8, ^3J = 1.5, H–C(3) of Py); 9.16 (*d*, ^2J = 5.5, H–C(6) of Py). Anal. calc. for $C_{15}H_{14}Cl_2N_2OPd$: C 43.35, H 3.40, N 6.74; found: C 43.34, H 3.61, N 6.74.

*Synthesis of (Diaqua){(*S*)-4-benzyl-4,5-dihydro-2-(pyridin-2-yl-*κ*N)oxazole-*κ*N}palladium(II) Trifluoromethanesulfonate* (**5b**). $[PdCl_2[(S)$-4-benzyl-4,5-dihydro-2-(pyridin-2-yl)oxazole$\}$ (1.61 g, 3.9 mmol) was suspended in 300 ml of dry THF; 2.1 g (8.2 mmol, 1.05 equiv.) of AgOTf in 50 ml of THF was slowly added to this mixture, and the resulting suspension was stirred for 2 h at r.t. The Ag salt formed was removed by filtration on *Celite*, and the filtrate was reduced to *ca*. 20 ml. This soln. was added to 120 ml of cold pentane; the precipitate was quickly filtered and then dried *in vacuo* to give **5b** (1.87 g, 2.8 mmol, 71%). Beige powder. ^{1}H-NMR: 2.6–3.7 (br., 2 H_2O); 2.97 (*dd*, ^2J = 13.8, ^3J = 8.0, 1 H, PhCH_2); 3.37 (*d*, ^2J = 13.8, 1 H, PhCH_2); 4.84–4.93 (*m*, H–C(4), 2 H–C(5)); 7.28–7.44 (*m*, 5 arom. H); 7.80 (*d*, ^2J = 7.8, H–C(3) of Py); 7.88 (*t*, ^2J = 6.1, H–C(5) of Py); 8.29 (*t*, ^2J = 7.8, H–C(4) of Py); 8.53 (br., H–C(6) of Py). Anal. calc. for $C_{17}H_{18}F_6N_2O_9PdS_2$ (678.9): C 30.08, H 2.67, N 4.13; found: C 31.47, H 3.11, N 3.55.

*Synthesis of {(*S*)-4-Benzyl-4,5-dihydro-2-(pyridin-2-yl-*κ*N)oxazole-*κ*N}(dimethyl)palladium(II)* $[PdMe_2$(tmeda)] (500 mg, 1.98 mmol) was dissolved in 12 ml of benzene at r.t., and 496 mg (2.08 mmol, 1.05 equiv.) of (*S*)-4-benzo-4,5-dihydro-2-(pyridin-2-yl)oxazole in 4 ml of benzene was added to the resulting soln. After 5 min, 24 ml of pentane was added, and the mixture was stirred for 2 h. Evaporation of the solvent and trituration of the residue with Et_2O gave the desired complex as a pale yellow powder (402 mg, 1.07 mmol, 54.3%). ^{1}H-NMR: 1.17 (*s*, PdMe); 1.25 (*s*, PdMe); 2.79 (*dd*, ^2J = 13.8, ^3J = 7.7, 1 H, PhCH_2); 2.96 (*dd*, ^2J = 13.8, ^3J = 3.8, 1 H, PhCH_2); 3.61 (*dd*, ^2J = 8.8, ^3J = 9.5, 1 H–C(5)); 3.85 (*dd*, ^2J = 8.8, ^3J = 6.2, 1 H–C(5)); 4.19–4.28 (*m*, 1 H–C(4)); 6.38 (*t*, ^3J = 5.1, H–C(5) of Py); 6.64 (*t*, ^3J = 7.7, H–C(4) of Py)); 6.89 (*d*, ^3J = 7.7, H–C(3) of Py)); 6.92–7.01 (*m*, 3 arom. H); 7.13–7.16 (*m*, 2 arom. H); 8.48 (*d*, ^3J = 5.1, H–C(6) of Py). In the NOESY spectrum (C_6D_6, 25°), the Me group at 1.17 ppm shows a NOE to H–C(5) of Py and the Me group at 1.25 ppm shows a NOE to H–C(4) and to PhCH_2. Anal. calc. for $C_{17}H_{20}N_2OPd$ (374.78): C 54.48, H 5.38, N 7.47; found: C 54.30, H 5.44, N 7.43.

Synthesis of {(S)-4-Benzyl-4,5-dihydro-2-(pyridin-2-yl-κN)oxazole-κN}(chloro)(methyl)palladium(II) (**10**). AcCl (370 mg, 4.72 mmol, 5.2 equiv.) was added to 339 mg (0.91 mmol) of the dimethyl complex described above, dissolved in 30 ml of benzene. After stirring for 0.5 h at r.t., the solvent was removed under reduced pressure to give **10** (332 mg, 0.84 mmol, 93%). Yellow powder. ^{1}H-NMR: 1.61 (*s*, PdMe); 2.52 (*dd*, ^2J = 14.0, ^3J = 7.9, 1 H, PhCH_2); 2.72 (*dd*, ^2J = 14.0, ^3J = 3.6, 1 H, PhCH_2); 3.86–3.97 (*m*, 2 H–C(5)); 4.08–4.22 (*m*, H–C(4)); 6.44 (*t*, ^3J = 5.0, H–C(5) of Py); 6.58 (*t*, ^3J = 7.7, H–C(4) of Py); 6.89 (*d*, ^3J = 7.7, H–C(3) of Py); 6.92–7.04 (*m*, 5 arom. H); 9.05 (*d*, ^3J = 5.0, H–C(6) of Py). The Me group at 1.61 ppm shows a NOE to the H–C(4) and the PhCH_2. Anal. calc. for $C_{16}H_{17}ClN_2OPd$ (395.20): C 48.63, H 4.34, N 7.09; found: C 51.65, H 4.78, N 6.42.

Synthesis of (Acetonitrile-κN){(S)-4-benzyl-4,5-dihydro-2-(pyridin-2-yl-κN)oxazole-κN}(methyl)palladium(II) Trifluoromethanesulfonate (**11**). A soln. of 174 mg (0.68 mmol, 1.05 equiv.) AgOTf in 8 ml of MeCN was slowly added to 250 mg (0.63 mmol) of **10** in MeCN. After stirring for 1 h, the formed AgCl salt was removed by filtration over *Celite*, and the yellow filtrate was concentrated under reduced pressure to give **11** (248 mg, 0.62 mmol, 98%). Pale yellow powder. ^{1}H-NMR: 1.17 (*s*, PdMe); 2.55 (*s*, PdNC*Me*); 2.85 (*dd*, ^2J = 14.0, ^3J = 8.2, 1 H, PhCH_2); 3.15 (*dd*, ^2J = 14.0, ^3J = 3.6, 1 H, PhCH_2); 4.54–4.64 (*m*, 1 H–C(4)); 4.74–4.87 (*m*, 2 H–C(5)); 7.25–7.35 (*m*, 5 arom. H); 7.79 (*d*, ^3J = 7.8, H–C(3) of Py); 7.94 (*t*, ^3J = 5.0, H–C(5) of Py); 8.12 (*t*, ^3J = 7.8, H–C(4) of Py); 8.80 (*d*, ^3J = 5.0, H–C(6) of Py). In the NOESY spectrum (C_6D_6, 25°) the Me group shows a NOE to H–C(4) and PhCH_2.

Reaction of **11** *with CO.* A CD_2Cl_2 soln. of compound **11** in a NMR tube was saturated with labelled (or unlabelled) CO at −78° to give *(acetonitrile-κN)(acetyl){(S)-4-benzyl-4,5-dihydro-2-(pyridin-2-yl-κN)oxazole-κN}palladium(II)trifluoromethanesulfonate* (**12**) with *ca.* 20% of *(acetyl){(S)-4-benzyl-4,5-dihydro-2-(pyridin-2-yl-κN)oxazole-κN}(carbonyl)palladium(II)trifluoromethanesulfonate* (**13**). ^{1}H-NMR of **12** (300 MHz, CD_2Cl_2, 25°): 2.55 (*s*, NC*Me*); 2.59 (*d*, ^2J(C,H) = 6.3, Pd^{13}CO*Me*); 3.00–2.76 (*m*, 2 H–C(5)); 4.55–4.37 (*m*, 1 H–C(4)); 4.80–4.67 (*m*, PhCH_2); 7.37–7.14 (*m*, 5 arom. H); 7.89–7.86 (*m*, 1 H of Py); 7.79 (*d*, ^3J(H,H) = 7.6, 1 H of Py); 8.08 (*td*, ^3J(H,H) = 7.6, ^4J(H,H) = 1.4, 1 H of Py); 8.68 (*d*, ^3J(H,H) = 4.8, 1 H of Py). ^{13}C-NMR (75 MHz, CD_2Cl_2, 25°): 219.10 (Pd^{13}*C*OMe). In the NOESY spectrum (C_6D_6, 25°), the Me group at 2.59 ppm shows a NOE to H–C(4) of the ligand. After *ca.* 14 h, **12** completely disappeared from the mixture to give **13**. ^{1}H-NMR of **13** (300 MHz, CD_2Cl_2, 25°): 3.00–2.62 (br., 6 H, H–C(5), Pd^{13}CO*Me*); 4.55–4.37 (br., 1 H–C(4)); 4.84–4.68 (br., PhCH_2); 7.37–7.14 (br., 5 arom. H); 7.89–7.83 (br., 1 H of Py) 7.98–7.90 (br., 1 H of Py); 8.26–8.15 (br., 1 H of Py); 8.64–8.53 (br., 1 H of Py). ^{13}C-NMR (75 MHz, CD_2Cl_2, 25°): 172.91 (Pd^{13}CO); 211.51 (Pd^{13}*C*OMe). The acyl Me group shows an NOE to the pyridine H-atom at 8.64 ppm in the NOESY spectrum (C_6D_6, 25°).

Copolymerization Experiments. A 250-ml stainless-steel autoclave under N_2 was charged with 1,4-benzoquinone (0.216 g; 2.0 mmol). The Pd complex (0.11 mmol) was dissolved in MeOH (10 ml) in a *Schlenk* tube, and the mixture was stirred for 15 min. After adding styrene (50 ml, 435 mmol), the soln. was transferred to the pre-evacuated autoclave. After pressurizing with CO, the autoclave was placed in an oil bath, and the mixture was stirred and heated to 50°. The reaction was stopped by cooling the autoclave to r.t., and the residual gas was released. The mixture was poured into MeOH, and the insoluble copolymer was filtered off, washed again with MeOH and dried under reduced pressure. Prior to NMR analysis, some of the recovered copolymer was extracted with MeOH in a *Kumagawa* extractor.

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