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High Stereocontrol and Efficiency in CO/Styrene Polyketone Synthesis Promoted by Azabis(oxazoline)−Palladium Complexes

Alexander Schätz,[†] Alessandro Scarel,[‡] Ennio Zangrando,[‡] Luca Mosca,[§] Carla Carfagna,[§]
Anja Gissibl,[†] Barbara Milani,*,[‡] and Oliver Reiser*,[†]

*Institut für Organische Chemie, Universität Regensburg, Universitätsstrasse 31,
93053 Regensburg, Germany, Dipartimento di Scienze Chimiche, Università di Trieste,
Via Licio Giorgieri 1, 34127 Trieste, Italy, and Istituto di Scienze Chimiche, Università di Urbino,
Piazza Rinascimento 6, 61029 Urbino, Italy*

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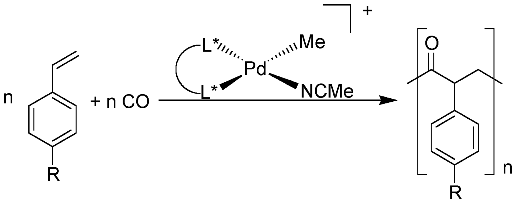
Summary: Palladium−azabis(oxazoline) complexes proved to be highly selective and efficient in the asymmetric copolymerization of styrene and CO at ambient pressure.

Stereoregular polymers, like isotactic polypropylene, have changed the world due to their extraordinary material properties. Such polymers possess mirror planes and are consequently not chiral. Nevertheless, metal-promoted polymerization using chiral catalysts has proved to be the most powerful tool to achieve the stereocontrolled synthesis of these macromolecules.[1]

Few examples of polymers characterized by main-chain chirality are known to date, although they have considerable potential for application as optically active materials.[2] Isotactic polyketones, being obtained by copolymerization of vinyl monomers and CO, are among these, possessing a true stereocenter along the polymer backbone (Scheme 1).[3] Several catalytic systems have been reported to afford the synthesis of isotactic CO/vinyl arene copolymers; all of them are based on palladium(II) complexes modified with enantiomerically pure ligands of different nature. Nitrogen-donor chelating ligands (N*-N*),[4] the phosphino−phosphito derivative BINAPHOS,[5] or hybrid P-N ligands[6] have been successfully employed, yielding polyketones with impressively high stereoregularity. The systems based on N*-N* ligands appear to be especially attractive, since they are not prone to oxidative degradation like their phosphine counterparts and, moreover, they do not require high CO pressure like the P-N-containing catalysts. However, due to the comparatively weak coordination of nitrogen ligands, their palladium complexes suffer from a rather poor stability, which have prevented so far the synthesis of isotactic polyketones in high yields and with high molecular weight values.

Scheme 1. Asymmetric CO/Styrene Copolymerization with Pd^{II} Complexes of Enantiomerically Pure Ligands (R = H, Me, ^{t}Bu)



Work by Brookhart[4a] and co-workers has demonstrated that Pd^{II} complexes of the bis(oxazoline) species **1** (Figure 1) promote the copolymerization of *p-tert*-butylstyrene, representing one of the most reactive substrates for this process, and CO to completely isotactic polyketone, albeit with low yield. Similarly, fully isotactic CO/styrene or CO/*p*-methylstyrene copolymers were obtained by means of Pd^{II} complexes with the bioxazoline **2** (Figure 1), however, always with low productivity.[4b,c]

Very recently, we reported that the yield of the isotactic CO/styrene copolymer is remarkably enhanced when the copolymerization, promoted by the complex [Pd(Me)(MeCN)((*S,S*)-*i*Pr-BIOX)][X] (X = BArF (BArF = B(3,5-$(CF_3)_2C_6H_3)_4$), PF_6^-, OTf (OTf = triflate)), is carried out in 2,2,2-trifluoroethanol (TFE) instead of dichloromethane or methanol.[7] At the same time, however, the variation of the reaction medium resulted in a partial loss of the stereochemical control during the polymerization process, and polyketones with a prevailing (61−76% of the *ll* triad content), but not fully isotactic, microstructure have been obtained.

With the goal of finding a catalyst able to synthesize the CO/vinyl arene polyketones in high yield and at the same time with complete isospecificity, we focused our attention on the nitrogen-bridged azabis(oxazoline)[8] **3** ((*S,S*)-*i*Pr-AZABOX; Figure 1). Indeed, azabis(oxazolines) with their electron-

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* To whom correspondence should be addressed. Fax: +49-941-943 4121 (O.R.). E-mail: Oliver.Reiser@chemie.uni-regensburg.de (O.R.); milani@dsch.units.it (B.M.).

[†] Universität Regensburg.

[‡] Università di Trieste.

[§] Università di Urbino.

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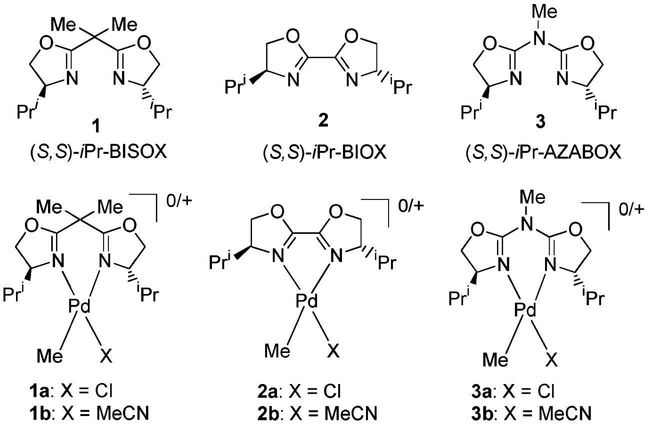

Figure 1. Bis(oxazolines) **1**−**3** and their neutral (**1a**−**3a**) and monocationic (**1b**−**3b**) Pd^{II} complexes.

Table 1. CO/Styrene Copolymerization in 2,2,2-Trifluoroethanol:[a] Effect of the Nitrogen Donor Ligand

N*-N*	amt of CP[b] (g)	g CP/g Pd	M_w (M_w/M_n)[c]	ll[d] (%)	$[\alpha]^{25}_{568}$[e] (deg)
1	0.120	88	4600 (1.7)	>99	−338
2	1.013	750	3000 (1.3)	73	−267
3	0.285	210	22 000 (1.2)	>99	−363

[a] Catalyst precursor: [Pd(Me)(MeCN)(N*-N*)][PF$_6$] (**1b**−**3b**). Reaction conditions: n_{Pd} = 12.8 × 10^{-6} mol; styrene V = 10 × 10^{-3} L; p_{CO} = 1 bar; [BQ]/[Pd] = 40; T = 30 °C; solvent V = 20 mL of TFE; t = 24 h. [b] Isolated copolymer. [c] Determined by GPC measurements versus polystyrene. [d] Content of the *ll* triad determined by integration from ^{13}C NMR. [e] 0.25 g/L in CHCl$_3$.

donating amino group in the central bridge are in general considerably more electron rich than the corresponding bis(oxazolines), resulting in metal complexes with greatly improved stability.[9,10] Moreover, the electronic properties of these ligands can be tuned through alkylation on the central nitrogen, thus allowing a broader scope of certain catalytic asymmetric transformations such as the cobalt-catalyzed conjugate reduction[11] or the copper-catalyzed benzoylation of diols.[12]

With ligands **1**−**3** we synthesized the monocationic Pd^{II} complexes [Pd(Me)(MeCN)(N*-N*)][PF$_6$] (**1b**−**3b**; N*-N* = **1**−**3**) through a dehalogenation reaction of the corresponding neutral derivatives **1a**−**3a** (Figure 1). Complexes **1b**−**3b** were tested as precatalysts in the copolymerization of CO and styrene, the last species being the most readily available vinyl arene but also being known as a substrate with much lower reactivity for this process with respect to its para-substituted derivatives. The reactions were carried out in trifluoroethanol at 30 °C under 1 bar of CO pressure, in the presence of an excess of 1,4-benzoquinone (BQ) with respect to palladium ([BQ]/[Pd] = 40). The solids isolated at the end of the runs were perfectly alternating polyketones.

Complex **2b**, containing the (*S,S*)-*i*Pr-BIOX ligand, was found to be the most active among the three tested (Table 1); however, in agreement with our previous data,[7] the polyketones obtained were of low molecular weight and isotacticity. Perfectly isotactic copolymer was obtained with complex **1b** containing the (*S,S*)-*i*Pr-BISOX ligand, but a significant loss of productivity was found. With complex **3b** having the (*S,S*)-*i*Pr-AZABOX ligand incorporated, while still producing exclusively isotactic copolymer, the productivity more than doubled, and moreover, the molecular weight of the polymer obtained was 5 times higher with a narrow molecular weight distribution compared to the case for **1b** (Table 1).

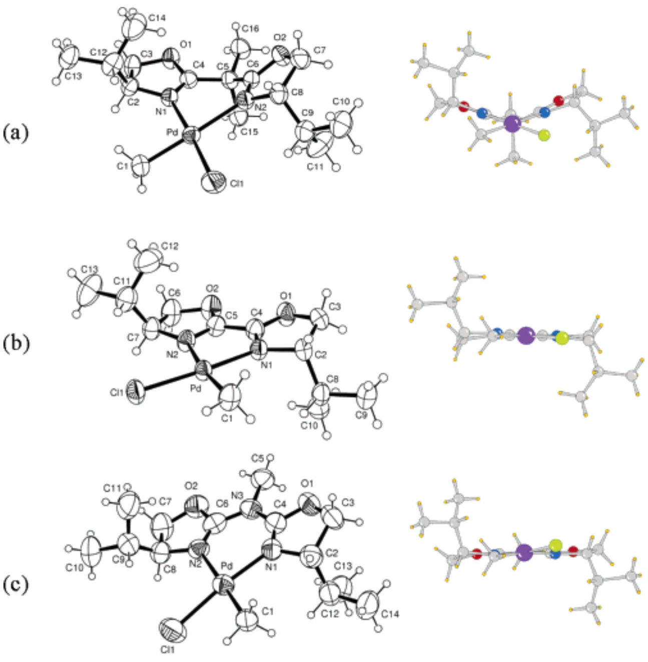

Figure 2. ORTEP drawings (ellipsoids at 40% probability level) and side views of complexes (a) **1a**, (b) **2a**, and (c) **3a**.

Comparison of the crystal structures[13] of **1a**−**3a** (Figure 2) reveals that **3** binds more tightly to palladium compared to **1** and **2**, as judged by the shortening of the Pd−N(2) bond from 2.20 to 2.10 Å (Table 2).[14] The increased stability of palladium complexes with **3** is also observed experimentally with the decomposition to black palladium for complex **1b** but not for **3b** during the copolymerization at standard reaction conditions (Table 1). In parallel to the shortened Pd−N(2) bond, the translocated Pd−C(1) bond is significantly prolonged in **3a** from 2.03 to 2.09 Å, indicating a greater lability of the methyl substituent on palladium, a necessary requirement for the copolymerization to proceed. Consequently, these data provide

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(13) The crystal structure of **2a** was reported in ref 7. CCDC 603141 (**1a**) and 603142 (**3a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, U.K.; fax (+44) 1223−336−033; deposit@ccdc.cam.ac.uk). CIF files of **1a** and **3a** are also part of the Supporting Information available with this publication. Crystal data for **1a**: $C_{16}H_{29}ClN_2O_2Pd$, M_r = 423.26, orthorhombic, space group $P2_12_12_1$, a = 9.197(3) Å, b = 9.923(4) Å, c = 20.785(4) Å, V = 1896.9(10) Å^3, Z = 4, D_c = 1.482 g/cm^3, μ(Mo Kα) = 1.127 mm^{-1}, F(000) = 872, θ_{max} = 29.60°, final R1 = 0.0349, wR2 = 0.0691, S = 0.981 for 199 parameters and 21 076 collected reflections, 4886 unique reflections (R_{int} = 0.0537), residuals in ΔF map 0.546, −0.290 e Å^{-3}. Crystal data for **3a**: $C_{14}H_{26}ClN_3O_2Pd$, M_r = 410.23, orthorhombic, space group $P2_12_12_1$, a = 9.944(3) Å, b = 11.180(3) Å, c = 16.186(5) Å, V = 1799.5(9) Å^3, Z = 4, D_c = 1.514 g/cm^3, μ(Mo Kα) = 1.187 mm^{-1}, F(000) = 840, θ_{max} = 27.10°, final R1 = 0.0512, wR2 = 0.1283, S = 0.950 for 190 parameters and 17 933 collected reflections, 3157 unique (R_{int} = 0.0350), residuals in ΔF map 0.702, −0.329 e Å^{-3}.

(14) The higher Lewis basicity of ligand **3** with respect to that of ligand **1** has been confirmed even in solution by an in situ NMR competition experiment: mixing 1 equiv of **1** and 1 equiv of **3** in CD$_2$Cl$_2$ at room temperature followed by addition of 1 equiv of [Pd(COD)(Me)(Cl)] showed the formation of the palladium complex **3a** over **1a** with a preference of >90:<10.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complexes 1a−3a[a]

	1a	**2a**[7]	**3a**
Pd−N(1)	2.060(3)	2.059(4)	2.051(7)
Pd−N(2)	2.202(3)	2.189(3)	2.101(6)
Pd−C(1)	2.027(4)	2.017(4)	2.091(6)
Pd−Cl	2.306(1)	2.302(15)	2.303(3)
C(1)−Pd−N(1)	90.55(15)	93.8(2)	94.7(3)
N(1)−Pd−N(2)	86.64(11)	77.88(15)	86.3(3)
C(1)−Pd−Cl	86.07(13)	91.50(16)	83.1(2)
N(2)−Pd−Cl	96.76(8)	96.79(11)	96.50(18)

[a] For atom numbering, see Figure 2.

Table 3. CO/Styrene Copolymerization in 2,2,2-Trifluoroethanol:[a] **Effect of Reaction Time, Temperature, and [BQ]/[Pd] Ratio**

entry	time (h)	T (°C)	[BQ]/[Pd]	g CP/g Pd	M_w (M_w/M_n)[b]	$[\alpha]^{25}_{586}$[c] (deg)
1	16	30	40	81	13 400 (1.1)	
2	24	30	40	210	22 000 (1.2)	−363
3	48	30	40	503	25 000 (1.4)	−372
4	24	30	0	89		
5	24	30	5	111	19 900 (1.2)	−365
6	24	30	20	178	23 600 (1.2)	−363
7	24	30	30	229	31 500 (1.3)	−378
8	24	30	40	210	22 000 (1.2)	−363
9	24	45	20	243	29 700 (1.4)	
10	24	45	30	255	28 100 (1.6)	−414
11	24	45	40	338	18 100 (1.9)	
12	24	56	30	74	8100 (1.9)	

[a] Catalyst precursor: [Pd(Me)(MeCN)(**3**)][PF_6]. Reaction conditions: $n_{Pd} = 12.8 \times 10^{-6}$ mol; styrene $V = 10 \times 10^{-3}$ L; solvent $V = 20 \times 10^{-3}$ L of TFE; $p_{CO} = 1$ bar. [b] Determined by GPC measurements versus polystyrene. [c] 0.25 g/L in $CHCl_3$.

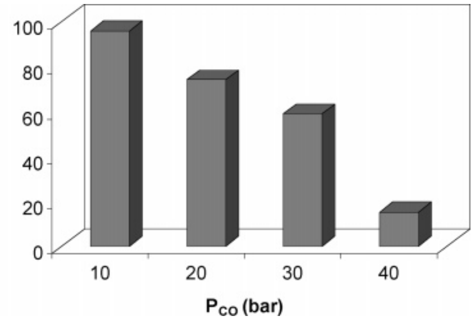
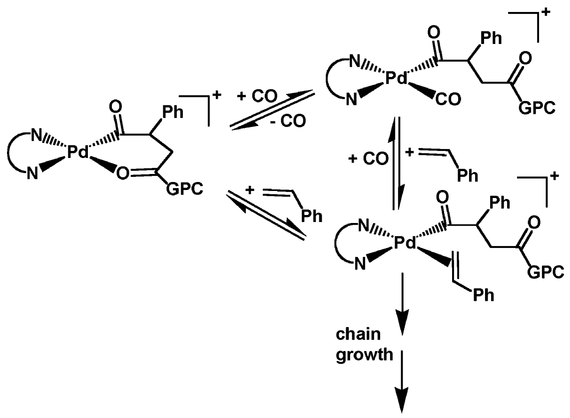


Figure 3. CO/styrene copolymerization: effect of CO pressure. The catalyst precursor was [Pd(Me)(MeCN)(**3**)][PF_6]. Reaction conditions: $n_{Pd} = 12.8 \times 10^{-6}$ mol; styrene $V = 30 \times 10^{-3}$ L; [BQ]/[Pd] = 20; $T = 50$ °C; solvent $V = 20 \times 10^{-3}$ L of TFE; $t = 24$ h.

Scheme 2. Key Steps of the Copolymerization Process



an explanation for the increased productivity of **3b** with respect to **1b**; however, the respective bond lengths of **2a** do not fit into this picture.

We assume that the N−Pd−N coordination angle must also exert a significant effect on the productivity and tacticity of the copolymer being obtained. While in **1a** and **3a** N−Pd−N coordination angles of around 86° are observed in their X-ray structures, in **2a** this angle is decreased to 78°, which could be a factor for the increased productivity of the catalyst **2b** but at the same time for the partial loss of the control of the stereochemistry during the polymerization. Indeed, the six-membered palladacycle formed by ligands **1** and **3** approaches better the angle for the ideal square-planar geometry around palladium than the five-membered palladacycle involving ligand **2**. In the latter case the deviation from the ideal square-planar geometry could cause the opening of one Pd−N bond during the copolymerization in TFE, resulting in isomerization equilibria that could decrease the efficiency of the enantioface selection. Finally, the control of the tacticity seems not to be related to the distortion of the ligand evidenced by the side view of the complexes **1a** and **3a** (Figure 2).

Working with [Pd(Me)(MeCN)(**3**)][PF_6], the effect of several parameters was investigated. Productivity increases with time by reaching the value of 503 g of CP/g of Pd after 48 h, without any decomposition to palladium metal (Table 3, entries 1−3). The M_w values indicate the presence of a chain transfer reaction (Table 3, entries 1−3).

1,4-Benzoquinone is a necessary component of this catalytic system: low productivity together with formation of palladium black was observed in its absence (Table 3, entry 4). The optimum benzoquinone to palladium ratio ranges between 30 and 40, depending on reaction temperature (Table 3, entries 5−11). For instance, the productivity was raised to 338 g of CP/g of Pd by increasing the reaction temperature to 45 °C and with [BQ]/[Pd] = 40. A further increase of temperature, up to 56 °C, resulted in a dramatic loss of productivity (Table 3, entries 7, 10, and 12). The effect of these parameters on the length of the polymeric chains is as previously observed with complex **2b**:[7] both an excess of BQ with respect to palladium and an increase of temperature cause a decrease of the M_w values. It is important to note that in all cases copolymers with a complete isotactic microstructure were obtained.

A dramatic decrease of productivity was found on increasing the CO pressure from 10 to 40 bar (Figure 3), in contrast with other catalysts that require high CO pressures.[6] No formation of inactive palladium metal was observed, indicating that the loss of catalytic activity is due to the inhibiting effect of CO rather than to catalyst decomposition.

The higher Lewis basicity of **3** with respect to that of **1** accounts also for the observed CO inhibiting effect. Very recently, we have found that the step mainly affected by the CO pressure is the equilibrium between the Pd−acyl−carbonyl species, which represents the resting state of the catalytic cycle, and the Pd−acyl−alkene intermediate (Scheme 2).[15] The position of this equilibrium is sensitive to the electron density on palladium: the Pd−acyl−carbonyl species is stabilized by the presence of electron-rich ligands on the metal, while the formation of the Pd−acyl−alkene intermediate is favored with ligands bearing electron-withdrawing substituents. Apparently, the more electron rich azabis(oxazoline) ligand **3** provides a sufficiently stable palladium complex (no palladium black

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formation as observed with the bis(oxazoline) ligand **1**), which leads to good productivities at atmospheric CO pressure but which is inhibited by the formation of the palladium−acyl−carbonyl species upon higher CO pressures. The results reported are in perfect agreement with this trend.

The good catalytic behavior of the (*S*,*S*)-*i*Pr-AZABOX-containing catalyst is not restricted to styrene but has also been observed in the CO/*p*-methylstyrene copolymerization. A productivity of 273 g of CP/g of Pd was achieved in the synthesis of the fully isotactic CO/*p*-methylstyrene polyketone with an M_w value of 17 000 ($M_w/M_n = 1.7$) under the reaction conditions reported in Table 1 ([BQ]/[Pd] = 30).

In conclusion, for the synthesis of fully isotactic CO/vinyl arene polyketones in alcoholic medium at ambient pressure (*S*,*S*)-*i*Pr-AZABOX exceeds previously known ligands in terms of productivity and molecular weight, which could be rationalized by a structural analysis of the catalyst precursors.

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Supporting Information Available: Text giving a full description of the experimental details, CIF files giving crystallographic data, and a figure giving sample spectra of the polymers synthesized. This material is available free of charge via the Internet at http://pubs.acs.org.

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