The Control of the Stereochemistry in the Palladium-Catalyzed Alternating Styrene/Carbon Monoxide Copolymerization: Effect of the Chirality of the Ligand and of the Ligand-to-Palladium Ratio

Preliminary Communication

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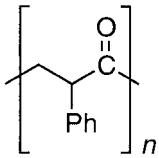
Dedicated to Professor *Dieter Seebach* on the occasion of his 65th birthday

Diaquapalladium(2+) trifluoromethanesulfonates modified with (4*R*,4′*S*)- or (4*S*,4′*S*)-2,2′-bis(4-benzyl-4,5-dihydrooxazole) (C_s- and C_2-ligands) produce isotactic poly(1-oxo-2-phenylpropane-1,3-diyl) through copolymerization of styrene with carbon monoxide. However, the same *meso*-catalyst in the presence of the free ligand leads to prevailingly syndiotactic growth of the copolymer, whereas the optically active catalyst, when used in the presence of the free enantiomeric ligand, gives an atactic copolymer.

Asymmetric catalysis leading to the synthesis of stereoregular copolymers has been a matter of intense interest [1] since the discovery of isotactic polypropylene and its rationalization based on the existence of enantiomorphic catalytic sites [2]. The discovery of the relationship between the symmetry properties of the catalytic system and the microstructure of the produced polymers in the case of the propene polymerization by zirconocene catalytic systems is particularly intriguing [3][4].

Despite the development of a variety of palladium-nitrogen-donor ligands catalytic systems to promote the synthesis of stereoregular styrene/carbon monoxide (CO) copolymers **1** [5], the factors involved in the enantioface discrimination during the related copolymerization of olefins with CO are much less understood [6][7].



1

We showed that $[Pd(PP)(H_2O)_2][OTf]_2$ complexes (where PP is either (1*R*,1′*S*)-or (1*RS*,1′*RS*)-1,2-bis[1,1′-(diphenylphosphino)ethyl]benzene, OTf = trifluoromethanesulfonate), when used as catalyst precursors for the copolymerization of propene with CO, produce both isotactic poly(1-methyl-2-oxopropane-1,3-diyl) [8]. The *meso*-ligand shows higher stereospecificity and much higher catalytic activity than the *racemic*-

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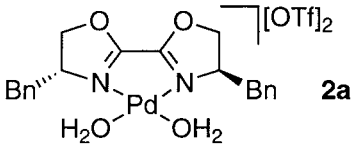
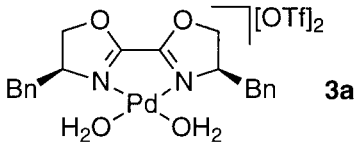
ligand, possibly due to the highly stereo- and regiospecific formation of the olefin intermediate responsible for insertion. On the other hand, it has been reported that [Pd(CH_3)(N*N*)(MeCN)](BARF) (where N*N* is optically pure 2,2′-propane-1,3-diylbis(4,5-dihydro-4-methyloxazole)) produces isotactic poly(1-oxo-2-phenylpropane-1,3-diyl) from styrene and CO; when used in the presence of 1 equiv. of the alternative enantiomer ligand, the copolymer forms at a higher rate and with a prevailingly syndiotactic structure [9][10]. Rapid exchange of the ligand with respect to chain growth and enantiomorphic site control of the stereochemistry of the polymerization explain these findings. We speculated that, for related complexes containing *meso*-ligands with C_s-symmetry, the direct availability of enantiotopic coordination sites (see **3a**) might, therefore, result in higher reactivity towards the formation of a syndiotactic copolymer. To verify this hypothesis, we synthesized (4*S*,4′*S*)-**2** and (4*R*,4′*S*)-2,2′-bis(4-benzyl-4,5-dihydrooxazole) (**3**), and their corresponding diaquapalladium(II) triflate complexes, **2a** and **3a**, and used them as catalyst precursors for the copolymerization of styrene with CO.



2a



3a

In contrast to our expectations, copolymerization with the *meso*-ligand gives a copolymer with a prevailing isotactic structure (*Table* and *Figure*, *c*). The ^{13}C-NMR spectrum in the region of the *ipso*-C-atom shows a sharp band associated, at least, with the *ll*-triad [11]. The material is comparable with that obtained with the optically pure ligands (*Figure*, *a*), which shows high optical activity [12]. It is, however, remarkable that, when the copolymerization reaction is carried out with **3a** in the presence of 1 mol-equiv. (with respect to the catalyst precursor) of the free ligand **3** under otherwise the same reaction conditions, poly(1-oxo-2-phenylpropane-1,3-diyl) with a prevailingly syndiotactic structure forms at a lower reaction rate (*Table* and *Figure*, *d*); the most intense group of bands is in the region of the *uu*-triad [11]. Furthermore, when the copolymerization is carried out with only MeOH as the solvent instead of the 10:1 mixture of CH_2Cl_2 and MeOH, the C_s-system **3a** again produces a prevailingly syndiotactic copolymer.

Table. *Copolymerization of Styrene and CO*[a])

Catalyst	Reaction time [h]	Polymer [g]	Productivity [g/gPd·h]	Mn ($\times 10^{-3}$)
2a	2.75	0.62	20	2.2
2a[b])	16.5	0.10	0.4	5.5
3a	6.25	0.38	4	12
3a[c])	16	0.26	1	7.9

[a]) Reaction conditions: 0.15 mmol of catalyst precursor, 2 mmol of benzoquinone, 50 ml of styrene, 1 ml of MeOH, 9 ml of CH_2Cl_2, 1.5 bar of CO, 25°. [b]) 1 Equiv. of (*R*,*R*)-ligand added to the reaction mixture. [c]) 1 Equiv. of *meso*-ligand added to the reaction mixture.

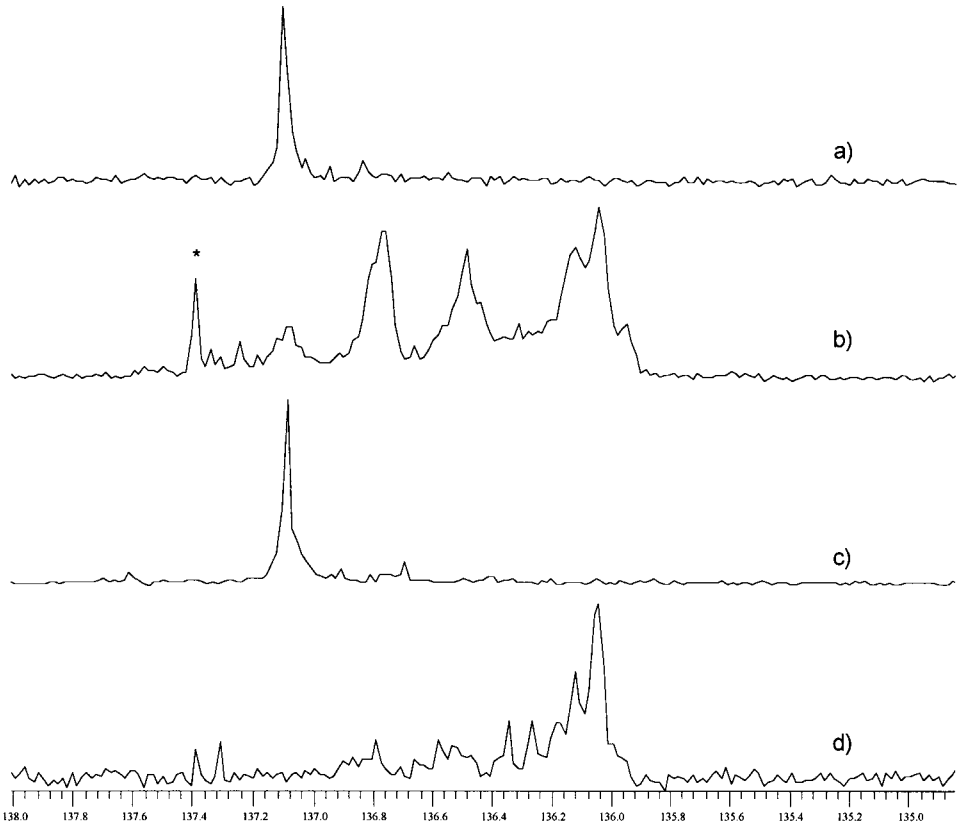
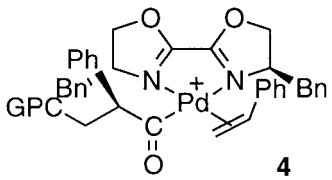


Figure. *^{13}C-NMR* ((D$_2$)-HFIP/CDCl$_3$, *ipso*-C-atom region, ppm) *of poly(1-oxo-2-phenylpropane-1,3-diyl) prepared with catalyst precursors* **2a** *and* **3a** *under different reaction conditions. a*) **2a**; *b*) **2a** + 1 equiv. of (*R*,*R*)-ligand **2**; *c*) **3a**; *d*) **3a** + 1 equiv. *meso*-ligand **3** (* = styrene impurity).

As reported in [12], the optically active catalyst precursor **2a** gives the expected isotactic copolymer. When **2a** is used in the presence of 1 mol-equiv. of the alternative enantiomeric ligand, the copolymerization takes place only very slowly (*Table*), in contrast to the case of the aforementioned chiral 2,2′-propanediylbis(4,5-dihydro-4-methyloxazole) system [10]. Moreover, the stereochemistry of the produced copolymer changes from isotactic, leading to the formation of an essentially atactic material (*Figure*, *a* and *b*). The different behavior with respect to the reaction rate of the two C_2 systems possibly reflects the putatively stronger coordination of the bis(4,5-dihydro-4-benzyloxazole) ligands. Association of the free ligand in solution with the catalytic complex depresses the catalytic activity by occupation of the coordination sites on the catalyst.

As far as the stereochemical outcome of the reactions is concerned, the production of the isotactic copolymers using the C_s-system, in spite of the accessibility of the syndiotactic structure, is regarded to be evidence for the existence of similar olefin

intermediates for the two systems with different geometry (C_s and C_2, **5** and **4**, GPC = growing polymer chain).



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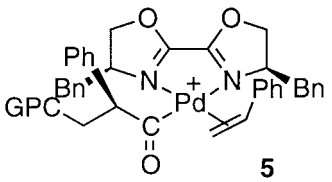

5

The prevailing formation of *l*-dyads found with the C_s-symmetry system probably implies site-selective coordination of the olefin substrate to maintain discrimination of the same enantioface that is determined by the center of chirality at C(4) of the dihydrooxazole ring [13][14]. As a consequence, it also seems that isomerization does not occur during the growth of the chain. On the other hand, the variation in the microstructure of the copolymer observed upon addition of the free ligand is probably due mainly to the isomerization of the intermediate **5** to a structure in which the coordination sites of the olefin and the growing chain are interchanged. Indeed, exchange of the *meso*-ligand by itself cannot change the nature of the catalytic species. The isomerization of the coordination site might be caused by association of the free ligand with the formation of sterically labile five-coordinated intermediates [15]. The chemical behavior of the related species in solution was investigated by means of NMR spectroscopy. When 1 mol-equiv. of the *meso*-ligand **3** is added to a solution of the Pd-Me derivative [Pd(Me)(**3**)(MeCN)][OTf] (**3b**), free MeCN is formed, and no signal due to free bioxazoline is observed. Therefore, complete substitution of MeCN with the second molecule of **3** occurred, yielding a [Pd(Me)(**3**)$_2$][OTf] species **3c** with both molecules of the bioxazoline ligand coordinated to Pd. These two molecules are involved in dynamic processes that are fast on the NMR time-scale, thus making them equivalent. Reaction of both solutions of **3b** and **3c** with labeled (and unlabeled) CO leads to the formation of the corresponding acetyl products. In the case of **3b**, the palladium-acyl-carbonyl species [Pd(C(O)Me)(CO)(**3**)][OTf] is obtained (two *singlets* at 209.96 and 170.35 ppm in ^{13}C NMR spectrum). For **3c**, a broad signal at 222.19 ppm is also observed, which is assigned to the acyl species with the two molecules of bioxazoline coordinated [Pd(C(O)Me)(**3**)$_2$][OTf]. Moreover, in the corresponding ^{1}H-NMR spectrum, all the signals due to the bioxazoline ligand are broad, even at low temperature (203 K), thus again indicating a dynamic process. Similar behavior was reported for the [Pd(Me)(phen)$_2$][OTf] complexes [16]. These experiments clearly indicate that association of a second molecule of the ligand takes place, yielding a five-coordinated species, which is involved in fluxional processes [15]. Complete exchange between the bound and the free ligand was found to occur in the aforementioned Pd-bioxazoline [10]. Association of the free ligand in solution with the catalytic complex eventually leads to ligand exchange at a rate comparable to that of copolymerization. Therefore, in the case of the C_2-system, enantiomerization of the catalytic complex leads to the formation of a mostly atactic copolymer.

The change in the microstructure of the copolymer produced with MeOH as the only solvent with the *meso*-system is most probably a consequence of ion-pairing effects on the stereochemistry of the copolymerization [17]. A stronger labilization of the ion

pair by the more polar solvent might cause a greater separation of the ion pair with easier isomerization at the level of intermediate **5** [18]. The effect of the anion both on the activity and the stability of the catalytic system used for the CO/styrene copolymerization has been reported [19]. Experiments are in progress to detect the effect, if any, of the anion on the stereochemistry of the produced copolymer.

The data obtained evidence that C_2- and C_s-symmetric $[Pd(H_2O)_2(N^*N^*)][OTf]_2$ complexes, with N*N* either an optically active or a *meso*-bioxazoline ligand, catalyze the copolymerization of styrene and CO to isotactic poly(1-oxo-2-phenylpropane-1,3-diyl) **1**. Depending on the reaction conditions, the *meso*-ligands can alternatively produce a copolymer with a prevailingly syndiotactic structure, whereas the racemic ligand gives an atactic copolymer. Finally, the present results suggest that the control of the stereochemistry in the aforementioned copolymerization reaction is related not only to the chirality of the ligand, but also to other factors such as the ligand-to-palladium ratio and the strength of the ion pair.

REFERENCES

[1] G. W. Coates, *J. Chem. Soc., Dalton Trans.* **2002**, 467.
[2] G. W. Coates, *Chem. Rev.* **2000**, *100*, 1223.
[3] M. Farina, G. Di Silvestro, A. Terragni, *Macromol. Chem. Phys.* **1995**, *196*, 353.
[4] F. J. Gómez, R. M. Waymouth, *Science* **2002**, *295*, 635.
[5] M. T. Reetz, G. Aderlein, K. Angermund, *J. Am. Chem. Soc.* **2000**, *122*, 996.
[6] E. Drent, P. H. M. Budzelaar, *Chem. Rev.* **1996**, *96*, 663.
[7] C. Bianchini, A. Meli, *Coord. Chem. Rev.* **2002**, *225*, 35.
[8] B. Sesto, G. Consiglio, *J. Am. Chem. Soc.* **2001**, *123*, 4097.
[9] M. Brookhart, M. I. Wagner, G. G. A. Balavoine, H. A. Haddou, *J. Am. Chem. Soc.* **1994**, *116*, 3641.
[10] M. Brookhart, M. I. Wagner, *J. Am. Chem. Soc.* **1996**, *118*, 7219.
[11] M. Barsacchi, A. Batistini, G. Consiglio, U. W. Suter, *Macromolecules* **1992**, *25*, 3604.
[12] A. Gsponer, T. M. Schmid, G. Consiglio, *Helv. Chim. Acta* **2001**, *84*, 2986.
[13] M. Sperrle, A. Aeby, G. Consiglio, A. Pfaltz, *Helv. Chim. Acta* **1996**, *79*, 1387.
[14] A. Aeby, A. Gsponer, M. Sperrle, G. Consiglio, *J. Organomet. Chem.* **2000**, *603*, 122.
[15] R. Romeo, L. Fenech, S. Carnabuci, M. R. Plutino, A. Romeo, *Inorg. Chem.* **2002**, *41*, 2839.
[16] B. Milani, A. Marson, E. Zangrando, G. Mestroni, J. M. Ernsting, C. J. Elsevier, *Inorg. Chim. Acta* **2002**, *327*, 188.
[17] M.-C. Chen, T. J. Marks, *J. Am. Chem. Soc.* **2001**, *123*, 11803.
[18] P. W. N. M. van Leeuwen, C. F. Roobeek, H. van der Heijden, *J. Am. Chem. Soc.* **1994**, *116*, 12117.
[19] A. Macchioni, G. Bellachioma, G. Cardaci, M. Travaglia, C. Zuccaccia, B. Milani, G. Corso, E. Zangrando, G. Mestroni, C. Carfagna, M. Formica, *Organometallics* **1999**, *18*, 3061.

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