Regioselectivity of the insertion of propene with achiral Pd(II) catalysts to highly isotactic poly[1-oxo-2-methylpropane-1,3-diyl]. Is the syndiotactic structure accessible?

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Achiral cationic palladium catalysts, modified with 1,2-bis-(diarylphosphinomethyl)benzene ligands with different electronic properties, can efficiently produce poly(propene-*alt*-CO) with essentially complete regioregularity and high isotacticity, depending on the aryl substituent; the stereochemistry of the copolymers obtained is barely, if at all, influenced by the regiochemistry of the olefin insertion.

The alternating copolymerization of aliphatic olefins with carbon monoxide has attracted much attention in the last few years.[1–5] Useful catalytic systems in terms of productivity for this process are cationic palladium complexes of the type [(P–P)Pd(S)$_2$](X)$_2$ [P–P is a chelate diphosphine ligand, typically
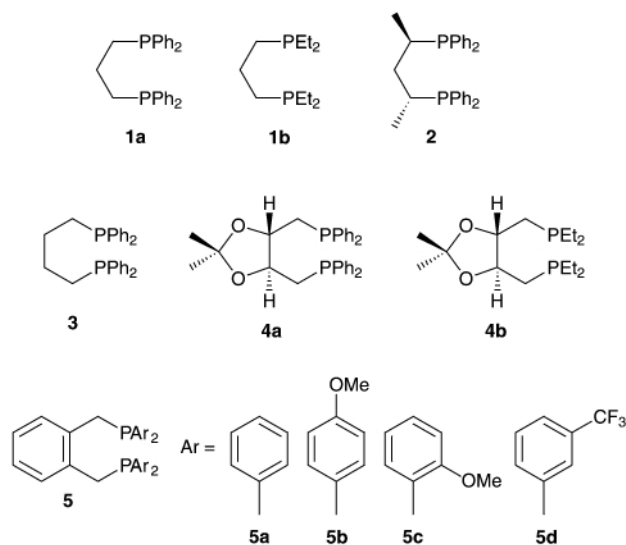

Fig. 1

1,3-bis(diphenylphosphino)propane **1a** (Fig. 1), S is a solvent molecule and X a weakly coordinating anion].[6]

When 1-olefins are used as the substrate, the microstructure of the produced copolymers depends on the characteristics of the regio- and stereo-chemistry of the step that corresponds to the migratory insertion of the olefin.[7] For the series of 1,3-propanediyl ligands tested so far in the copolymerization of aliphatic olefins, two factors have been identified as playing a role in the production of stereo- and regio-regular copolymers: chirality of the catalytic system, which brings about efficient enantioface discrimination and basicity of the ligand necessary to achieve regiospecificity during the insertion process.[8] The two selectivities seem to influence each other. Whereas the prototypical catalyst precursor **1a** leads to the production of stereoirregular poly(propene-*alt*-CO) (Scheme 1), which has a maximum head-to-tail (ht) diad content of *ca.* 60%,[9] the ht diad content for **2** can be as high as 90%[8] and is *ca.* 100% for **1b**[10] or for similar alkyl substituted ligands. At the same time a shift towards the preferential formation of *l*-sequences is observed.
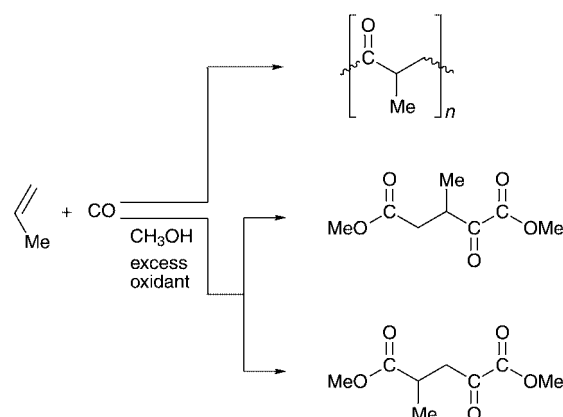
Scheme 1

The activity of ligand **3** was similar to that of ligand **1a**, but it showed somewhat better regioselectivity.[6,9]

Based on the above results, it was expected that **4a** would produce a substantially stereoregular material, which however is not the case.[9,11] Even **4b** did not seem to be very efficient from a stereochemical point of view, considering that the reported optical rotation of the produced copolymer is quite low.[12,13] The characteristics of these catalytic systems are clearly influenced to a considerable extent by the size of the coordination ring on the metal. We have continued our study, the aim of which is the identification of the factors involved in the regio- and stereo-chemical control of the insertion of the olefin substrate for this important carbonylation reaction, with the ultimate goal of achieving syndiotactic copolymerisation of aliphatic 1-olefins. We made the unexpected observation that electronic factors can substantially influence the regioselectivity and the enantioface discrimination of the efficient and largely regioregular copolymerization of propene with carbon monoxide caused by ligand **5a**.

Starting with ligands **5** (**5a** and **5c** have already been used for related copolymerization reactions[14,15]), the corresponding [(P–P)Pd(H$_2$O)$_2$](CF$_3$SO$_3$)$_2$ derivatives **6** were synthesized[16] and used as catalyst precursors for the copolymerization of propene with carbon monoxide as well as for the triple carbonylation to dimethyl 3- and 4-methyl-2-oxopentanedioates (Table 1 and Scheme 1).[17] The catalytic activity of **5a** is about four times larger than that of **1a** under the same reaction conditions. Electron withdrawing and electron donating aryl substituents result in lower catalytic activity. The activity loss is larger for the latter substituents, particularly in conjunction with steric effects (**5b** and **5c**). Moreover, the results presented in Table 1 and in Fig. 2 reveal the good performance of the tested catalysts, especially of **5d**, with respect to regio- and stereo-chemistry. The concentration of the band associated to the isotactic pentad (82%) implies that the content of *l*-diads is >96%.[18]

The regioselectivity of the olefin insertion is inferred from the isomeric ratio of 3- to 4-methyl-2-oxopentanedioate

Table 1 Copolymerization of propene with carbon monoxide using **6**[a]

Ligand	Reaction time/h	Productivity[b]/ g(g(Pd) h)$^{-1}$	Regioregularity[c]			Stereoregularity[d]	Regioselectivity[e]
			hh	ht	tt		
5a	21.5	233	0.04	1.00	0.05	79	66/34
5b	142	11	0.06	1.00	0.11	54	34/66
5c	26.3	89	<0.01	1.00	0.04	73	19/81
5d	5.6	126	<0.01	1.00	0.02	82	~100/0

[a] *Reaction conditions*: 19 g of propene in 75 ml THF and 4.5 ml MeOH; 0.03 mmol catalyst precursor; 80 bar CO; 1.5 mmol 1,4-naphthoquinone; 44 °C. [b] Mean molecular masses were 5100, 9700, 4100 and 3500, respectively. [c] Relative intensity of signals centered at δ *ca.* 223, 219 and 214, respectively (Fig. 2). [d] Intensity (%) of the most intense band in the ht range of the CO signals in the ^{13}C NMR spectra (Fig. 2). [e] Isomeric ratio of 3- to 4-methyl-2-oxopentanedioate, both of which are formed under similar reaction conditions but in the presence of excess of 1,4-benzoquinone.
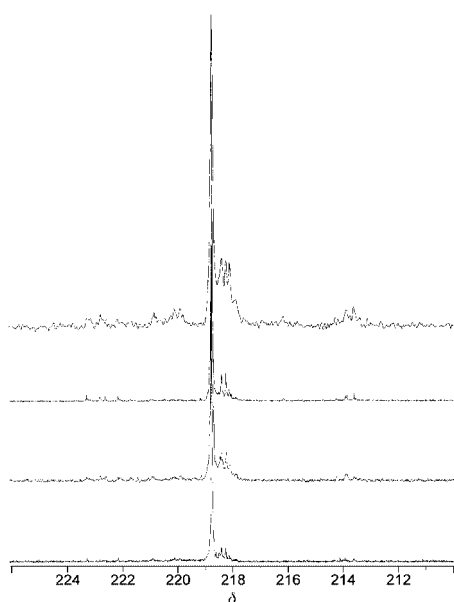

Fig. 2 ^{13}C NMR [125 MHz, (CF$_3$)$_2$CDOD] spectrum of the carbonyl region of poly(propene-*alt*-CO) prepared with catalysts **5** (from the bottom to the top: **5d**, **5b**, **5a** and **5c**).

(Scheme 1), which is affected by the tendency of propene to insert with primary or with secondary regiochemistry into a L$_n$Pd–CO–OMe intermediate.[17] Catalysts **5c** and **5d** display an essentially reversed regioselectivity but, nevertheless both systems give poly(propene-*alt*-CO) with quite high regioregularity and a largely prevailing isotactic structure. Even though **5c** and **5d** are regioisomerically different, the position of the trifluoromethyl substituent in **5d** should have no influence on the electronic characteristics of the catalytic system.[19] Considering the achiral nature of the ligands,[20] it seems obvious that the enantioface discrimination during the copolymerization process is chain-end controlled. Chain-end control and secondary insertion result in the formation of syndiotactic copolymers

during the related styrene copolymerization.[21] Therefore the reported results raise doubts about the accessibility of syndiotactic copolymerization of aliphatic 1-olefins with catalyst precursors containing diphosphines.

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