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Stereochemical Control and Reactivity of Pd Complexes with Meso and Racemic Ligands in the Isotactic Alternating Propene−Carbon Monoxide Copolymerization

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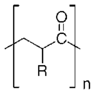
We report here that C_2- and C_s-symmetric $[(P\wedge P)Pd(H_2O)_2](SO_3CF_3)_2$ complexes, P∧P being either a *rac*- or a *meso*-diphosphine ligand, catalyze the copolymerization of propene and carbon monoxide to isotactic poly(1-methyl-2-oxo-1,3-propanediyl) (**1a**); the meso ligands are even more stereoselective than the racemic ligands and display much higher catalytic activity.



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1a R = CH_3

The relationship between the geometric characteristics of the catalytic system and the microstructure of the produced polymer has received much attention in recent years,[1] particularly in the field of the polymerization of olefins by metallocenes.[2] Thus, C_2-symmetric catalysts,[3,4] in which the alternative coordination sites are homotopic,[5,6] give isotactic polymers, whereas C_s-catalysts with enantiotopic coordination sites give syndiotactic polymers.[7] Similarly, C_2-symmetric palladium catalyst precursors enable the copolymerization of aliphatic or aromatic olefins with carbon monoxide to polyketones **1**,[8] which have a highly isotactic microstructure.[9−13] With C_1-symmetric catalyst precursors, isotacticity in the copolymerization was also achieved,[14−17] as was the case for poly-1-olefins with some C_1-metallocene systems.[18,19] The role of square planar C_s-catalysts in the copolymerization reaction is still unclear with respect to the possible synthesis of materials with an unknown microstructure as well as to the mechanistic implications for the catalysis.

Table 1. Copolymerization of Propene and Carbon Monoxide[a]

cat.	reaction time [h]	polymer [g]	productivity [g/(g Pd·h)]	M_n (10^{-3})	regioregularity[b] H−H/H−T/T−T
2a	19	8.5	70	5.5	0.40/1/0.40
3a	31	13.6	140	5.7	0.17/1/0.17
4a[c]	76	6.4	26	0.9	0.12/1/0.12
5a	45	16.0	233	4.0	0.04/1/0.05
6a	21	22.2	331	14.9	0/1/0
7a	93	1.2	4	4.7	0.04/1/0.04

[a] Reaction conditions: propene (19 g, 45 mmol); THF (75 mL); methanol (4.5 mL); 1,4-naphthoquinone (0.237 g, 1.5 mmol); catalyst precursor (0.03 mmol); 80 bar of CO; reaction temperature 44 °C. [b] Relative intensity of the ^{13}C NMR bands centered at 223, 219, and 214 ppm, respectively. [c] The (2*S*,4*S*)-ligand was used.

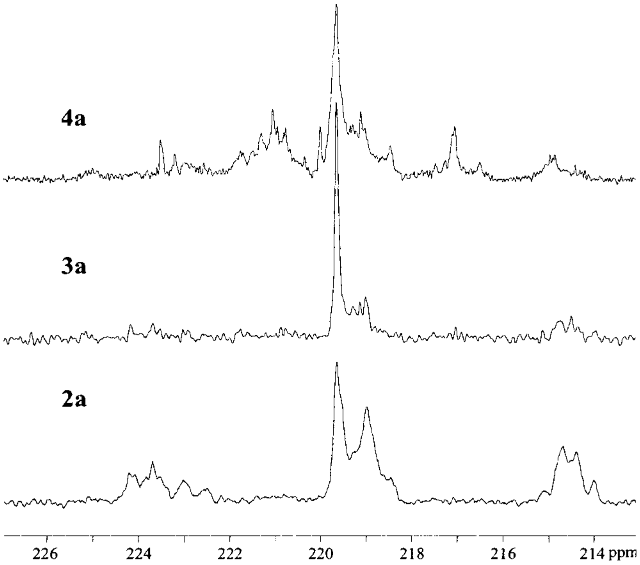

Figure 1. ^{13}C NMR (HFIP-d_2, 125 MHz, carbonyl region) of the poly(propene-*alt*-CO) copolymers prepared with the catalyst precursors **2a, 3a**, and with **4a**.

A first comparison was made with the $[(P\wedge P)Pd(H_2O)_2](SO_3CF_3)_2$[20] complexes **2a**−**4a**, modified with the corresponding ligands **2**−**4**, for the copolymerization of propene (Table 1). Systems containing **2** and **4** had already been used as catalysts.[21] The results in Table 1 and the ^{13}C NMR spectra in the region of the carbonyl resonances of the synthesized copolymers (Figure 1) clearly show that the meso ligand has much better stereochemical control and higher catalytic activity. In the related ethene copolymerization, the activity of the system modified by **3** was only 1.4 times higher than the corresponding system modified by **4**.[22]

Due to the possible implications of the incomplete regioselectivity exhibited by catalyst precursors **2a** to **4a**, however, we used systems that show better control of the regiochemistry of the insertion of propene, namely systems related to the recently investigated **5**.[23] Ligands **6** and **7** were synthesized from **5** by using a slightly modified form of the procedure reported for their 1,3-isomers;[24] they were stereochemically identified by ^{31}P NMR

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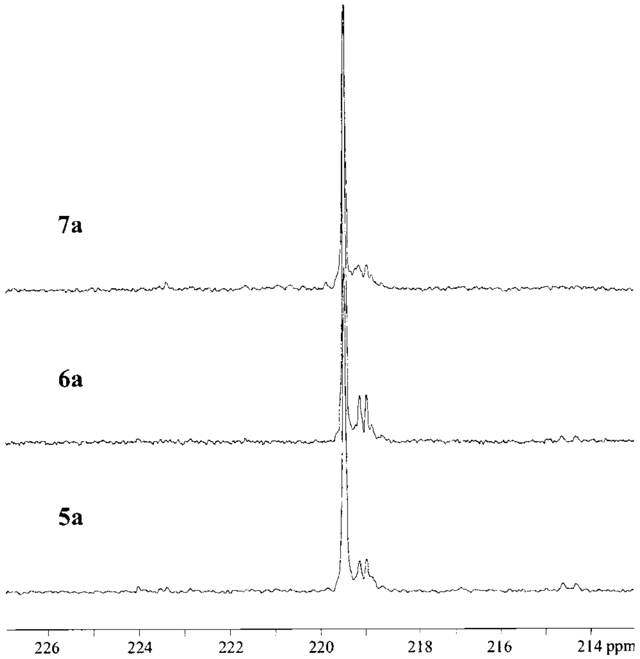
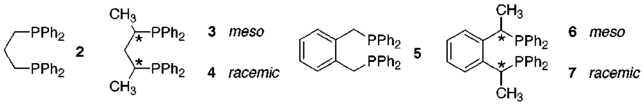


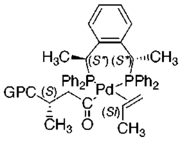
Figure 2. ^{13}C NMR (HFIP-d_2, 125 MHz, carbonyl region) of the poly(propene-*alt*-CO) copolymers prepared with the catalyst precursors **5a**, **6a**, and with **7a**.

through an exchange reaction of PPh_3 from $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl]$ (single line vs AB quartet).[25] Table 1 shows the corresponding copolymerization results, and Figure 2 shows the ^{13}C NMR spectra of the carbonyl region of the copolymers.



The meso-ligand **6** generally performs better than the achiral ligand **5** and much better than the racemic ligand **7**. The catalytic activity of **6a** is about 2 orders of magnitude higher than that of **7a**; the reactivity ratio is about 2.4 for ethene. The produced copolymer is essentially regioregular and is one of the most isotactic poly(1-methyl-2-oxo-1,3-propanediyl)s ever produced.[11,26,27] According to a previously reported analysis, the content of the *l*-dyads was evaluated to be 96% for **6a** and 95% for **7a**.[14]

These results can be explained by considering the olefin intermediates[28,29] prior to the primary insertion of propene,[8,30,31] which causes the chain to grow. The relative energy of the involved species has also been theoretically analyzed.[32] Having used racemic **7**, the actual stereochemical relationship to the ligand is unknown, since we have no information about the optical activity of the copolymer;[14,31] therefore, the corresponding chirality descriptors are labeled.



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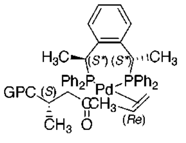

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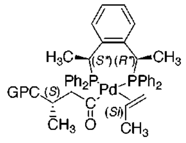

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Formation of the prevailingly isotactic copolymer by using the chiral ligand **7** implies that the corresponding intermediate **8**, in which the relative topicity between the last asymmetric center of the growing chain and the enantioface of the coordinated olefin is *like* ((*S*) vs (*Si*)), inserts much more rapidly than the alternative *unlike* intermediate **9** ((*S*) vs (Re)). The same situation ((*S*) vs (*Si*)) is found for the meso-ligand **6** where the intermediate **10** is responsible for the insertion. The overall large difference in the polymerization rate can be explained by assuming the formation of the involved intermediate **8** in low concentration.[33] The concentration may be low as a result of an unfavorable steric situation arising from the geometry of the center of chirality of the ligand in the cis-position with respect to the coordinated olefin (*lk*-topicity, (*S**) vs (*Si*)). For the system containing the meso-ligand, this situation does not occur (*ul*-topicity, (*R**) vs (*Si*)) with the intermediate (**10**) that is responsible for the growth of the isotactic chain. Similar considerations can be applied to the catalytic systems **3a** and **4a**. An increase in the rate of the insertion, due to the "matched" relative topicity of the ligand and of the olefin enantioface, was observed in the related copolymerization of 4-*tert*-butylstyrene by palladium systems modified with the C_2-symmetric 4,4′,5,5′-tetrahydro-2,2′-isopropylidene-4,4′-dimethylbis[oxazole].[34]

The two coordination sites, which are available for the growing chain and the olefin, are enantiotopic in intermediate **10**. ^{31}P NMR of the [(**6**)$PdCl_2$] complex shows a single line, consistent with a very symmetric geometry of the diphosphine ligand, in contrast to the spectrum of [(**7**)$PdCl_2$], which shows two lines that reveal an AB system at low temperature.[35] The copolymer produced with **6a** is highly isotactic and, therefore, site-selective coordination of the olefin prior to insertion is assumed; this might be caused by a stereospecific interaction of the growing chain with the palladium center.[8]

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