Enantioselective Dicarbonylation of Styrene to Isotactic Poly[1-oxo-2-phenylpropane-1,3-diyl] with Phosphinodihydrooxazole-palladium(II) Complexes: Model Studies for Enantioface Selection

Preliminary Communication

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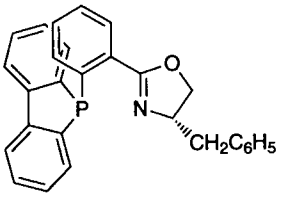
The first steps, believed to be involved in the highly enantioselective copolymerization of styrene and carbon monoxide to poly[1-oxo-2-phenylpropane-1,3-diyl] with phosphinodihydrooxazole-palladium(II) complexes, were investigated. The insertion of carbon monoxide into [Pd(Me)(P^N)(solvent)] TfO (P^N = (*S*)-2-[2-(5*H*-benzo[*b*]phosphindol-5-yl)phenyl]-4-benzyl-4,5-dihydrooxazole (**1**)) and of styrene into [Pd(COMe)(P^N)(solvent)] TfO were highly regioselective (alkyl and acyl substituents *trans* to N); moreover, the olefin insertion took place with essentially complete enantioface discrimination.

The alternating copolymerization of olefins with carbon monoxide has attracted much attention in recent years as a consequence of the foreseen and, indeed, realized commercialization of 'carilon', a terpolymer containing ethene and propene [1]. Numerous model studies of the steps believed to be responsible for chain growth at the cationic Pd catalyst during the copolymerization process, namely the formation of alkyl and acyl substituents, have been published [2]. In addition to systems containing monodentate ligands [3], palladium complexes, modified by C_2-symmetric ligands [4] using ethene or norbornene as the olefin substrate, were usually the subject of these investigations. C_s-Symmetric ligands have not been studied to such an extent [4c][5], but revealed useful for recognizing the migration of the alkyl group in the step corresponding to the acyl formation [6]. Only two studies have been published on the insertion reaction of prochiral olefins, namely 4-(*tert*-butyl)styrene [7] and propene [8]; in particular, the latter approached the problem of enantioface selection during the copolymerization process using a chelate C_1-ligand. This aspect is important not only to control the copolymerization process in a largely enantioselective way [9] for producing optically pure copolymers [10], but also because of its similarity with the *Ziegler-Natta* catalysis [11] and for the possible role of catalytic systems, similar to those systems described in the present paper, in polymerization processes using alk-1-enes [12].

Catalysts containing enantiomerically pure bis-dihydrooxazole [13] or hybrid (diphenylphosphino)dihydrooxazole ligands [14] give highly isotactic, optically active poly[1-oxo-2-phenylpropane-1,3-diyl]. The investigation of the terpolymerization of ethene and styrene using the latter catalytic systems provided some evidence that a similarly very high enantioface selection may take place during styrene insertion, independently of the nature of the last inserted olefin unit (either ethene or styrene) [15]. We report on model studies which help to clarify the mechanistic aspects of this highly enantioselective process with the above-mentioned hybrid ligand.

Due to the beneficial effect of the phosphindole moiety with respect to the diphenylphosphino substituent for regio- and enantioselectivity in carbonylation reactions of styrene [16], we used ligand (*S*)-**1** (hereafter designated P^N) to synthesize the monomethyl cationic complex **4** (*Scheme*) *via* the complexes [Pd(Me)$_2${(*S*)-**1**}] (**2**) and [PdCl(Me){(*S*)-**1**}] (**3**) (see *Exper. Part*).



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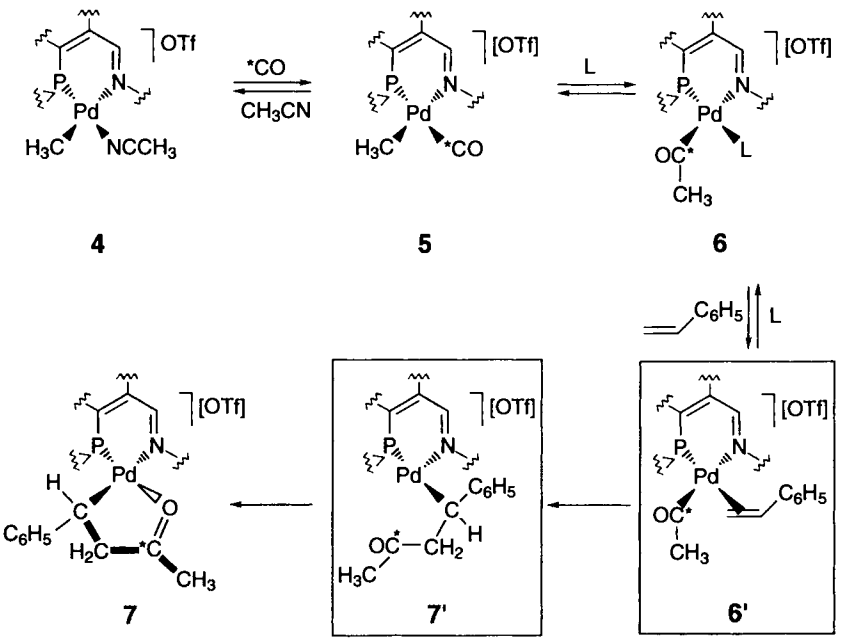
The carbonylation of **4** was carried out in CD_2Cl_2 under one bar of either ^{13}C-labeled or unlabeled carbon monoxide and was monitored by multinuclear NMR spectroscopy. Displacement of MeCN by CO led to complex **5** (*Scheme*) with essentially complete retention of the geometry. However, the reaction was not complete (**4**/**5** *ca.* 60:40 at 163 K, by ^1H-NMR) and disfavoured **5** at higher temperatures (**4**/**5** *ca.* 68:32 at 203 K). The ^{31}P-NMR signals of **4** and **5** are both rather broad down to 163 K, showing that exchange processes are probably operative. No formation of **6** was observed at 203 K during a 2 h period. Increasing the temperature to 243 K led to the disappearance of the signal of **5** and to the formation of traces of **6** (L probably MeCN), the ^{31}P-NMR signal

Scheme



of which being also rather broad. A 30% conversion to **6** was reached in *ca.* 2 h at 263 K and complete conversion within *ca.* 17 h at room temperature. The addition of a stoichiometric amount of styrene to a mixture of **4** and **6** (68:32; obtained from non-isolated **4**/**5**) at 273 K not only caused slow formation of **7** (sharp band in the ^{31}P-NMR), but also seemed to force formation of **6** at the expense of **4**. The complete transformation of the system to **7** was essentially reached within *ca.* 18 h at room temperature (the species **6′** and **7′** correspond to postulated intermediates).

In addition to the information on complex geometry as derived from the NMR data (see *Exper. Part*) and shown in the *Scheme*, two further aspects related to the styrene insertion reaction are of significance. In contrast to the similar chemistry using 4-(*tert*-butyl)styrene and the 2,2′-bipyridine-modified system [7], we observed neither the formation of the π-benzyl complex related to **7′** nor the evolution of species **7** to an acylcarbonyl intermediate corresponding to **6** (L=CO). The latter observation is consistent with the reaction order with respect to the carbon monoxide concentration observed for the two catalytic systems [7][17] during styrene copolymerization. Most importantly, the simplic-

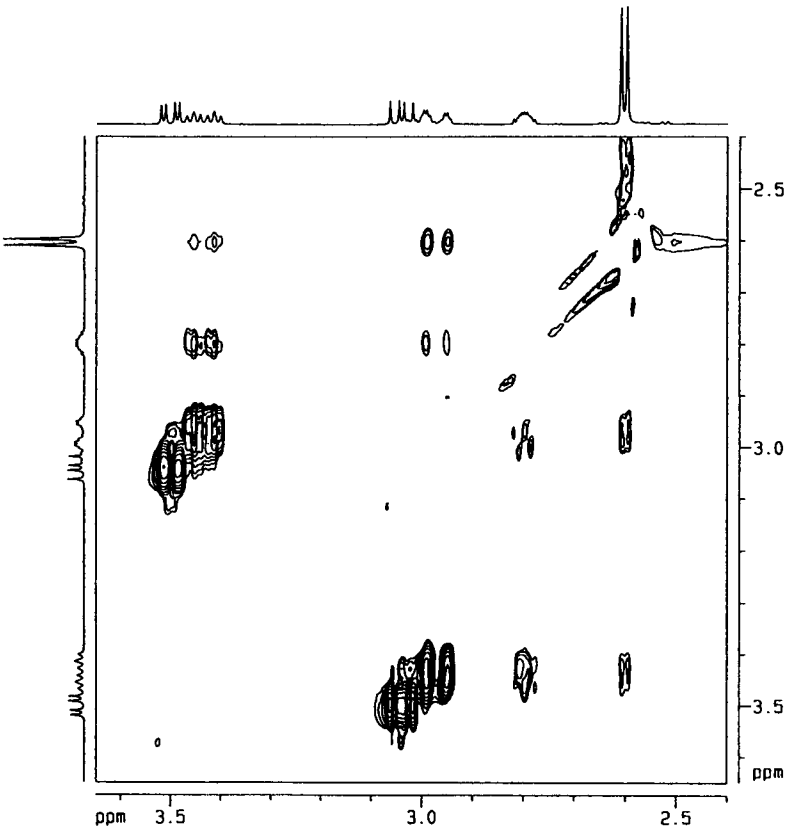


Figure. *NOESY Spectrum* (CD_2Cl_2, 25°) *of* **7** *showing a correlation of the Me group with the two methylene protons but none with the methine proton of the inserted styrene unit.* Positive NOE signals are shown, negative signals of the diagonal are supressed.

ity of all NMR spectra (^{31}P, ^{13}C, ^{1}H) of **7** is consistent with the formation of a single species in yields higher than 98%, arising from an essentially complete enantioface discrimination during the insertion process.

Unfortunately, NOESY experiments, even though clearly confirming the structure of **7** (*Fig.*), gave no information about the relative configuration of the chiral ligand and the newly formed asymmetric C-atom. However, a *u*-relationship, which can be easily understood on the basis of steric interactions between the ligand and the coordinated olefin in the postulated intermediate **6′** [14], is strongly suggested as follows. When used as the catalyst precursor for the copolymerization of styrene, **4** shows an activity that is approximately twice as large as that of the corresponding diphenylphosphino complex. In residual solutions from copolymerization carried out in the presence of 1,4-benzoquinone [14], traces of (*R*)-dimethyl 2-phenylbutanoate (95.4% enantiomeric excess) were found. The produced highly isotactic poly[1-oxo-2-phenylpropane-1,3-diyl] (CD: 284 nm ($\Delta\varepsilon = -11.8\,l \cdot mol^{-1} \cdot cm^{-1}$)) had an optical rotation ($[\alpha]_D^{25} = -423$) consistent with the same absolute configuration (*R*) [13][14]. We could not detect any diastereoisomeric relationship associated with the $MeOOCCH_2C^*H(Ph)CO$ end group in the copolymers. In a similar copolymerization experiment, carried out in chlorobenzene as the solvent without an oxidant, 1,4-diphenylpent-1-en-3-one (24% enantiomeric excess) was identified. In contrast to the previous end group, in this case, a diastereomer ratio of *ca.* 60:40 for the $MeC^*(Ph)COCH_2C^*H(Ph)CO$ termination was found for the co-produced copolymer.

The reported results are consistent with a low enantioface discrimination in the formation of the first acyl group through styrene insertion into an initiating [Pd–H(P^N)] species. In contrast, insertion into a [Pd-(CO–X)(P^N)] species seems to be equally effective, independent of the nature of the X group (Me, MeO, or growing polymer chain). The striking similarity with metallocene poylmerization catalysis of alk-1-enes is thus evidenced [18].

Experimental Part

Syntheses. Ligand (*S*)-**1** (designated P^N) and the corresponding complex $[Pd(Me)_2(P^N)]$ (**2**) were synthesized as described in [19] for analogous compounds. Reaction of **2** with acetyl chloride [20] to [PdCl(Me)(P^N)] (**3**), followed by treatment with silver trifluoromethanesulfonate in MeCN [4b], gave with 100% regioselectivity the monomethyl cationic complex **4**.

Selected Spectroscopic Data. (S)-2-[2-(5H-Benzo[b]phosphindol-5-yl)phenyl]-4-benzyl-4,5-dihydrooxazole ((*S*)-**1**): ^{31}P-NMR (121.5 MHz, $CDCl_3$, 25°): −14.95.

{(S)-2-[2-(5H-Benzo[b]phosphindol-5-yl-κP)phenyl]-4-benzyl-4,5-dihydrooxazole-κN}dimethylpalladium (**2**): ^{1}H-NMR (300 MHz, C_6D_6, 25°): 0.88 (*d*, $^{3}J(P,H) = 9.6$, Me–Pd *trans* to N); 1.30 (*d*, $^{3}J(P,H) = 7.1$, Me–Pd *trans* to P). ^{31}P-NMR (121.5 MHz, C_6D_6, 25°): 12.45. ^{13}C-NMR (75.5 MHz, C_6D_6, 25°): −5.9 (*d*, $^{2}J(P,C) = 6.1$, Me–Pd *trans* to N); 7.9 (*d*, $^{2}J(P,C) = 115.4$, Me–Pd *trans* to P). NOESY (C_6D_6, 25°): NOE between *Me*–Pd *trans* to P and *H*–C(4) of the ligand.

{(S)-2-[2-(5H-Benzo[b]phosphindol-5-yl-κP)phenyl]-4-benzyl-4,5-dihydrooxazole-κN}chloro(methyl)palladium (**3**). ^{1}H-NMR (200 MHz, CD_2Cl_2, 25°): 0.27 (*d*, $^{3}J(P,H) = 4.3$, Me–Pd *trans* to N). ^{31}P-NMR (81.0 MHz, CD_2Cl_2, 25°): 26.05. ^{13}C-NMR (75.5 MHz, CD_2Cl_2, 25°): −0.6 (*d*, $^{2}J(P,C) = 1.7$, Me–Pd *trans* to N. NOESY ($CDCl_3$, 25°): no NOE between *Me*–Pd and *H*–C(4) of the ligand.

(Acetonitrile-κN){(S)-2-[2-(5H-benzo[b]phosphindol-5-yl-κP)phenyl]-4-benzyl-4,5-dihydrooxazole-κN}methylpalladium(1+) Trifluoromethanesulfonate (**4**). ^{1}H-NMR (200 MHz, CD_2Cl_2, 25°): 0.19 (*d*, $^{3}J(P,H) = 2.4$, Me–Pd *trans* to N); 2.14 (*s*, MeCN). ^{31}P-NMR (81.0 MHz, CD_2Cl_2, 25°): 28.71. ^{13}C-NMR (50.3 MHz, CD_2Cl_2, 25°): 2.2 (*d*, $^{2}J(P,C) = 2.2$, Me–Pd *trans* to N); 2.8 (*s*, *Me*CN–Pd *trans* to P).

{(S)-2-[2-(5H-Benzo[b]phosphindol-5-yl-κP)phenyl]-4-benzyl-4,5-dihydrooxazole-κN}[(¹³C)carbonyl](methyl)palladium(1+) Trifluoromethanesulfonate (**5**): ^{1}H-NMR (500 MHz, CD_2Cl_2, −110°): −0.13 (*d*, ^3J(P,H) = 2.6, Me−Pd *trans* to N). ^{31}P-NMR (202.5 MHz, CD_2Cl_2, −110°): 21.69 (*d*, ^2J(C,P) = 124.7). ^{13}C-NMR (125.8 MHz, CD_2Cl_2, −110°): −3.46 (*d*, ^2J(P,C) = 1.9, Me−Pd *trans* to N); 176.0 (*d*, ^2J(C,P) = 124.4, O^{13}C−Pd *trans* to P)).

(Acetonitrile-κN){(S)-2-[2-(5H-Benzo[b]phosphindol-5-yl-κP)phenyl]-4-benzyl-4,5-dihydrooxazole-κN}[(1-¹³C)acetyl]palladium(1+) Trifluoromethanesulfonate (**6**): ^{1}H-NMR (500 MHz, CD_2Cl_2, 0°): 1.80 (*dd*, ^2J(C,H) = 6.0, ^4J(P,H) = 1.9, Me^{13}C(O)−Pd *trans* to N). ^{31}P-NMR (202.5 MHz, CD_2Cl_2, 0°): 14.44 (*d*, ^2J(C,P) = 6.8). ^{13}C-NMR (125.8 MHz, CD_2Cl_2, −10°): 225.2 (*d*, ^2J(P,C) = 6.8, Me^{13}C(O)−Pd).

{(S)-2-[2-(5H-Benzo[b]phosphindol-5-yl-κP)phenyl]-4-benzyl-4,5-dihydrooxazole-κN}[4-phenyl(2-¹³C)butan-2-one-κC⁴,κO]palladium(1+) Tetrafluoromethanesulfonate (**7**): ^{1}H-NMR (500 MHz, CD_2Cl_2, 25°): 2.60 (*d*, ^2J(C,H) = 5.8, *Me*^{13}COCH$_2$CHPh); 2.78–2.82 (*m*, Me^{13}COCH$_2$*CH*Ph); 2.95–3.01 (*m*, 1 H, Me^{13}COC*H*$_2$CHPh), 3.43 (*ddd*, ^2J(H,H) = 20.3, ^2J(C,H) = 6.0, ^3J(H,H) = 7.2, 1 H, Me^{13}COC*H*$_2$CHPh). ^{31}P-NMR (202.5 MHz, CD_2Cl_2, 25°): 25.34 (*d*, ^3J(C,P) = 1.2). ^{13}C-NMR (125.8 MHz, CD_2Cl_2, 25°): 28.6 (*dd*, ^1J(C,C) = 40.8, ^4J(P,C) = 14.0, *Me*^{13}COCH$_2$CHPh); 46.0 (*d*, ^2J(C,C) = 19.1, Me^{13}COCH$_2$*C*HPh); 57.8 (*d*, ^1J(C,C) = 40.0, Me^{13}CO*C*H$_2$CHPh); 235.3 (*d*, ^3J (P,C) = 1.2, Me^{13}*C*OCH$_2$CHPh).

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