Communications to the Editor

Highly Enantioselective Alternating Copolymerization of Propene with Carbon Monoxide Catalyzed by a Chiral Phosphine−Phosphite Complex of Palladium(II)

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Alternating copolymerization of α-olefins with carbon monoxide catalyzed by chiral transition metal complexes is an attractive methodology to obtain optically active polymers[1] because (1) main-chain chirality can be efficiently built from the prochiral monomers and (2) the polymer contains ketonic groups that are capable of further functionalization.[2] Recently, a few examples of successful asymmetric alternating copolymerization of CO with α-olefins catalyzed by chiral palladium(II) complexes have been reported by Sen,[2c,3] Consiglio,[4] and Brookhart.[5] In all those reports, however, the highest stereoregularities have been obtained with C_2 symmetric chiral *cis* bidentate ligands.[6,7] Here we report a highly enantioselective alternating copolymerization of propene and carbon monoxide catalyzed by Pd(II) complexes bearing the unsymmetrical phosphine−phosphite ligand (*R*,*S*)-BINAPHOS.[8] The important roles played by the two nonequivalent coordination sites in the chain-growth steps are also revealed.

The highest molecular weight (MW = 104 400) and the highest molar optical rotation ($[\Phi]_D$ = +40°) for poly(propene-*alt*-CO) have been attained by use of [Pd((*R*,*S*)-BINAPHOS)(Me)(CH_3CN)][BAr_4] (Ar = 3,5-bis(trifluoromethyl)phenyl) (**1**) as a catalyst (eq 1). The simplicity of the $^{13}C\{^1H\}$ NMR spectrum shown in Figure 1 leads us to conclude that the polymerization is almost completely diastereoselective.[9,11] Moreover, the extremely high molar optical rotation indicates that the polymerization proceeds in very high enantioselectivity.[12,13]

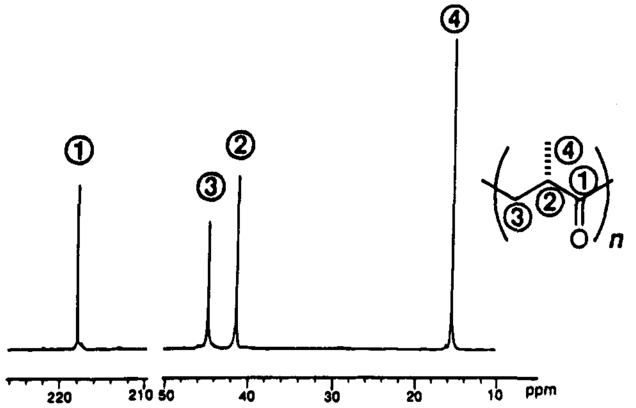
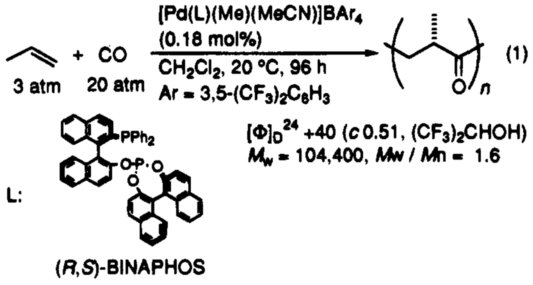


Figure 1. ^{13}C NMR spectrum of poly(propene-*alt*-CO) (in $(CF_3)_2CDOD$).

The structures of all the intermediate complexes involved in the early stages of chain growth have been determined. The cationic complex **1** exists as a single species containing bidentate BINAPHOS; the relative positions of the methyl group and CH_3CN have not been established.[14] Acetylpalladium **2**, alkylpalladium **3**, the longer acylpalladium **4**, and the longer alkylpalladium **5** were all obtained as single species (Chart 1). By using ^{13}CO, the *cis*/*trans* stereochemistries of complexes **2**−**5** have been determined on the basis of their $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$



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[1] For general references to these polymers, see: (a) Sen, A. *Acc. Chem. Res.* **1993**, *26*, 303. (b) Drent, E.; Van Broekhoven, J. A. M.; Doyle, M. J. *J. Organomet. Chem.* **1991**, *417*, 235. (c) For a recent mechanistic study on the origin of copolymerization, see: Rix, F. C.; Brookhart, M. *J. Am. Chem. Soc.* **1995**, *117*, 1137.

[2] Some examples of the functionalization of poly(α-olefins-*alt*-CO): (a) Brubaker, M. M.; Coffman, D. D.; Hoehn, H. H. *J. Am. Chem. Soc.* **1952**, *74*, 1509. (b) Green, M. J.; Lucy, A. R.; Lu, S.; Paton, R. M. *J. Chem. Soc., Chem. Commun.* **1994**, 2063. (c) Jiang, Z.; Sen, A. *J. Am. Chem. Soc.* **1995**, *117*, 4455.

[3] With propene: Jiang, Z.; Adams, S. E.; Sen, A. *Macromolecules* **1994**, *27*, 2694.

[4] With propene: Bronco, S.; Consiglio, G.; Hutter, R.; Batistini, A.; Suter, U. W. *Macromolecules* **1994**, *27*, 4436 and references cited therein.

[5] With 4-*tert*-butylstyrene: Brookhart, M.; Wagner, M. I.; Balavoine, G. G. A.; Haddou, H. A. *J. Am. Chem. Soc.* **1994**, *116*, 3641.

[6] The identification of intermediate complexes has been reported by using C_2 symmetric diimines; see: (a) Brookhart, M.; Rix, F. C.; DeSimone, J. M. *J. Am. Chem. Soc.* **1992**, *114*, 5894. (b) Van Asselt, R.; Gielens, E. E. C. G.; Rülke, R. E.; Elsevier, C. J. *J. Chem. Soc., Chem. Commun.* **1993**, 1203. (c) Van Asselt, R.; Gielens, E. E. C. G.; Rülke, R. E.; Vrieze, K.; Elsevier, C. J. *J. Am. Chem. Soc.* **1994**, *116*, 977. (d) Markies, B. A.; Kruis, D.; Rietveld, M. H. P.; Verkerk, K. A. N.; Boersma, J.; Kooijman, H.; Lakin, M. T.; Spek, A. L.; Van Koten, G. *J. Am. Chem. Soc.* **1995**, *117*, 5263.

[7] For polymerization of unsymmetrical chiral *cis* bidentate ligands, see refs 3 and 5.

[8] (*R*,*S*)-BINAPHOS = (*R*)-2-(diphenylphosphino)-1,1′-binaphthalen-2′-yl (*S*)-1,1′-binaphthalene-2,2′-diyl phosphite: Sakai, N.; Mano, S.; Nozaki, K.; Takaya, H. *J. Am. Chem. Soc.* **1993**, *115*, 7033.

[9] Signals due to the carbonyl carbons of stereoirregular polyketones are not observed in the range of δ 218−220 in $(CF_3)_2CDOD$[3,4] with the lowest detection limit of signal/noise = 115, which shows that head-to-head, tail-to-tail, and syndiotactic polymers are not formed.[10]

[10] The exclusive head-to-tail copolymerization of propene with carbon monoxide has been reported by both Consiglio and Sen. See refs 2c, 3, and 4.

[11] Poly(spiroketal) is known to be formed in the presence of protic solvents, but was not detected in the present system. (a) Batistini, A.; Consiglio, G. *Organometallics* **1992**, *11*, 1766. (b) Wong, P. K.; Van Doorn, J. A.; Drent, E.; Sudmeijer, O.; Stil, H. A. *Ind. Eng. Chem. Res.* **1993**, *32*, 986.

[12] Sen has reported that the polyketone with MW = 36 000 and higher than 90% ee has a molar optical rotation of $[\Phi]_D$ = +22°. The much higher optical rotatory power of the present polymer might result from its higher molecular weight. In fact, a polymer with a lower molecular weight (MW = 48 000) obtained by quenching the polymerization in a shorter reaction time (24 h) exhibited a lower optical rotation value ($[\Phi]_D$ = +32°). However, there might exist some other factors since several samples obtained under different reaction conditions (pressures and temperatures) afforded varying optical rotation values ($[\Phi]_D$ = +23 to +40°) regardless of their molecular weights, though they have equally high stereoregularities. In those cases, no significant correlation between molecular weight and optical rotation value has been observed.

[13] The cationic complex **1** catalyzes 4-*tert*-butylstyrene−CO copolymerization with lower stereoregularity (M_w = 5600, M_w/M_n = 1.3, and $[\Phi]^{23}_D$ −492° (*c* 0.50, CH_2Cl_2) at 20 °C for 96 h) than that accomplished by Brookhart. See ref 5.

[14] A neutral catalyst precursor Pd((*R*,*S*)-BINAPHOS)(Me)(Cl) is a *cis*/*trans* mixture in a ratio of 5:1. Treatment of the *cis*/*trans* mixture with $NaBAr_4$ afforded cationic complex **1** as a single product.

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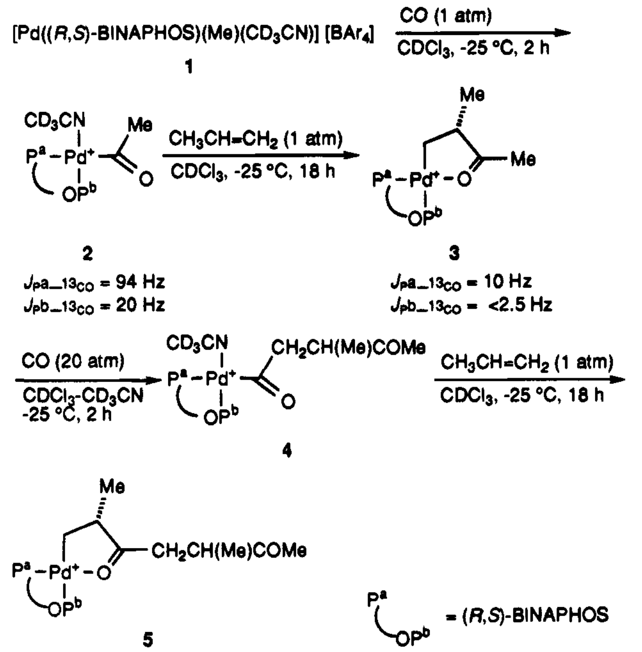
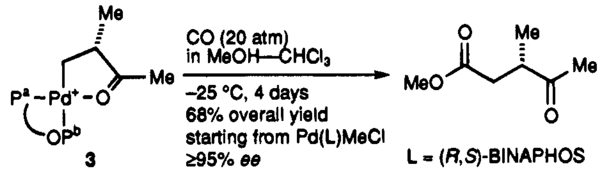
Chart 1



NMR spectral data.[15] The results can be summarized as follows: (1) Acyl groups are always *trans* to the phosphine in acyl complexes **2** and **4**. (2) Alkyl groups always occupy the position *trans* to the phosphite in alkyl complexes **3** and **5**. In each alkyl complex, the ketonic oxygen is coordinated intramolecularly to the central palladium atom, forming a five-membered metallacycle.[17]

Thus the two vacant *cis* coordination sites on the palladium center are shared alternately by acyl group and alkyl group at the resting steps. If we assume that all those complexes are involved in the actual catalytic cycle, the following characteristic features of the present system should be evident: (1) CO always coordinates to the position *trans* to the phosphine ligand (P^a) in alkyl complexes **1** and **3**. Migration of the alkyl group[18] to the coordinated CO gives the acyl complexes **2** or **4**. (2) Propene always coordinates to the position *trans* to phosphite (P^b) by replacing acetonitrile in acyl complexes **2** and **4**. Migration of the acyl group[17] affords alkyl complex **3** or **5** with a five-membered metallacycle. Accordingly, the palladium complex divides its two vacant coordination sites between CO and propene.

The absolute configuration of the α-carbon has been determined by carbomethoxylation of the five-membered alkylpalladium complex **3** as shown in eq 2. The sign of optical rotation of the obtained γ-keto ester is consistent with an *S*-configuration for the α-carbon atom.[19]



(2)

The very high *re*- or *si*-face selection of propene observed in the present system may be mainly controlled as follows. Propene will coordinate to the palladium(II) center of the acylpalladium complexes, such as **2** or **4**, by displacing acetonitrile at the position *cis* to the phosphine. If we assume olefin insertion to be irreversible,[20] steric repulsion between the phenyl groups of the phosphine and the methyl group of the propene is likely to strongly influence enantioface selection. The very high enantioselectivity can be attributed to invariable coordination of propene to a fixed coordination site.

Thus we have shown that BINAPHOS−Pd(II) complexes are highly efficient catalysts for an isotactic alternating copolymerization of propene and carbon monoxide. The stereochemistries and mechanism of this novel copolymerization have also been elucidated.

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Supporting Information Available: Experimental procedures and spectral data for all products (6 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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[15] Spectral data for the characterization of complexes **2**−**5** are given as supporting information.[16]

[16] Chain end analysis by Consiglio and Sen has also established about the regioselectivity that primary insertion of propene takes place in palladium-catalyzed copolymerization. (a) Reference 4. (b) Jiang, Z.; Dahlen, G. M.; Houseknecht, K.; Sen, A. *Macromolecules* **1992**, *25*, 2999.

[17] The formation of five-membered chelates through intramolecular coordination of carbonyl oxygen has been shown in many cases. For example: (a) Brumbaugh, J. S.; Whittle, R. R.; Parvez, M.; Sen, A. *Organometallics* **1990**, *9*, 1735. (b) Ozawa, F.; Hayashi, T.; Koide, H.; Yamamoto, A. *J. Chem. Soc., Chem. Commun.* **1991**, 1469. (c) References 6c,d.

[18] (a) Migratory insertion of CO to alkylplatinum or arylpalladium bonds by using an unsymmetrical bidentate diphosphine ligand has recently been proposed. Van Leeuwen, P. W. N. M.; Roobeek, C. F.; Van der Heijiden, H. *J. Am. Chem. Soc.* **1994**, *116*, 12117. (b) Using a monodentate phosphine ligand; see: Kayaki, Y.; Kawataka, F.; Shimizu, I.; Yamamoto, A. *Chem. Lett.* **1994**, 2171.

[19] Methyl 2-methyl-4-oxopentanoate was obtained in 95% ee (determined by GLC analysis using a chiral column (CP-cyclodextrin-β-236M-19, Chrompack) at 100 °C) after distillation (80 °C, 1.0 Torr) of the reaction mixture which contained palladium species; $[\alpha]^{26}_{D}$ −54° (*c* 0.42, THF); lit. $[\alpha]_D$ −28° (*c* 1.5, THF) for a sample of 43% ee (*S*). Distillation of the γ-keto ester in the presence of palladium species at 160 °C (20 Torr) resulted in considerable racemization of the product. (a) Blanco, L.; Rousseau, G.; Barnier, J.-P.; Guibé-Jampel, E. *Tetrahedron: Asymmetry* **1993**, *4*, 783. (b) Enders, D.; Gerdes, P.; Kipphardt, H. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 179.

[20] We think that the rate-determining step is CO insertion into the alkyl complexes such as **3** and **5** because elevated CO pressure is necessary for the present polymerization to take place. Since CO insertion into alkyl complex **1** having no ketonic group proceeds under much milder conditions (1 atm of CO pressure at −25 °C) than that for the five-membered alkyl complex **3** (20 atm of CO pressure at −25 °C), the replacement of the ketonic oxygen in **3** with CO seems to require the highest activation energy. However, enantioface selection of the olefin has already occurred before this rate-determining step, if the olefin insertion is irreversible.