

Highly Screw-Sense Selective Polymerization of 1,2-Diisocyano-3,6-di-*p*-tolylbenzene Initiated by Optically Active Binaphthylpalladium(II) Complexes

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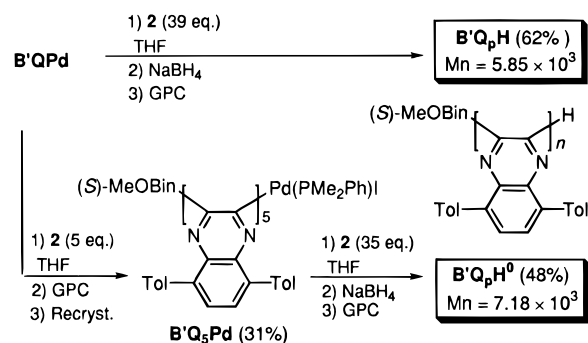
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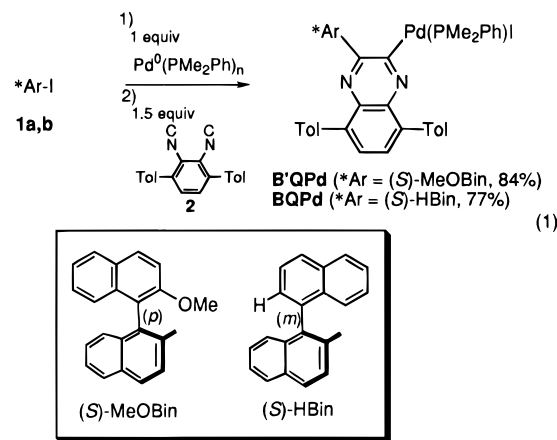
Synthesis of new polymers, which are featured by their secondary structures as well as main chain structure, is desired for directing toward functional materials. Synthetic construction of polymers with well-defined stable helices has been a challenging subject, since helical structures are characteristic of important biopolymers such as DNA and peptides.¹ We reported a new synthesis of helical poly[2,3-(1,4-diazaphthalene)]species (i.e., poly(2,3-quinoxaline)) by methylpalladium(II)-catalyzed polymerization of 1,2-diisocyanobenzene.² The aromatizing polymerization proceeds with successive insertion of the two isocyno groups into the palladium–carbon bond of the growing [poly(quinoxalanyl)]palladium(II) complexes, which are isolable. Although a methylpalladium(II) complex bearing bis((*S*)-2-methylbutyl)phenylphosphine as a chiral ligand failed to induce screw-sense selection in the polymerization of 1,2-diisocyno-3,6-di-*p*-tolylbenzene, the ligands allowed us to separate right- and left-handed helices in the form of diastereomeric [penta(quinoxalanyl)]palladium(II) complexes.³ Of interest is that the polymerization of 1,2-diisocyanobenzene derivatives with the [penta(quinoxalanyl)]palladium(II) complexes of pure screw-sense thus isolated proceeded with retention of their screw-sense. Herein, we disclose highly screw-sense selective polymerization of 1,2-diisocyno-3,6-di-*p*-tolylbenzenes initiated by enantiomerically pure binaphthylpalladium(II) complexes, whose substituents on the binaphthyl groups crucially affected the selectivity. A stable and rigid helical structure of the growing [oligo(quinoxalanyl)]palladium(II) complex was revealed by an X-ray analysis.

Enantiomerically pure catalysts for the polymerization of the 1,2-diisocyanobenzene were prepared from (*p*)-(*S*)-2-iodo-2'-methoxy-1,1'-binaphthyl **1a** and (*m*)-(*S*)-2-iodo-1,1'-binaphthyl **1b** with the axial chirality (eq 1).⁴ Oxidative addition of **1** onto the palladium(0) complex generated in situ from (cyclopentadienyl)(π -allyl)palladium(II) and 3 equiv of dimethylphenylphosphine gave binaphthylpalladium(II) iodide complexes,⁵ which were then reacted with 1,2-diisocyno-3,6-di-*p*-tolylbenzene **2** to afford the corresponding [2-(2-binaphthyl)quinoxalin-

Scheme 1



3-yl]palladium(II) complexes **B'QpPd** and **BQpPd** in good yields as yellow crystalline solids.⁶



(1)

In the presence of a catalytic amount of **B'QpPd**, polymerization of **2** (39 equiv) in THF proceeded at room temperature to give, after quenching the reaction with NaBH₄, polymer **B'QpH** ($M_n = 5.85 \times 10^3$, 62% yield),⁷ which exhibited a CD spectrum with a Cotton effect characteristic of the optically active, helical poly(2,3-quinoxaline)species (Scheme 1, Figure 1). The oligomerization of **2** (5 equiv based on the palladium catalyst) permitted us to separate and isolate [penta(quinoxalanyl)]palladium(II) complex **B'Q5Pd** in 31% yield as reddish crystals from a mixture of the corresponding oligomers (Scheme 1).⁸ A 400 MHz ¹H NMR spectrum of the complex exhibited the distinct ten methyl singlets of the tolyl groups and one methyl singlet of the methoxynaphthyl group.

An X-ray crystal analysis of **B'Q5Pd** revealed a right-handed helical structure in which the two adjacent quinoxaline rings Q(1)–Q(2), Q(2)–Q(3), Q(3)–Q(4), and Q(4)–Q(5) were arranged at the dihedral angles of +151°, +148°, +148°, and +171°, respectively, with an iodo(dimethylphenylphosphine)-palladium terminus intramolecularly coordinated by a nitrogen atom of the fourth quinoxaline Q(4) (Figure 2).⁹ The helical

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(2) Ito, Y.; Ihara, E.; Murakami, M.; Shiro, M. *J. Am. Chem. Soc.* **1990**, *112*, 6446.

(3) (a) Ito, Y.; Ihara, M.; Murakami, M. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1509. (b) Ito, Y.; Ihara, E.; Murakami, M.; Sisido, M. *Macromolecules* **1992**, *25*, 6810. (c) Ito, Y.; Kojima, Y.; Murakami, M. *Tetrahedron Lett.* **1993**, *51*, 8279. (d) Ito, Y.; Kojima, Y.; Sugimoto, M.; Murakami, M. *Heterocycles* **1996**, *42*, 597–615.

(4) The notation (*p*) or (*m*) (*plus* or *minus*, respectively) represents the sense of the chirality of binaphthyl groups without considering their substituents. Hattori, T.; Hotta, H.; Suzuki, T.; Miyano, S. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 613–622.

(5) For the generation of phosphine–palladium(0) complexes from (cyclopentadienyl)(π -allyl)palladium(II), see: Bennett, M. A.; Chiraratvata, C.; Robertson, G. B.; Tooptakong, U. *Organometallics* **1988**, *7*, 1403–1409 and references therein.

(6) No diastereoisomerism was observed for **BQpPd** and **B'QpPd** at room temperature. Enantiomerically pure **B'QpPd** was confirmed by HPLC analysis (a Chiralcel OD-H column) of the corresponding methyl ester, prepared by the reaction of **B'QpPd** with CO (20 atm) in MeOH at 100 °C.

(7) Molecular weights were estimated by analytical GPC using poly(styrene) species as standard. According to the GPC estimation, penta quinoxaline **B'Q5H** (fw = 1826) prepared by the reaction of **B'Q5Pd** with NaBH₄ was calculated to have lower molecular weights ($M_n = 1.28 \times 10^3$).

(8) The mixture contained tetra-, penta-, and [hexa(quinoxalanyl)]-palladium complexes, each of which may consist of both of the right- and left-handed helices. In fact, when the mixture was treated with NaBH₄ to remove the palladium moiety, two diastereomeric hexamers, which exhibited CD spectra corresponding to opposite screw-sense, were isolated by GPC and subsequent HPLC purification (see supporting information).

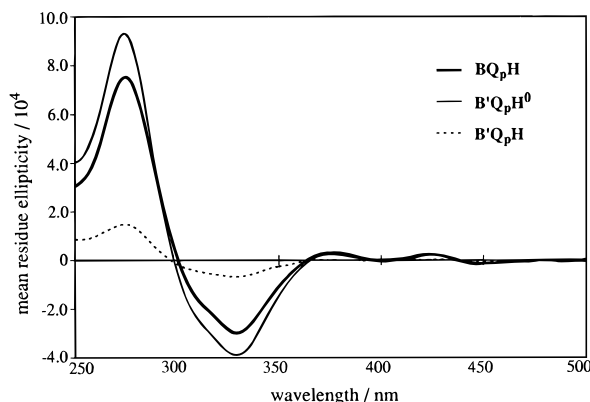


Figure 1. CD spectra of the optically active poly(2,3-quinoxaline) species $B'Q_pH$, $B'Q_pH^0$, and BQ_pH .

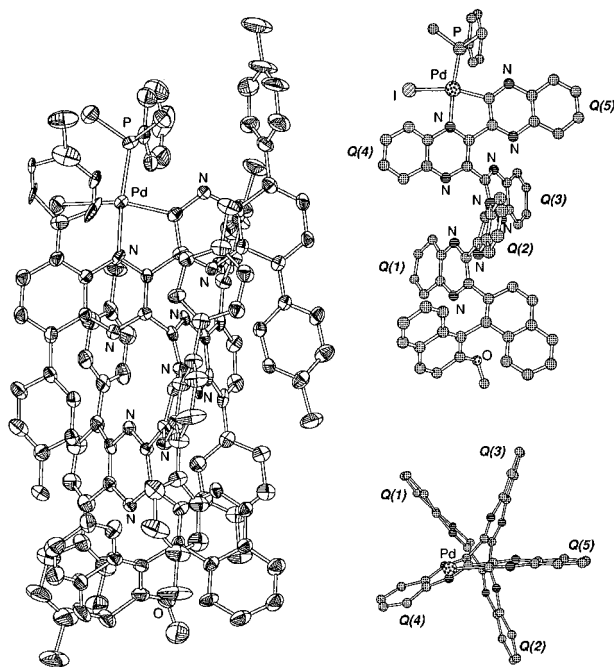


Figure 2. Molecular Structure of $B'Q_5Pd$. ORTEP drawing (left; 30% probability), a side view (top right; tolyl groups are omitted), and a top view (bottom right; binaphthyl, tolyl, Me_2PhP , and iodo groups are omitted).

structure once formed was stable with no change of CD spectrum even on heating in benzene at 80 °C for 24 h.

The stable palladium(II) complex $B'Q_5Pd$ was still active and induced the polymerization of **2** at room temperature, producing poly(2,3-quinoxaline) species $B'Q_pH^0$ ($M_n = 7.18 \times 10^3$) after reduction with $NaBH_4$ (Scheme 1). The polymers showed a

(9) Crystal data for $B'Q_5Pd$: crystal size $0.30 \times 0.20 \times 0.50$ mm; monoclinic, space group $P2_1$ (No. 4), $Z = 2$; $a = 12.853$ (4), $b = 40.251$ (9), $c = 12.486$ (3) Å; $\beta = 117.36$ (2)°; $V = 5737$ (2) Å³, $\rho_{calcd} = 1.27$ g/cm³; $\mu = 40.22$ cm⁻¹; max $2\theta = 125^\circ$ (Cu $K\alpha$, $\lambda = 1.54178$ Å, graphite monochromator, $\omega/2\theta$ scan, $T = 293$ K); 10431 reflections measured, 9746 independent, 8803 included in the refinement, Lorentzian polarization; direct methods, anisotropic refinement for non-hydrogen atoms by full-matrix least-squares against $|F|$ with program package CrystanG (Mac Science), 1376 parameters; $R = 0.070$, $R_w = 0.091$. Molecular packing diagram is shown in the supporting information.

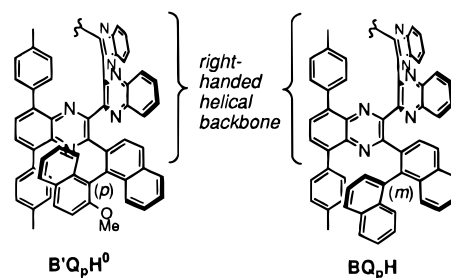
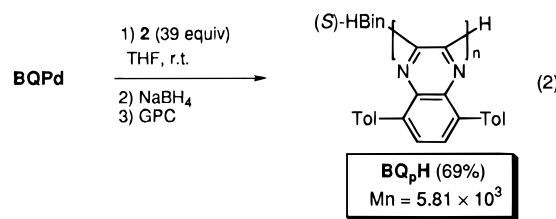


Figure 3. Possible orientations of the binaphthyl terminus of the optically active polymers $B'Q_pH^0$ and BQ_pH .

remarkably strong CD spectrum between 250 and 370 nm (Figure 1). This finding may suggest that the palladium(II) complex $B'Q_5Pd$ promotes the polymerization of **2** with retention of its preorganized screw-sense resulting in highly pure, right-handed helical structure. On the basis of the intensity of the CD spectrum of $B'Q_pH^0$, the palladium(II) complex catalyst $B'QPd$, which is not yet helically preorganized, induced the polymerization of **2** only in low screw-sense selectivity.

It should be noted that the highly screw-sense selective polymerization of **2** was promoted by the palladium(II) complex catalyst $BQPd$, in which the chiral binaphthyl group has no substituent (eq 2). A polymerization of **2** (39 equiv) was catalyzed at room temperature by $BQPd$ to afford, after quenching the reaction with $NaBH_4$, poly(2,3-quinoxaline)-species BQ_pH ($M_n = 5.81 \times 10^3$) with a CD spectrum bearing ca. 80% intensity of $B'Q_pH^0$ (Figure 1).



The CD spectrum of BQ_pH , which exhibits Cotton effect of the same sign as $B'Q_pH^0$, indicates that the initiator $BQPd$ induces the formation of the right-handed helix with high screw-sense selectivity. Plausible arrangements of the binaphthyl terminus of the polymer chains are illustrated on the basis of the X-ray structure of $B'Q_5Pd$ (Figure 3). It is noted that the benzene rings of the terminal naphthyl groups ($C5'-C10'$) are oppositely oriented in polymers $B'Q_pH^0$ and BQ_pH .

In conclusion, highly screw-sense selective polymerization and oligomerization of the 1,2-diisocyanobenzene were developed by use of the optically active palladium initiator with simple chiral auxiliary, leading to practical preparation of new and stable helical molecules.

Supporting Information Available: Detailed experimental procedures, characterization of the new compounds, and molecular packing diagram, tables of final atomic coordinates, thermal parameters, bond distances, and bond angles for compound $B'Q_5Pd$ (17 pages). See any current masthead page for ordering and Internet access instructions.

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