Journal of Organometallic Chemistry 738 (2013) 55–58

Contents lists available at SciVerse ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Note

Synthesis of novel polyfluorene with defined group in the center using aryl dipalladium complex as an initiator

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ARTICLE INFO

Article history:
Received 28 February 2013
Received in revised form
9 April 2013
Accepted 10 April 2013

Keywords:
Palladium complex
Catalyst
Chain-growth polycondensation
Conjugated polymer

ABSTRACT

Dinuclear Pd(II) complex **DiPd–DPE** with a bridging ligand $C_6H_4OC_6H_4$-4,4′ was successfully synthesized by double oxidative addition reaction of $Pd(PCy_3)_4$ with 4,4′-dibromodiphenyl ether in good yield. X-ray crystal structure analysis reveals that the Pd atoms have the nearly square-planar coordination geometry with the similar bond lengths of two Pd–Br as well as four Pd–P, implying that two Pd(II) centers have similar reactivity. Using the dinuclear Pd(II) complex **DiPd–DPE** as an initiator, novel polyfluorene (PF) with a defined group ($C_6H_4OC_6H_4$-4,4′) in the middle of polymer main chain was prepared, demonstrated by MALDI-TOF analysis.

1. Introduction

Conjugated polymers have drawn a great deal of attention owing to their potential applications in organic light-emitting diodes (OLEDs) [1–8], field-effect transistors (OFETs) [9–11] and photovoltaic cells (OPVs) [12,13]. These polymers have been commonly synthesized by conventional step-growth polycondensation [14–16], displaying broad molecular weight distribution. Chain-growth polymerization, however, could address this issue and obtaining polymers with controlled molecular weight and low polydispersity [17–20]. The representative work involves the Ni-catalyzed polycondensation of Grignard-type monomer which was extensively used in the synthesis of regioregular poly(3-alkylthiopherens) (P3ATs) as an electron-donating material for OPVs [20–23]. The controlled regioregular polythiophenes with low polydispersity show superior electronic and optical properties over the regiorandom analogs. Recently, Yokozawa reported a three-coordinate complex $[({}^tBu_3P)Pd(Ph)Br]$ used as an initiator in the chain-growth Suzuki–Miyaura polycondensation reaction of AB-type aromatic monomer. The polycondensation proceeded from the defined phenyl unit derived from the catalyst $[({}^tBu_3P)Pd(Ph)Br]$ and achieved polymers with well-defined end groups [24–26]. Nevertheless, even with these advantages, the unsaturated-coordination catalyst $[({}^tBu_3P)Pd(Ph)Br]$ has not been widely investigated in polymerization reaction due to its relatively poor stability, which must be strictly operated and stored under inert atmosphere at low temperature.

Inspired by these ideas, we speculate that if the polymerization starts from a saturated-coordination dinuclear palladium initiator with a bridging functional group between two Pd centers and proceeds in a chain-growth polymerization, the defined functional group would serve as an initiator unit and be incorporated in the center of polymer main chain. Therefore, we focus on the development of dipalladium catalyst [27–31], in which the choice of phosphine ligand is very critical. The bulky tricyclohexyl phosphine (PCy_3) was chosen as the auxiliary ligand because it has high activity in the reductive elimination step and could effectively inhibit the aryl–aryl exchange side reaction without the additional phosphine ligand [32–35]. In addition, diphenyl ether with simple structure and sufficient space is chosen as the bridging ligand. Finally, We successfully synthesized the dinuclear palladium complex **DiPd–DPE** by double oxidative addition of 4,4′-dibromodiphenyl ether to $Pd(PCy_3)_4$, and preliminarily investigate the polymerization behavior of AB-type fluorene monomer using **DiPd–DPE** as an initiator (Scheme 1).

2. Results and discussions

2.1. Synthesis of dipalladium complex **DiPd–DPE**

Based on the consideration of thermal stability, we initially attempted to prepare the dinuclear Pd(II) complex **DiPd–DPE** at

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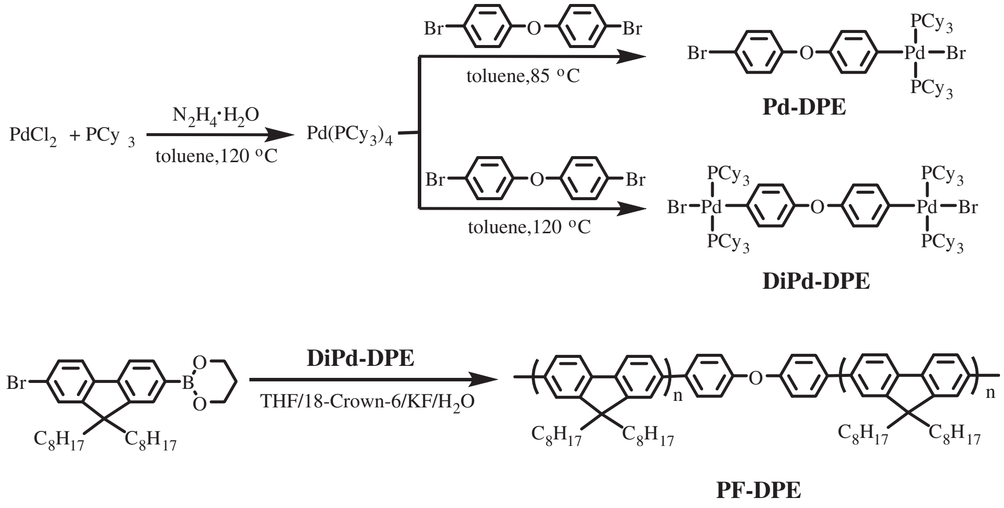
http://dx.doi.org/10.1016/j.jorganchem.2013.04.016



Scheme 1. Synthesis of dipalladium catalyst **DiPd–DPE** and polymer **PF–DPE**.

85 °C by double oxidative addition reaction of 4,4′-dibromodiphenyl ether with $Pd(PCy_3)_4$ generated *in situ* in a ratio of 1:2.5 in toluene, however, only mononuclear complex **Pd–DPE** was isolated in good yield, confirmed by ^1H NMR spectrum and X-ray crystallography. Increase of the reaction temperature to 120 °C leads to the target dipalladium complex **DiPd–DPE** in 72% yield, which means that the double oxidative addition could be carried out smoothly at higher temperature [24]. The chemical structure of **DiPd–DPE** was determined by ^1H NMR and ^{31}P NMR. ^{31}P NMR spectrum shows a singlet at 19.3 ppm, indicative of its symmetric structure, which is in accordance with a *trans* configuration having four magnetically equivalent PCy_3 ligands. The dipalladium(II) complex **DiPd–DPE** has better stability compared with monomeric three-coordination arylpalladium(II) halide complex $[(^tBu_3P)Pd(Ph)Br]$, which renders the operation easier. Indeed, complex **DiPd–DPE** can be weighted, transferred in air, and recrystallized from the solvents without distillation treatment. Furthermore, it is worth noting that the dipalladium(II) complex **DiPd–DPE** can be preserved in the Schlenk flask under argon at room temperature for two month with the catalytic activity unchanged.

2.2. X-ray characterization of **DiPd–DPE** and **Pd–DPE**

The molecular structures of complexes **DiPd–DPE** and **Pd–DPE** are shown in Figs. 1 and 2, and selected bond distances and angles were summarized in Table 1. Complex **DiPd–DPE** adopts the expected *trans* configuration with a nearly square-planar geometry around central Pd atoms, supported by the bond angle of C1–Pd1–Br1, P1–Pd1–P2, C10–Pd2–Br2 and P3–Pd2–P4 (166.15–173.80°), which are approximate to 180°. The four *cis* angles around each Pd atom are close to orthogonal (89.76–93.67° and 87.10–92.48°, respectively). The two planes defined by Pd1Br1P1P2C1 and Pd2Br2P3P4C10 are twisted with dihedral angle of 50.71°. Each phenyl ring is almost perpendicular to the adjacent Pd(II)-centered plane with the dihedral angles of 85.74 and 84.83°. In addition, the bond length of Pd1–Br1 [2.5324(7) Å] and Pd2–Br2 [2.5104(9) Å] are similar to each other as well as the four Pd–P bond distances. All of the results illustrate that two Pd(II) centers should have similar chemical reaction activity. Accordingly, the bridging group $C_6H_4OC_6H_4$-4,4′ would be introduced in the center of polymer main chain when the dipalladium(II) complex **DiPd–DPE** is used as an initiator in the polycondensation reaction.

2.3. Synthesis and polymerization behavior study of polyfluorene

The polymerization of AB-type monomer 2-(7-bromo-9,9-dioctylfluoren-2-yl)-1,3,2-dioxaborinane with dipalladium(II) complex **DiPd–DPE** was carried out at 25 or 75 °C for 12 h in the presence of KF/18-crown-6. THF with a small amount of water for dissolving KF was chosen as the reaction solvents because they could form a homogeneous system facilitating the polymerization process. After the reaction was quenched with 1 M hydrochloric acid, the crude product was filtered and washed with acetone via a Soxhlet apparatus to remove low-molecular-weight fractions. Molecular weights and polydispersity indices (PDI) of polyfluorene **PF–DPE** were determined by gel permeation chromatography (GPC) analysis with a polystyrene standard calibration. The number average molecular weight (M_n) of **PF–DPE** (25 °C) is 12,320 g/mol with a PDI of 1.84, and **PF–DPE** (75 °C) exhibits a higher M_n of 15,670 g/mol with a slightly broader PDI of 2.09. These results reveal that high temperature is beneficial for the proceeding of Suzuki–Miyaura coupling polymerization of fluorene-based monomer.

The polymerization behavior was further evaluated by MALDI-TOF mass spectrometry. The mass spectrum for polyfluorene obtained at 75 °C (Fig. 3) shows a series of major peaks accompanied with two sets of minor peaks. All of the mass differences between

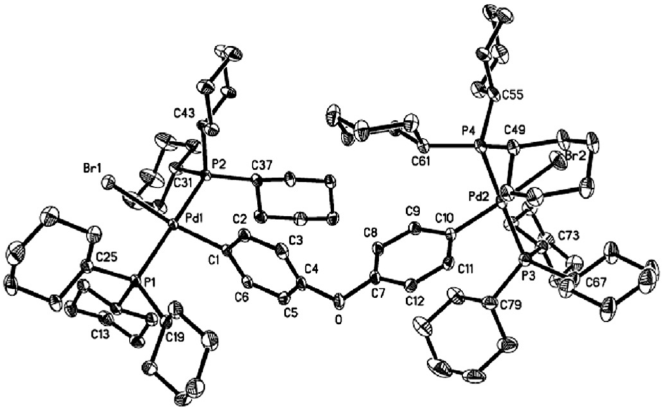


Fig. 1. An ORTEP drawing of **DiPd–DPE** showing the atom-labeling scheme and 30% probability thermal ellipsoids, H atoms and solvent molecule are omitted for clarity.