Ferrocene in Boron-Nitrogen Coordination Polymers

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Abstract

Ferrocene is frequently used in polymer chains owing to their electrochemical properties. The paper aims at identifying novel routes to synthesize a dinuclear complex 1.pyz.1 and a poly [2.pyz]_n. The complex 1.pyz.1 is synthesized from the reaction of pyrazine with solution of 1 while the poly is obtained from the reaction of solution of 2 with pyrazine. Following the synthesis these complexes were structurally characterized by X-ray crystallography.

Introduction

Macromolecules containing metal exhibit electrical, magnetical, and optical properties due to electron delocalization. These electrochemical properties are inherent in the ferrocene nucleus which is useful when incorporating ferrocene into polymer chains.
Three major pathways to ferrocenes have been developed namely: (i) polycondensation reactions using difunctional ferrocenes, (ii) the synthesis of ferrocene derivatives bearing polymerizable substituents, (iii) the thermal or catalytic ring-opening polymerization of strained [1]- and [2]-ferrocenophanes.

**Objective**

This paper dwells on developing new synthetic routes to low-dimensional ferrocenes. The paper reports the synthesis and the structural characterization of a dinuclear complex 1.pyz.1 and of a poly [2.pyz]n. This complex consists of diborylated units 2,5 linked by pyrazine (pyz) bridges. The synthesis of this complex is based on the facile formation of boron-nitrogen adduct bonds. This process combines the advantages of coordination polymer synthesis with the unique properties of ferrocene building blocks.

**Methodology**

*Experimental Setup:* The synthesis of starting materials was carried out under controlled conditions, using Schlenk techniques to exclude moisture and air to maintain dry and prepurified argon atmosphere. All solvents were distilled under N₂ prior to use. MS: Finnigan MAT 90. IR: Perkin-Elmer 1650 FTIR. NMR: JOEL JMN-GX 400 and Bruker DPX 400. ¹¹B NMR spectra were referenced to external BF₃.Et₂O. Thermal analyses: Netzsch DSC 404 high-temperature furnace, thermocouple Pt/Rh, Perkin-Elmer TGA 7 thermobalance equipped with a Balzers QNC 420 mass spectrometer.
Starting Materials: ferrocene derivatives 1 and 2

Preparation of 1.pyz.1: A colorless solution of pyrazine in toluene was added in drops to an orange-red solution of 1 at ambient temperature. The reaction mixture was stirred for 2 hours before reducing the amount of solvent in vacuo which results in a purple microcrystalline precipitate. This precipitate is collected on a frit, triturated with hexane and finally dried in vacuo. The filtrate is kept overnight at -30 °C to yield a second crop of dark reddish-brown X-ray quality crystals of 1.pyz.1.

Preparation of [2.pyz]$_n$. A red solution of 2 in CH$_2$Cl$_2$ was layered in a Schlenk tube with toluene and then with a solution of pyrazine in toluene. This solution is kept for 7 days which yields a homogeneous purple reaction mixture which is further stored for several days at 5 °C to yield a dark green X-ray quality crystals of [2.pyz]$_n$.

Results and Discussions

X-ray structure determination

- 1.pyz.1: Data was collected on an air-stable dark reddish-brown needle at -110 ± 3 °C by using a NONIUS CAD4 diffractometer with graphite-monochromated Mo Kα radiation.

- [2.pyz]$_n$: Data was collected on an air-stable dark green platelet at 20 ± 1 °C by using an image plate diffraction system with graphite-monochromated Mo Kα radiation.
X-ray structure analysis showed all crystals under study to be partial meroedic twins. All nontwinned parts were integrated using a software program called TWIN. This resulted in two half-records which were used to solve and refine the structure. All non-hydrogen atoms were refined anisotropically, while all hydrogen atoms were analyzed using X-ray crystallography.

This review shows that the electronic and photophysical properties of organic conducting polymers can be modulated through the incorporation of Lewis acidic boron centers into the polymer backbones. The different data for neutral atom scattering factors for all the atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken form the International tables for X-ray crystallography.

**Conclusion**

Metallocene polymerization (polymerization catalyzed by metallocenes) is the current interest in the research field these days as it is very useful in the synthesis of vinyl polymers. Vinyl polymers are polymers made from vinyl monomers; that is, small molecules containing carbon-carbon double bonds. They make up largest family of polymers, for example polyethylene. Metallocenes makes polymers with specific tacticity. Tacticity is nothing but the way the side-chains are attached to the main backbone chain of polymers. However, the polymerization process is not discussed in this review. But the polymerization is of much interest since the invention of Ziegler-Natta Polymerization, which is important because it allows one to make polymers of specific tacticity as aforementioned.
Reference


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