

中性リンドナーを含む[NPN]三座配位子から成る Zr 錯体の合成およびオレフィン重合活性評価

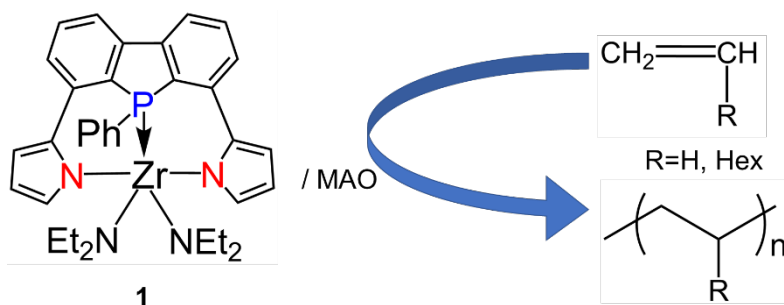
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Synthesis and Its Olefin Polymerization Activity of a Zr Complex with [NPN] Tridentate Ligand Having Neutral Phosphine Donor (¹Nagaoka University of Technology, ²Niigata University, ³National Institute of Technology, Oyama College, ⁴Hirosaki University) ○Yuzuki Kasahara,¹ Tomoyuki Toda,¹ Jin Iwasaki,¹ Katsuhiko Takenaka,¹ Ayana Wakatsuki,² Yoshihiro Matano,² Kei Nishii,³ Shun Ohta⁴

In the design of polymerization catalysts, hard bases are often used as the ligands for group 4 metals that classified as hard acids. Moreover, the introduction of sulfur, a soft base acts as donor moiety, in the ancillary ligands serves as hard bases has been reported to improve the ethylene polymerization activity.¹ In this context, phosphine, a soft base, is also expected to exhibit a similar effect. However, there have been very few examples of the synthesis and polymerization of group 4 metal catalysts with hard base ligands containing phosphorous as donor moiety.² In this study, we synthesized a zirconium complex **1** with a [NPN] tridentate ligand, analyzed its molecular structure, and evaluated its ability of olefin polymerization. Ethylene polymerization was conducted by complex **1** activated with methylaluminoxane (MAO). As a result, the catalytic system gave the linear polyethylene (PE) with a high activity of 367 kg(PE)/mol(Zr) h.

Keywords : Coordination Polymerization; Group 4 Metal Complex; Polymerization Catalyst; Phosphorus

重合触媒の設計において、硬い酸である4族金属の補助配位子には硬い塩基が利用されることが多い。また、硬い塩基を基盤とする配位子に柔らかい塩基である硫黄を導入することによりエチレン重合活性が大幅に向上することが報告されている¹⁾。硫黄と同様、柔らかい塩基であるリンでも同様の効果が期待できるが、リンと硬い塩基を併せ持つ混合ドナー配位子を有する4族金属触媒の合成・重合例は非常に少ない²⁾。本研究では中性リンドナーを含む[NPN]三座配位子から成るジルコニウム錯体**1**を合成し、分子構造の解析とオレフィン重合活性の評価を行った。錯体**1**をメチルアルミノキサンで活性化してエチレン重合を行ったところ、367 kg(PE)/mol(Zr) h という比較的高い活性で直鎖状ポリエチレン(PE)が得られた。



1) A. van der Linden, *et al.*, *J. Am. Chem. Soc.* **1995**, *117*, 3008. 2) R. J. Long, *et al.*, *Organometallics* **2008**, *27*, 235.