

博士論文(要約)

**Studies on Transformation of Olefins
Mediated by Earth-Abundant Elements**

(地球に豊富に存在する元素が介在する
オレフィン類の変換に関する研究)

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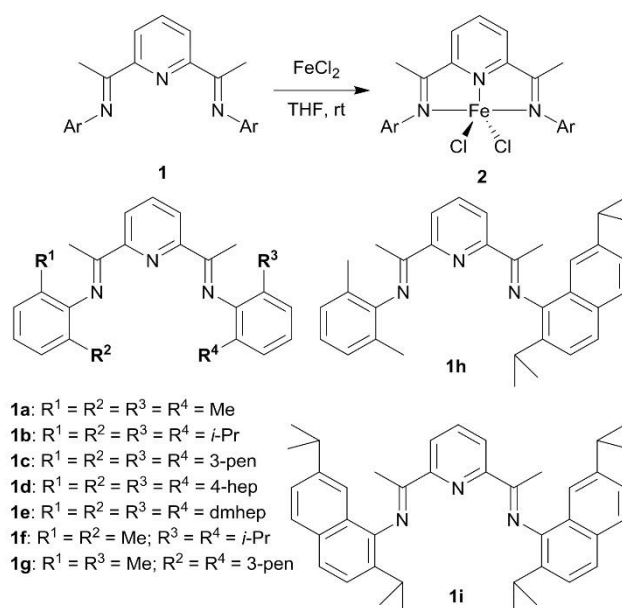
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[1. General Introduction]

Humankind has long been benefited by chemical industry. To date, tremendous effort has been made on transformation of chemical feedstocks to commodity chemicals. In that context, olefin is one of the most important class of compounds, as the largest class of chemical feedstocks produced not only from fossil fuel but also from bio-based renewable sources. Wide variety of chemical transformation using olefin as substrate were utilized and that bring about transformation of our society. Majority of such transformations were depending on precious metal catalyst. Although the continuous effort devoted to modifications and optimizations have led to the development of highly selective and efficient catalytic system, there are still nonnegligible demands for sustainable catalyst technology. At this point, in recent decades, earth abundant elements mediated systems drawing significant attention as an alternative to precious metal based one. In this thesis, I focused on the following topics: "Iron-catalyzed homo- and copolymerization of propylene"

[2. Iron-Catalyzed Homo- and Copolymerization of Propylene]

Iron, the 4th most abundant element on earth, has long been utilized in human society. As for the transformation of olefin, iron based catalytic system for hydrosilylation, hydroamination, and many other reactions, have been developed.[1] In terms of the utilization of olefins, polymerization of them is one of the most important technology. Synthetic polymers such as polyethylene and polypropylene have wide variety of application although low polarity of them decrease their efficacy to some extent when utilized in combination with polar materials. To overcome that drawback copolymerization of olefins with monomers bearing functional groups is one of the most attractive way.[2] Iron(II)/bis(imino)pyridine complexes are an important class of catalysts which successfully promote olefin polymerization.[3] Although Small and Brookhart[3a] and Pellecchia, et al.[3b] independently reported that the iron complexes produce isotactic polypropylene in their seminal study, most of the following studies have focused on the oligomerization or polymerization of ethylene, and much less attention has been paid to that of propylene. In addition, there was no report on iron-catalyzed copolymerization of propylene with another comonomer. In this work, a series of iron complexes bearing a bis(imino)pyridine ligand were synthesized and examined as a precatalyst for the homopolymerization of propylene and the copolymerization of propylene with allyl comonomers.

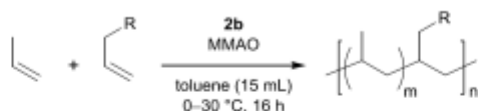


Scheme 1. Preparation of Iron Complexes

Table 1. Propylene Polymerisation by Iron Catalysts

Entry	catalyst	yield (g)	activity (g/mmol-h)	$M_n/10^3$	M_w/M_n	$[\eta]^4$
1	2a	1.4	72	1.6	2.1	39
2	2b	1.0	200	4.7(9.0)	2.5	54
3	2c	0.065	0.82	3.4	2.4	60
4	2d	0.041	0.76	4.5	2.1	53
5	2f	1.5	290	4.1	2.3	57
6	2g	0.68	34	6.6(9.5)	2.9	54
7	2h	1.8	350	3.2	2.6	52
8	2i	1.3	67	3.2	4.1	59

Homopolymerization of propylene was investigated using iron complexes **2** activated by modified methylaluminoxane (MMAO) (Table 1). I hypothesised that the longer alkyl chain could block the axial position of the iron center and inhibit β -hydride elimination and/or chain transfer to afford high-molecular-weight polypropylenes.[4] Then, I examined catalysts bearing different length of alkyl substituents (entries 1–4). The results suggest that the substituents also severely inhibited the coordination and insertion of propylene. Next, I focused on ligands bearing unsymmetrically substituted aryl groups. It should be noted that **2g** produced the highest molecular weights of the polypropylenes and **2h** gave the highest catalytic activity (entry 7).

Table 2. Copolymerisation of Propylene and Allyl Monomers by Iron Complex **2b**.

entry	R in comonomer	comonomer (mL)	propylene (g)	T (° C)	yield (g)	activity (g·mmol ⁻¹ ·h ⁻¹)	M _n /10 ³ (g/mol)	M _w /M _n	incorp. (%)
1	R = OAc	0.20	9.4	30	2.7	8.5	3.3	6.9	0
2	R = OMe	0.40	9.2	30	0.37	1.1	3.7	2.1	0
3	R = OSiPr ₃	0.40	9.2	30	2.7	8.4	2.4	2.0	0
4	R = Ph	0.40	5.7	30	2.3	7.2	0.97	2.1	1.4
5	R = SiMe ₃	0.40	7.0	30	1.4	4.5	1.3	7.8	2.1
6	R = SiMe ₂ Ph	0.40	7.3	30	0.67	2.1	2.0	1.9	1.7
7	R = Si(OEt) ₃	0.40	11	0	0.44 ^c	1.3	3.2	2.4	0.30

Copolymerization of propylene with a range of allyl monomers was examined using catalyst **2b** (Table 2). First, I investigated copolymerization with polar monomers, such as allyl acetate (entry 1), allyl ether (entry 2), and allyl silyl ethers (entry 3). In all the attempts, however, the corresponding functionality was not incorporated. In contrast, allylbenzene (entry 4) and allylsilanes (entries 5–7) could be incorporated into the polypropylene chain.

[3. References]

- [1] (a) I. Bauer, H.-J. Knölker, *Chem. Rev.*, **2015**, *115*, 3170–3387 (b) V. Rodriguez-Ruiz, R. Carlino, S. Bezzenine-Lafollée, R. Gil, D. Prim, E. Schulz, J. Hannedouche *Dalton Trans.*, **2015**, *44*, 12029–12059 (c) J. R. Ludwig, P. M. Zimmerman, J. B. Gianino, C. S. Schindler *Nature*, **2016**, *533*, 374–379 [2] A. Nakamura, T. M. J. Anselment, J. P. Claverie, B. Goodall, R. F. Jordan, S. Mecking, B. Rieger, A. Sen, P. W. N. M. van Leeuwen, K. Nozaki, *Acc. Chem. Res.*, **2013**, *46*, 1438–1449. and references cited therein. [3] (a) B. L. Small, M. Brookhart, *Macromolecules*, **1999**, *32*, 2120–2130. (b) C. Pellecchia, M. Mazzeo, D. Pappalardo, *Macromol. Rapid Commun.*, **1998**, *19*, 651–655. [4] (a) Y. Ota, S. Ito, J. Kuroda, Y. Okumura, K. Nozaki, *J. Am. Chem. Soc.*, **2014**, *136*, 11898–11901. (b) D. H. Camacho, Z. Guan, *Chem. Commun.*, **2010**, *46*, 7879–7893.