

博士論文（要約）

**Studies on Olefin Polymerization by
Bisphosphine Monoxide-Palladium Complexes**

（ビスホスフィンモノオキシド-パラジウム錯体による
オレフィン重合の研究）

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1. Introduction

Late transition-metal-catalyzed copolymerization of olefins with polar monomers has drawn much attention as a new method to synthesize functionalized polyethylenes.[1] This method can copolymerize ethylene with common polar monomers and potentially allows precise control of polymer microstructures, which is difficult to achieve by other copolymerization methods.

In 2012, Nozaki group reported the synthesis of bisphosphine monoxide-palladium (BPMO-Pd) complexes (Figure 1) and their reactivity toward olefin polymerization.[2] BPMO-Pd complexes could catalyze the copolymerization of ethylene with various polar monomers to afford linear functionalized polyethylenes. Before this report, phosphine-sulfonate/palladium catalysts, first reported by Drent and coworkers,[3] were the only system which was tolerant of a wide range of polar monomers.[1] In this context, the report of BPMO-palladium catalysts is notable because it demonstrated that an electronically unsymmetric structure composed of a strong electron donation moiety and a weak electron donation moiety in a bidentate ligand other than the combination of phosphine and sulfonate could lead to the palladium catalysts which are able to copolymerize ethylene with polar monomers. Although this report offered important insights into a ligand design, the derivatization of BPMO ligands was not fully investigated and the polymerization mechanism of BPMO-Pd catalysts remained unclear.

Here in this study, the mechanistic studies on the BPMO-Pd catalyzed copolymerization of ethylene with methyl acrylate (MA) are described. It was found that the regioselectivity of MA insertion could be controlled by changing the substituents on the phosphine moiety and this regioselectivity of MA insertion affected the rate of copolymerization dramatically.

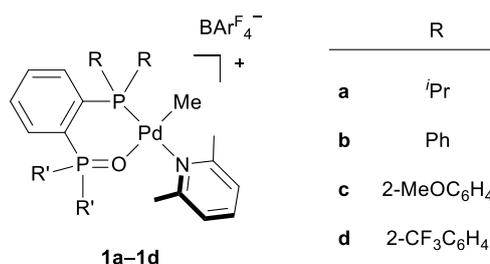
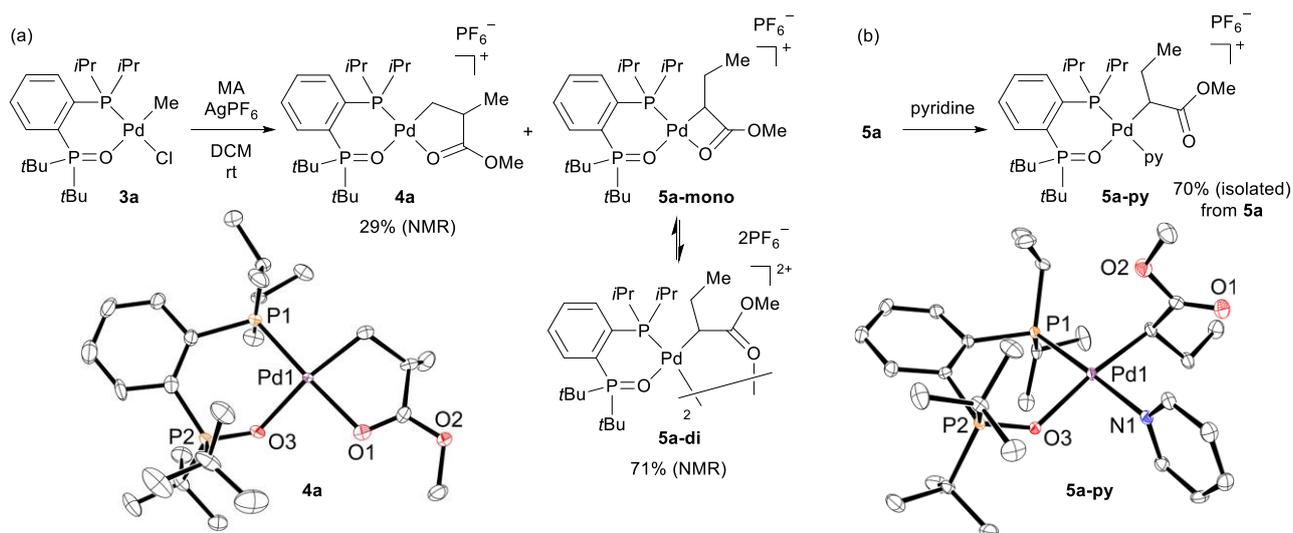


Figure 1. Examples of BPMO-Pd complexes. Ar^F = 3,5-bis(trifluoromethyl)benzene

2. This Work

The original BPMO-palladium catalyst (an analog of **1a** bearing SbF₆⁻ in place of BAr^F₄⁻) was not applicable to the copolymerization of ethylene and MA. This observation was puzzling considering that MA has been the most reactive comonomer for copolymerization with ethylene,[2] and I set out to elucidate the reason of this phenomenon.

A stoichiometric reaction of a BPMO-palladium complex having a dialkylphosphino group with MA was first tried to gain insight into the structure of any potential deactivated catalyst states. Treatment of chloro(methyl)palladium complex **3a** with silver hexafluorophosphate in the presence of MA led to the formation of two distinct palladium products, **4a** and **5a**, in 29% and 71% NMR yield, respectively (Scheme 1). Recrystallization of **4a** from (trifluoromethyl)benzene/diethyl ether provided single crystals of **4a** suitable for X-ray analysis (Scheme 1a). The formation of **4a** must occur by initial 1,2-insertion of MA into the Pd–C bond of **3a**, which is an uncommon mode of regioselectivity.[4] On the other hand, the characterization of **5a** was difficult due to the equilibrium between **5a-mono** and **5a-di**, but it was found that **5a** reacted with pyridine to give a single new species (**5a-py**), the structure of which was successfully determined by X-ray analysis (Scheme 1b). This complex was formed by 2,1-insertion of MA into the Pd–C bond of **3a**. Thus, both



Scheme 1. (a) Stoichiometric reaction of methyl acrylate with complex **3a** and (b) reaction of **5a** mixture with pyridine.

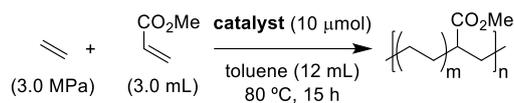
Table 1. Homopolymerization of ethylene by BPMO-Pd complexes **3a**, **4a** and **5a**.

entry	catalyst	yield (g)	activity (kg mol ⁻¹ h ⁻¹)	M_n (10 ³)	M_w/M_n
1	3a + AgSbF ₆	2.51	420	23	3.3
2	4a	0.05	8	30	2.3
3	5a-mono/5a-di	0.32	54	23	3.0

organometallic products **4a** and **5a** arise from migratory insertion of MA with opposite regioselectivity.

The catalytic activities of isolated metallacycles **4a** and **5a-mono/5a-di** towards ethylene polymerization were compared to that of typical catalyst **3a** mixed with silver hexafluorophosphate (Table 1). The results of these experiments clearly indicate that both palladacycle complexes react more slowly than methylpalladium precatalyst **3a**. Notably, 5-membered palladacycle **4a** is also significantly less reactive towards ethylene insertion compared to the dynamic mixture of 4-membered palladacycle **5a-mono** and dimer **5a-di**. These data suggest that any new BPMO-Pd catalyst that is active for polymerizations of acrylates likely would need to enforce high 2,1-insertion regioselectivity to avoid catalyst inhibition through formation of a stable 5-membered palladacycle.

Most importantly, a significant improvement in the catalytic activity for ethylene/MA copolymerization was observed when BPMO-Pd catalysts that possess an *ortho*-substituted diarylphosphino moiety were used (Table 3). Complex **1b** with a diphenylphosphino fragment were inert for copolymerization (entry 2), but **1c** or **1d** exhibited dramatically high activity (entries 3 and 4). In order to get insight into the high catalytic activity of BPMO-Pd complexes bearing *ortho*-functionalized aryl groups, a stoichiometric reaction of **3c** with MA was conducted. The reaction of **3c** with silver hexafluorophosphate in the presence of MA followed by trapping with pyridine afforded **5c-py** in high overall yield (90%) as determined by ¹H NMR yield (Scheme 2). Importantly, a palladium complex corresponding to 1,2-insertion of MA was not detected, which indicated that the

Table 3. Copolymerization of ethylene and methyl acrylate in the presence of BPMP-O-Pd complexes.

entry	catalyst	yield (g)	activity (kg mol ⁻¹ h ⁻¹)	M _n /10 ³	M _w /M _n	incorp. (mol%)
1	1a	0.03	0.2	1.6	1.7	2.5
2	1b	0	---	---	---	---
3	1c	0.61	4.1	33	2.3	2.3
4	1d	0.89	5.9	14	2.1	0.9

high catalytic activity of BPMP-O-Pd complexes bearing an *ortho*-substituted diarylphosphino group should be accomplished by the exclusive 2,1-insertion of MA.

3. References

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