

Copolymerization of Polar Monomers with Olefins Using Transition-Metal Complexes

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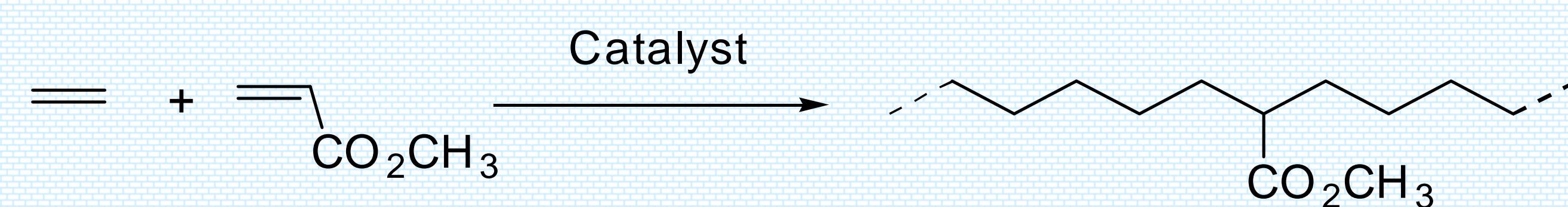
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Introduction

Transition-metal catalysts long ago made it from the laboratory bench to the polymerization reactor. Indeed, they are being used around the world to make more than 70 million tons of polyethylene and polypropylene a year. Transition-metal catalysts give polyolefin producers unprecedented flexibility in process and polymer design. However, there are still new worlds for catalysts to conquer. One of the most challenging targets is the controlled copolymerization of simple olefins with polar functional monomers. Success in this area would mark a quantum advance in polyolefin field.

Research Goal

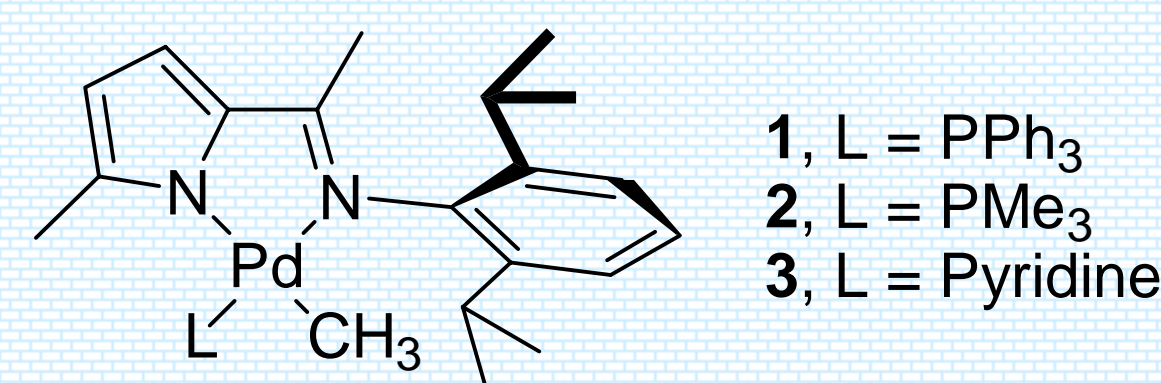
- Developing transition-metal catalysts for copolymerization of polar monomers with olefins
- Exploring the polymerization mechanism



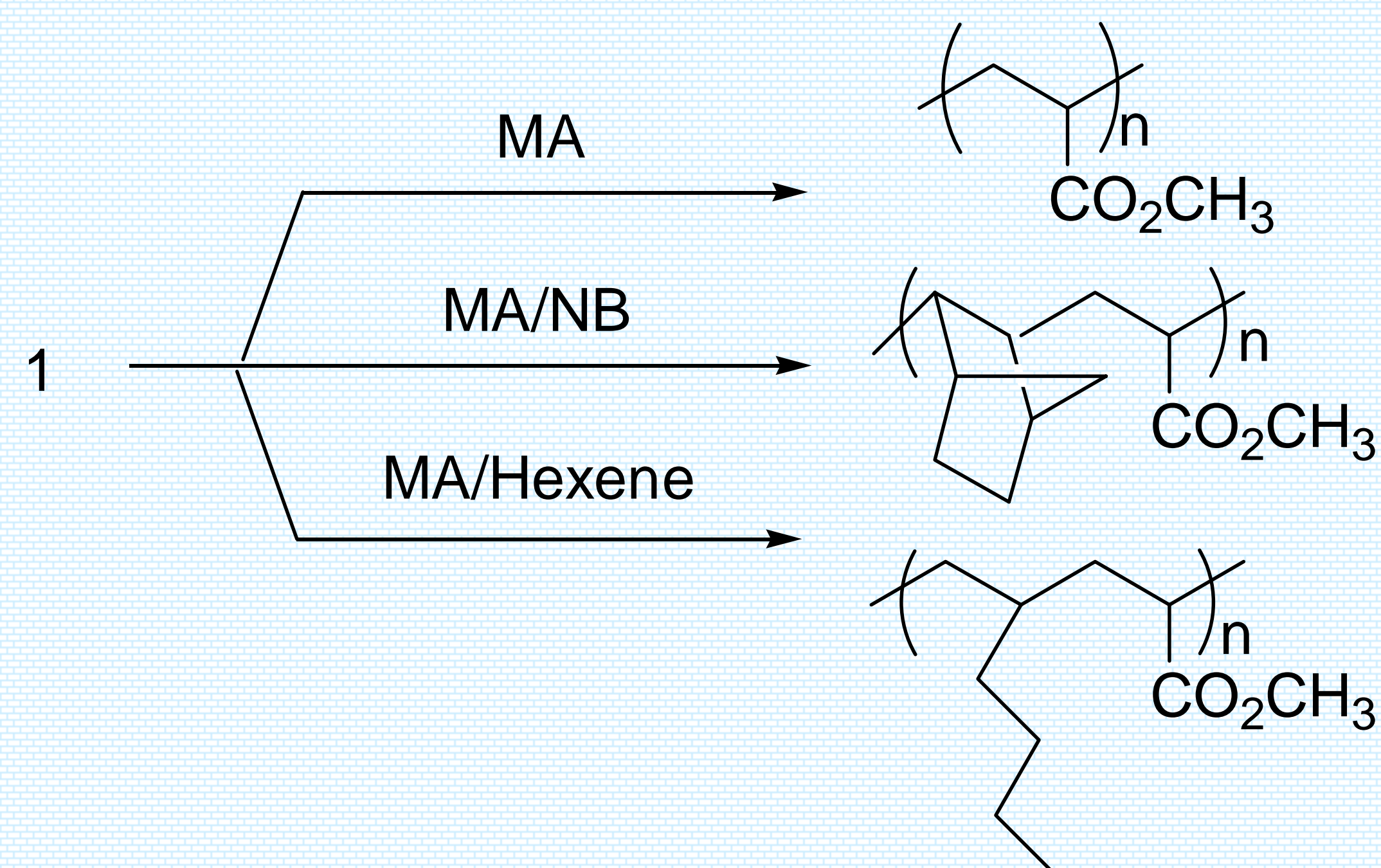
Neutral Palladium Alkyls

Normally, transition-metal catalysts could not tolerate polar monomers. The interactions between metal center and heteroatoms (such as O, N and S) poison the catalysts.

In order to reduce the Lewis acidity of metal center, we have synthesized a series of neutral palladium alkyl complexes possessing negatively charged 2-iminopyrrole ligands.



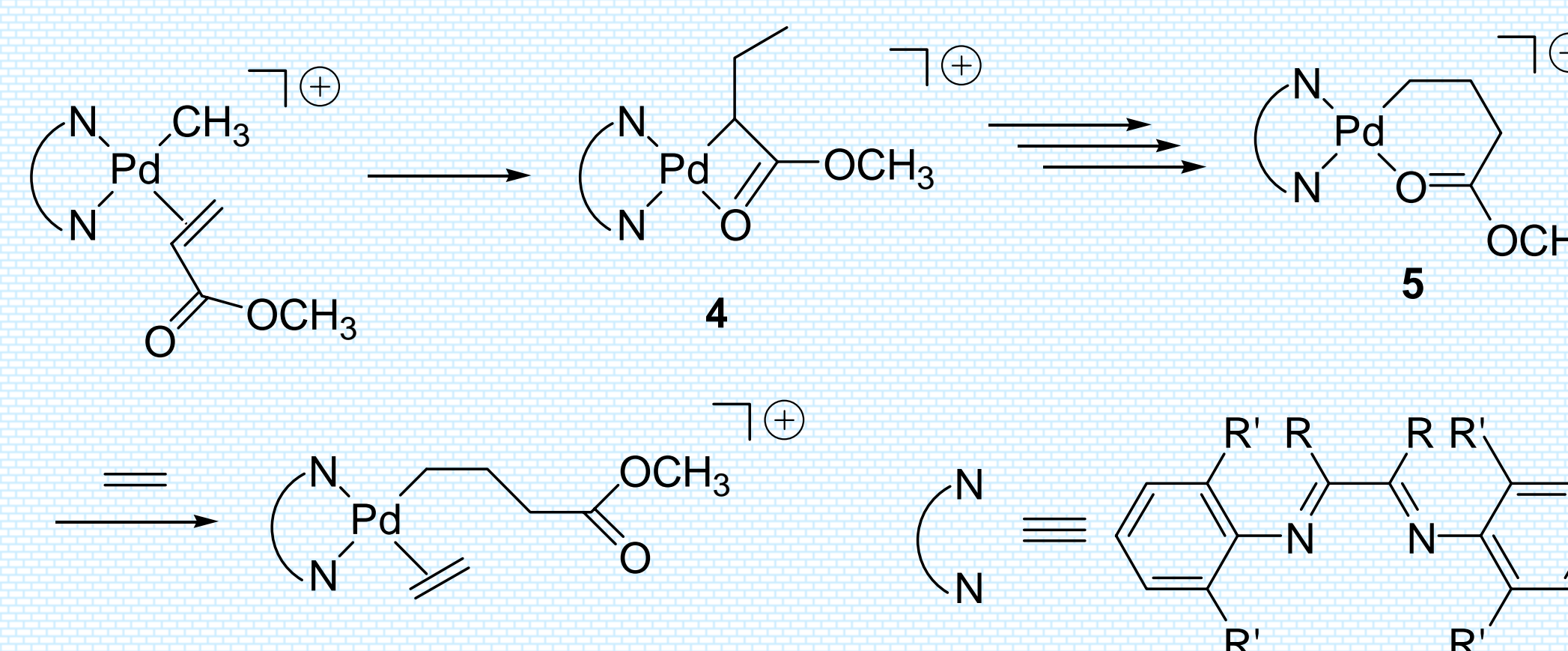
Attempts to polymerize olefins using these complexes were so far unsuccessful. However, they were found to be highly active toward methyl acrylate (MA) homo- and co- polymerizations. Further studies indicated that the propagation mechanism is free radical rather than the sought after metal-mediated type.



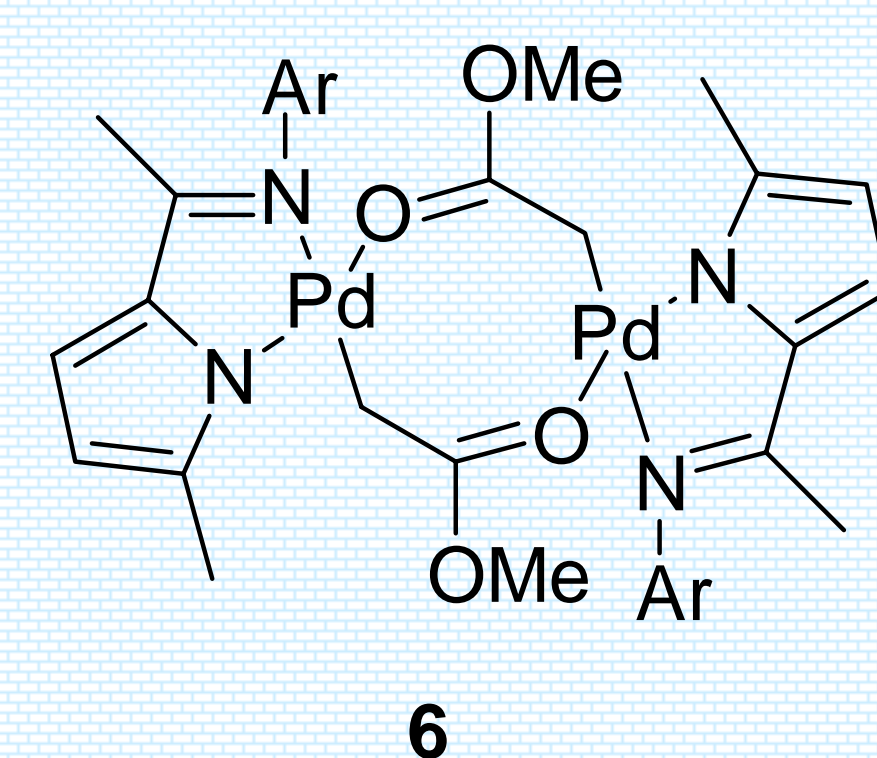
Particular caution is suggested when selecting radical inhibitors as simple phenoxy inhibitors are not effective in inhibiting radical chain processes in presence of these palladium complexes.

Palladium Enolate

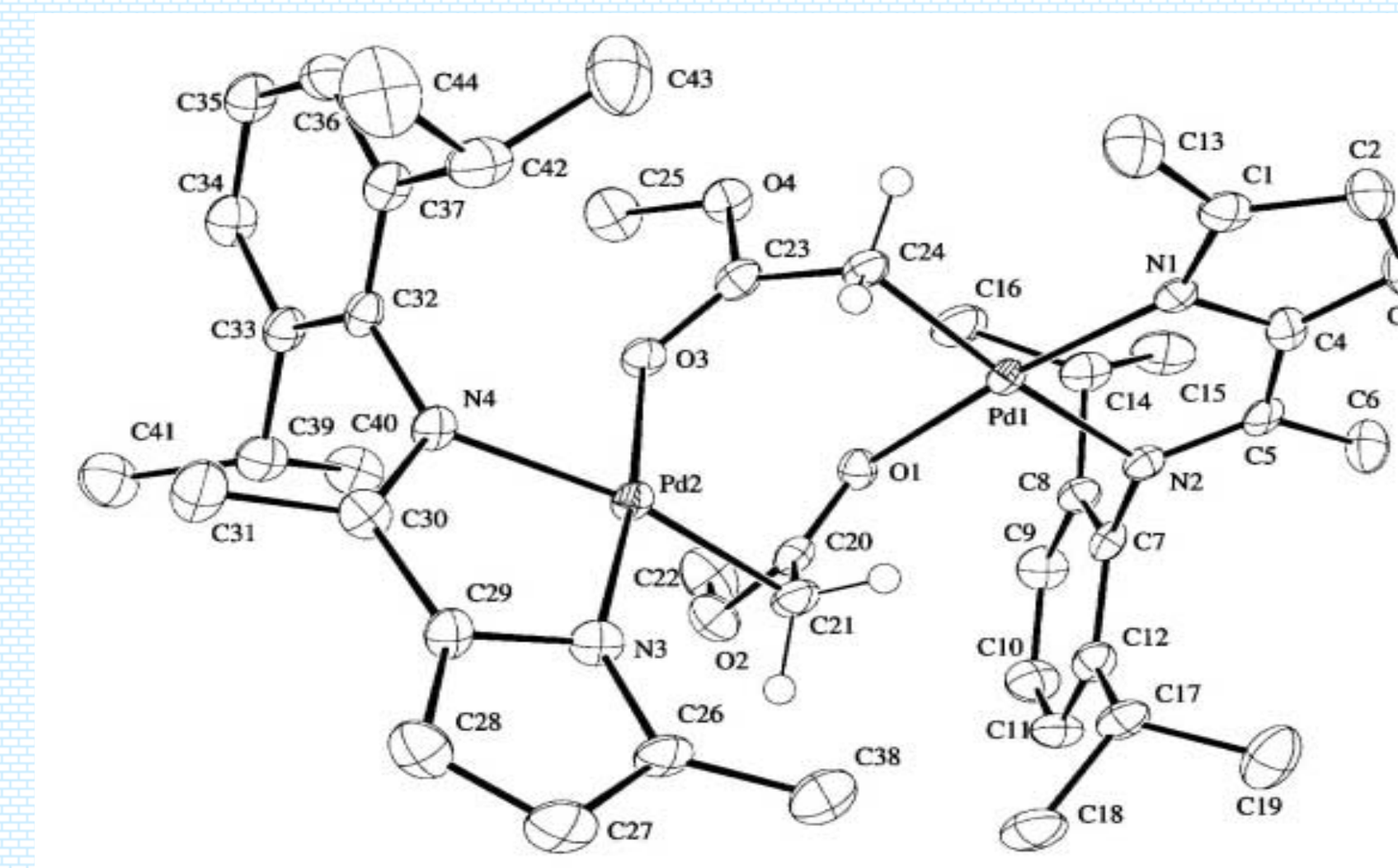
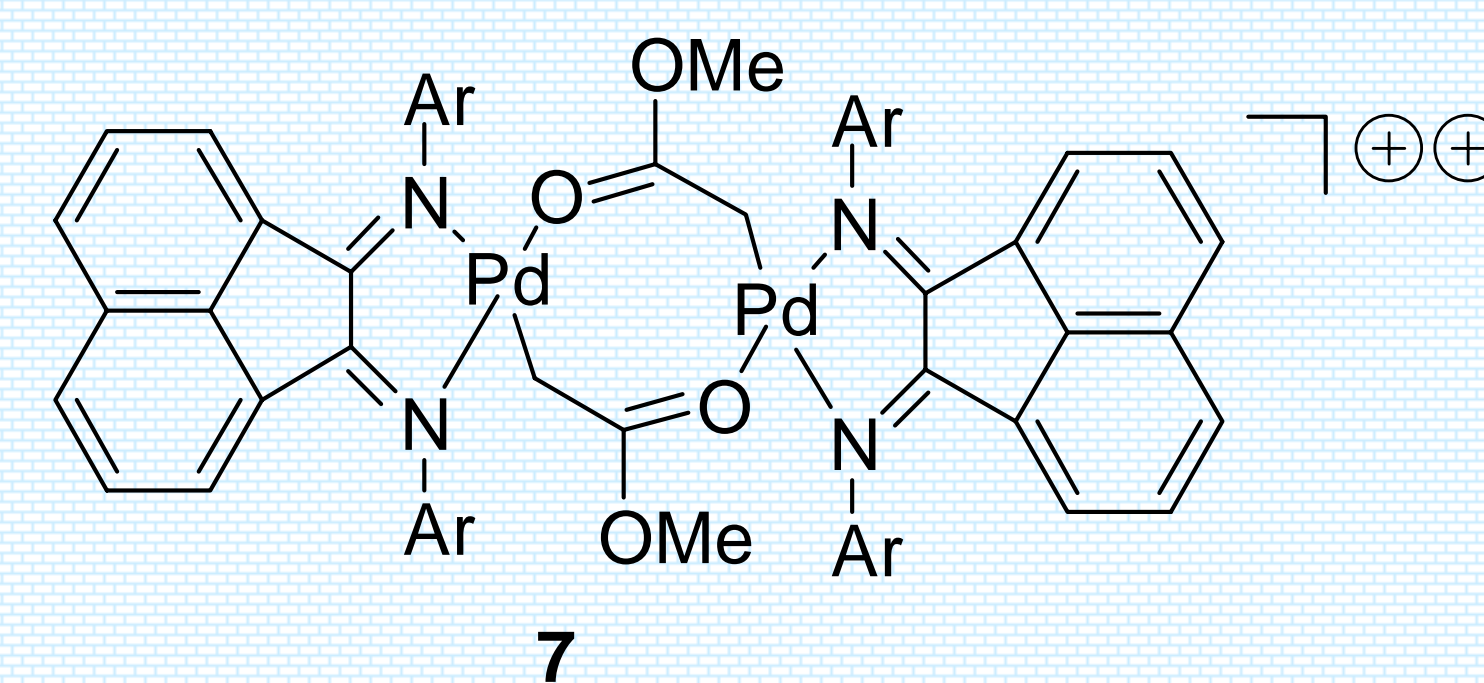
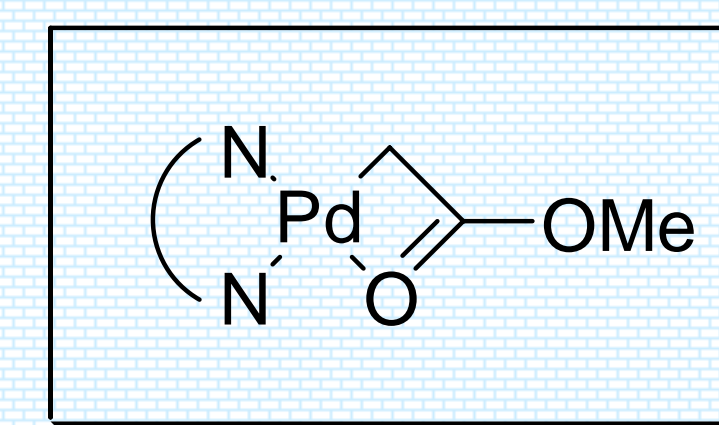
Brookhart and Johnson have reported the copolymerization of ethylene and methyl acrylate using cationic palladium catalysts. Palladium enolate (**4**) has been proposed as the key reaction intermediate, but it has not been structurally characterized.



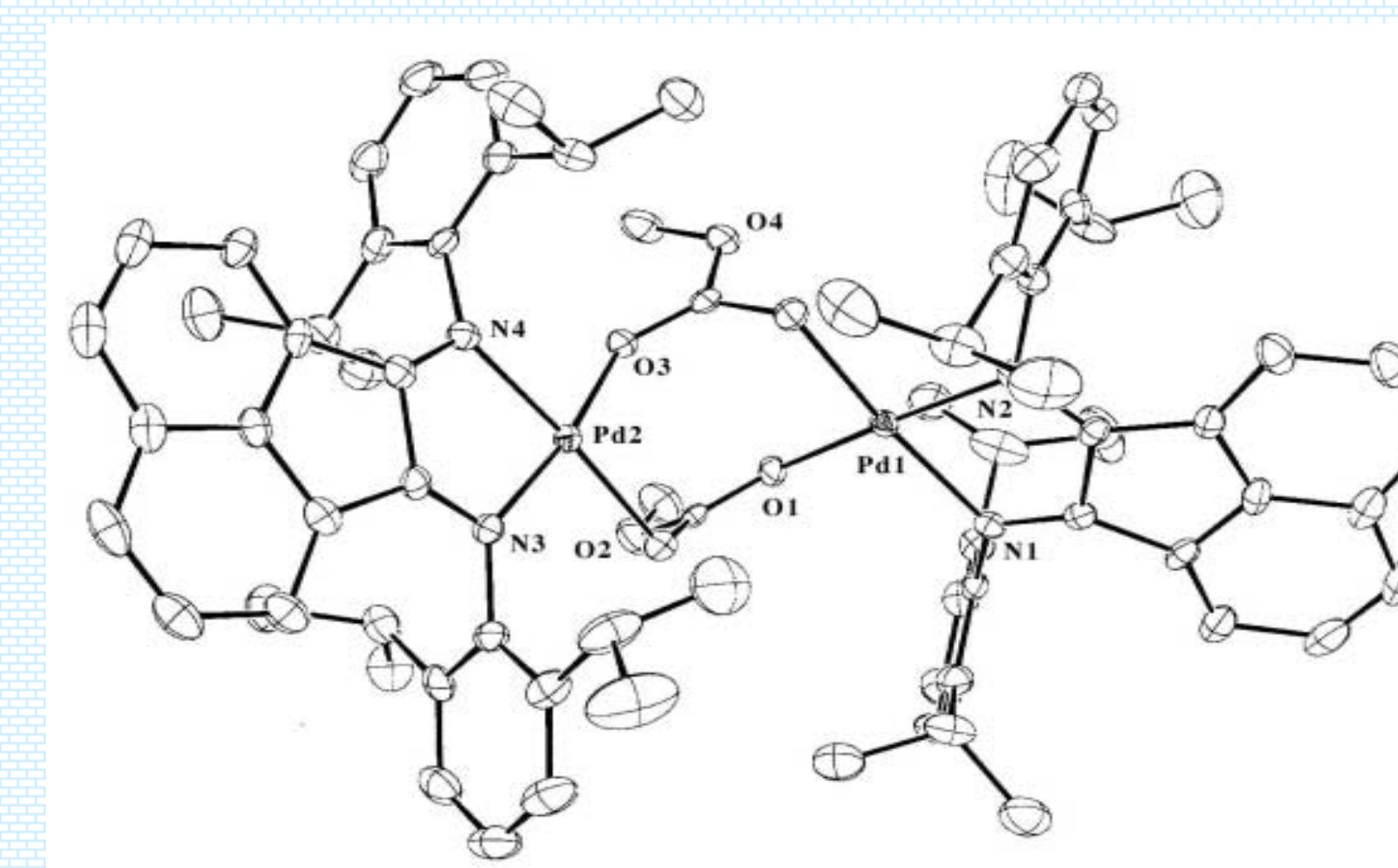
Characterization of the structure of palladium enolate would provide clearer insight into the polymerization mechanism. Therefore, we have prepared two different types of palladium enolates, **6** (neutral) and **7** (cationic), and determined their crystal structures. Both enolates adopt a dimeric structure instead of the assumed four-membered ring chelate.



Rather than

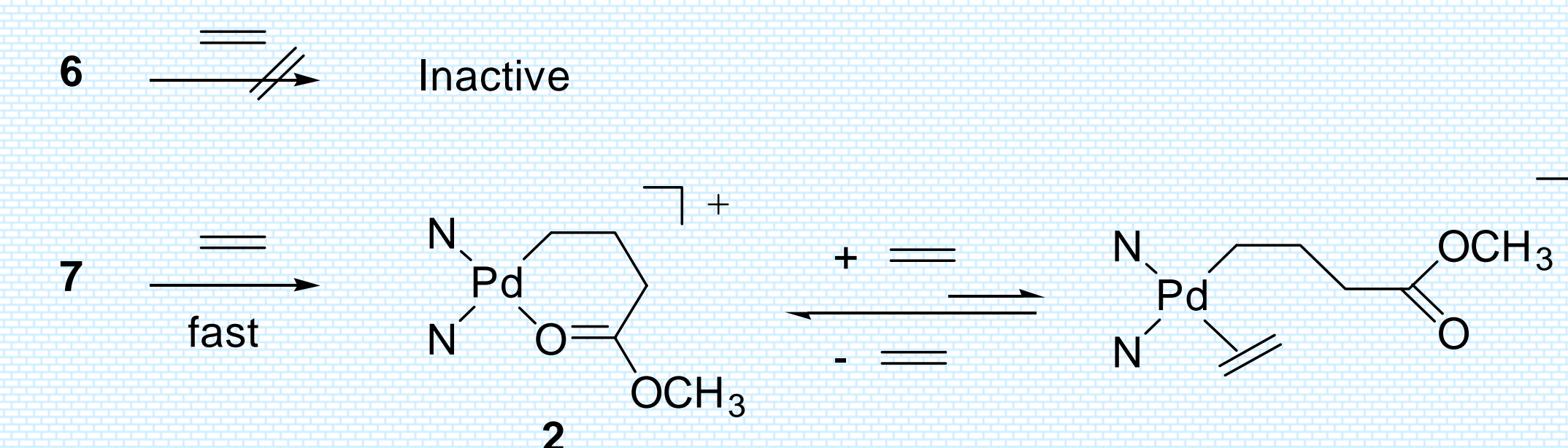


Crystal structure of **6**



Crystal structure of **7**

Cationic enolate **7** showed the same activities as catalyst **5**. NMR polymerization studies revealed a facile ethylene insertion into the Pd-CH₂CO₂CH₃ bond and the formation of six-membered ring chelate as the rest state. Valuable information of polymerization can be deduced from these studies.



Conclusions

- Neutral palladium complexes have been synthesized and found to be capable of copolymerizing MA with olefins through a radical mechanism.
- Studies on palladium enolates have provided a new insight into the reaction mechanism of ethylene-MA copolymerization.
- Application of the above results into catalyst design could result in better control over polymerization reactions.