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Synthesis of triazacyclononane iron complexes bearing pseudo-halogen ligands and their application to catalytic reactions

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Abstract

In our previous papers, we have prepared a series of Fe(II) complexes bearing N,N',N''-trialkylated-1,4,9-triazanonane (R_3 TACN) ligands. These complexes are useful for well-controlled atom transfer radical polymerization (ATRP) of styrene, methyl methacrylate, and butyl acrylate. We wish to report synthesis of a series of $(R_3\text{TACN})\text{FeY}_2$ analogues having Y =pseudo-halogen ligands such as sulfonates and alkoxides, and their catalytic performance toward ATRP.

1. Introduction

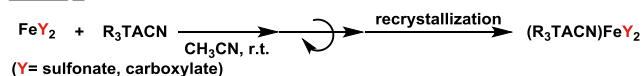
In general, halogen salt of the transition metals is used as a precursor for many catalysts, while some reactions have been reported by using catalysts which have metal-oxygen bonds as a precursor such as sulfonate salt, carboxylate salt, and alkoxide salt. These salts have a redox potential, structure, and coordinative design different from metal-halogen salt.

In our laboratory, we have focused on the synthesis of iron complexes which are induced by iron salts with iron-oxygen bonds. In some literatures, we have already reported the way to synthesize $\text{Fe}(\text{OSO}_2\text{R})_2$, $\text{Fe}(\text{OCOR})_2$, and $\text{Fe}(\text{OR})_2$. However, iron complexes synthesis by using those starting materials and its study of the catalytic reactions are hardly to investigate. Moreover, it is difficult to study the fundamental reactivity and identify the structure of those compounds using paramagnetic methods. That makes it difficult to design catalysts and catalytic reactions.

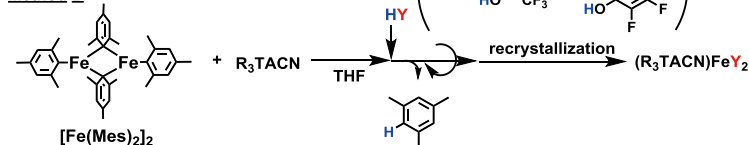
We have focused on the strong coordination ligand of its bearing ring frame; that is N,N',N''-trialkyl-1,4,9-triazacyclononane ligand (R_3 TACN) and synthesis of R_3 TACN comprising $\text{Fe}(\text{OSO}_2\text{R})_2$, $\text{Fe}(\text{OCOR})_2$, and $\text{Fe}(\text{OR})_2$. We examined the ligand R_3 TACN into two types; R = Me, or R = *i*Pr to study the steric bulk property of the alkyl (R) group.

First of all, we have synthesized seven kinds of $\text{Fe}(\text{OSO}_2\text{R})_2$, $\text{Fe}(\text{OCOR})_2$ related to the published procedure. We divided the synthesis method of iron complexes into two ways which are method A and B. Method A is the way that iron salts react with two R_3 TACN ligands directly and purify by recrystallization, and method B is the way that iron dimesityl $[\text{Fe}(\text{Mes})_2]_2$ reacts with alcohol and R_3 TACN ligand, then purify by recrystallization same as the synthesis way of $(R_3\text{TACN})\text{Fe}(\text{OR})_2$ (**Scheme 1**)

Method A



Method B



Scheme 1. Synthesis method for TACN complexes bearing pseudo-halogen ligands.

2. Results

We have gotten eight single crystals of iron complexes and then examined complexes **1-8** structure by X-ray diffraction and ESI-MS analysis (**Figure 1**).

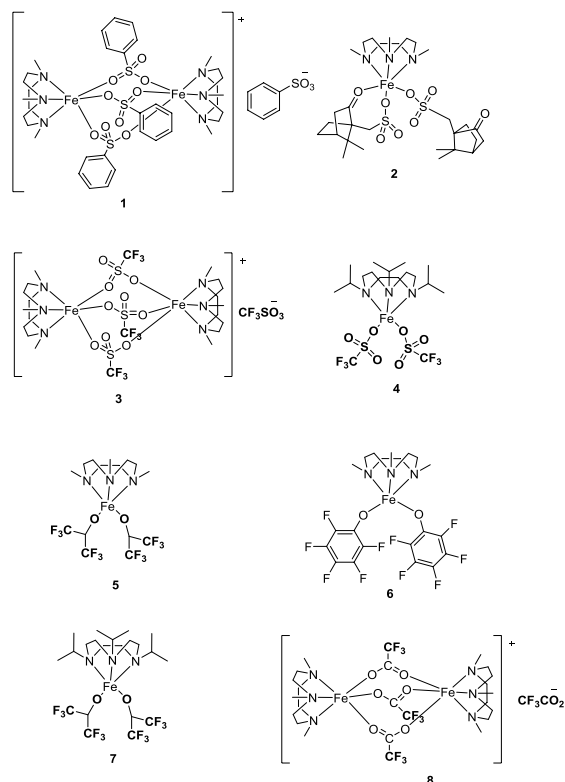
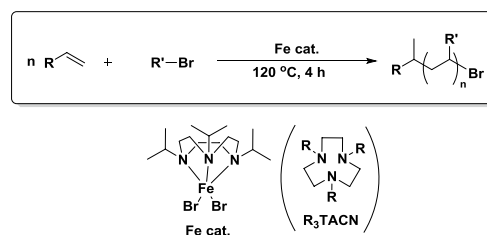


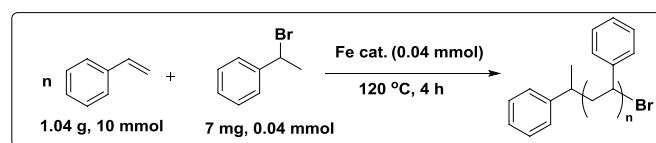
Figure 1. Synthesized series of TACN complexes bearing pseudo-halogen ligands.

In X-ray diffraction analysis result, we have found that complexes **1**, **3**, **8** have three pseudo-halogen ligands with cross-linked binuclear structure and complexes **2**, **4-7** have mononuclear structure. In case of complex **2**, it will have a mononuclear intramolecular carbonyl group coordination structure on the ligand in the crystal phase but in the liquid phase it will show a binuclear structure instead. In equilibrium between mononuclear and binuclear structure, we have studied the catalyst properties by comparing to known $(R_3TACN)FeX_2$ with cyclic voltammetry and Lewis acidity determination experiments. Moreover, we have succeeded in development of the iron(II) complexes which have excellent activity for good controlled radical polymerization method of vinyl monomer called Atom Transfer Radical Polymerization(ATRP)(Scheme 2).



Scheme 2. Our laboratory developed TACN iron catalyst and Atom Transfer Radical Polymerization (ATRP)

For catalytic activity of complexes **2**, **5**, and **6** in order to verify polymerization living property were investigated by ATRP reaction using styrene as a monomer and (1-bromoethyl) benzene as an initiator. (Scheme 3)



Scheme 3. Their catalytic performance toward ATRP.

3. Conclusion

We have succeeded in synthesizing a series of TACN Fe(II) complexes bearing pseudo-halogen ligands such as sulfoates, alkoxides, and carboxylates. Their molecular structures have been determined. Their catalytic performance toward ATRP have been examined and showed the activity.

Reference

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