

論文 / 著書情報
Article / Book Information

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Title(English)	
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学位種別(和文)	博士論文
Category(English)	Doctoral Thesis
種別(和文)	論文要旨
Type(English)	Summary

(博士課程)
Doctoral Program

論文要旨

THESIS SUMMARY

専攻 : Department of	13D32100	専攻	申請学位 (専攻分野) : Academic Degree Requested	博士 工学 Doctor of
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要旨 (英文 800 語程度)

Thesis Summary (approx.800 English Words)

The author investigated ligand transfer reactions of aryl platinum(II) complexes and macrocyclization of bridged-Tröger's base ligand in this thesis. Macrocyclization is one of the attractive research fields of synthetic chemistry. The author employed ligand transfer reaction of organometallic compounds to synthesize macrocycles because it was easy to control transmetallation by the condition such as temperature, solvent, and ancillary ligand. This doctoral thesis is composed of 7 chapters as below.

In chapter 1, the author made an introduction of the thesis, which contained the previous research reports of organic ligand transfer reaction, especially about transmetallation. Also, typical strategies for synthesis of macrocyclic compound such as one-step cyclization, step-wise cyclization, template method, and metathesis method, were described. Among these strategies, the author emphasized that it was the most effective method to form macrocycles by metathesis of the equilibrated bond exchange (e.g. imine metathesis, alkyne metathesis, and alkene metathesis) under thermodynamic control. At the end of chapter 1, the author claimed the reversible transmetallation and similar organometallic reactions would be useful for synthetic application of the macrocyclization.

In chapter 2, the author developed new reversible intramolecular transmetallation of aryl platinum(II) complexes. Diarylplatinum complexes with 1,5-cyclooctadiene (cod) as ancillary ligand were employed. Reaction of $\text{Pt}(\text{C}_6\text{H}_5)_2(\text{cod})$ (**1-H**₂) and $\text{Pt}(\text{C}_6\text{H}_4\text{-4-F})_2(\text{cod})$ (**1-F**₂) in C_6D_6 at 50 °C gave a mixture of **1-H**₂, **1-F**₂ and $\text{Pt}(\text{C}_6\text{H}_4\text{-4-F})(\text{C}_6\text{H}_5)(\text{cod})$ (**1-FH**) in statistical molar ratio (51:49:102). Dissolution of **1-FH** in C_6D_6 at 50 °C gave similar mixture of platinum complexes, indicating the reversibility of the ligand exchange reaction. The second-order rate constants (k_1 and k_{-1}) of the comproportionation reaction of **1-H**₂ and **1-F**₂ were determined to be $(6.4 \pm 0.6) \times 10^{-6}$ and $(2.0 \pm 0.2) \times 10^{-6} \text{ M}^{-1}\text{s}^{-1}$, respectively. The kinetic parameters such as $\Delta S^\ddagger = -46 \pm 84 \text{ J mol}^{-1} \text{ K}^{-1}$, were calculated by temperature dependence on the k_1 and k_{-1} , which indicated the associative transition state of two platinum complexes with four membered Pt-C-Pt-C ring. The existence of free cod in the reaction mixture did not affect rate constant significantly that indicated cod ligand coordinated tightly during the transmetallation. DFT studies revealed the effect of ancillary ligand that increased HOMO-LUMO interaction between the platinum complexes to form the above associative transition state.

In chapter 3, the author developed new method of synthesis for macrocycle via the dinuclear macrocyclic complexation by the combination of organometallic reactions. Tröger's base (TB), which has a pair of right-angled aromatic rings, was employed as

bridging ligands of dinuclear complexes. Reaction of $\text{Me}_3\text{Sn}-\text{C}_6\text{H}_3-\text{C}_3\text{H}_6\text{N}_2-\text{C}_6\text{H}_3-\text{SnMe}_3$ ($\text{TB}-(\text{SnMe}_3)_2$) and $\text{PtCl}_2(\text{cod})$ in THF under reflux condition yielded macrocyclic dinuclear Pt(II) complex composed of two Tröger's base ligands. Following reductive elimination was induced by addition of 10 equivalent of PPh_3 yielding macrocyclic dimer of Tröger's base (*cyclic-11*₂). Based on the NMR spectroscopy of *cyclic-11*₂ and DFT calculation, the author revealed *cyclic-11*₂ had most distorted TBs with angle of arene rings ($\phi = 65^\circ$) reported so far. Reaction of $\text{HCC}-\text{C}_6\text{H}_3-\text{C}_3\text{H}_6\text{N}_2-\text{C}_6\text{H}_3-\text{CCH}$ ($\text{TB}-(\text{CCH})_2$) and $\text{PtCl}_2(\text{dppf})$ ($\text{dppf} = 1,1'$ -bis(diphenylphosphino)ferrocene) in the presence of CuI in THF/*i* Pr_2NH at room temperature induced similar transmetallation to yield the macrocycle, *cyclic-[(dppf)Pt-CC-TB-CC-]₂*. Oxidative addition of $\text{TB}-\text{I}_2$ to $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ ($\text{dba} = \text{dibenzylideneacetone}$) in the presence of $\text{Me}_2\text{N}-\text{C}_2\text{H}_4-\text{NMe}_2$ (TMEDA) gave **11**- $\{\text{Pd}(\text{tmeda})\}_2$, followed by the transmetallation of bis(arylboronic acid-pinacol ester)-oligo ethylene glycol, $(\text{pin})\text{B}-\text{C}_6\text{H}_4\text{O}-(\text{CH}_2\text{O})_4-\text{C}_6\text{H}_4-\text{B}(\text{pin})$ or $(\text{pin})\text{B}-\text{C}_6\text{H}_4\text{O}-(\text{CH}_2\text{O})_3-\text{C}_6\text{H}_4-(\text{OCH}_2)_4-\text{OC}_6\text{H}_4-\text{B}(\text{pin})$ ($\text{pin} = \text{pinacolate}$), and reductive elimination to yield *cyclic-11-14e* or *cyclic-11-15*.

In chapter 4 and 5, the author investigated Lewis acid-promoted polycondensation of ferrocene and aldehyde as well as the characterization of the products which contained *linear*- and *cyclic*-oligo(ferrocenylene alkylene)s. Reaction of ferrocene and 1-alkylaldehyde, such as *n*- $\text{C}_7\text{H}_{15}-\text{CHO}$, $\text{Et}-\text{CHO}$ and $^t\text{Bu}-\text{CHO}$, in the presence of $\text{BF}_3 \cdot \text{OEt}_2$ in $(\text{CH}_2\text{Cl})_2$ at 30°C yielded a mixture of *linear*- and *cyclic*-oligo(ferrocenylene alkylene)s, while polycondensation of ferrocene and arylaldehyde, such as $\text{C}_6\text{F}_5-\text{CHO}$, $\text{CF}_3\text{C}_6\text{H}_4-4-\text{CHO}$ and $\text{MeC}_6\text{H}_4-4-\text{CHO}$, gave the linear oligomers exclusively. Their terminal groups of linear oligomers, -ferrocenyl or $-\text{CH}_2$ -aryl group, were characterized by HRESI-TOMS. Condensations of α -hydroxyalkylferrocene, such as 1-ferrocenyloctanol and ferrocenylmethanol, gave similar mixture of linear and cyclic oligomer, indicating the propagation of the above polycondensation contained terminal 1-hydroxyalkyl-ferrocenylene group, $-\text{Fe}(\text{C}_5\text{H}_4)[\text{C}_5\text{H}_4\{\text{CH}(\text{OH})\text{R}\}]$. Polycondensation of diferrocenylmethane with paraformaldehyde dimethylacetal yielded a mixture of oligomers composed of an odd and an even number of ferrocenylene groups, indicating the above polycondensation contained depolymerization process. The trimer synthesized from ferrocene and paraformaldehyde-dimethylacetal contained 1,1'-, 1,2-, and 1,3-ferrocenylene units, suggesting that the oligomers obtained from alkyl and aryl aldehydes were also composed of these structural units. At the end of chapter 5, the author suggested the mechanism of condensation by consideration of the above result.

In chapter 6, the author described the summary of this thesis and outlooks of the method of the macrocyclization.

In chapter 7, experimental procedures and data of compounds were described in detail.

備考：論文要旨は、和文 2000 字と英文 300 語を 1 部ずつ提出するか、もしくは英文 800 語を 1 部提出してください。

Note: Thesis Summary should be submitted in either a copy of 2000 Japanese Characters and 300 Words (English) or 1 copy of 800 Words (English).

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