

Synthesis, Structures, and Catalytic Activity of Transition-Metal Complexes with a 1,8-Naphthyridine-Based Bis(silyl) Supporting Ligand

著者	INDRA Kusuma
号	80
学位授与機関	Tohoku University
URL	http://hdl.handle.net/10097/00122941

論文内容要旨

(NO. 1)

氏名	Indra Kusuma	提出年	平成29年
学位論文の 題目	Synthesis, Structures, and Catalytic Activity of Transition-Metal Complexes with a 1,8-Naphthyridine-Based Bis(silyl) Supporting Ligand (1,8-ナフチリジンを基本骨格とするビス(シリル)支持配位子を持つ遷移金属錯体の合成, 構造および触媒活性)		

論文目次

Chapter 1: General Introduction**Chapter 2:** Synthesis of Precursors of 1,8-Naphthyridine-Based Bis(silyl) Supporting Ligands**Chapter 3:** Synthesis and Structures of Transition-Metal Complexes with a 1,8-Naphthyridine-Based Bis(silyl) Ligand**Chapter 4:** Catalytic Activity of a Diruthenium Complex with a 1,8-Naphthyridine-Based Bis(silyl) Ligand Toward Reactions of Alkynes with Hydrosilanes**Chapter 5:** Conclusion

論文内容要旨

Dinuclear transition-metal complexes bearing silyl-containing multidentate ligands are expected to show high reactivity towards bond activation because this reactivity is possibly enhanced by cooperative effect of not only two metal centers but also silyl ligand moieties that possess both strong σ -donating ability and strong *trans* influence. Furthermore, due to this strong *trans* influence, dimetallic cores bearing silyl coordinating moieties are also expected to have some specific structural and electronic features caused by weakening of metal–metal or metal–element bond(s) located *trans* to the silyl silicon atoms. In this study, I developed an unprecedented 1,8-naphthyridine-based ligand having two coordinating moieties in substituents at the 2,7-positions for the synthesis of dinuclear transition-metal bis(silyl) complexes. For that purpose, I designed SiNNSi-type tetradentate ligand precursors, namely 2,7-bis[(dialkylsilyl)methyl]-1,8-naphthyridine (abbreviated as $^R\text{NBSi}(\text{H})_2$), to synthesize dinuclear complexes **A** (eq. 1). As a representative reaction system to investigate the catalytic performance of one of the complexes **A**, I selected the reactions of alkynes with hydrosilanes.

In **Chapter 2**, details of the experimental results of the synthesis of $^R\text{NBSi}(\text{H})_2$ were described (eq. 2). The first example of a 1,8-naphthyridine-based ligand precursor bearing (hydrosilyl)methyl groups at the 2,7-positions, i.e. $^t\text{-BuNBSi}(\text{H})_2$ (**1a**), was successfully synthesized by six-step reactions from 2-aminopyridine via 2,7-dimethyl-1,8-naphthyridine **B** as an intermediate (eq. 2). On the other hand, when a silyl group with less bulky isopropyl substituents was used, compound **1b** bearing a bis(diisopropylsilyl)methyl group at the 2-position of the

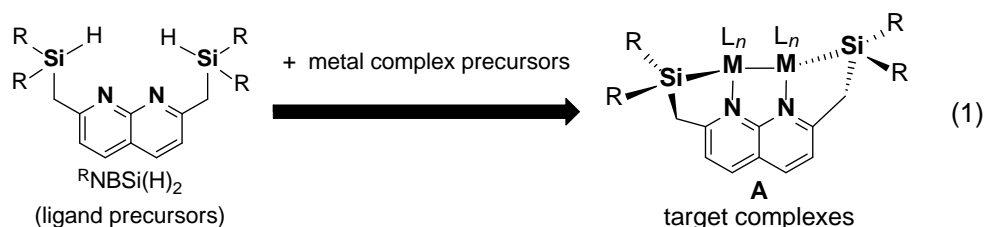
1,8-naphthyridine ring was obtained as the main product. This result indicates that the bulkiness of substituents on Si is crucial for selective synthesis of the desirable ligand precursor $^R\text{NBSi}(\text{H})_2$.

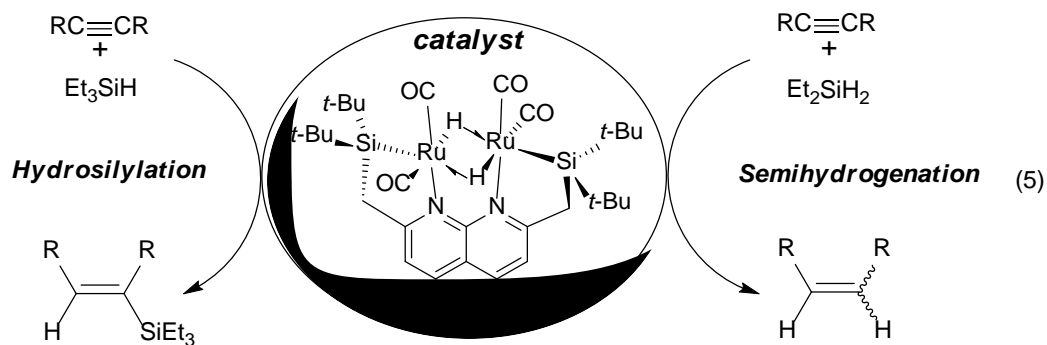
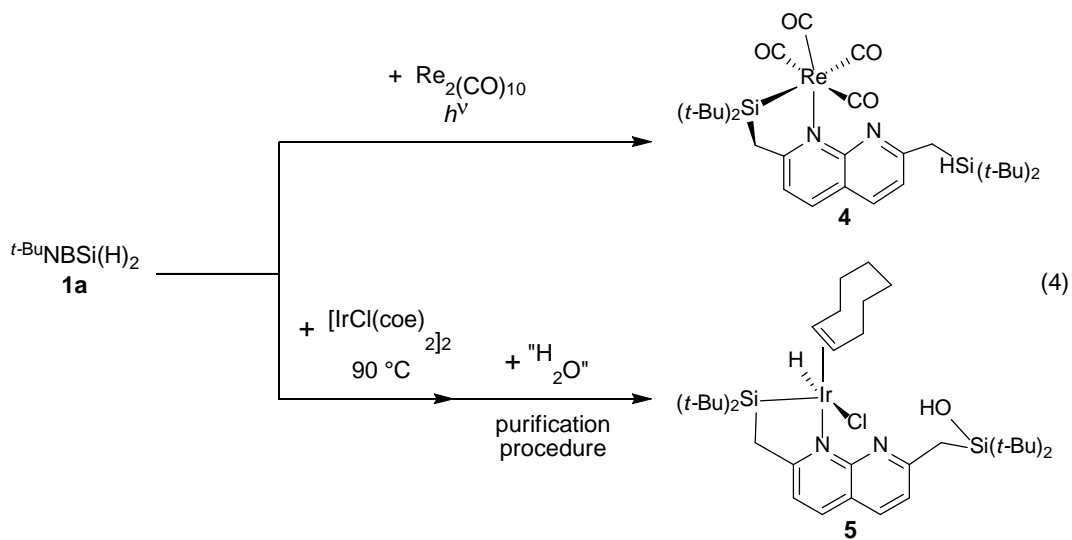
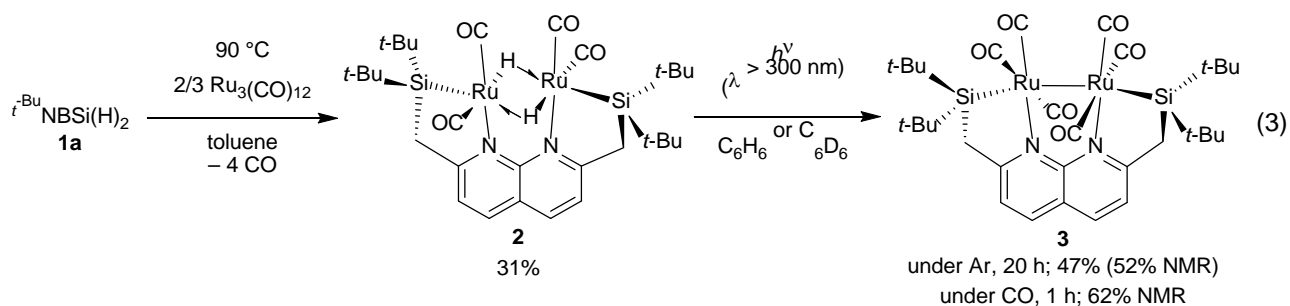
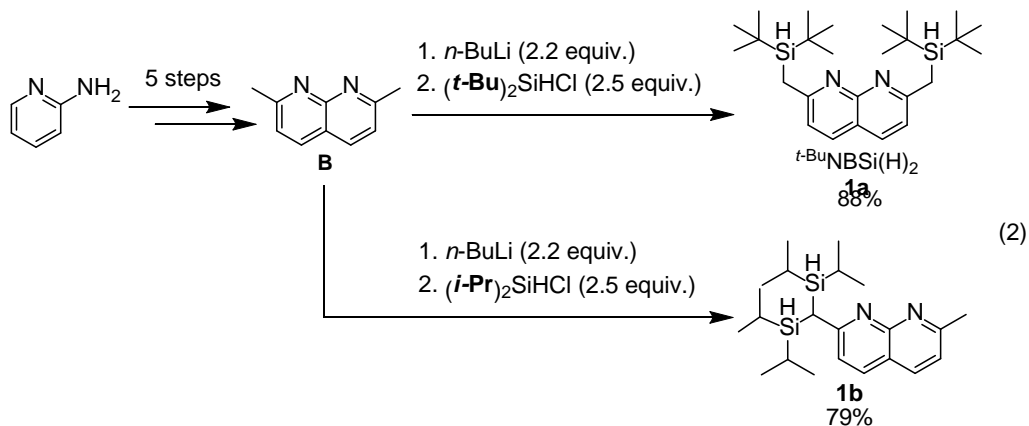
In **Chapter 3**, details of the examinations of the reactions of $\text{Ru}_3(\text{CO})_{12}$, $\text{Re}_2(\text{CO})_{10}$, and $[\text{IrCl}(\text{coe})_2]_2$ with a ligand precursor **1a** to synthesize the target dinuclear complexes **A** and structures of products obtained from the reactions were described (eqs. 3 and 4). Diruthenium(II,II) complex $(^t\text{BuNBSi})\text{Ru}_2(\mu\text{-H})_2(\text{CO})_4$ (**2**) was successfully synthesized by a thermal reaction of ligand precursor **1a** with 2/3 molar equiv. of $\text{Ru}_3(\text{CO})_{12}$ (eq. 3). Crystal structure analysis of **2** revealed that the Si–Ru–Ru–Si linkage adopts a zigzag arrangement. A DFT optimized structure of a simplified model complex of **2**, i.e. $(^{\text{Me}}\text{NBSi})\text{Ru}_2(\mu\text{-H})_2(\text{CO})_4$, clearly showed that each of the two hydrido ligands asymmetrically bridges two Ru atoms where the Ru–H bonds trans to Si are longer than those trans to CO evidently due to strong trans influence of the silyl ligand moieties.

Photoirradiation of a benzene solution of complex **2** resulted in the formation of an air stable (hexacarbonyl)diruthenium(I,I) complex $(^t\text{BuNBSi})\text{Ru}(\text{CO})_6$ (**3**) as a dark brown powder (eq. 3). The change of the oxidation number of each of the Ru centers from +2 (complex **2**) to +1 (complex **3**) indicates that $^t\text{BuNBSi}$ is able to support dinuclear ruthenium cores with some different oxidation states. The Si–Ru–Ru–Si linkage in **3** adopts a roughly linear arrangement in which each of the silyl silicon atoms is located trans to the Ru–Ru bond. Two $\text{RuN}(\text{CO})_3$ fragments are mutually twisted around the Ru–Ru bond due to the steric repulsion between CO ligands, and the Ru–Ru bond in **3** (2.8579(3) Å) is elongated in comparison with those of related Ru_2 complexes with 1,8-naphthyridine-based ligands (normally shorter than 2.7 Å), obviously because of strong *trans* influence of the silyl ligands.

On the other hand, reactions of **1a** with $\text{Re}_2(\text{CO})_{10}$ under photoirradiation and with $[\text{IrCl}(\text{coe})_2]_2$ under heating at 90 °C gave mononuclear complexes $[^t\text{BuNBSi}(\text{H})]\text{Re}(\text{CO})_4$ (**4**) and $[^t\text{BuNBSi}(\text{OH})]\text{Ir}(\text{H})\text{Cl}(\text{coe})$ (**5**), respectively, instead of dinuclear ones (eq. 4).

In **Chapter 4**, the catalytic activity of diruthenium complex **2** toward the reactions of alkynes with triethylsilane and diethylsilane was described (eq. 5). Complex **2** was found to catalyze both hydrosilylation and semihydrogenation reactions of alkynes with triethylsilane and diethylsilane, respectively (eq. 5). In the latter reaction, dehydrogenative coupling of diethylsilanes is considered to occur first to generate dihydrogen that is subsequently used for the semihydrogenation.





別紙

論文審査の結果の要旨

二核遷移金属錯体は、2つの金属中心の協働効果により基質分子の配位および活性化を行うため、単核錯体とは異なる様式での物質変換反応を起こすことで、独自の触媒機能を発現すると期待されている。Kusuma は、二核錯体を合成するための新しい支持配位子として、1,8-ナフチリジン骨格の 2,7 位の置換基末端にシリル配位部位 (σ -供与性とトランス影響がともに大きく、金属中心の反応性を向上させる作用を持つ) を 1 つずつ導入した新規の SiNNSi 型多座配位子 $t\text{-BuNBSi}$ を開発した。また、当該配位子を持つ二核錯体への誘導および触媒反応に関して、詳細な研究を行った。本研究の主な成果を以下に列記する。

(1) 1,8-ナフチリジンを基本骨格とする配位子前駆体 2,7-ビス[(ヒドロシリル)メチル]-1,8-ナフチリジン誘導体 $t\text{-BuNBSi(H)}_2$ の合成に初めて成功した。

(2) 前駆錯体 $\text{Ru}_3(\text{CO})_{12}$ と配位子前駆体 $t\text{-BuNBSi(H)}_2$ との Si-H 酸化的付加を経る反応により、架橋ヒドリド配位子を持つ二核ルテニウム(II,II)ビス(シリル)錯体($t\text{-BuNBSi}$) $\text{Ru}_2(\mu\text{-H})_2(\text{CO})_4$ (**A**) を合成した。次いで、錯体 **A** が光反応により $\text{Ru}_2(\text{I,I})$ 錯体($t\text{-BuNBSi}$) $\text{Ru}_2(\text{CO})_6$ (**B**)へと変換されることを見出した。この結果は、 $t\text{-BuNBSi}$ が異なる酸化状態にある複数種類の二核金属中心を保持できることを示している。X 線結晶構造解析の結果より、Si-Ru-Ru-Si 部分が **A** ではジグザグ型の配列をとり、一方 **B** では直線型の配列となることがわかった。また、錯体 **B** は、トランス影響の大きなシリル配位部位の効果により Ru-Ru 結合が伸長した構造的特徴を持つこともわかった。

(3) 二核ルテニウム錯体 **A** が、末端あるいは内部アルキンとヒドロシランとの反応に対する触媒となることを明らかにした。第三級シランを用いた場合はヒドロシリル化生成物を与えるのに対し、第二級シランを用いた場合には、アルキンからアルケンへの部分水素化が化学選択的に起こることを見出した。

本論文の研究結果は、二核錯体を保持する新しい種類の支持配位子を開発するという観点で、金属錯体化学および有機金属化学の分野の発展に大きく貢献するものである。得られた知見を、今後、様々な種類の遷移金属を持つ二核ビス(シリル)錯体の合成と触媒反応の開発研究へと発展させることが可能であり、その結果として、この種の支持配位子を持つ錯体を触媒とした新反応の発見も期待される。上記の成果を挙げたことは、Kusuma が自立して研究活動を行うのに十分な研究能力と学識を有することを示している。したがって、Indra Kusuma 提出の博士論文は、博士(理学)の学位論文として合格と認める。