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Studies on Clarification of Characteristic Features of
Low-Valent Rare Earth Reagents under
Photoirradiation and Application to
Polysilane Synthesis

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Doctoral Thesis at Osaka Prefecture University
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Chapter 1  General Introduction

Rare earth elements (Ln) involve seventeen chemical elements comprised of the fifteen lanthanoid elements from lanthanum (La) through lutetium (Lu) in the periodic table and additionally scandium (Sc) and yttrium (Y).

The fifteen lanthanides have similar chemical features, because 4f orbitals are located in somewhat inner atomic shell and covered with 6s and 5d orbitals. For example, trivalent oxidation state (Ln$^{3+}$) is the most stable, and trivalent ions have a high Lewis acidity. In recent years, these element features are often included in any general discussion of the lanthanide chemistry.

In synthetic organic chemistry, Ce(IV) is a strong oxidizing reagent such as CAN (cerium(IV) ammonium nitrate), because Ce can exist as tetravalent state. On the other hand, samarium (Sm), europium (Eu), and ytterbium (Yb) are stable as divalent state, and thus, the Ln$^{2+}$ act as reducing reagents similarly to the alkali metal compounds.$^{1}$ In particular, samarium diiodide (SmI$_2$) is widely employed as a single-electron reducing reagent, because of the adequate reducing ability and the suitable solubility in organic solvent such as THF.$^{2}$ SmI$_2$ is usually employed as stoichiometric reagent, and examples of catalytic use of SmI$_2$ are limited (e.g., the intramolecular Tishchenko reaction,$^{3}$ epoxide rearrangement$^{4}$, Michael and aldol reactions,$^{5}$ and Diels-Alder reaction$^{6}$). It is important to enhance the reducing ability of SmI$_2$. From this point
of view, recent investigations have established several activation methods of SmI$_2$, e.g., SmI$_2$-HMPA, SmI$_2$-H$_2$O, SmI$_2$-acid, and SmI$_2$-base. In our laboratory, the combination of SmI$_2$ and Sm metal enhances the reducing ability compared with their single systems.\textsuperscript{7,8} Furthermore, visible light irradiation dramatically enhances the reducing ability of SmI$_2$.\textsuperscript{9,10} Therefore, it is of great importance to explore these activation methods for development of novel progressive usage of rare earths in synthetic organic chemistry.

This thesis consists of six chapters, and the main objects are to clarify the characteristic features of low-valent rare earth reagents under photoirradiation, and to apply them to the synthesis of highly pure polysilanes.

Chapter 1 deals with the general information (background, purpose, and outline of this investigation). Chapter 2 deals with the activation method of rare earth reagents. Chapter 3 deals with the carbonylation of organic halides with carbon monoxide mediated by samarium diiodide. Some improvement methods and mechanistic investigations are described. Chapter 4 deals with photoaccelerated reductive coupling of acid chlorides with conjugate dienes and styrenes by use of neodymium metal in $N,N$-dimethylacetamide. Chapter 5 deals with construction of Si-Si linkages by reductive coupling of organochlorosilanes using photoinduced SmI$_2$/Sm system.

In many scientific fields, rare earths attract much attention, because of their photonic or physical properties based on f-electronic transition. For synthetic organic chemistry viewpoints,
rare earths play important roles, as Lewis acids, oxidants, and reductants. The present photoirradiation systems are expected to open up a new field in organic synthesis as well as materials science.
References


Chapter 2  The Activation Method of Rare Earth Reagents

2-1 Introduction

Lanthanide elements have electron(s) in f-orbitals, and should indicate characteristic reactivities on the basis of the nature of f-electrons. However, systematic studies on the reactivities of a series of lanthanoid species are still rare. During the course of our study on the clarification of the characteristic features of rare earth compounds and their application to synthetic reactions, two novel findings have been revealed in our laboratory: (i) the combination of samarium (II) diiodide and samarium metal enhances the reducing ability compared with that of their single systems; (ii) visible light irradiation dramatically enhances the reducing ability of SmI$_2$. To clarify whether similar enhancement of the reducing ability is observed concerning a series of rare earth species$^{1,2}$, the author has investigated systematically the reduction of 1-iodododecane, as a model compound, by using low-valent species of a series of rare earths upon photoirradiation or in the dark. This thesis deals with a novel finding that most of low-valent rare earth species exhibit their potentially excellent reducing abilities under photoirradiation.
2-2 Results and Discussion

2-2-1 Preparation of “LnI$_2$/Ln” reagents

At first, the author prepared the mixed system of rare earths (“LnI$_2$/Ln”) by the reaction of excess amount of rare earth metal and 1,2-diiodoethane in THF (Scheme 1).

Scheme 1. Preparation of “LnI$_2$/Ln” reagents

A mixture of Ln powder (1.0 mmol) and 1,2-diiodoethane (0.2 mmol) in THF (2 mL) was stirred at room temperature for 1.5 h under nitrogen atmosphere, and in this stage, the color of the solution changed as follows (Scheme 2): Sc (yellow), Y (yellow), La (gray), Ce (ocher), Pr (gray), Nd (gray), Sm (blue), Eu (brown), Gd (yellow), Tb (yellow), Dy (deep green), Ho (yellow), Er (yellow green), Tm (yellow), Yb (reddish brown), and Lu (yellow). In the cases of Sm, Eu, and Yb, the corresponding divalent diiodides (LnI$_2$) were apparently formed, according to the literature.$^3$ Similar observation concerning other rare earths strongly suggests the generation of low-valent rare earth species such as LnI$_2$. 

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A possible reaction pathway for this reduction is shown in Scheme 3. Most probably, the reduction may proceed via the single-electron transfer from rare earth species to iodododecane generating dodecyl radical. Further reduction of dodecyl radical with rare earth species leads to dodecylanion species, which is protonated with water during workup. On the other hands, dimerization of dodecyl radicals affords tetracosane, and disproportionation leads to equimolar of dodecene and dodecane.
2-2-2 Reduction of 1-iodododecane with “LnI$_2$/Ln” reagents

Next, the author examined the reduction of 1-iodododecane by use of this binary systems of divalent and zero-valent rare earth reagents (“LnI$_2$/Ln”) in the presence of 2-propanol as a proton source (Scheme 4), and the results are summarized in Figure 1. As can be seen from Figure 1, the reduction took place successfully in the cases of La, Ce, Pr, Nd, Sm, Eu, and Yb, and dodecane was obtained as the major product along with small amounts of the corresponding coupling product (tetracosane) and disproportionation products (dodecene and dodecane)."}

**Figure 1.** Reduction of 1-iodododecane with “LnI$_2$/Ln” system (r.t., 3 h)
When the same reduction of 1-iodododecane was attempted by using only Ln metals under the identical conditions (room temperature, 3 h), no reaction took place at all.\textsuperscript{4,5} Furthermore, when the reduction of 1-iodododecane was carried out by employing equimolar amounts of Ln metal (1.0 mmol) and ICH\textsubscript{2}CH\textsubscript{2}I (1.0 mmol) (which may form “LnI\textsubscript{2}” reagents), the desired reduced products were obtained in very low yields: the yields of dodecane were 10\% (La); 27\% (Ce); 12\% (Pr); 7\% (Nd); 8\% (Sm); 1\% (Yb).\textsuperscript{7} These results are summarized in Figure 2, and strongly suggest the binary systems of “Ln(0)/Ln(II)” exhibit higher reducing ability compared with the Ln(0) or “LnI\textsubscript{2}” single system.

**Scheme 4.** Reduction of 1-iodododecane by use of low-valent rare earth reagents

\[
\begin{align*}
\text{C}_{12}\text{H}_{25}\text{I} & \quad \text{Ln (1.0 mmol), ICH}_2\text{CH}_2\text{I (1.0 mmol)} \\
2\text{-PrOH, THF, r.t., 3 h} & \quad \text{C}_{12}\text{H}_{26}
\end{align*}
\]

**Rare earth reagents:**

“LnI\textsubscript{2}/Ln” [Ln (1.0 mmol), ICH\textsubscript{2}CH\textsubscript{2}I (0.2 mmol)]

“LnI\textsubscript{2}” [Ln (1.0 mmol), ICH\textsubscript{2}CH\textsubscript{2}I (1.0 mmol)]

Ln (1.0 mmol)
Figure 2. Reduction of 1-iodododecane by use of low-valent rare earths reagents (r.t., 3 h)
**2-2-3 Photoinduced reduction of 1-iodododecane with “LnI₂/Ln” reagents**

In the case of Sm, it has been revealed in our laboratory that a dark blue solution of SmI₂ in THF was activated by irradiation with the light of wavelength between 560 and 700 nm. Mixed systems of other rare earths indicated several colors in THF, and therefore, similar photoinduced enhancement of the reducing ability may be observed. To clarify the photoinduced reducing ability, the author examined the same reduction of 1-iodododecane by using a series of “LnI₂/Ln” system upon irradiation through Pyrex (>300 nm) with a Xe lamp (500 W) during the reactions (“LnI₂/Ln/hν” system).

Interestingly, the reduction using the “LnI₂/Ln/hν” system proceeded very smoothly in the cases of La, Ce, Pr, Nd, Sm, Eu, and Yb. In the cases of Pr and Nd, remarkable photoinduced enhancement of the reducing ability was obtained [yield of dodecane; Nd: 33 % (dark), 67 % (hν), Pr: 41 % (dark), 75 % (hν)]. Noteworthy is that, by using heavy rare earths such as Gd, Tb, and Ho, the reduction took place upon photoirradiation conditions [yield of dodecane; 12 % (Gd), 23 % (Tb), and 7 % (Pr)], despite the same reduction in the dark did not occur at all. Furthermore, the attempted photoinduced reduction using “LnI₂/Ln/hν” systems of Y, Dy, and Er suggests the possibility of the photoactivation.
The author compiled these results compared with the results under the dark conditions (Figure 3). Figure 3 clearly indicates the photoirradiation increases the reducing ability of a series of low-valent rare earths species for the reduction of 1-iodododecane.

To reveal the photoinduced activation more remarkably, the author examined the reaction under refluxing condition of THF (67 °C) for extended reaction time (20 h) (Figure 4). The “LnI2/Ln” systems of Y and heavy rare earths as Gd, Tb, Dy, Ho, Er, and Tm worked well for the reduction of 1-iodododecane under reflux for 20 h, especially under photoirradiation conditions.

In the case of Tb and Dy upon photoirradiation, the yields of dodecane were almost the same as those when the reaction was conducted at 67 °C for 20 h in the dark [yield of dodecane; Tb: 70 % (dark), 74 % (hv), Dy: 68 % (dark), 75 % (hv)]. However, the decrease in the reaction time (8 h) clearly indicates that the influence of the photoirradiation was recognized more definitely: the yields of dodecane were 2% (dark), 33% (hv) [Tb]; 3% (dark), 46% (hv) [Dy].

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Figure 3. Influence of photoirradiation on the "LnI$_2$/Ln"-induced reduction of 1-iodododecane with heavy rare earth reagents (67 °C, 20 h).

Figure 4. Reduction of 1-iodododecane with heavy rare earth reagents (67 °C, 20 h).
2-2-4 Novel photoinduced reduction of haloalkanes with rare earth metals

To elucidate the reducing ability of rare earth metals toward the reductive dehalogenation of haloalkanes, the author selected 1-iodododecane as a model substrate and examined the reduction using a series of rare earth metals in THF. Except europium, high-grade rare earth metals powders (40 mesh) are commercially available. Thus, the reduction of 1-iodododecane was attempted by employing these commercially available powders without further activation, but the desired reduction did not occurred at all. As to europium metal, the author filed Eu ingot to prepare powder (ca. 20 mesh) in a grove box under nitrogen atmosphere. Surprisingly, the desired reduction took place successfully to afford dodecane (2), tetracosane (3), and dodecane (4) in 54 %, 18 %, and 2 %, respectively, as can be seen from Eq. (1) and Fig. 5.

\[ \text{\( C_{12}H_{25}I \)} \xrightarrow{\text{Ln (1.0 mmol)}} \text{\( C_{12}H_{26} \)} + \text{\( C_{24}H_{50} \)} + \text{\( C_{10}H_{21}CH=CH_2 \)} \]

1 (0.5 mmol)

2 3 4
To clarify whether the reducing ability observed in the case of europium powder depends on the preparation method of lanthanoid powders, the author next examined the same reduction of 1-iodododecane by using some other rare earth powders prepared by the same procedure in the case of europium. The author prepared fine powder (ca. 20 mesh) of Y, Pr, Gd, Dy, and Er from their ingot in a grove box under nitrogen atmosphere and examined the reduction of 1-iodododecane. However the desired reduction did not occur at all in the dark. These results suggest that europium metal has an excellent reducing ability. This is supported by the fact that europium metal easily undergoes air-oxidation compared with other rare earth metals.
In our laboratory, a novel photoinduced reduction system of SmI$_2$ has been developed: visible light irradiation leads to the excitation of SmI$_2$, which makes it possible to transfer electrons efficiently to organic compounds such as organic halides and chalcogenides, etc. Although the reduction of 1-iodododecane with a series of rare earth metals did not proceed at all in the dark, as described in next section, the reaction solution indicates the change of color, which suggests the formation of small amount of soluble lanthanoid(II) species in THF.

Thus, the author examined the reduction of 1-iodododecane using a series of rare earth metals upon irradiation through Pyrex with a Xe lamp, and the results are summarized in Eq. (2) and Fig. 6.

\[
\text{Ln (1.0 mmol), } h\nu \\
\rightarrow \text{2-PrOH (2 mmol), THF (4 mL), r.t., 3 h}
\]

\[
^nC_{12}H_{26} + \text{Ln (1.0 mmol)} \\
\rightarrow ^nC_{12}H_{26} + \text{(0.5 mmol)} \\
\rightarrow \text{Ln (1.0 mmol), h\nu} \\
\rightarrow \text{2-PrOH (2 mmol), THF (4 mL), r.t., 3 h}
\]

**Figure 6.** Photoinduced reduction of 1-iodododecane with Ln metals

<table>
<thead>
<tr>
<th>Yield (%)</th>
<th>Sc</th>
<th>Y</th>
<th>La</th>
<th>Ce</th>
<th>Pr</th>
<th>Nd</th>
<th>Sm</th>
<th>Eu</th>
<th>Gd</th>
<th>Tb</th>
<th>Dy</th>
<th>Ho</th>
<th>Er</th>
<th>Tm</th>
<th>Yb</th>
<th>Lu</th>
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<tbody>
<tr>
<td>$^nC_{12}H_{26}$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$^nC_{24}H_{50}$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>13</td>
<td>0</td>
<td>20</td>
<td>4</td>
<td>24</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$^nC_{10}H_{21}CH=CH_2$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>3</td>
<td>1</td>
<td>3</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>
Very interestingly, light rare earth metals such as Ce, Nd, Sm, and Eu exhibited good reducing abilities toward the reduction of 1-iodododecane under photoirradiation conditions. On the other hand, heavy rare earth metals indicated no reducing ability even upon photoirradiation.

A possible reaction pathway for this reaction is shown in Scheme 5. Most probably, the reduction may proceed via the single-electron transfer process from rare earth metal to 1-iodododecane generating dodecyl radical. Further reduction of dodecyl radical with rare earth species leads to dodecyl lanthanoid iodide, which is protonated with water during workup. On the other hand, dimerization of dodecyl radicals affords tetracosane.

Scheme 5. Preparation of “SmI₂/Ln” reagents

\[
\begin{align*}
\text{\( ^\text{n} \text{C}_{12}\text{H}_{25}\text{I} \)} & \xrightarrow{\text{Ln}-\text{hv}} \text{\( ^\text{n} \text{C}_{12}\text{H}_{25}\cdot \)} & \xrightarrow{\text{dimerization}} & \text{\( ^\text{n} \text{C}_{24}\text{H}_{50}\)} \\
\text{\( ^\text{n} \text{C}_{12}\text{H}_{25}^- \)} & \xrightarrow{\text{Lee-\text{hv}}} & \text{\( ^\text{n} \text{C}_{12}\text{H}_{25}\cdot \)} & \xrightarrow{\text{H}^+} & \text{\( ^\text{n} \text{C}_{12}\text{H}_{26}\)}
\end{align*}
\]

In the case of Sm, the product selectivity to give dodecane is higher compared with the cases of other rare earth metals. This is probably because the solubility of samarium diiodide in THF is superior to other divalent rare earth species: dodecyl radical intermediate formed in situ may be immediately reduced by the homogeneous low-valent samarium species (SmI₂) in
In the case of europium metal, photoirradiation clearly accelerated the reduction of 1-iodododecane (See Eq. (2), Ln = Eu), although the product ratio of 2/3 was similar to that in the dark. The influence of the photoirradiation on the reduction can be understood by the results of the reduction at lower temperature (see Table 1). At low temperature (-23 °C), photoirradiation is effective for the reduction of 1-iodododecane. In the dark, the conversion of the reduction dramatically decreased as dropping the reaction temperatures (entries 1 and 2). Even at -23 °C, however, the reduction proceeded efficiently under photoirradiation conditions (entry 3).

Table 1. Reduction of 1-iodododecane with Eu metal

<table>
<thead>
<tr>
<th>entry</th>
<th>temperature (°C)</th>
<th>nC\textsubscript{12}H\textsubscript{26}</th>
<th>nC\textsubscript{24}H\textsubscript{50}</th>
<th>nC\textsubscript{10}H\textsubscript{21}CH=CH\textsubscript{2}</th>
<th>nC\textsubscript{12}H\textsubscript{25}I</th>
</tr>
</thead>
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<tr>
<td>1\textsuperscript{c}</td>
<td>10</td>
<td>58</td>
<td>23</td>
<td>2</td>
<td>8</td>
</tr>
<tr>
<td>2\textsuperscript{c}</td>
<td>-23</td>
<td>4</td>
<td>trace</td>
<td>0</td>
<td>95</td>
</tr>
<tr>
<td>3\textsuperscript{d}</td>
<td>-23</td>
<td>82</td>
<td>10</td>
<td>trace</td>
<td>5</td>
</tr>
</tbody>
</table>

\textsuperscript{a}nC\textsubscript{12}H\textsubscript{25}I (0.5 mmol), Eu (1.0 mmol), 2-PrOH (2.0 mmol), THF (4 mL), 3h. \textsuperscript{b}Determined by GC. \textsuperscript{c}In the dark. \textsuperscript{d}Irradiation through Pyrex with a Xe lamp (500 W).
2-2-5 Novel reducing properties by the combination of SmI₂ and a series of rare earth metals

The author examined to prepare the “SmI₂/Ln” reagent (Scheme 6). A mixture of the appropriate Ln metal powder (0.8 mmol), Sm powder (0.2 mmol), and 1,2-diiodoethane (0.2 mmol) in THF (2 mL) was stirred at room temperature for 1.5 h under nitrogen atmosphere. After stirring, the color of solution changed dark blue. This clearly indicated the generation of SmI₂, because other divalent rare earth species do not exhibit the blue color. Unreacted Ln metal remained insoluble in THF.

Scheme 6. Preparation of “SmI₂/Ln” reagents

\[
\text{Ln} + \text{ICH}_2\text{CH}_2\text{I} + \text{Sm} \quad \text{THF (2 mL)} \quad \text{r.t., 1.5 h} \quad \text{SmI}_2 + \text{Ln} + \text{LnI}_2
\]

A mixture of dodecyl iodide (0.5 mmol) as a model compound and 2-propanol (2.0 mmol) as a proton source in THF (2 mL) was dropped into the prepared “SmI₂/Ln” reagent in THF. After the reaction, the resulting products were analyzed by GC, and the results are shown in Scheme 7 and Figure 7.
Scheme 7. Reaction of 1-iodododecane by use of “SmI$_2$/Ln” reagents

$^{n}$C$_{12}$H$_{26}$I $\xrightarrow{\text{"SmI}_2$/Ln" reagent}$ $^{n}$C$_{12}$H$_{26}$ + $^{n}$C$_{24}$H$_{50}$ + $^{n}$C$_{10}$H$_{21}$CH=CH$_2$

1 (0.5 mmol)

Figure 7. Photoinduced reduction of 1-iodododecane with “SmI$_2$/Ln” reagents

In the cases of scandium (Sc) and yttrium (Y), the reduction of dodecyl iodide with SmI$_2$/Ln did not proceed at all. Sc and Y are among group 3 transition metal elements, but they have no 4f-orbital electron. Lutetium (Lu) also indicated no reducing ability in the presence of SmI$_2$. In the case of Lu, all 4f-orbitals are perfectly occupied by electrons, and therefore, Lu is very stable and less reactive.
Except Sc, Y, and Lu, the mixed systems by the combination of other rare earth metals and SmI$_2$ exhibited reducing ability toward the reduction of dodecyl iodide. In particular, in the cases of light rare earth elements (LREE) such as lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), Sm, and europium (Eu), the reduction of dodecyl iodide proceeded efficiently to give dodecane selectively. On the other hand, in the cases of heavy rare earth elements (HREE) such as terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), and thulium (Tm), their reducing abilities were lower compared with LREE, and the yields of dodecane decreased in proportion to the increase in atomic numbers.

Noteworthy is that the SmI$_2$/gadolinium (Gd) and SmI$_2$/ytterbium (Yb) systems indicated somewhat different reactivities. In both cases, tetracosane and 1-dodecene were formed besides dodecane (e.g., yield of tetracosane: 24 % (Gd), 24% (Yb)). Gd is known as the inflection point in a series of rare earth elements concerning various physical and chemical properties. These phenomena are explained reasonably by the electron state of Gd having unpaired electrons in all 4f-orbitals. On the other hand, Yb is a single-electron-deficient element from closed shell of Lu, and therefore specialized properties and reactivities are sometimes observed, based on the driving force that Yb prefers to have 14 electrons in 4f-orbitals.

In a series of SmI$_2$/Ln systems, if only SmI$_2$ acts as the reducing agent and lanthanoid
metals only work to regenerate SmI₂, the results of the reduction may be similar each other. Very interestingly, however, these results mentioned above clearly indicated the characteristic features of individual rare earth elements.

A possible pathway for the reduction of dodecyl iodide with SmI₂/Ln is shown in Scheme 8. C₁₂H₂₅I undergoes single-electron transfer from SmI₂/Ln species to give the corresponding dodecyl radical, which is reduced to dodecyl anion species. Protonation of the dodecyl anion species affords dodecane. On the other hand, tetracosane and 1-dodecene are obtained by the dimerization and disproportionation of dodecyl radicals, respectively.

Scheme 8. Reaction of 1-iodododecane by use of “SmI₂/Ln” reagents

\[
\begin{align*}
C_{12}H_{25}^- & \xrightarrow{SmI_2/Ln} C_{12}H_{25}^- + \text{dimerization} \rightarrow C_{24}H_{50}^- \\
C_{12}H_{25}^- & \xrightarrow{SmI_2/Ln} C_{12}H_{25}^- + H^+ \rightarrow C_{12}H_{26}^- \\
C_{12}H_{25}^- & \xrightarrow{dimerization} C_{24}H_{50}^- \\
C_{12}H_{25}^- & \xrightarrow{disproportionation} C_{10}H_{21}CH=CH_2^- + C_{12}H_{26}^-
\end{align*}
\]

2-3 Conclusion

In summary, the author has investigated the generation and reducing ability of a series of low-valent rare earths systematically. In the case of light rare earths (La, Ce, Pr, Nd, Sm, and Eu)
and Yb, it has been shown that the mixed systems of rare earths ("LnI₂/Ln") indicate potentially higher reducing ability, compared with Ln or LnI₂ single system. More importantly, it has been revealed that photoirradiation can induce excellent reducing ability of most of low-valent rare earths species. This suggests that “the excited low-valent rare earth species” exhibits higher reducing ability than “the low-valent rare earth species in the ground state”.

Furthermore, the author has revealed that europium metal can be employed as an excellent reducing agent for the reduction of 1-iodoalkanes. It has been found that the photoinduced reduction of 1-iodododecane with several light rare earth metals such as Ce, Nd, Sm and Eu takes place successfully. In this reaction, the reaction solution indicates characteristic color, i.e., Ce (ocher), Nd (gray), Sm (blue), and Eu (dark green), and therefore, the corresponding divalent species are formed in situ. The photoirradiation may activate the divalent species, although the precise mechanism requires further detailed investigations. In addition, the author has investigated the generation and reducing abilities of a series of “SmI₂/Ln” reagent systematically. It is strongly suggested that electron states of rare earth elements effect the reducing abilities of SmI₂/Ln. The SmI₂/Ln systems make it possible to use three electrons of lanthanoid metals for reductive transformations.

The author believes these finding will open up a new field of rare earth chemistry.
2-4 Experimental Section

**General comments.** Gas chromatography (GC) spectra were recorded on Shimadzu GC-14A instrument equipped a flame ionizing detector and equipped using a capillary column (0.25 mm x 30 m). A Xe lamp by Ushio Optical Modulex (SX-UI500XQ) was employed.

**Reduction of 1-iodododecane with “LnI\textsubscript{2}/Ln” reagents:** In a three-necked flask equipped with a reflux condenser and a dropping funnel were placed rare earth (Ln) powder (1.0 mmol), 1,2-diiodoethane (0.2 mmol), and freshly distilled (sodium/benzophenone ketyl) THF (2 mL) under nitrogen atmosphere. The mixture was stirred for 1.5 h at room temperature (to attain the identical conditions). In the case of all rare earths, the color of the solutions was changed as shown in Scheme 2. To the resulting THF solution of “LnI\textsubscript{2}/Ln” were added dropwise a solution of 1-iodododecane (0.5 mmol), 2-propanol (2.0 mmol), and tetradecane (an internal standard for GC analysis) in THF (2 mL) for 1 h, and the reaction was continued for additional 2 h. To quench the reaction, the flask was exposed to air. Aqueous HCl (1.5 mol/L) was added to the resulting mixture, and then the products were extracted with diethyl ether (10 mL x 3). The combined organic layer was washed with saturated NaHCO\textsubscript{3} solution, dried over anhydrous MgSO\textsubscript{4}, and filtered. The resulting ethereal solution was analyzed by GC.\textsuperscript{11}
**Reduction of 1-iodododecane with LnI₂ systems:** In a three-necked flask equipped with a reflux condenser and a dropping funnel were placed rare earth (Ln) powder (1.0 mmol), 1,2-diiodoethane (1.0 mmol), and freshly distilled (sodium/benzophenone ketyl) THF (2 mL) under nitrogen atmosphere. The mixture was stirred for 1.5 h at room temperature. In all cases, insolved metals were existed. To the resulting THF solution of “LnI₂” were added dropwise a solution of 1-iodododecane (0.5 mmol), 2-propanol (2.0 mmol), and tetradecane in THF (2 mL) for 1 h, and the reaction was continued for additional 2 h. To quench the reaction, the flask was exposed to air. After similar workups, the resulting ethereal solution was analyzed by GC.

**Reduction of 1-iodododecane with “LnI₂/Ln/hν” systems:** To the THF solution of “LnI₂/Ln” prepared in a similar manner as mentioned above, were added dropwise a solution of 1-iodododecane (0.5 mmol), 2-propanol (2.0 mmol), and tetradecane (an internal standard for GC analysis) in THF (2 mL) for 1 h, and the reaction was continued for additional 2 h. Irradiation through Pyrex with a Xe lamp (500 W) was performed during the reaction. To quench the reaction, the flask was exposed to air. After similar workups, the resulting ethereal solution was analyzed by GC.

**Reduction of 1-iodododecane with Ln metal system:** In a three-necked flask equipped with a
reflux condenser and a dropping funnel were placed rare earth (Ln) powder (1.0 mmol) and freshly distilled (sodium/benzophenone ketyl) THF (2 mL) under nitrogen atmosphere. The mixture was stirred for 1.5 h at room temperature (to attain the identical conditions). In the case of all rare earths, the color of the solutions was not changed, and insolved metal was existed. To the resulting THF solution of Ln were added dropwise a solution of 1-iodododecane (0.5 mmol), 2-propanol (2.0 mmol), and tetradecane in THF (2 mL) for 1 h, and the reaction was continued for additional 2 h. To quench the reaction, the flask was exposed to air. After similar workups, the resulting ethereal solution was analyzed by GC.

**Reduction of 1-iodododecane with “SmI$_2$/Ln”:** In a three-necked flask equipped with a reflux condenser and a dropping funnel were placed rare earth (Ln) powder (0.8 mmol), samarium powder (0.2 mmol), 1,2-diiodoethane (0.2 mmol), and freshly distilled (sodium/benzophenone ketyl) THF (2 mL) under nitrogen atmosphere. The mixture was stirred for 1.5 h at room temperature (to attain the identical conditions). In the case of all rare earths, the color of the solutions changed dark blue. To the resulting THF solution of “SmI$_2$/Ln” were added dropwise a solution of 1-iodododecane (0.5 mmol), 2-propanol (2.0 mmol), and tetradecane in THF (2 mL) for 1 h, and the reaction was continued for additional 2 h. To quench the reaction, the flask was exposed to air. After similar workups, the resulting ethereal solution was analyzed by GC.
2-5 References


2. Standard oxidation potentials ($E^0$, Ln$^{3+}$/Ln$^{2+}$), ionic radii of Ln$^{2+}$ (R), thermodynamic functions for the formation of the aquo-ions of Ln$^{2+}$, and the enthalpies of hydration of the gaseous Ln$^{2+}$ ions are known. See: Mikheev, N. B. Russ. J. Inorg. Chem. 1984, 2, 251.


4. In general, high-grade lanthanoid powders (40 mesh) are commercially available and can be used without further activation. However, Eu powder is not commercially available as high-grade powder. Thus, the author filed Eu ingot to prepare the corresponding powder in a grove box under nitrogen atmosphere and used directly for the reduction of 1-iodododecane. See: Tomisaka, Y.; Tsuchii, K.; Ogawa, A. J. Alloys Compd. 2006, 408-412, 427.

5. The reduction of 1-iodododecane with Ln metal can proceed at the THF refluxing temperature for 2 h. See: (a) Nishino, T.; Nishiyama, Y.; Sonoda, N. J. Org. Chem. 2002, 67, 966. (b)
6. In the case of Yb, the reductive dimerization product (tetracosane) was obtained in the similar yield as that of the reduction product (dodecane). Relatively lower solubility of YbI$_2$ in THF may contribute to the dimerization of dodecyl radical.

7. The color of solutions changed similarly as described about the Ln(0)/Ln(II) binary system. In the case of Gd, Tb, Dy, Ho, Er, Tm, and Lu, however, most of metals were seemed to remain unchanged.


9. Ce, Nd, and Sm metals indicate effective reducing abilities toward the deiodination of 1-iodododecane, when the size of metals is even 40 mesh.


11. We attempted the preparation of LnI$_2$ by the reaction of Ln (1.0 mmol) with I$_2$ (0.2 mmol) in freshly distilled (sodium/benzophenone ketyl) THF (2 mL) under a nitrogen atmosphere, and
then examined the reduction of 1-iodododecane. The yields of dodecane were 4% (Sm and Yb); trace (Pr, Nd, Gd, Dy, Ho, Er, and Tm). Therefore, 1,2-diiodoethane is more suitable additive for the preparation of divalent rare earth species.
Chapter 3 Carbonylation of Organic Halides with Carbon Monoxide Mediated by Samarium Diiodide: Improvement and Mechanistic Investigations

3-1 Introduction

Under the atmospheric pressure of carbon monoxide, the photoinduced reductive carbonylation of organic halides (RX) with samarium diiodide (SmI$_2$) successfully takes place to provide the corresponding unsymmetrical ketones (RC(O)CH$_2$R) in good yields. Mechanistic insight into this carbonylation, especially the pathway for the generation of acylsamarium species (RC(O)SmI$_2$) as a key intermediate, is also investigated in detail.

Transition-metal-catalyzed carbonylation of organic halides with carbon monoxide via oxidative addition of organic halides to the transition metal catalysts is a synthetically very useful process in organic synthesis. In contrast, examples of reductive carbonylation of organic halides involving electron-transfer process are rare. In our laboratory, a novel reductive carbonylation of organic halides (RX) with carbon monoxide (50 atm) mediated by samarium diiodide (SmI$_2$) has been developed. This carbonylation takes place successfully upon visible-light irradiation and the corresponding unsymmetrical ketones (RC(O)CH$_2$R) are obtained in good yields.$^1$ Further detailed study on this carbonylation has led to an interesting finding that this SmI$_2$-induced reductive carbonylation of haloalkanes does proceed under the atmospheric pressure of CO upon
visible-light irradiation, as shown in Eq. (1). Moreover, the atmospheric carbonylation is advantageous to get insight into the present carbonylation pathway. In this thesis, the author wishes to report the atmospheric carbonylation of organic halides with SmI\(_2\) upon visible-light irradiation and its detailed mechanistic aspects.

\[
2 \text{RX} + 2 \text{CO} \xrightarrow{\text{1 atm}} \overset{\text{SmI}_2}{\text{R-C\R}}
\]  

(1)

### 3-2 Results and Discussion

Initially, the influence of the visible-light irradiation on this reductive carbonylation under the atmosphere of carbon monoxide was investigated. When the reaction of 1-iodododecane (0.5 mmol) with CO (1 atm) was carried out using SmI\(_2\)/Sm (2 mmol/2 mmol)\(^2\) mixed system upon irradiation with a Xe lamp through Pyrex, reductive carbonylation took place successfully, to give 58% of dodecyl tridecyl ketone, which consisted of two dodecyl and two CO units. In contrast, no reductive carbonylation took place at all in the dark, as shown in Eq. (2). A deep blue color solution of SmI\(_2\) in THF, exhibits its absorption maxima in visible region (\(\lambda_{\text{max}} = 565, 617 \text{ nm}\)), which can be assigned as a 4f\(^6\)\(\rightarrow\)4f\(^5\)5d\(^1\) transition. In our laboratory, it has been reported that the irradiation with the light of wavelength between 500 and 700 nm is effective for the excitation of SmI\(_2\), which leads to the dramatical enhancement of its reducing ability compared with SmI\(_2\) in the ground state.\(^3\)
Table 1. Atmospheric carbonylation of organic halides

<table>
<thead>
<tr>
<th>entry</th>
<th>R-X</th>
<th>product</th>
<th>yield (%)&lt;sup&gt;a&lt;/sup&gt;</th>
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<td>2</td>
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<td>&lt;sup&gt;n&lt;/sup&gt;C&lt;sub&gt;12&lt;/sub&gt;H&lt;sub&gt;25&lt;/sub&gt;CO&lt;sup&gt;n&lt;/sup&gt;C&lt;sub&gt;12&lt;/sub&gt;H&lt;sub&gt;25&lt;/sub&gt;</td>
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<td>&lt;sup&gt;c&lt;/sup&gt;C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;11&lt;/sub&gt;CO&lt;sup&gt;c&lt;/sup&gt;C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;11&lt;/sub&gt;</td>
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<td>4</td>
<td>&lt;sup&gt;c&lt;/sup&gt;C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;11&lt;/sub&gt;I</td>
<td>&lt;sup&gt;c&lt;/sup&gt;C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;11&lt;/sub&gt;CO&lt;sup&gt;c&lt;/sup&gt;C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;11&lt;/sub&gt;</td>
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</tr>
<tr>
<td>5</td>
<td>CH₂=CH(CH₂)₄Br</td>
<td>CH₂=CH(CH₂)₄CO(CH₂)₄CH=CH₂</td>
<td>68</td>
</tr>
</tbody>
</table>

<sup>a</sup>RX (0.5 mmol), SmI₂ (2 mmol), Sm (2 mmol), THF (15 mL), CO (1 atm), r.t., 6 h, *hν*; Xe lamp (500 W), Pyrex.

Table 1 summarizes the results of the photoinduced carbonylation of several organic halides with SmI₂/Sm under the atmosphere of CO. The primary alkyl halides such as chloro-, bromo-, and iodododecanes (entries 1-3) could be employed for the photoinduced atmospheric
carbonylation, and the corresponding unsymmetrical ketones were obtained in moderate yields. Similarly, cyclohexyl iodide as a secondary alkyl iodide underwent the atmospheric carbonylation to provide the unsymmetrical ketones in good yield (entry 4).

The present photoinduced carbonylation may involve the formation of acylsamarium species (RC(O)SmI$_2$) as a key intermediate from haloalkane (RX), CO, and SmI$_2$. Kagan et al. previously reported that the reduction of acyl chloride (RC(O)Cl) by excess amounts of SmI$_2$ provided the corresponding unsymmetrical ketones (RC(O)CH$_2$R) and suggested that a possible pathway to give the unsymmetrical ketones might involve the dimerization of acylsamarium species and the subsequent further reduction with SmI$_2$, as shown in Eq. (3).$^4$

![Diagram](image)

In this thesis, thus, mechanistic study is focused on the carbonylation step to generate the acylsamarium species from haloalkanes and CO in the presence of low-valent samarium reagent (SmI$_2$/Sm). Scheme 1 indicates some possible reaction pathways for the formation of acylsamarium species (RC(O)SmI$_2$).
In the first pathway, in situ generated alkyl radical (R·) reacts with CO to give acyl radical species (RC(O)·)\(^5\) and the subsequent reduction of the acyl radical with SmI\(_2\) forms acylsamarium species (Path A). To elucidate whether this atmospheric carbonylation includes the formation of acyl radical intermediates, the photoinduced carbonylation of 5-hexenyl bromide with SmI\(_2\) under the atmospheric pressure of CO was examined. Scheme 2 summarizes several kinetic data concerning this reaction system.\(^6\) As can be seen from Scheme 2, the rate for the 5-\(exo\) cyclization of 5-hexenyl radical is \(k_1 = 2.3 \times 10^5\) \(s^{-1}\) (25 °C). Contrary to this, the rate for the reduction of 5-hexenyl radical and the rate for the carbonylation of 5-hexenyl radical can be estimated roughly to be \(k_{Sm}[SmI_2] = \sim 10^4\) \(s^{-1}\) and \(k_{CO}[CO] = \sim 10^3\) \(s^{-1}\), respectively. These kinetic data strongly suggest that the 5-\(exo\) cyclization of 5-hexenyl radical takes place preferentially and,
in contrast, the direct carbonylation of 5-hexenyl radical is an unfavorable process at least under the atmosphere of CO. Surprisingly, however, the expected cyclic carbonylated product was not obtained at all, and instead acyclic ketone was obtained in 68% yield. This result can not be accounted for by the free radical pathway (Path A in Scheme 1).

**Scheme 2.** Photoinduced atmospheric carbonylation of 5-hexynyl bromide with SmI₂

\[
\begin{align*}
\text{Br} & \quad \text{Sml₂} \\
\text{SmI₂} & \quad \text{hv} \\
\text{CO} & \quad \text{k}_\text{CO} \ [\text{CO}] = 10^{-3} \\
\text{Sml₂} & \quad \text{k}_\text{Sm} \ [\text{Sml₂}] = 10^{-4} \\
5\text{-exo} & \quad k_f = 10^{-5} \\
\text{not detected} & \quad 68 \% \\
\text{CO} & \quad \text{SmI₂} \\
\text{CO} & \quad \text{SmI₂} \\
\text{I₂Sm} & \quad \text{SmI₂} \\
\end{align*}
\]

\[
\begin{align*}
\text{k}_\text{CO} & = 6.3 \times 10^5 \text{ M}^{-1}\text{s}^{-1} (80 \degree \text{C}); [\text{CO}] = 1.01 \times 10^5 / 8.31 \times 10^3 \times 298 = 4 \times 10^{-2}, \\
\text{k}_\text{CO}[\text{CO}] & = 6.3 \times 10^5 \times 4 \times 10^{-2} = 10^5, \\
\text{k}_\text{Sm} & = 10^5 \text{ M}^{-1}\text{s}^{-1} (40 \degree \text{C}, \text{Sml₂-THF}); [\text{Sml₂}] = 0.2 \text{ mmol/L}, \text{k}_\text{Sm}[\text{Sml₂}] = 10^5 \times 10^{-1} = 10^4, \\
k_f & = 2.3 \times 10^5 \text{ s}^{-1} (25 \degree \text{C})
\end{align*}
\]
Since the free radical pathway (Path A) is not suitable for the formation of acylsamarium species, the author next investigated about the organosamarium pathway, which consists of the reduction of haloalkanes (RX) with SmI₂ to generate organosamarium species (RSmI₂), followed by the carbonylation of RSmI₂ with CO to give acylsamarium species (Path B in Scheme 1). Thus, the reaction of RSmI₂ with CO (1 atm) was examined. Dodecylsamarium diiodide was prepared by the reaction of 1-iodododecane (0.5 mmol) with SmI₂/Sm (2 mmol/2 mmol) at room temperature for 1.5 h upon irradiation with Xe lamp through Pyrex. Then, atmospheric CO was introduced into the solution upon photoirrradiation (r.t., 4.5 h). However, the desired unsymmetrical ketone was not obtained at all, as shown in Eq. (4).

\[ 2 \, ^nC_{12}H_{25}I \xrightarrow{\text{SmI}_2, h\nu, \text{r.t., 1.5 h}} 2 \left[ ^nC_{12}H_{25}SmI_2 \right] \xrightarrow{\text{CO (1 atm), h\nu, \text{r.t., 4.5 h}}} ^nC_{12}H_{25}SmI_2 + ^nC_{12}H_{25} \]

To ascertain whether dodecylsamarium diiodide is formed properly in this reaction system, capturing dodecylsamarium diiodide with excess amounts of diethyl ketone was attempted. However, this Grignard-type reaction did not occur, and instead dodecane and dodecene were obtained in 45% and 38% yields, respectively, as a result of the reduction and disproportionation shown as Eq. (5). Furthermore, the same reaction was exercised at –15 °C to 5 °C, but the addition product was not detected at all.
These results suggest that the alkylsamarium diiodide is unstable under the conditions, and thus decomposed before the reaction with CO. Accordingly, the pathway through the generation of alkylsamarium species (Path B) is unfavorable for this carbonylation, because of the instability of alkylsamarium species as the intermediate.

During the course of our study on this carbonylation, the author found that the reducing ability of SmI$_2$ was intensively reduced in the presence of CO (Table 2). For example, when the photoinduced reduction of 2-octanone by SmI$_2$ was conducted at room temperature for 1 h in the absence of CO, 2-octanol (1) was obtained as the major product, along with small amounts of vic-diol (2) as a pinacol-type product and ketone (3) as a pinacol rearrangement product (entry 1). The same reaction without photoirradiation led to similar results as the case with photoirradiation (entry 2). In the presence of CO, however, the photoinduced reaction of 2-octanone afforded the desired alcohol (1) in very poor yield, and the starting material was recovered mainly (entry 3). It is clear that the existence of CO decreases the reducing ability of SmI$_2$, most probably by the coordination of CO to samarium species.$^8$

$$\begin{align*}
nC_{12}H_{25}I & \xrightarrow{\text{SmI}_2-h\nu} \text{r.t., 1.5 h} \quad nC_{12}H_{26} \text{SmI}_3 \\
& \quad \xrightarrow{\text{Et}_2\text{CO (3 eq), } h\nu} \text{r.t., 2 h} \quad nC_{12}H_{25} \text{Et} + nC_{12}H_{26} + \text{Et}_2\text{CO (3 eq), } h\nu
\end{align*}$$

$$\begin{align*}
nC_{12}H_{26} + nC_{12}H_{24} & + nC_{12}H_{25} \text{Et} \\
45 \% & + \quad 38 \% \quad \text{not formed}
\end{align*}$$
With these results in mind, a possible pathway for the formation of acylsamarium species (Path C in Scheme 1) is shown as follows: dodecyl iodide undergoes single-electron transfer from SmI₂ to generate dodecyl radical in an inner sphere, which may be captured rapidly with the CO coordinated to the samarium species and simultaneously undergoes single electron reduction with SmI₂(CO)ₙ generating acylsamarium species.
3-3 Conclusion

In conclusion, the photoirradiated atmospheric carbonylation of organic halides with samarium diiodide occurred. Under the atmospheric pressure of carbon monoxide, the photoinduced reductive carbonylation of organic halides (RX) with samarium diiodide (SmI$_2$) successfully took place to provide the corresponding unsymmetrical ketones (RC(O)CH$_2$R) in good yields. Mechanistic insight into this carbonylation, especially the pathway for the generation of acylsamarium species (RC(O)SmI$_2$) as a key intermediate, was also investigated in detail.

3-4 Experimental Section

**General comments.** Gas chromatography (GC) spectra were recorded on Shimadzu GC-14A instrument equipped a flame ionizing detector and equipped using a capillary column (0.25 mm x 30 m). A Xe lamp by Ushio Optical Modulex (SX-UI500XQ) was employed.

**Atmospheric carbonylation:** In a 20 mL of three-necked glass flask (Pyrex) equipped with a dropping funnel, a cooler, and an inlet, were placed under the atmosphere of nitrogen Sm powder (4 mmol, 0.601 g), 1,2-diiodoethane (2 mmol, 0.564 g), and THF (10 mL). The resulting mixture was stirred magnetically for 1.5 h to prepare a SmI$_2$/Sm reagent, and then carbon monoxide was introduced into the vessel. Upon irradiation with a Xe lamp (500 W), haloalkane (0.5 mmol) was added dropwise to the mixture over 1 h, and then the reaction was continued for another 5 h.
After the decomposition of excess SmI$_2$/Sm with air, and then 1 mol·L$^{-1}$ HCl, the product was extracted with ether. The extracts were dried (MgSO$_4$) and concentrated in vacuo. Purification of the product was performed by preparative HPLC or PTLC.
3-5 References


2 By using only SmI$_2$ (i.e., in the absence of Sm metal), the same reductive carbonylation of dodecyl iodide with CO could proceed, but the yield of dodecyl tridecyl ketone was lower, compared with the reaction using the SmI$_2$/Sm-mixed system. The combination of SmI$_2$ and Sm metal was reported to exhibit higher reducing power compared with SmI$_2$ or Sm metal itself. See: Ogawa, A.; Takami, N.; Sekiguchi, M.; Ryu, I.; Kambe, N.; Sonoda, N. J. Am. Chem. Soc. 1992, 114, 8729.


8 The existence of CO also decreases the reducing ability of SmI$_2$ in the reduction of 1-iodododecane. See, ref. 1 (b).
Chapter 4 Photoaccelerated Reductive Coupling of Acid Chlorides with Conjugate Dienes and Styrenes by Use of Neodymium Metal in N,N-Dimethylacetamide

4-1 Introduction

Recently lanthanoid metal salts and organolanthanoid compounds have been widely employed in organic synthesis. Among them, divalent lanthanoid salts, especially samarium diiodide, work as useful reducing agents in organic synthesis. Zero-valent lanthanoid metals also bear potential reducing ability. However, the use of zero-valent lanthanoid metals themselves directly in organic synthesis is still rare. The advantages of the use of lanthanoid metals are the electron economies compared with divalent lanthanoid species, because lanthanoid metals can afford three electrons to form the stable trivalent state. In addition, another advantage of the use of lanthanoid metals is easy operation. However, the problems of the use of lanthanoid metals are the heterogeneous nature in organic solvents and lower reactivity. In order to increase the reducing ability of lanthanoid metals, some additives are employed. For example, Nishiyama et al. found that iodoalkanes could be reduced with lanthanum metal in the presence of a catalytic amount of iodine$^1$. Samarium metal$^{2a,2b}$ and cerium metal$^{2c}$ have been reported to promote pinacol coupling reactions by using iodine as the activating reagent. The silyl group activated coupling reaction mediated by ytterbium/Me$_3$SiBr in hexamethylphosphoramide (HMPA) has also been
reported by Fujiwara et al.\textsuperscript{3} Talukdar and Fang described the coupling reaction of aromatic aldehydes mediated by samarium in the presence of aqueous hydrochloric acid.\textsuperscript{4}

In our laboratory, it has been found that photoirradiation dramatically enhances the reducing ability of some rare earth metals (e.g., Ce, Nd, Sm, and Eu) toward the reduction of iodoalkanes.\textsuperscript{5} This thesis describes that neodymium metal upon photoirradiation (Nd/$h\nu$) acts as an electron-economical reducing agent for the reductive coupling of aroyl chlorides with conjugate dienes and styrenes with easy operation.\textsuperscript{6,7}

**4-2 Results and Discussion**

When a mixture of benzoyl chloride (1 mmol) and 2,3-dimethyl-1,3-butadiene (2 mmol) in DMA ($N,N$-dimethylacetamide) (5 mL) was treated with lanthanide metal powder (0.5 mmol) such as samarium, cerium, neodymium, and europium under photoirradiation conditions for 2 h,\textsuperscript{8} the corresponding coupling product was obtained in good yield. It should be noted that, when the reaction was performed in the dark, the yield of the coupling product was low. When the reaction was performed in THF, acetonitrile, or DME, no reaction took place at all (Table 1).
**Table 1.** Reductive coupling of benzoyl chloride with a 1,3-diene

![Reductive coupling of benzoyl chloride with a 1,3-diene](image)

<table>
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<tr>
<th>Ln</th>
<th>condition</th>
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<td>6</td>
<td>20</td>
</tr>
<tr>
<td>Nd</td>
<td>h&lt;sub&gt;v&lt;/sub&gt;</td>
<td>DMA</td>
<td>2</td>
<td>83</td>
</tr>
<tr>
<td>Eu</td>
<td>dark</td>
<td>DMA</td>
<td>6</td>
<td>55</td>
</tr>
<tr>
<td>Eu</td>
<td>h&lt;sub&gt;v&lt;/sub&gt;</td>
<td>DMA</td>
<td>2</td>
<td>78</td>
</tr>
</tbody>
</table>

<sup>a</sup>Reaction conditions: benzoyl chloride (1 mmol), 2,3-dimethyl-1,3-butadiene (2 mmol), Ln (0.5 mmol), h<sub>v</sub> (Xe lamp), DMA = N,N-dimethylacetamide. <sup>b</sup>Isolated yield based on benzoyl chloride.

By using neodymium metal powder under photoirradiation, 4-toluoyl chloride and 4-chlorobenzoyl chloride can also react with 1,3-diene smoothly to give the corresponding coupling products in high yield, as shown in Eq. (1).

![Reductive coupling of benzoyl chloride with a 1,3-diene](image) (1)

R = H, Me, Cl  
DMA = N,N-dimethylacetamide  
yields = 85-95 %
Under the same reaction conditions, the cross coupling of benzoyl chloride with isoprene was also examined. The benzoyl radical C selectively attacks the site of isoprene to give the coupling product A in good yield. The product B formed through b attack was not obtained at all (Scheme 1). This regioselectivity can be explained by the difference in stability between allylic radical intermediates D and E.

**Scheme 1.** Photoinduced reductive coupling of benzoyl chloride with isoprene in the presence of Nd

Next, the reductive coupling by using a cyclic diene was examined. When the photoirradiated reaction of benzoyl chloride (1 mmol) with 1,3-cyclohexadiene (1.1 mmol) was
conducted in the presence of neodymium metal powder (0.5 mmol), another type of coupling product $F$ was obtained in 65% yield (Scheme 2). In this case, the allyl radical $G$ formed in situ from acryl radical and 1,3-cyclohexadiene is a secondary radical, and does not undergo homocoupling, most probably owing to steric factor. The aclyl radical $G$ undergoes single-electron-transfer from low-valent Nd species, to generate acryl anion species $H$, which is acylated with allyl chloride to give the coupling product $F$.

**Scheme 2.** Photoinduced reductive coupling of benzoyl chloride with 1,3-cyclohexadiene in the presence of Nd

Furthermore, the present photoinduced coupling reaction of acyl chlorides with conjugated dienes using Nd metal powder can be applied to reductive coupling with styrene derivatives (Scheme 3).
Scheme 3. Photoinduced reductive coupling of benzoyl chloride with styrene in the presence of Nd

\[
\text{PhCl} + \text{PhCH} = \text{CH}_2 \xrightarrow{\text{Nd-h} \nu \text{DMA}} \text{PhCH} = \text{CHCO} \text{Ph} \quad 80\%
\]

In this case, the reductive coupling reaction proceeded similarly to the case of cyclic dienes, and the corresponding coupling product derived from two molecules of benzoyl groups and one molecule of styrene was obtained successfully. Representative results of the reductive coupling of aroyl chlorides with styrenes using the Nd/h ν system are shown in Scheme 4.

Scheme 4. Photoinduced reductive coupling of aroyl chloride with styrene in the presence of Nd

\[
\begin{align*}
\text{PhCl} & \quad \text{PhCH} = \text{CHCH}_2 \text{Cl} \\
\text{PhCl} & \quad \text{PhC} = \text{CHCH}_2 \text{Cl} \\
\text{PhCl} & \quad \text{PhCH} = \text{CHCH}_2 \text{Cl}
\end{align*}
\]

80 %

74 %

85 %

70 %

55 %
4-3 Conclusion

In summary, under photoirradiation, lanthanide metals, such as cerium, neodymium, samarium, and europium metals indicated higher reducing abilities toward the reductive transformation of acid chlorides. By using these novel photoinduced reduction systems of rare lanthanide metals, benzoyl chloride reacted with dienes and styrenes, giving the corresponding coupling products in good yields.

4-4 Experimental Section

General comments. $^1$H NMR spectra were recorded on a JEOL JNM-AL (300 Hz) spectrometer using CDCl$_3$ as the solvent with tetramethylsilane (TMS) as the internal standard. $^{13}$C NMR spectra were obtained on a JEOL JNM-AL (75 Hz) spectrometer using CDCl$_3$ as the solvent. Chemical shifts in $^{13}$C NMR were measured relative to CDCl$_3$ and converted to δ TMS values by using δ 77.0 ppm. Mass spectra were obtained on a JEOL JMS-DX303 instrument in the analytical section of Osaka University. Elemental analyses were also performed there.

Reductive coupling of benzoyl chloride with a 1,3-diene by Ln metal: To a mixture of Ln powder (1 mmol), benzoyl chloride (1 mmol) and 1,3-diene (2 mmol, freshly distilled) in freshly distilled DMA ($N,N$-dimethylacetamide) was added at room temperature with magnetic stirring under nitrogen atmosphere. The resulting solution turned yellow-green within 15 min and an
exothermic reaction occurred. After completion of the reaction (about 1 h), dilute hydrochloric acid (2 M, 5 mL) was added and the resulting mixture was extracted with diethyl ether (20 mL x 3). The combined organic layer was washed with brine, dried over anhydrous sodium sulphate, and concentrated under reduced pressure. The residue was separated by column chromatography on silica gel with ethyl acetate and cyclohexane (1:6) as an eluent to afford the coupling products.

**Photoinduced reductive coupling of benzoyl chloride with a 1,3-diene by Ln metal:** The Ln in DMA was prepared in a similar manner as mentioned above. Irradiation through Pyrex with a Xe lamp (500 W) was performed during the reaction (2 h). The resulting solution turned yellow-green within 15 min and an exothermic reaction occurred. After completion of the reaction (for about 1 h), dilute hydrochloric acid (2 M, 5 mL) was added and the resulting mixture was extracted with diethyl ether (20 mL x 3). The combined organic layer was washed with brine, dried over anhydrous sodium sulphate, and concentrated under reduced pressure. The residue was separated by column chromatography on silica gel with ethyl acetate and cyclohexane (1:6) as an eluent to afford the coupling products.
4-5 References


In the stoichiometric reaction, Ln metals changed to LnCl₃, and the resulting solution was homogeneous.

Only *E,E*-isomer was obtained, and no formation of *Z*-isomers were confirmed (see ref. 6):

*E,E*-isomer: IR (KBr) ν<sub>max</sub>: 3062, 2949, 1686, 1596, 1580, 1448 cm<sup>-1</sup>. ¹H NMR δ<sub>H</sub> (CDCl₃): 8.01–7.96 (m, 4H), 7.58–7.55 (m, 2H), 7.48–7.44 (m, 4H), 5.31 (d, 2H, J = 1:2 Hz), 3.64 (s, 4H), 2.13–2.11 (t, 4H, J = 3:2 Hz), 1.68 (s, 6H). ¹³C NMR δ<sub>c</sub> (CDCl₃): 182.4, 120.6, 116.6, 113.4, 112.7, 112.1, 112.0, 49.3, 33.0, 11.7. MS (EI) m/z (%): 347 (M⁺ + 1, 0.72), 346 (M⁺, 1.56), 241 (0.68), 226 (2.17), 173 (5.11), 105 (100.00), 77 (50.93).

Benzoyl chloride (1 mmol), styrene (1.1 mmol), and Nd powder (0.5 mmol) were usually employed for the reductive coupling reaction with styrenes. Similar results were obtained when benzoyl chloride (2 mmol), styrene (1.1 mmol), and Nd (0.8 mmol) were used.
Chapter 5 Construction of Si-Si Linkages by Reductive Coupling of Organochlorosilanes Using Photoinduced SmI$_2$/Sm System

5-1 Introduction

Polysilanes have recently attracted considerable attention in materials science, because of their characteristic structures and physical properties.$^1$ For example, polysilanes indicate excellent conductive and optical properties based on the $\pi$ and $\sigma-\pi$ conjugation. For synthetic methods of polysilanes, Wurtz-type coupling reaction of dichlrosilanes with alkali metals has been employed generally, as well as the electrolytic polymerization of dichlorosilanes and the dehydrogenative polymerization of hydrosilanes.$^2$

However, Wurtz-type coupling reaction has several problems, in a word, which are the difficulty in controlling the reactions, the wide molecular weight distribution, and the limitation of functional groups. These are owing to the powerful reducing ability of alkali metals.$^3$

This chapter deals with the reductive coupling of oraganochlorosilanes by using Sm/SmI$_2$-mixed system.
5-2 Results and Discussion

5-2-1 Selection of solvent

Samarium diiodide (SmI$_2$) is well-known to be a mild, single-electron reducing reagent in organic synthesis.$^4$ However, SmI$_2$ had not been employed for the reductive coupling of chlorosilanes. This is because silyl iodide, which is formed in situ from chlorosilanes and SmI$_2$, acts as a ring-opening silyliodination reagent toward THF as a general solvent in the reactions with SmI$_2$. Therefore, a variety of solvents such as HMPA-toluene, propylene glycol 1-monoethyl ether 2-acetate (PGMEA), and 1,2-dimethoxyethane (DME) were checked. Among the solvents employed, DME, bearing similar polarity to THF$^5$, was found to be an excellent solvent for this purpose. Thus, by using DME as solvent, a novel reductive coupling of chlorosilanes with SmI$_2$-based system was developed.

5-2-2 SmI$_2$/Sm-induced reductive dimerization of dimethylphenylchlorosilane

As a starting point for the synthesis of disilanes, initially, the author examined to study the reductive conversion of dimethylphenylchlorosilane to the corresponding disilane mediated by the SmI$_2$/Sm reagent, as shown in Eq. (1).
After detailed studies concerning the optimization of solvents, ratios of SmI₂/Sm, and reaction temperatures (Table 1), the best result was obtained when the reaction was conducted using a 3:1 molar ratio of Sm/SmI₂ in refluxing 1,2-dimethoxyethane (84 °C) for 12 h (entry 6). Control experiments clearly indicated that both samarium powder and samarium diiodide are essential for the formation of Me₂PhSiSiPhMe₂ from dimethylphenylchlorosilane. When samarium powder or samarium diiodide was used alone, no reaction occurred (entries 3, 4, and 9).

Table 1. SmI₂/Sm-induced reductive dimerization of dimethylphenylchlorosilane

<table>
<thead>
<tr>
<th>entry</th>
<th>Sm (mmol)</th>
<th>SmI₂ (mmol)</th>
<th>solvent</th>
<th>reaction time (h)</th>
<th>yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3</td>
<td>1</td>
<td>THF</td>
<td>24</td>
<td>0ᵇ</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>1</td>
<td>CH₃CN</td>
<td>24</td>
<td>NR</td>
</tr>
<tr>
<td>3</td>
<td>-</td>
<td>1</td>
<td>DME</td>
<td>12</td>
<td>NR</td>
</tr>
<tr>
<td>4</td>
<td>-</td>
<td>3</td>
<td>DME</td>
<td>12</td>
<td>trace</td>
</tr>
<tr>
<td>5</td>
<td>3</td>
<td>1</td>
<td>DME</td>
<td>5</td>
<td>46ᶜ</td>
</tr>
<tr>
<td>6</td>
<td>3</td>
<td>1</td>
<td>DME</td>
<td>12</td>
<td>76ᶜ</td>
</tr>
<tr>
<td>7</td>
<td>3</td>
<td>0.5</td>
<td>DME</td>
<td>24</td>
<td>54ᶜ</td>
</tr>
<tr>
<td>8ᵈ</td>
<td>3</td>
<td>1</td>
<td>DME</td>
<td>36</td>
<td>NR</td>
</tr>
<tr>
<td>9</td>
<td>3</td>
<td>-</td>
<td>DME</td>
<td>24</td>
<td>NR</td>
</tr>
</tbody>
</table>

ᵇReaction condition: PhMe₂SiCl (1 mmol), solvent (4 mL), reflux (DME, 84 °C; THF, 65 °C; CH₃CN, 82 °C).  
ᶜSilylative ring opening of THF with silyl iodide (formed in situ from the substrates chlorosilanes and SmI₂) took place successively.  
ᶜIsolated yields based on 1.  
The reaction was conducted using a 3:1 molar ratio of Sm/SmI₂ in refluxing 1,2-dimethoxyethane (84 °C) for 12 h (entry 6). Control experiments clearly indicated that both samarium powder and samarium diiodide are essential for the formation of Me₂PhSiSiPhMe₂ from dimethylphenylchlorosilane. When samarium powder or samarium diiodide was used alone, no reaction occurred (entries 3, 4, and 9).
In order to clarify the scope and the limitations of this reaction, a number of different organochlorosilanes were allowed to react with the SmI$_2$/Sm system under the optimized reaction conditions (entry 6 in Table 1). As shown in Table 2, substituted aromatic chlorosilanes could undergo reductive dimerization to give the corresponding disilanes in good to excellent yield. In the case of diphenylvinylchlorosilane (entry 6), the vinyl group was unaffected under these reaction conditions. It is remarkable that an aliphatic organochlorosilane, tert-butyl(dimethyl)chlorosilane, also reacted to form disilane using the SmI$_2$/Sm system, although longer reaction times (20 h) were required (entry 7).

**Table 2.** SmI$_2$/Sm-induced reductive dimerization of organochlorosilanes

<table>
<thead>
<tr>
<th>entry</th>
<th>chlorosilane</th>
<th>disilane</th>
<th>yield (%)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Me$_2$PhSiCl</td>
<td>Me$_2$PhSiPhMe$_2$</td>
<td>a 76</td>
</tr>
<tr>
<td>2</td>
<td>MePh$_2$SiCl</td>
<td>MePh$_2$SiPh$_2$Me</td>
<td>b 90</td>
</tr>
<tr>
<td>3</td>
<td>Ph$_3$SiCl</td>
<td>Ph$_3$SiPh$_3$</td>
<td>c 80</td>
</tr>
<tr>
<td>4</td>
<td>MePhHSiCl</td>
<td>MePhHSiHPhMe</td>
<td>d 64$^c$</td>
</tr>
<tr>
<td>5</td>
<td>Ph$_2$HSiCl</td>
<td>Ph$_2$HSiHPh$_2$</td>
<td>e 70</td>
</tr>
<tr>
<td>6$^d$</td>
<td>(vinyl)Ph$_2$SiCl</td>
<td>(vinyl)Ph$_2$SiPh$_2$(vinyl)</td>
<td>f 85</td>
</tr>
<tr>
<td>7</td>
<td>tBuMe$_2$SiCl</td>
<td>tBuMe$_2$SiMe$_2$Bu</td>
<td>g 81</td>
</tr>
</tbody>
</table>

$^a$Unless, otherwise noted, organochlorosilanes (1 mmol) were allowed to react with Sm (3 mmol) and SmI$_2$ (1 mmol) in DME at 84 °C for 12-14 h. $^b$Isolated yields based on chlorosilane 1. $^c$Ratio of diastereomers is about 50/50. $^d$20 h.
5-2-3 SmI₂/Sm-induced reductive polymerization of organochlorosilanes

Interestingly, when 1,4-bis(dimethylchlorosilyl)benzene (1 mmol) was treated with Sm (3 mmol)/SmI₂ (1 mmol) in refluxing DME for 24 h, the corresponding poly(disilanyleneophenylene) was formed in good yield (73%), as shown in Eq. (2). The polymer was purified by precipitation from its THF solution by addition of EtOH, followed by freeze-drying. The molecular weight distribution of this polymer was determined by gel permeation chromatography (GPC) calibrated by polystyrene standards with chloroform as the eluent ($M_n = 2480, M_w/M_n = 1.2$). This result suggests that the SmI₂/Sm system is a promising reagent for the construction of a $\zeta$−$\pi$ conjugate system of poly(disilanyleneophenylene).

Since the synthesis of disilanes was successful, the reductive polymerization of dichloromethylphenylsilane was also carried out under the reaction conditions mentioned above. When dichloromethylphenylsilane (2 mmol) was treated with Sm (3 mmol)/SmI₂ (1 mmol) in refluxing DME for given times, the poly(methylphenyl)silane was obtained in moderate yield, as shown in Table (3). When magnesium⁶ was used as the coreductant, the molecular weight distribution of the poly(methylphenyl)silane ($M_w/M_n = 1.5$, $M_n = 4650$) was much narrower than that
of the product prepared by using a SmI$_2$/Sm mixed system in the absence of Mg ($M_w/M_n = 2.6, M_n = 1450$) (Table 3). However, when samarium powder or samarium diiodide was not employed with Mg in the reduction system, the reactive coupling failed (entries 5 and 6). The product was identified based on the analysis of $^1$H NMR, IR, and UV spectra ($\lambda_{\text{max}} = 334$ nm, which shows the high purity of the polysilane).

Table 3. Reductive polymerization of dichloromethylphenylsilane mediated by the SmI$_2$/Sm system

<table>
<thead>
<tr>
<th>entry</th>
<th>MePhSiCl$_2$ (mmol)</th>
<th>Sm (mmol)</th>
<th>SmI$_2$ (mmol)</th>
<th>Mg (mmol)</th>
<th>time (h)</th>
<th>yield (%)$^a$</th>
<th>$M_w$</th>
<th>$M_n$</th>
<th>$M_w/M_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>3</td>
<td>1</td>
<td>-</td>
<td>12</td>
<td>33</td>
<td>3740</td>
<td>1560</td>
<td>2.4</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>3</td>
<td>1</td>
<td>-</td>
<td>24</td>
<td>42</td>
<td>3770</td>
<td>1450</td>
<td>2.6</td>
</tr>
<tr>
<td>3</td>
<td>4</td>
<td>3.9</td>
<td>0.1</td>
<td>10</td>
<td>36</td>
<td>38</td>
<td>7040</td>
<td>4400</td>
<td>1.6</td>
</tr>
<tr>
<td>4</td>
<td>2</td>
<td>1.5</td>
<td>1</td>
<td>10</td>
<td>24</td>
<td>43</td>
<td>6980</td>
<td>4650</td>
<td>1.5</td>
</tr>
<tr>
<td>5</td>
<td>0.5</td>
<td>2</td>
<td>-</td>
<td>10</td>
<td>24</td>
<td>0$^b$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>0.5</td>
<td>-</td>
<td>0.5</td>
<td>10</td>
<td>24</td>
<td>0$^b$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$Isolated yield based on 1. $^b$In the absence of SmI$_2$ or Sm powder, no reaction occurred.

Finally, in order to investigate the limitations of this reductive polymerization, the reductive polymerization of dichlorosilanes bearing vinyl group was carried out with SmI$_2$/Sm mixed system in refluxing DME for 24 h. As shown in Table 4, both phenylvinyldisilane and methylvinyldisilane afforded the corresponding polysilanes [$R = \text{Ph}, M_n = 1760, M_w/M_n = 2.5, R$]
These results suggest that the SmI₂/Sm mixed system is promising reagent for the construction of a \( \zeta - \zeta \) conjugate system such as poly(vinylalkylsilane). These vinyl dichlorosilanes can be converted into the corresponding polyvinylsilanes without affecting the vinyl group. These vinyl polymers are profitable to form several functional polysilanes.

**Table 4.** Polymerization of R(vinyl)SiCl₂ with SmI₂/Sm in DME

\[
\begin{align*}
\text{Cl-Si-Cl} & \quad \text{SmI}_2 (1 \text{ mmol})/\text{Sm (3 mmol)} \quad \text{EtOH} \\
1 \; (1 \text{ mmol}) & \quad \text{DME (10 mL), reflux, 24 h} \\
& \quad \text{EtO}(\text{Si} \; \text{OEt})_n
\end{align*}
\]

<table>
<thead>
<tr>
<th>R</th>
<th>( M_n )</th>
<th>( M_w/M_n )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me</td>
<td>1740</td>
<td>2.3</td>
</tr>
<tr>
<td>Ph</td>
<td>1760</td>
<td>2.5</td>
</tr>
</tbody>
</table>

In summary, an efficient reductive dimerization of chlorosilanes has been achieved by the SmI₂/Sm mixed system in DME. A variety of chlorosilanes bearing hydrogen, vinyl, and tert-butyl groups can be converted conveniently into the corresponding disilanes. The procedure is applicable for the synthesis of poly(disilanylenephenylene) and poly(methylphenyl)silane.
5-2-4 Photoinduced reductive coupling reaction of silyl chlorides

As previous work, it is indicated that the visible-light irradiation extremely enhanced the reducing ability of SmI$_2$. Thus, the reductive coupling of organochlorosilanes by using this SmI$_2$-$h\nu$ system was attempted. At first, the visible-light-irradiated reductive dimerization of monochlorosilanes was examined (Table 5).

**Table 5. Photoinduced reductive coupling of organochlorosilanes**

<table>
<thead>
<tr>
<th>entry</th>
<th>$R^1R^2R^3Si$-Cl</th>
<th>SmI$_2$ (0.5 mmol)/Sm (1.5 mmol)</th>
<th>DME (2 mL), reflux, 3 h</th>
<th>$R^1R^2R^3Si$-$SiR^2R^3Si$</th>
<th>yield of 2 (%)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>dark $^b$</td>
</tr>
<tr>
<td>1</td>
<td>Ph$_2$MeSi</td>
<td>1b</td>
<td></td>
<td></td>
<td>64</td>
</tr>
<tr>
<td>2$^b$</td>
<td>Ph$_2$MeSi</td>
<td>1b</td>
<td></td>
<td></td>
<td>80</td>
</tr>
<tr>
<td>3</td>
<td>PhMe$_2$Si</td>
<td>1a</td>
<td></td>
<td></td>
<td>16</td>
</tr>
<tr>
<td>4</td>
<td>PhMeHSi</td>
<td>1d</td>
<td></td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>5$^c$</td>
<td>PhMeHSi</td>
<td>1d</td>
<td></td>
<td></td>
<td>10</td>
</tr>
<tr>
<td>6</td>
<td>SiPh$_2$</td>
<td>1f</td>
<td></td>
<td></td>
<td>61</td>
</tr>
</tbody>
</table>

$^a$Determined by $^1$H NMR. $^b$Reaction time: 5 h. $^c$Reaction time: 7 h.

Upon treatment with Sm/SmI$_2$ (3 equiv/1 equiv) in refluxing DME (84 °C) for 3 h in the dark, methyldiphenylsilyl chloride (1b) underwent reductive dimerization to give the corresponding disilane (2b) in 64 % yield (entry 1). Prolonged reaction time increased the yield of 2b (80 %, entry 2). Upon photoirradiation ($h\nu > 300$ nm), the desired disilane (2b) was obtained in higher
yield (90 %). The reductive dimerization of PhMe$_2$SiCl (1a) with Sm/SmI$_2$ in the dark for 3 h resulted in poor yield of the disilane (2a), whereas the photoirradiated reaction afforded the disilane (2a) in good yield (entry 3). In the case of PhMeHSiCl (1c), the reductive dimerization proceeded slowly (entry 4). However, the photoirradiation for 7 h improved the yield of the disilane (2c) (entry 5). Vinylic chlorosilane (1f) also underwent reductive dimerization successfully without affecting the vinyl group (entry 6).

5-2-5 Synthesis of polysilanes

Next, the reductive polymerization of dichloromethylphenylsilane (PhMeSiCl$_2$, 3) was examined by using the SmI$_2$/hν system and compared with the results of the polymerization with Sm/SmI$_2$ in the dark (Table 6). When dichloromethylphenylsilane (1 mmol) was treated with Sm (3 mmol)/SmI$_2$ (1 mmol) in refluxing DME (10 mL) for 24 h in the dark, the corresponding poly(phenylmethyl)silane (4) was formed in 78 % yield after quenching by EtOH (entry 1). The molecular weight distribution of this polymer was determined by gel permeation chromatography (GPC) calibrated by polystyrene standards with THF as the eluent ($M_n = 600, M_w/M_n = 2.1$). In contrast, when the same polymerization of PhMeSiCl$_2$ was conducted under photoirradiation ($h\nu > 315$ nm) for 6 h, the desired polysilane (4) was obtained in 66 % yield. The average molecular
weight and distribution of this polysilane are as follows: \( M_a = 2300, \frac{M_w}{M_n} = 1.1 \) (entry 2).

Compared with the polysilane obtained in the dark, the molecular weight was apparently increased, and the molecular weight distribution was extremely narrow (Table 6).

Table 6. Photoinduced polymerization of PhMeSiCl\(_2\) with SmI\(_2\)/Sm in DME\(^a\)

<table>
<thead>
<tr>
<th>entry</th>
<th>wavelength</th>
<th>yield of 4 (%)</th>
<th>( M_n )</th>
<th>( M_w/M_n )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>dark</td>
<td>78(^a)</td>
<td>600</td>
<td>2.1</td>
</tr>
<tr>
<td>2</td>
<td>&gt;315 nm</td>
<td>66</td>
<td>2300</td>
<td>1.1</td>
</tr>
<tr>
<td>3</td>
<td>&gt;350 nm</td>
<td>66</td>
<td>2300</td>
<td>1.2</td>
</tr>
<tr>
<td>4</td>
<td>&gt;435 nm</td>
<td>68</td>
<td>2400</td>
<td>1.3</td>
</tr>
<tr>
<td>5</td>
<td>&gt;455 nm</td>
<td>64</td>
<td>2200</td>
<td>1.2</td>
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<tr>
<td>6</td>
<td>&gt;485 nm</td>
<td>59</td>
<td>2400</td>
<td>1.2</td>
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<tr>
<td>7</td>
<td>&gt;550 nm</td>
<td>61</td>
<td>2300</td>
<td>1.2</td>
</tr>
</tbody>
</table>

\(^a\)DME reflux for 24 h.

Furthermore, the dependence of wavelength on this photoinduced reductive polymerization of 3 with Sm/SmI\(_2\) was investigated. The polymerization of PhMeSiCl\(_2\) with Sm/SmI\(_2\) was attempted by varying the wavelengths of light. The molecular weight of the polysilanes obtained is from 2200 to 2400, and the molecular weight distribution is from 1.1 to 1.3: the present SmI\(_2\)/h\(\nu\) system attains the extremely narrow molecular weight distribution.

UV-vis and photoluminescence spectra of the obtained polysilanes are shown in Fig. 1. The absorption peak at 317 nm and the emission peak at 351 nm are observed. These results
suggest the high purity of the polysilane (4) based on σ-conjugation. Owing to excellent oxygen affinity of samarium, oxygen and water contaminated in the reaction system were selectively trapped by samarium species, not forming -Si-O-Si- linkage.

Figure 1. UV-vis spectrum and emission spectrum of polysilane obtained upon photoirradiation (hν > 435 nm)

5-3 Conclusion

In summary, a novel photoinduced reduction of Si-Cl bond with Sm/SmI$_2$ mixed reagents in DME has been developed. We succeeded the synthesis of highly pure polysilanes, which has narrow molecular weight distribution ($M_w/M_n$ = 1.1-1.2).
5-4 Experimental Section

General comments. $^1$H NMR spectra were recorded on a JEOL JNM-AL (300 MHz) spectrometer using CDCl$_3$ as the solvent with tetramethylsilane (TMS) as the internal standard. $^{13}$C NMR spectra were obtained on a JEOL JNM-AL (75 MHz) spectrometer using CDCl$_3$ as the solvent. Chemical shifts in $^{13}$C NMR were measured relative to CDCl$_3$ and converted to δ TMS values by using δ 77.0 ppm. IR spectra were determined on a Perkin-Elmer Model 1600 spectrometer. Melting points were determined on a Yanagimoto micro melting point apparatus. Mass spectra were obtained on a JEOL JMS-DX303 instrument in the analytical section of Osaka University. Elemental analyses were also performed there.

DME was freshly distilled from sodium–benzophenone ketyl prior to use. Unless otherwise noted, chemical reagents were obtained from commercial suppliers and used directly. Samarium powder in oil (99.9%) was purchased from High Purity Chemicals and was used after washing with dry pentane, followed by drying for 4 h under reduced pressure. 1,2-Diiodoethane was purified by washing of its ether solution with saturated sodium thiosulfate, followed by removal of ether under reduced pressure.
Representative procedure for the reductive dimerization of organochlorosilanes mediated by the SmI\textsubscript{2}/Sm−DME mixed system. In a 20 mL two-necked flask equipped with a reflux condenser and a dropping funnel was placed samarium powder (4 mmol), 1,2-diiodoethane (1 mmol), and freshly distilled (sodium–benzophenone ketyl) DME (4 mL) under nitrogen atmosphere. The mixture was stirred at ambient temperature for 1 h, resulting in the formation of a dark blue solution of SmI\textsubscript{2}. After the addition of the substrates (1 mmol) to the solution, the flask was set in an oil bath maintained at 90 °C and the reaction mixture was stirred at the refluxing temperature for about 12 h. After the resulting solution was cooled to room temperature, the reaction mixture was treated with hydrochloric acid (1.5 mol/L, 20 mL) and extracted with methyl tert-butyl ether (10 mL x 3). The combined organic layer was washed with saturated NaHCO\textsubscript{3} solution and brine, dried over anhydrous MgSO\textsubscript{4}, and filtered. The solvent was removed under reduced pressure. Products were isolated by HPLC (silica gel 40–63 μm), with hexane or a mixture of hexane and dichloromethane (9:1) as an eluent.
Spectral and Analytical Data.

(a) 1,1,2,2-Tetramethyl-1,2-diphenyldisilane (2a) [1145-98-8].

\[
\text{Yield: 103 mg (76 %). Mp: 33–35 °C (mp 34–35 °C). } \]
\[
\text{H NMR } \delta (\text{CDCl}_3): 0.32 (s, 12H), 7.25–7.55 (m, 10H). \]
\[
\text{C NMR } \delta (\text{CDCl}_3): -3.93, 127.78, 128.49, 133.98, 139.10. \]
\[
\text{IR (neat) } \nu_{\text{max}}: 3049, 2956, 1427, 1259, 1105, 792, 698 \text{ cm}^{-1}. \]
\[
\text{MS: } m/z \text{ (relative intensity) 270 (10, M}^+) , 255 (5), 135 (100). \]

(b) 1,2-Dimethyl-1,1,2,2-tetraphenyldisilane (2b) [1172-76-5].

\[
\text{Yield: 177 mg (90 %). Mp: 143–145 °C (a white solid from ethanol) (mp 142–146 °C). } \]
\[
\text{H NMR } \delta (\text{CDCl}_3): 0.65 (s, 6H), 7.24–7.38 (m, 20H). \]
\[
\text{C NMR } \delta (\text{CDCl}_3): -5.14, 127.03, 128.14, 134.44, 135.80. \]
\[
\text{IR (KBr) } \nu_{\text{max}}: 3021, 1420, 1259, 1100 \text{ cm}^{-1}. \]
\[
\text{MS: } m/z \text{ (relative intensity) 394 (10, M}^+) , 379 (15), 197 (100). \]
(c) 1,1,1,2,2,2-Hexaphenyldisilane (2c) [1450-23-3].

\[
\text{Yield: 207 mg (80 %). Mp: 371 °C (a white solid from ethanol) (mp 365–367 °C). } ^1\text{H NMR } \delta_{\text{H}} (\text{CDCl}_3): 7.25–7.70 \text{ (m, 30H).} \quad ^{13}\text{C NMR } \delta_{\text{C}} (\text{CDCl}_3): 128.16, 130.40, 135.29, 136.79. \quad \text{IR } (\text{KBr}) \nu_{\text{max}}: 3040, 1423, 1105, 792, 698 \text{ cm}^{-1}. \quad \text{MS: } m/z \text{ (relative intensity) 518 (5, M$^+$), 259 (100).}
\]

(d) 1,1,1,2,2,2-Hexaphenyldisilane (2d) [1450-23-3].

\[
\text{Yield: 78 mg (64 %). Colorless oil (mp 105 °C (0.6 mmHg)). } ^1\text{H NMR } \delta_{\text{H}} (\text{CDCl}_3): 0.43 \text{ (d, 6H, } J = 2.7 \text{ Hz), 4.40 \text{ (q, 2H, } J = 3.3 \text{ Hz), 7.25–7.57 \text{ (m, 10H).} } ^{13}\text{C NMR } \delta_{\text{C}} (\text{CDCl}_3): -7.52, -7.73, 128.12, 129.17, 135.05, 137.45. \quad \text{IR (neat) } \nu_{\text{max}}: 3051, 2954, 2360, 2120, 1427, 1261, 1105, 792, 698 \text{ cm}^{-1}. \quad \text{MS: } m/z \text{ (relative intensity) 242 (5, M$^+$), 227 (5), 121 (100).} \quad \text{Anal. Calcd for C}_{14}\text{H}_{18}\text{Si}_{2}: \text{ C, 69.35; H, 7.48.} \quad \text{Found: C, 69.38; H, 7.52.}
\]
(e) 1,1,2,2-Tetraphenyldisilane (2e) [16343-18-3].

Yield: 128 mg (70 %). Mp: 77–78 °C (a white solid from ethanol) (mp 76.5–80.5 °C). $^1$H NMR $\delta_H$ (CDCl$_3$): 5.18 (s, 2H), 7.45–7.48 (m, 8H), 7.25–7.38 (m, 12H). $^{13}$C NMR $\delta_C$ (CDCl$_3$): 128.15, 129.51, 132.51, 136.12. IR (KBr) $\nu_{max}$: 3064, 3043, 2360, 2119, 1483, 1425, 1261, 1101, 1024, 790, 738, 694, 657 cm$^{-1}$. MS: $m$/z (relative intensity) 366 (10, M$^+$), 183 (100). HRMS: $m$/z calcd, 366.613 08; $m$/z found, 366.613 15. Anal. Calcd for C$_{24}$H$_{22}$Si$_2$: C, 78.63; H, 6.05. Found: C, 78.35; H, 6.06.
(f) 1,1,2,2-Tetraphenyl-1,2-divinyldisilane (2f).

\[
\begin{align*}
\text{Yield: } & 178 \text{ mg (85 \%)} . & \text{Mp: } 125−127 ^\circ \text{C (a white solid from methanol)}. & \text{\textsuperscript{1}H NMR } \delta_{\text{H}} (\text{CDCl}_3): \\
& 5.68 (\text{dd}, 2\text{H}, J = 3.6, 20.1 \text{ Hz}), & 6.19 (\text{dd}, 2\text{H}, J = 3.6, 14.4 \text{ Hz}), & 6.52 (\text{dd}, 2\text{H}, J = 14.4, 20.1 \text{ Hz}), \\
& 7.23−7.62 (\text{m}, 20\text{H}). & \text{\textsuperscript{13}C NMR } \delta_{\text{C}} (75 \text{ MHz, CDCl}_3): & 128.01, 129.35, 134.42, 134.56, 136.29, \\
& & & 136.45. & \text{IR (KBr) } \nu_{\text{max}}: & 3068, 3049, 2960, 2360, 1593, 1427, 1255, 1116, 794, 732, 698 \text{ cm}^{-1}. \\
& & & \text{MS: } m/z (\text{relative intensity}) & 418 (5, \text{M}^+), & 390 (10), & 263 (7), & 259 (65), & 209 (50), & 183 (100). & \text{Anal. Calcd for } \text{C}_{28}\text{H}_{26}\text{Si}_2: & \text{C, 80.32; H, 6.26. Found: C, 80.69; H, 6.29.} \\
\end{align*}
\]

(g) 1,2-Di-tert-butyl-1,1,2,2-tetramethyldisilane (2g).

\[
\begin{align*}
\text{Yield: } & 93 \text{ mg (81 \%)} . & \text{Mp: } 60 ^\circ \text{C (70 mmHg)}. & \text{\textsuperscript{1}H NMR } \delta_{\text{H}} (\text{CDCl}_3): & 0.06 (\text{s}, 12\text{H}), & 0.88 (\text{s}, 18\text{H}). & \text{\textsuperscript{13}C NMR } \delta_{\text{C}} (\text{CDCl}_3): & -3.73, 18.22, 25.59. & \text{IR (neat) } \nu_{\text{max}}: & 2954, 2892, 1251 \text{ cm}^{-1}. \\
& & & \text{MS: } m/z (\text{relative intensity}) & 230 (4, \text{M}^+), & 173 (5), & 158 (7), & 143 (6), & 115 (100). & \text{Anal. Calcd for } \text{C}_{12}\text{H}_{30}\text{Si}_2: & \text{C, 62.52; H, 13.12. Found: C, 62.48; H, 13.09.} \\
\end{align*}
\]
Reductive dimerization of chlorodiphenylmethylsilane mediated by the SmI$_2$/Sm–DME mixed system. In a 100 mL two-necked flask equipped with a reflux condenser and a dropping funnel were placed samarium powder (15 mmol), 1,2-diiodoethane (5 mmol), and freshly distilled (sodium–benzophenone ketyl) DME (40 mL) under nitrogen atmosphere. The mixture was stirred at ambient temperature for 1.5 h, resulting in the formation of a dark blue solution of SmI$_2$. After the addition of chlorodiphenylmethylsilane (10 mmol) to the solution, the flask was set in an oil bath maintained at 90 °C and the reaction mixture was refluxed for about 12 h. After the resulting mixture was cooled to room temperature, the reaction mixture was treated with hydrochloric acid (1.5 mol/L, 20 mL) and extracted with diethyl ether (40 mL x 3). The combined organic layer was washed with saturated NaHCO$_3$ solution and brine, dried over anhydrous MgSO$_4$, and filtered. The solvent was removed under reduced pressure. The crude product was purified by recrystallization from ethanol.

1,2-Dimethyl-1,1,2,2-tetraphenyldisilane (2b). Yield: 1.812 g (92 %). Mp: 144−146 °C. $^1$H NMR $\delta_H$ (CDCl$_3$): 0.66 (s, 6H), 7.30–7.41 (m, 20H). $^{13}$C NMR $\delta_c$ (CDCl$_3$): −5.14, 127.03, 128.14, 134.44, 135.80. IR (KBr) $\nu_{max}$: 3021, 1420, 1255, 1100 cm$^{-1}$. 
General procedure for the reductive polymerization of 1,4-bis(dimethylchlorosilyl)benzene mediated by the SmI$_2$/Sm−DME system. In a 50 mL three-necked flask equipped with a reflux condenser and a dropping funnel were placed samarium powder (8 mmol), 1,2-diiodoethane (2 mmol), and freshly distilled (sodium–benzophenone ketyl) DME (20 mL) under nitrogen atmosphere. The mixture was stirred at ambient temperature for 1 h, resulting in the formation of a dark blue solution of SmI$_2$. After the addition of 1,4-bis(dimethylchlorosilyl)benzene (2 mmol) to the solution, the flask was set in an oil bath maintained at 90 °C. The reaction mixture was refluxed for another 24 h. After the resulting mixture was cooled to room temperature, the reaction mixture was treated with EtOH (5 mL), poured into hydrochloric acid (1.5 mol/L, 30 mL), and extracted with diethyl ether (40 mL x 3). The combined organic layer was washed with saturated NaHCO$_3$ solution and brine, dried over anhydrous MgSO$_4$, and filtered. The solvent was removed under reduced pressure, providing a white crude product. The residual crude polymer was dissolved in THF (2 mL) and purification of the product was performed by precipitation by the addition of ethanol (100 mL) to the solution.

Poly(disilanylene phenylene). Yield: 282 mg (73 %). $^1$H NMR $\delta$$_H$ (CDCl$_3$): 0.25–0.46 (m, 12H), 7.24–7.46 (m, 4H). IR (KBr) $\nu_{max}$: 3066, 3049, 2956, 1427, 1259, 1105, 1066, 1026, 792, 696 cm$^{-1}$. $M_n$ = 2480, $M_w$ = 2976, $M_w/M_n$ = 1.2.
**Polymerization of dichloromethylphenylsilane with the SmI$_2$/Sm–DME system.** In a 250 mL three-necked flask equipped with a reflux condenser and a dropping funnel were placed samarium powder (40 mmol), 1,2-diiodoethane (10 mmol), and freshly distilled (sodium–benzophenone ketyl) DME (100 mL) under nitrogen atmosphere. The mixture was stirred at ambient temperature for 1.5 h, resulting in the formation of a dark blue solution of SmI$_2$. After the addition of dichloromethylphenylsilane (10 mmol) to the solution, the flask was set in an oil bath maintained at 90 °C. The reaction mixture was refluxed for additional 24 h. After the resulting mixture was cooled to room temperature, the reaction mixture was treated with EtOH (20 mL), poured into hydrochloric acid (1.5 mol/L, 40 mL), and extracted with diethyl ether (50 mL x 3). The combined organic layer was washed with saturated NaHCO$_3$ solution and brine, dried over anhydrous MgSO$_4$, and filtered. The solvent was removed under reduced pressure, providing a white crude product. The residual crude polymer was dissolved in THF (50 mL) and the desired polymer was precipitated by the addition of ethanol (300 mL) to the solution. The molecular weight of the polymer was determined by gel permeation chromatography (GPC) calibrated by polystyrene standards with chloroform as the eluent.

**Poly(methylphenyl)silane.** Yield: 0.492 g (41 %). $^1$H NMR $\delta$ (CDCl$_3$): $-0.85$–$0.86$ (m, 3H), $6.40$–$7.46$ (m, 5H). IR (KBr) $\nu_{\text{max}}$: 3056, 2956, 1427, 1250, 1105 cm$^{-1}$. UV (THF): $\lambda_{\text{max}}$ (log $\varepsilon$) 338 nm. $M_n = 1550, M_w = 3906, M_w/M_n = 2.52$. 


Polymerization of dichloromethylphenylsilane with the SmI\(_2\)/Sm/Mg–DME system. In a 50 mL three-necked flask equipped with a reflux condenser and a dropping funnel was placed samarium powder (2.5 mmol), 1,2-diiodoethane (1 mmol), magnesium (10 mmol), and freshly distilled (sodium–benzophenone ketyl) DME (20 mL) under nitrogen atmosphere. The mixture was stirred at ambient temperature for 1 h. After the addition of dichloromethylphenylsilane (2 mmol) to the solution, the flask was set in an oil bath maintained at 90 °C. The reaction mixture was refluxed for additional 24 h. After the resulting mixture was cooled to room temperature, the reaction mixture was treated with EtOH (5 mL), poured into hydrochloric acid (1.5 mol/L, 30 mL), and extracted with diethyl ether (40 mL x 3). The combined organic layer was washed with saturated NaHCO\(_3\) solution and brine, dried over anhydrous MgSO\(_4\), and filtered. The solvent was removed under reduced pressure, providing a white crude product. The residual crude polymer was dissolved in THF (2 mL) and the desired polymer was precipitated by the addition of ethanol (100 mL) to the solution. Yield: 0.103 g (43 %). \(^1\)H NMR δ\(\text{H}\) (CDCl\(_3\)): −0.84 to −0.88 (m, 3H), 6.41–7.47 (m, 5H). IR (KBr) \(\nu_{\text{max}}\): 3056, 2956, 1427, 1250, 1105 cm\(^{-1}\). UV (THF): \(\lambda_{\text{max}}\) (log \(\varepsilon\)): 338 nm. \(M_n = 4650\), \(M_w = 6975\), \(M_w/M_n = 1.5\).
5-5 References


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Chapter 6  Conclusion

In this research, the author has clarified characteristic features of low-valent rare earth reagents under photoirradiation and has developed useful synthetic methods of polysilanes.

In chapter 2, the author has investigated the generation and reducing ability of a series of low-valent rare earths systematically. In the cases of La, Ce, Pr, Nd, Sm, Eu, and Yb, it has been shown that the mixed systems of rare earths (“LnI$_2$/LnI”) indicate potentially higher reducing ability, compared with Ln or LnI$_2$ single system. More importantly, it has been revealed that photoirradiation can induce excellent reducing ability of low-valent rare earths in the cases of most of rare earths species. It is expected that “the excited low-valent rare earth” exhibits higher reducing ability than “the low-valent rare earth species in the ground state”.

In chapter 3, the author has developed the photoirradiated atmospheric carbonylation of organic halides with samarium diiodide. Under the atmospheric pressure of carbon monoxide, the photoinduced reductive carbonylation of organic halides (RX) with samarium diiodide (SmI$_2$) successfully took place to provide the corresponding unsymmetrical ketones (RC(O)CH$_2$R) in good yields. Mechanistic insight into this carbonylation, especially the pathway for the generation of acylsamarium species (RC(O)SmI$_2$) as a key intermediate, was also investigated in detail.

In chapter 4, the author has developed that lanthanide metals, such as Ce, Nd, Sm, and Eu metals indicate higher reducing abilities under photoirradiation toward the reductive transformation
of acid chlorides. By using these novel photoinduced reduction systems of rare earth metals, benzoyl chloride reacts with dienes and styrenes, giving the corresponding coupling products in good yields.

In chapter 5, the author has developed a novel photoinduced reduction of Si-Cl bond with SmI$_2$/Sm mixed reagents in DME. The author has succeeded the synthesis of polysilanes, and the obtained polysilane has narrow molecular weight distribution ($M_w/M_n = 1.1 - 1.2$). It should be noted that the SmI$_2$-$h\nu$ system is valuable for synthesis of highly pure polysilanes. Furthermore, vinyl group-substituted polysilanes can be obtained, and therefore these reaction systems are useful for creating polysilane materials.
List of Publication

The content of this thesis has been published in the following papers.

1. A Novel Photoinduced Reduction of Haloalkanes with Rare Earth Metals  
   Tomisaka, Y.; Tsuchii, K.; Ogawa, A.  
   (Chapter 2)

2. On the Potentially Excellent Reducing Ability of a Series of Low-Valent Rare Earths Induced by Photoirradiation  
   Tomisaka, Y.; Nomoto, A.; Ogawa, A.  
   (Chapter 2)

3. Novel Reducing Properties by the Combination of SmI$_2$ and a Series of Lanthanoid Metals  
   Tomisaka, Y.; Yoshimura, A.; Nomoto, A.; Sonoda, M.; Ogawa, A.  
   (Chapter 2)

   Tomisaka, Y.; Harato, N.; Sato, M.; Nomoto, A.; Ogawa, A.  
   (Chapter 3)

5. Photoaccelerated Reductive Coupling of Acid Chlorides with Conjugate Dienes and Styrenes by Use of Neodymium Metal in N,N-Dimethylacetamide  
   Li, Z.; Tomisaka, Y.; Nomoto, A.; Zhang, Y.; Ogawa, A.  
   (Chapter 4)

6. New Entry to the Construction of Si-Si Linkages: Sm/SmI$_2$-Induced Efficient Reductive Coupling of Organochlorosilanes  
   (Chapter 5)
7. A Novel Synthetic Method of Highly Pure Polysilanes: Photoinduced Reductive Coupling of Organochlorosilanes by SmI$_2$/Sm in DME

Tomisaka, Y.; Nomoto, A.; Yoshimura, A.; Kusano, H.; Li, Z.; Sonoda, M.; Ogawa, A.


(Chapter 5)
List of Other Publication

1. Reductive Carboxylation of Alkyl Halides with CO₂ by Use of Photoinduced SmI₂/Sm Reduction System
   Nomoto, A.; Kojo, Y.; Shiino, G.; Tomisaka, Y.; Mitani, I.; Tatsumi, M.; Ogawa, A.

2. Cerium Reagents in Organic Synthesis
   Sumino, Y.; Tomisaka, Y.; Ogawa, A.

3. A Highly Efficient Reduction of Group 14 Heteroatom-Chlorine Single Bonds by Using Samarium Diiodide-Mediated Reaction System
   Kamiya, I.; Iida, K.; Harato, N.; Li, Z.; Tomisaka, Y.; Ogawa, A.

   Sumino, Y.; Harato, N.; Tomisaka, Y.; Ogawa, A.
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