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On the potentially excellent reducing ability of a series of low-valent rare earths induced by photoirradiation

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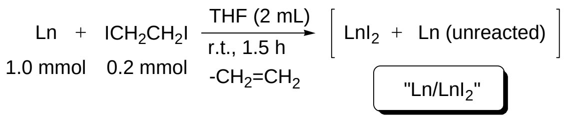
ABSTRACT

Mixed systems of a series of rare earth metals such as La, Ce, Pr, Nd, Sm, Eu, and Yb and their low-valent rare earth diiodides exhibit excellent reducing ability toward the reductive deiodation from 1-iodododecane as a model compound compared with their single systems. More importantly, *under photoirradiation conditions*, the C–I bond reduction using ‘Ln/LnI$_2$’ takes place efficiently in refluxing THF, even in the cases of heavy rare earths such as Gd, Tb, Dy, Ho, Er, and Tm.

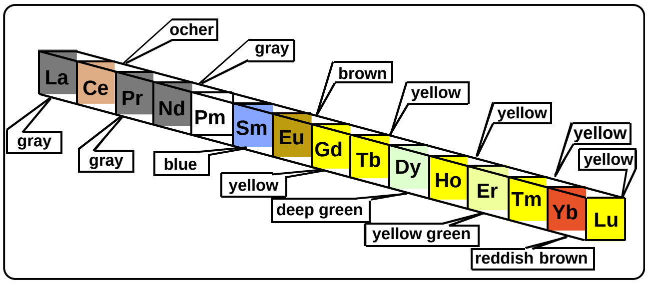
Lanthanoid elements have electron(s) in f-orbitals, and should indicate characteristic reactivities on the basis of the nature of f-electrons.[1] However, systematic studies on the reactivities of a series of lanthanoid species are still rare. During the course of our study on the clarification of the characteristic features of rare earth compounds and their application to synthetic reactions, we have revealed two novel findings: (i) the combination of samarium(II) diiodide and samarium metal enhances the reducing ability compared with that of their single systems;[2,3] (ii) visible light irradiation dramatically enhances the reducing ability of SmI$_2$.[4,5] To clarify similar enhancement of the reducing ability of other rare earth species by the combination of divalent and zerovalent species or by photoirradiation,[6,7] we have 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. In this Letter, we wish to report a novel finding that *most of low-valent rare earth species exhibit their potentially excellent reducing abilities under photoirradiation conditions*.

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

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 the Sm, Eu, and Yb, the corresponding divalent diiodides (LnI$_2$) were apparently formed, according to the literature.[8] Similar observation concerning other rare earths strongly suggests the generation of low-valent rare earth species such as LnI$_2$.



Scheme 1. Preparation of ‘Ln/LnI$_2$’ reagents.



Scheme 2. Color of the THF solution of ‘Ln/LnI$_2$’.

Next, we examined the reduction of 1-iodododecane by use of these binary systems of divalent and zero valent rare earth reagents (‘Ln/LnI$_2$’) in the presence of 2-propanol as a proton source (Scheme 3), and the results are summarized in Figure 1.[9] As can be seen from Figure 1, the reduction took place successfully in the cases of La, Ce, Pr, Nd, Sm, Eu, and Yb providing *n*-dodecane as the major product (shown in the third line in Fig. 1) along with small amounts of the corresponding coupling product (n-$C_{24}H_{50}$, the second line) and disproportionation products (n-$C_{10}H_{21}CH{=}CH_2$ (the first line) and n-$C_{12}H_{26}$).[10]

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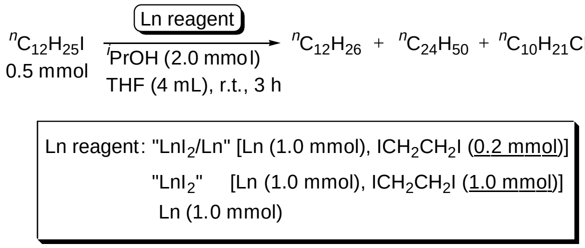

Scheme 3. Reduction of 1-iodododecane by use of rare earths reagents.

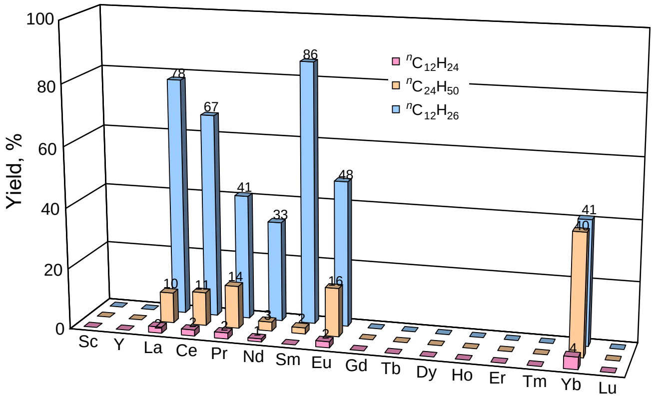

Figure 1. Reduction of 1-iodododecane with 'Ln/LnI$_2$' system (r.t., 3 h).

However, 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 (the first line in Fig. 2).[11–13] Furthermore, when the reduction of 1-iodododecane was carried out by employing equimolar amounts of Ln metal (1.0 mmol) and ICH$_2$CH$_2$I (1.0 mmol) (which may form 'LnI$_2$' reagents), the desired reduced products were obtained in very low yields (the second line in Fig. 2): the yields of n-$C_{12}H_{26}$ were 19% (La); 15% (Ce); 12% (Pr); 7% (Nd); 8% (Sm); 1% (Yb).[14,15] These results strongly suggest that the binary systems of 'Ln(0)/Ln(II)' (the third line) exhibit higher reducing ability compared with the Ln(0) or 'LnI$_2$' single system.

In the case of Sm, we have revealed that SmI$_2$ (a dark blue solution 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, we examined the same reduction of 1-iodododecane by using a series of 'Ln/LnI$_2$' systems upon irradiation through Pyrex (>300 nm) with a xenon lamp (500 W) during the reactions ('Ln/LnI$_2$/$h\nu$' systems[16]).

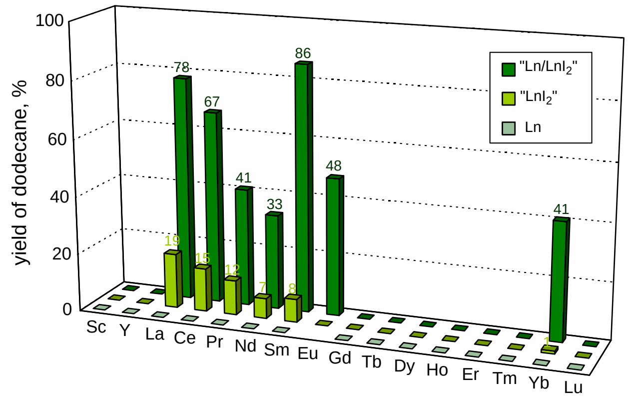

Figure 2. Reduction of 1-iodododecane by use of low-valent rare earths reagents (r.t., 3 h).

Interestingly, the reduction using the 'Ln/LnI$_2$/$h\nu$' systems proceeded very smoothly in the cases of La, Ce, Pr, Nd, Sm, Eu, and Yb.[17] In the cases of Pr and Nd, especially, the photoinduced enhancement of the reducing ability appeared remarkable [yield of dodecane; Nd: 33% (dark), 67% ($h\nu$), Pr: 41% (dark), 75% ($h\nu$)]. Noteworthy is that, in the cases of 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% (Ho)], despite the same reduction in the dark did not occur at all. Furthermore, the attempted photoinduced reduction using Y, Dy, and Er suggests the possibility of the photoactivation.

We compiled these results and compared with the results in the dark conditions (Fig. 3). Figure 3 clearly indicates that the photoirradiation increases the reducing ability of a series of low-valent rare earths species for the reductive deiodation of 1-iodododecane.

To increase the conversion, we examined the reaction under refluxing condition of THF (67 °C) for extended reaction time (20 h) (Fig. 4). The 'Ln/LnI$_2$' 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 cases of Tb and Dy upon photoirradiation, the yields of dodecane were almost the same as those when the reaction was

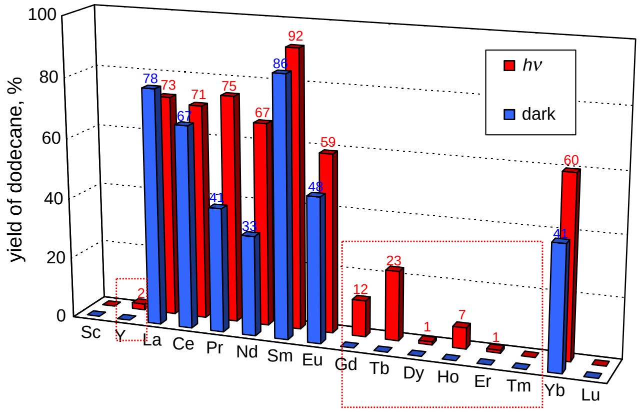

Figure 3. Influence of photoirradiation on the 'Ln/LnI$_2$'-induced reduction.

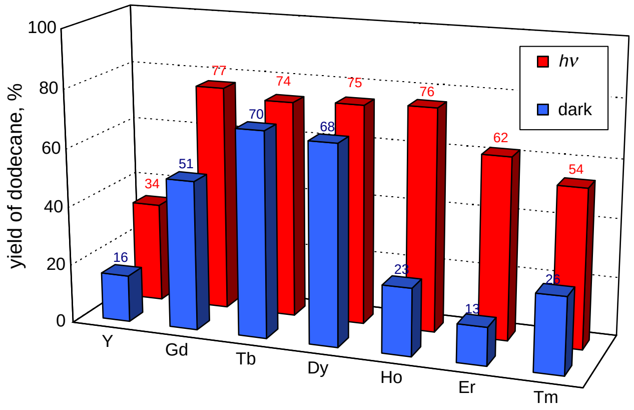

Figure 4. Reduction of 1-iodododecane with heavy rare earth reagents (67 °C, 20 h).

conducted at 67 °C for 20 h in the dark [yield of dodecane; Tb: 70% (dark), 74% ($h\nu$), Dy: 68% (dark), 75% ($h\nu$)]. However, the decrease in the reaction time (8 h) clearly indicates that the influence of the photoirradiation was recognized more definitely: the yields of n-$C_{12}H_{26}$ were 2% (dark), 33% ($h\nu$) [Tb]; 3% (dark), 46% ($h\nu$) [Dy].

In summary, we have investigated the generation and reducing ability of a series of low-valent rare earths systematically. In the case of light rare earths as La, Ce, Pr, Nd, Sm, Eu, and Yb, it has been shown that the mixed-valent rare earths ('Ln/LnI_2') 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. As shown in the cases of SmI_2 and YbI_2 typically, divalent lanthanoid diiodides have their absorption in near UV and/or visible region based on the 4f–5d excitation. Accordingly, it is expected that 'the photoinduced divalent rare earth species in the excited state' exhibits higher reducing ability than 'the divalent rare earth species in the ground state'.[4f,18] We believe that this finding will open up a new field of rare earth chemistry.

Acknowledgments

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7. 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.
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9. 'Ln/LnI_2' 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 (0.2 mmol), and freshly distilled (sodium/benzophenone ketyl) THF (2 mL) under a nitrogen atmosphere. The mixture was stirred for 1.5 h at room temperature. In all cases of rare earths, the color of the solution was changed, and unreacted Ln metal was insoluble in THF. To the resulting suspension of 'Ln/LnI_2' in THF were added dropwise a solution of 1-iodododecane (0.5 mmol), 2-propanol (2.0 mmol), and tetradecane (n-$C_{14}H_{30}$, 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.[19] Aqueous saturated $NaHCO_3$ (40 mL) was added to the reaction mixture, and the products were extracted with Et_2O (20 mL × 3). The combined extracts were dried over anhydrous $MgSO_4$, and filtered off. The resulting solution was analyzed by GC.[20]
10. In the case of Yb, the reductive dimerization product (n-$C_{24}H_{50}$) was obtained in the similar yield as that of the reduction product (n-$C_{12}H_{26}$). Relatively lower solubility of YbI_2 in THF may contribute to the dimerization of n-$C_{12}H_{25}$.
11. In general, high-grade lanthanoide 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, we filed Eu ingot to 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.
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13. Ln Systems: 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 a nitrogen atmosphere. The mixture was stirred for 1.5 h at room temperature (to attain the identical conditions). In all cases of rare earths, the color of the solution was not changed, and unreacted Ln metal was insoluble in THF. To the resulting suspension of Ln metal in THF 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.
14. The color of solutions changed similarly as described about the Ln(0)/Ln(II) binary system. In the cases of Gd, Tb, Dy, Ho, Er, Tm, and Lu, however, most of metals were observed to remain unchanged.
15. LnI_2 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 a nitrogen atmosphere. The mixture was stirred for 1.5 h at room temperature. In the cases of Ce, Pr, Nd and Sm, the color of the solution was changed and homogeneous solution was formed. In other rare earths, the color of the solution was not changed, and unreacted Ln metal existed. To the resulting THF solution or suspension of 'LnI_2' 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.
16. 'Ln/LnI_2/$h\nu$' systems: To the THF solution of 'Ln/LnI_2' 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 xenon 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.
17. In the cases of SmI_2 and YbI_2, similar reduction of the corresponding chloride and bromide took place successfully upon photoirradiation. See Refs. 4a and b: Ogawa, A.; Ohya, S.; Sumino, Y.; Sonoda, N.; Hirao, T. *Tetrahedron Lett.* **1997**, *38*, 9017.
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20. 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.