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Samarium(II)-Mediated Pinacol Coupling in Water: Occurrence of Unexpected Disproportionation and Action of Low-Valent Samarium as an Active Species

Satoru Matsukawa* and Yumi Hinakubo

Department of Science, Faculty of Education, Ibaraki University,
Mito, Ibaraki 310-8512, Japan

smatsuka@mx.ibaraki.ac.jp

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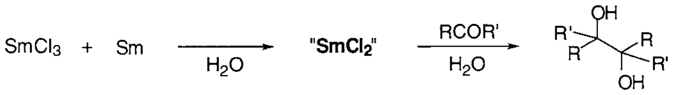
ABSTRACT



Mechanistic studies of one-electron reduction in water using samarium were carried out. Unexpected disproportionation in water was observed via UV–vis spectroscopic analysis. This fact indicates that low-valent samarium species can exist in water. Furthermore, the $SmCl_3$–Sm and $SmCl_3$–Mg systems were found to act as good one-electron reducing agents in water.

The use of samarium as a single electron transfer reagent in organic synthesis has been developed, and numerous examples, such as coupling, reduction, cyclization, and the Barbier reaction, have been widely studied and utilized.[1,2] On the other hand, the use of water as a solvent for organic reactions has been attracting attention because of its advantages with regard to environmental concerns, and numerous successful reactions have been reported.[3,4] Samarium-mediated reactions in aqueous media have also been reported; however, the mechanism underlying these reactions remains unclear.[5] To develop this environmentally benign method, we investigated the mechanism of these samarium-mediated reactions. A low-valent samarium species was found to exist in water and act as a one-electron reducing agent.

Initially, we conducted UV−vis spectroscopic analysis to obtain information on the reaction intermediates.[6] UV−vis

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[3] For reviews on organic reactions in water, see: (a) Li, C.-J. *Chem. Rev.* **1993**, *93*, 2023. (b) Lubineau, A.; Auge, J.; Queneau, Y. *Synthesis* **1994**, 741. (c) Li, C.-J.; Chen, T.-H. *Organic Reactions in Aqueous Media*; John Wiley & Sons: New York 1997. (d) *Organic Synthesis in Water*; Grieco, P. A., Ed.; Blackie Academic & Professional: Glasgow, 1998. (e) Li, C.-J.; Chen, T.-H. *Tetrahedron.* **1999**, *55*, 11149.

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[5] (a) Wang, L.; Zhang, Y. *Tetrahedron Lett.* **1998**, *39*, 5257. (b) Wang, L.; Zhang, Y. *Tetrahedron* **1999**, *55*, 10695. (c) Talukdar, S.; Fang, J.-M. *J. Org. Chem.* **2001**, *66*, 330. Reaction in MeOH, see: (d) Ghatak, A.; Becker, F. F.; Banik, B. K. *Tetrahedron Lett.* **2000**, *41*, 3793. (e) Yu, C.; Liu, B.; Hu, L. *J. Org. Chem.* **2001**, *66*, 919.

[6] Flowers reported mechanistic studies of Sm(II) species including UV−vis analysis of $SmCl_2$, $SmBr_2$, and SmI_2. (a) Miller, R. S.; Sealy, J. M.; Shabangi, M.; Kuhlman, M. L.; Fuchs, J. R.; Flowers, R. A., II. *J. Am. Chem. Soc.* **2000**, *122*, 7718. Also see: (b) Shabangi, M.; Sealy, J. M.; Fuchs, J. R.; Flowers, R. A., II. *Tetrahedron Lett.* **1998**, *39*, 4429. (c) Kuhlman, M. L.; Flowers, IR. A., II. *Tetrahedron Lett.* **2000**, *41*, 8049. (d) Knetlle, B. W.; Flowers, R. A., II. *Org. Lett.* **2001**, *3*, 2321.

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spectroscopic analysis indicated the existence of the low-valent samarium species (Figure 1). Addition of samarium powder to 0.1 M HCl resulted in a color change to reddish purple, and absorption was observed at about 560 nm, the characteristic absorption of Sm(II).[7] These results suggested that a low-valent samarium species such as $SmCl_2$ could exist and act as an active species in water. However, this solution was unstable, and the absorption immediately disappeared, accompanied by a color changed to yellow, possibly due to $SmCl_3$ formation. To obtain a more stable low-valent samarium species, another investigation was conducted using $SmCl_3$ and Sm powder. $SmCl_3$ in H_2O is a pale yellow solution. After Sm powder was added to the solution, the color gradually changed to reddish purple, and absorption was observed at about 560 nm. This result indicated that disproportionation occurred; that is, $SmCl_3$ was reduced by Sm powder.[8] This reddish purple solution was comparatively stable; indeed, absorption at 560 nm remained after 30 min. It is noteworthy that low-valent samarium species are known to be unstable in water;[9] however, this $SmCl_3$−Sm system gave stable low-valent samarium species, even in water (Scheme 1).

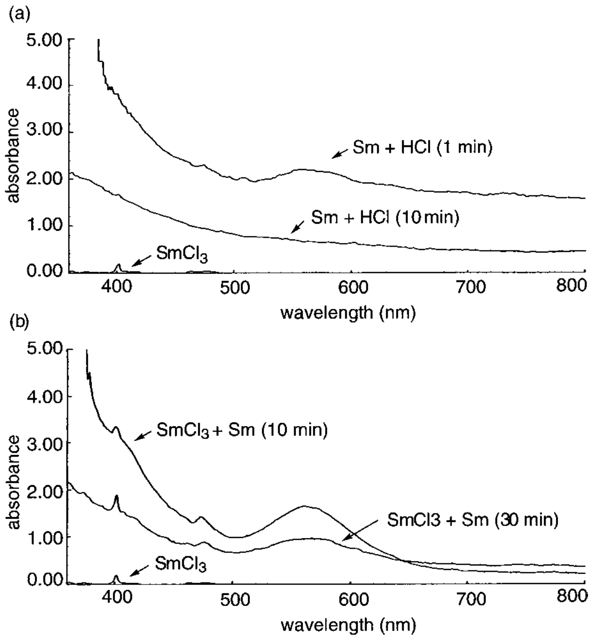


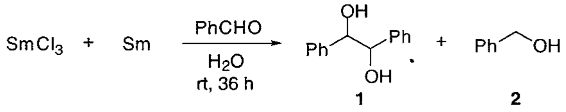
Figure 1. UV−vis spectra of samarium powder in 0.1 M HCl (a) and UV−vis spectra of $SmCl_3$ and samarium powder (b) at 20 °C.

Scheme 1

$$SmCl_3 + Sm \xrightarrow[H_2O]{} \text{"}SmCl_2\text{"}$$

To investigate this water-based $SmCl_3$−Sm system, it was applied to the pinacol coupling (Table 1).[10,11] As expected, the coupling product was obtained in good yield using 1 equiv of $SmCl_3$ and 3 equiv of Sm powder. The equimolar mixture of $SmCl_3$ and Sm powder was ineffective in this reaction, owing to their sluggish disproportionation. Interestingly, the $SmBr_3$−Sm and SmI_3−Sm systems exhibited lower reactivity.[12] Various aldehydes and ketones were screened to examine the generality of this reaction (Table 2). In the case of aromatic aldehydes and ketones, the coupling product

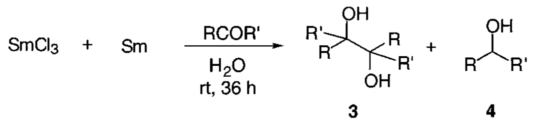
Table 1. $SmCl_3$-Sm-Mediated Pinacol Coupling of Benzaldehyde in Water



entry	ratio (mmol) (Sm/$SmCl_3$/PhCHO)	yield (%)	
		1 (*dl*/*meso*)[a]	**2**[a]
1	1.0:1.0:1.0	trace	5
2	2.0:1.0:1.0	52 (55:45)	2
3	3.0:1.0:1.0	81 (58:42)	2
4[b]	3.0:1.0:1.0	25 (51:49)	trace
5[c]	3.0:1.0:1.0	32 (43:57)	10
6	0:3.0:1.0	0	0
7	3.0:0:1.0	trace	0

[a] Isomeric ratio was detemrined by GC analysis and/or or ^1H NMR spectra. [b] $SmBr_3$ was used instead of $SmCl_3$. [c] SmI_3 was used instead of $SmCl_3$.

Table 2. $SmCl_3$−Sm-Mediated Pinacol Coupling in Water[a]



entry	RCOR′	yield (%)	
		3 (*dl*/*meso*)	4
1	PhCHO	81 (52:48)	2
2	4-$MeOC_6H_4CHO$	75 (52:48)	16
3	4-$CF_3C_6H_4CHO$	83 (56:44)	5
4	4-ClC_6H_4CHO	71 (56:44)	11
5	$PhCOCH_3$	75 (54:46)	2
6	3-$MeOC_6H_4COCH_3$	0	48
8	$PhCH_2CH_2COCH_3$	0	62

[a] Sm/$SmCl_3$/RCOR′ = 2:1:1. [b] Isomeric ratio was determined by ^1H NMR spectra.

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(7) (a) Evans, D. F.; Fazakerley, G. V.; Philips, R. F. *J. Chem. Soc. A* **1971**, 1931. (b) Girard, P.; Namy, J. L.; Kagan, H. B. *J. Am. Chem. Soc.* **1980**, *102*, 2693. Endo reported formation of SmI_2 from SmI_3 and Mg, which was detected by UV−vis analysis: Nomura, R.; Matsuno, T.; Endo, T. *J. Am. Chem. Soc.* **1996**, *118*, 11666.

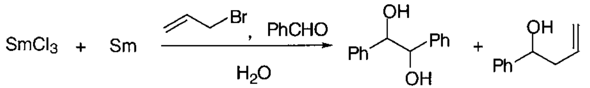
(8) Ogawa and Sonoda reported that SmI_3 was reduced by Sm powder in THF; see: Ogawa, A.; Takami, N.; Sekiguchi, M.; Ryu, I.; Kambe, N.; Sonoda, N. *J. Am. Chem. Soc.* **1992**, *114*, 8729. Also see: Murakami, M.; Hayashi, M.; Ito, Y. *Synlett* **1994**, 179.

(9) Although, addition of water to the SmI_2/THF system is reported to enhance the reductive potential, this is not supported by our research, see: Hasegawa, E.; Curran, D. P. *J. Org. Chem.* **1993**, *58*, 5008.

was obtained in good yield. On the other hand, unimolecular reduction occurred using aliphatic aldehydes and ketones. A solid substrate also resulted in good yield.

To obtain insight into the characteristic features of this low-valent samarium species, the Barbier reaction of benzaldehyde and allyl bromide was examined using the $SmCl_3$−Sm system (Scheme 2). Interestingly, the allylated product

Scheme 2



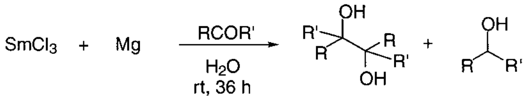
3 (*dl*/*meso*)
71 (51 : 49)

5
trace

was not obtained, while the coupling product was obtained in good yield.[13] In this case, allyl bromide might act as an activator of Sm metal. The detailed mechanism is now under investigation in our laboratory.

Furthermore, we found that the $SmCl_3$−Mg system also acts as a good one-electron reducing agent (Scheme 3).

Scheme 3



RCOR'	**3** (*dl*/*meso*)	**4**
PhCHO	78 (54 : 46)	trace
$PhCOCH_3$	58 (52 : 48)	trace

Indeed, the coupling products were obtained in good yield using 1 equiv of $SmCl_3$ and 3 equiv of Mg powder.

In summary, we demonstrated pinacol coupling using samarium in water. Unexpected disproportionation in water was detected via UV−vis spectroscopic analysis. This fact indicates that low-valent samarium species can exist in water. Furthermore, the $SmCl_3$−Sm and $SmCl_3$−Mg systems were found to act as good one-electron reducing agents in water. We believe that may provide a new method for water-mediated organic reactions.

Supporting Information Available: Experimental details for the Sm(II)-mediated pinacol coupling reactions in water. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) $SmCl_3$-associated electroreductions were reported; see: (a) Léonard, E.; Duñach, E.; Périchon, J. *J. Chem. Soc., Chem. Commun.* **1989**, 276. (b) Espanet, B.; Duñach, E.; Périchon, J. *Tetrahedron Lett.* **1992**, *33*, 2485. (c) Hébri, H.; Duñach, E.; Périchon, J. *J. Chem. Soc., Chem. Commun.* **1993**, 499.

(12) Flowers reported that $SmBr_2$ and SmI_2 are not as effective as $SmCl_2$ in pinacol coupling reactions in THF. See ref 6a.

(13) Banik reported samarium-mediated pinacol coupling in MeOH. In this paper, allyl bromide was used as an activator of Sm metal. See ref 2d.