

**The First Oxidative Addition of a Hypervalent Compound to Metallic Lanthanoid: Synthesis, Characterization, and Reaction of Samarium(II) Bis(trifluoromethanesulfonate) Derived from Metallic Samarium and 1,5-Dithioniabicyclo[3.3.0]octane Bis(trifluoromethanesulfonate)**

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**Introduction**

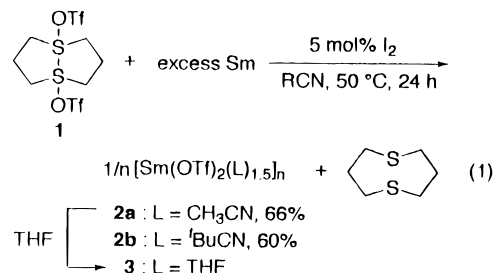
Diiodolanthanoid(II) compounds such as  $\text{SmI}_2$  and  $\text{YbI}_2$ , first introduced by Kagan, are versatile, homogeneous, and powerful reducing reagents<sup>1</sup> which have been utilized for chemo- and stereoselective C–C bond formation.<sup>2–9</sup> Recently, a new lanthanoid(II) reagent, a samarium(II) bistriflate “ $\text{Sm}(\text{OTf})_2$ ”, which is generated in situ by reducing  $\text{Sm}(\text{OTf})_3$  with Grignard reagents<sup>10</sup> or alkylolithium,<sup>11</sup> has been developed.<sup>12</sup> Despite its versatility, it has not been elucidated whether this Sm(II) species includes the complexation of a triflate anion with alkali and alkaline earth elements. Shibasaki et al. have reported that a lithium ate complex of lanthanum bearing chiral auxiliary binaphthoxy ligands is an excellent asymmetric catalyst for nitro-aldol reactions, in which the lithium plays an important role.<sup>13</sup> We anticipated that a salt-free, well-defined samarium(II) bistriflate compound would give direct information about the reactivity of Sm(II) supported with triflate ligands.

We have already reported that the reaction of oxidants such as disulfide with a metallic lanthanoid gave rise to salt-free lanthanoid thiolate complexes,<sup>14–18</sup> and we

proved that the hypervalent compound 1,5-dithioniabicyclo[3.3.0]octane (**1**), which has a transannular S–S bond,<sup>19</sup> was a highly reactive oxidant toward organo-metallic compounds.<sup>20</sup> Thus, these facts prompted us to investigate the reaction of lanthanoid metal with **1**. Herein, we report the first synthesis and characterization of salt-free samarium(II) bis(trifluoromethanesulfonate) complexes of the formula  $[\text{Sm}(\text{OTf})_2(\text{L})_{1.5}]_n$  (**2a**, L = MeCN; **2b**, L = *t*-BuCN; **3**, L = THF) and also report that the complex **2a** mediates intermolecular pinacol coupling reactions of aromatic ketones with high diastereoselectivity.

**Results and Discussion**

Complex **2a** can be prepared by the oxidative reaction of metallic samarium with **1** in acetonitrile. When a mixture of **1** and an excess of samarium metal in the presence of a catalytic amount of iodine in acetonitrile was stirred at 50 °C for 24 h, the complex **2a** was isolated as a purple powder in 66% yield (eq 1). A similar reaction

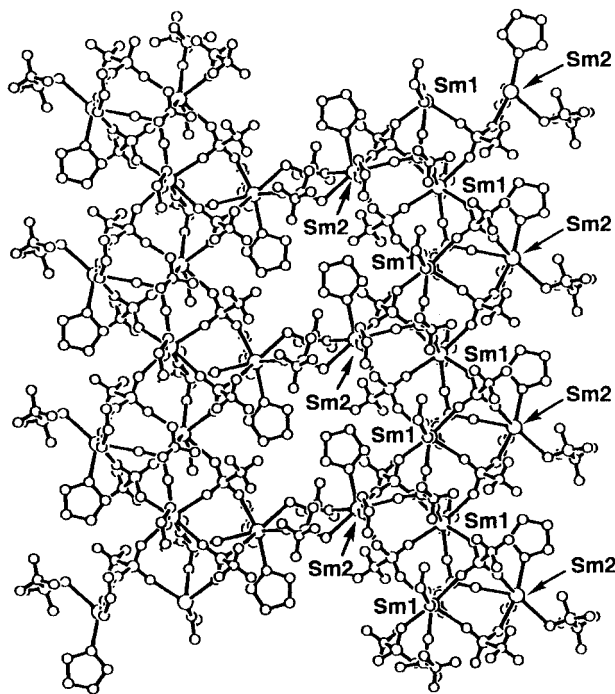


in pivalonitrile gave **2b** in 60% yield. Both complexes are highly air- and moisture-sensitive, but solid samples of these complexes can be stored under argon. Acetonitrile bound to the Sm center of **2a** was labile; thus, on dissolving the complex in THF at room temperature, the acetonitrile was easily replaced by THF to form  $[\text{Sm}(\text{OTf})_2(\text{thf})_{1.5}]_n$  (**3**) in quantitative yield. The addition of excess acetonitrile to **3** regenerates **2a**. The formulation of **3** was further confirmed by X-ray analysis; the complex **3** has an infinite 2D sheet structure (Figure 1),<sup>21</sup> though a one-dimensional coordination polymer of  $[\text{Eu}(\mu\text{-SePh})_2(\text{thf})_3]_n$  has been reported.<sup>22</sup>

The triflate complex **2a** was found to be an excellent reagent for pinacol coupling reactions of carbonyl compounds.<sup>23–25</sup> Coupling reactions of aromatic ketones, using stoichiometric amounts of **2a**, yielded the corresponding 1,2-diols. The results are summarized in Table 1. The pinacol coupling reaction of acetophenone using **2a** in acetonitrile proceeded smoothly at room temperature to give 2,3-diphenyl-2,3-butanediol in 99% yield with

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**Figure 1.** A drawing of the 2D sheet structure of **3**. All hydrogen atoms are omitted for clarity. Two samarium(II) centers, Sm1 and Sm2, have seven-coordinated geometry, a distorted capped octahedral geometry around Sm(1), and a distorted pentagonal bipyramidal geometry around Sm(2).

**Table 1. Pinacol Coupling of Carbonyl Compounds Mediated by **2a**<sup>a</sup>**

entry	substrate	solvent	temp (°C)	yield (%) <sup>b</sup>	<i>dl:meso</i> <sup>c</sup>
1	PhCOMe	CH <sub>3</sub> CN	rt	99	90:10
2	PhCOMe	CH <sub>3</sub> CN	-40	99	94:6
3	PhCOMe	EtCN	-78	60	94:6
4	PhCOMe	THF	rt	59	82:18
5	PhCOMe	THF	-78	20	88:12
6	PhCOMe	THF/HMPA <sup>d</sup>	rt	0	
7	PhCOEt	CH <sub>3</sub> CN	-40	92	95:5
8	<i>p</i> -MeC <sub>6</sub> H <sub>4</sub> COMe	CH <sub>3</sub> CN	-40	92	93:7
9	<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub> COMe	CH <sub>3</sub> CN	rt	74	78:22
10	<i>p</i> -MeOCC <sub>6</sub> H <sub>4</sub> COMe	CH <sub>3</sub> CN	-40	73	88:12
11	<i>p</i> -FC <sub>6</sub> H <sub>4</sub> COMe	CH <sub>3</sub> CN	-40	73	84:16

<sup>a</sup> Reaction conditions: ketone/**2a** = 1/1, 1 h. <sup>b</sup> Isolated yield of a mixture of diastereomers. <sup>c</sup> Ratio was determined by <sup>1</sup>H NMR. <sup>d</sup> Hexamethylphosphoramide (10 equiv) was added.

a high diastereoselectivity of *dl:meso* = 90:10 (entry 1). The highest diastereoselectivity of 94:6 was obtained when the same reaction took place at -40 °C in acetonitrile (entry 2) and at -78 °C in propionitrile (entry 3), though the yield of the 1,2-diol of entry 3 decreased to 60%.

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The choice of solvent is crucial in this reaction. The reaction conducted in THF decreased both in the diastereoselectivity and in the yield of the product (entry 4). The diastereoselectivity increased slightly to 88:12 at -78 °C in THF, though the yield decreased (entry 5). The addition of 10 equiv of hexamethylphosphoramide (HMPA) retarded the coupling reaction (entry 6), in sharp contrast to a previous finding that the addition of excess HMPA to Sm(OTf)<sub>2</sub> generated in situ dramatically accelerated the rate of the pinacol coupling reaction.<sup>11</sup> Thus, acetonitrile proved to be the best solvent, which corresponds to Kagan's finding that the pinacol coupling of acetophenone mediated by SmI<sub>2</sub> in the presence of a catalytic amount of NiBr<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> proceeded in pivalonitrile to give the diols with diastereoselectivity up to 79:21 (*dl:meso*).<sup>23e</sup> The pinacol coupling reaction of various aromatic ketones using **2a** gave the corresponding diols; the ester group remains intact (entry 10). It is assumed that mechanistically two adjacent Sm(II) centers binding a ketyl radical dimerize to give a bimetallopinacolate intermediate in which the two samarium atoms are connected by chelating triflate ligands and that minimization of steric interference through *anti*-orientation of the aryl groups explains the observed diastereoselectivity. The bimetallopinacolate complexes have been synthesized recently by the reaction of acetone with UCl<sub>4</sub>/Hg(Li)<sup>26</sup> and by the treatment of fluorenone with a samarium(II) alkoxide,<sup>27</sup> the latter a reversible conversion to the monomeric radical anion of fluorenone bound to the samarium center.

It is of interest to compare the reactivity of **2a** with that of in situ generated Sm(OTf)<sub>2</sub> species. When a tetrahydrofuran solution of Sm(OTf)<sub>2</sub>, which was derived from the reaction of Sm(OTf)<sub>3</sub> with ethylmagnesium bromide, was used for the reductive coupling of acetophenone at room temperature, the corresponding diols were obtained in 51% yield with 2 diastereoselectivity of 62:38 (*dl:meso*).<sup>10</sup> The coupling reaction of acetophenone by the in situ Sm(OTf)<sub>2</sub> species generated using *s*-BuLi in THF afforded the diols (67% yield) with a diastereoselectivity of 85:15 (*dl:meso*),<sup>11</sup> which is comparable to that obtained with **2a** in THF (the Sm(II) species in THF was **3**). These findings are consistent with the fact that the absorption spectrum of **3**<sup>28</sup> is almost the same as that of the Sm(OTf)<sub>2</sub> species generated using *s*-BuLi<sup>11</sup> but is much different from that of the Sm(OTf)<sub>2</sub> species generated using ethylmagnesium bromide,<sup>10</sup> suggesting that the former species is similar to the salt-free **3**, while the latter species likely involves an interaction with magnesium.

In summary, we demonstrated the new, salt-free divalent samarium triflates **2a**, **2b**, and **3**, which were synthesized by the novel oxidative reaction of metallic samarium with the hypervalent compound **1**. Complex **2a** was found to be an excellent reagent for the highly diastereoselective intermolecular pinacol coupling of aromatic ketones in acetonitrile.

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(28) UV spectra of Sm(II) species. Sm(OTf)<sub>2</sub>/EtMgBr system λ<sub>max</sub> (THF) (ε) 595 (240), 408 (390), 363 (400), 408 nm (460); Sm(OTf)<sub>2</sub>/*s*-BuLi system λ<sub>max</sub> (THF) (ε) 563 (110), 480 (85), 347 (270), 313 nm (320).

### Experimental Section

**General.** All manipulations involving air- and moisture-sensitive compounds were carried out using standard Schlenk techniques under argon. THF, toluene, diethyl ether, and hexane were dried over sodium-benzophenone ketyl and then distilled before use. Acetonitrile, propionitrile and pivalonitrile were distilled from CaH<sub>2</sub>. The compounds 1,5-dithionibicyclo-[3.3.0]octane bis(trifluoromethanesulfonate) (**1**)<sup>29</sup> and Sm(OTf)<sub>3</sub><sup>30</sup> were prepared according to the literature procedures. Metallic samarium was purchased from Nihon Yttrium Co. Ltd. Ethylmagnesium bromide (1.0 M diethyl ether solution) and *sec*-butyllithium were purchased from Kanto Chemical Co. Ltd.

**Preparation of 2a.** A mixture of **1** (1.392 g, 3.12 mmol), finely divided samarium metal (938 mg, 6.24 mmol), and iodine (39.5 mg, 0.156 mmol) in acetonitrile (40 mL) was stirred at 50 °C for 24 h. After excess samarium was removed by centrifugation, all volatiles were removed under reduced pressure. The crude product was dissolved in acetonitrile (5 mL), followed by precipitation by adding toluene (25 mL). The supernatant solution was removed by a syringe, and a purple powder **2a** (2.179 g) was obtained in 66% yield after being dried *in vacuo*: mp >230 °C (dec); IR (Nujol/KBr) 2267 (w), 1262 (s), 1045 (s), and 633 (s) cm<sup>-1</sup>. The composition of **2a** was determined both by iodometric titration and by the amount of the nitrile molecules estimated by the <sup>1</sup>H NMR of the decomposition product of **2a** with air. UV spectrum of **2a**: λ<sub>max</sub> (CH<sub>3</sub>CN) (ε) 659 nm (160).

The titration method<sup>31</sup> was as follows. An acetonitrile solution (1.0 mL) of compound **2a** (42.4 mg) in a Schlenk tube was titrated with a standard toluene solution of iodine (8.38 × 10<sup>-3</sup> mmol/mL) using a 1.0 mL syringe until the initial green solution of **2a** changed to pale yellow. This titration was repeated three times, and the averaged concentration of the solution of **2a** was determined to be 8.25 × 10<sup>-2</sup> mmol/mL.

Air oxidation of **2a** was accomplished as follows. Complex **2a** (7.2 mg) was dissolved into CDCl<sub>3</sub> (0.5 mL) containing dichloromethane (2.00 μL, 3.12 × 10<sup>-2</sup> mmol) as an internal standard. The mixture was exposed to air and then was passed through a short column of Na<sub>2</sub>SO<sub>4</sub> using CDCl<sub>3</sub> as an eluent. The <sup>1</sup>H NMR spectrum of the eluate showed a singlet signal due to the free acetonitrile and a singlet signal due to dichloromethane of the internal standard. Peak areas of the acetonitrile and the dichloromethane were given as follows: 213 for the acetonitrile (3 H) and 200 for dichloromethane (2 H). Thereby, the weight of acetonitrile was calculated to be 9.10 × 10<sup>-1</sup> mg (2.22 × 10<sup>-2</sup> mmol). This corresponds to the presence of 1.5 acetonitrile molecules per Sm(OTf)<sub>2</sub> fragment. The composition of **2a** obtained by this method agreed with that obtained by the iodometric titration.

**Preparation of 2b.** Similar procedures described for the

synthesis of **2a**, except for the use of pivalonitrile as a solvent, were conducted to give complex **2b** in 60% yield: mp >200 °C (dec); IR (Nujol/KBr) 2269 (w), 1271 (s), 1065 (s), 647 (s) cm<sup>-1</sup>. The composition of **2b** was also determined by iodometric titration and by the <sup>1</sup>H NMR spectrum of the decomposition product.

**Preparation of 3.** Complex **2a** (50.6 mg, 9.96 × 10<sup>-2</sup> mmol) was dissolved in 2 mL of THF. The resulting purple solution was stirred at room temperature for 5 min and then all volatiles were removed *in vacuo*. Complex **3** was obtained as a reddish purple powder in 97% yield (54.0 mg): mp >255 °C (dec); IR (Nujol/KBr) 1262 (s), 1039 (s), 887 (w), 623 (s) cm<sup>-1</sup>. The composition of **3** was also determined by similar methods to those employed for **2a**. UV spectrum of **3**: λ<sub>max</sub> (THF) (ε) 563 (340), 478 (230), 303 nm (180).

**Ligand Exchange Reaction of 3 with Acetonitrile.** An acetonitrile solution (2 mL) of **3** (45.0 mg, 8.09 × 10<sup>-2</sup> mmol) was stirred at room temperature for 5 min. All volatiles were removed, and the resulting purple powder was dried under vacuum. Complex **2a** was obtained in 95% yield (39.1 mg).

**Pinacol Coupling Reactions of Carbonyl Compounds Mediated by Complex 2a.** A typical procedure is described for the reaction of **2a** with acetophenone. A solution of **2a** (82.5 mg, 8.71 × 10<sup>-2</sup> mmol) in acetonitrile (1.0 mL) was cooled to -40 °C. Acetophenone (10.0 μL, 8.71 × 10<sup>-2</sup> mmol) was added via a microsyringe. After the mixture was stirred for 1 h at -40 °C, the reaction was quenched by adding silica gel and then hexane (3 mL). The organic products were passed through a short column of silica gel using ether as an eluent. The crude products obtained were subjected to preparative TLC (ethyl acetate/hexane 1:3) to give the 1,2-diols (10.4 mg, 99% yield). The diastereomeric ratio of the product was determined to be 94:6 (*dl:meso*) by <sup>1</sup>H NMR spectroscopy; a resonance (δ 1.52) due to the methyl group in the *dl*-isomer was observed further upfield than that (δ 1.59) in the *meso*-isomer.<sup>22</sup>

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**Supporting Information Available:** Structure, final positional parameters, final thermal parameters, bond distances, angles, and torsion angles for the complex **3** (15 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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