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A new convenient preparation of monocyclooctatetraenyl-lanthanide complexes from metallic lanthanides and oxidants

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Abstract

Treatment of lanthanide metals with cyclooctatetraene in the presence of an equimolar amount of iodine afforded cyclooctatetraenyl-iodolanthanide(III) complexes, $\mathrm{LnI}(\eta^8\text{-cot})(\mathrm{thf})_n$ (cot = cyclooctatetraenyl; **1a**: Ln = La, $n = 3$; **1b**: Ln = Ce, $n = 3$; **1c**: Ln = Pr, $n = 3$; **1d**: Ln = Nd, $n = 2$; **1e**: Ln = Sm, $n = 1$), in modest yields. Bromo and chloro-bridged dinuclear complexes of samarium, $[\mathrm{Sm}(\mu\text{-X})(\mathrm{cot})(\mathrm{thf})]_2$ (**2**: X = Br; **3**: X = Cl), are also prepared by the reaction of samarium metal with cyclooctatetraene in the presence of 1,2-dibromoethane or Ph_3PCl_2, respectively. The reaction of metallic samarium with cyclooctatetraene and diaryl disulfide or diphenyl diselenide in THF afforded cyclooctatetraenyl-thiolate or -selenolate complexes of samarium(III), $[\mathrm{Sm}(\mu\text{-EAr})(\eta^8\text{-cot})(\mathrm{thf})_n]_2$ (**4a**: EAr = SPh, $n = 2$; **4b**: $SC_6H_2Me_3$-2,4,6, $n = 2$; **4c**: $SC_6H_2{}^iPr_3$-2,4,6, $n = 1$; **5**: SePh, $n = 2$). The dimeric structure of **5** was revealed by X-ray crystallography [monoclinic, space group $P2_1/n$ with $a = 8.500(5)$, $b = 21.805(6)$, $c = 12.042(5)$ Å, $\beta = 105.98(4)°$, $V = 2145(1)$ Å^3, $Z = 2$, $R = 0.055$ for 2061 reflections with $I > 3\sigma(I)$ and 235 parameters]. A samarium(II) complex, $[\mathrm{Sm}(\eta^8\text{-cot})(\mathrm{thf})]_n$ (**6**), was also obtained by the direct reaction of samarium metal with cyclooctatetraene in THF with a catalytic amount of iodine. Reaction of **6** with iodine and diphenyl disulfide afforded **1e** and **4a**, respectively.

Key words: Lanthanide; Cyclooctatetraenyl; Thiolate; Selenolate; Samarium

1. Introduction

Most preparations of organolanthanide complexes have been by the metathesis of halide ligands with alkyl or aryl anions [1]. The synthesis of organolanthanide complexes bearing cyclooctatetraenyl ligand has also been based on the metathesis reaction [2–11]. In these preparations, the rather strong interaction of lanthanide cations with the metal halides disturbs the isolation and purification of the organometallic product. The introduction of bulkiness to the supporting ligands, examples being pentaalkylcyclopentadienyl and 2,6-dialkylphenoxo ligands, has been the main method to obtain salt-free organolanthanide complexes. The oxidation reaction of low valent organolanthanide complexes has been used as a new synthetic method to prepare Ln^{III} complexes, although for complexes of samarium and ytterbium this method has been limited to the oxidation state of two [12–16]. Recently, the synthesis of lanthanide complexes from the metallic state has been developed as an ideal method [17–20]. Here we report the direct one-pot synthesis based on the reaction of lanthanide metal and cyclooctatetraene in the presence of an oxidant to give the monocyclooctatetraenyl-lanthanide(III) complexes of general formula $[\mathrm{LnX}(\eta^8\text{-cot})(\mathrm{thf})_n]_m$ [17].

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2. Results and discussion

2.1. Preparation of cyclooctatetraenyl-lanthanide complexes.

The iodo(cyclooctatetraenyl) complexes of lanthanides **1**, LnI(η^8-cot)(thf)$_n$ (cot = cyclooctatetraenyl), have been prepared by the one-pot reaction of freshly cut metallic lanthanides with cyclooctatetraene in the presence of an equimolar amount of iodine in THF (eqn. 1). Samarium metal dissolved gradually in a hot (50°C) THF solution of cyclooctatetraene and iodine. In the course of reaction (24 h), the metal dissolved completely to give a clear violet solution, from which complex **1e** was isolated as violet crystals in 81% yield upon cooling the saturated THF solution. Ingot of metallic samarium can be employed for this reaction, though the reaction rate is slower than that of finely divided metal. As the source of iodine, 1,2-diiodoethane is also employed similar to the preparation of SmI_2 [21]. The complex **1e** rapidly becomes opaque upon removal of the solvent (THF) from crystalline product. The coordinated THF is slowly lost to form a complex **1e** having one THF ligand, which gave an elemental analysis consistent with the stoichiometry. This synthetic strategy can be applied for the preparation of complexes **1a–1d**, though the later organolanthanide complexes have not yet been prepared by this method. The formulations of **1a–1d** were also confirmed by elemental analyses and the monomeric structure of **1** was elucidated by the X-ray study of **1b** [17a]. The lability of THF ligand depends on the metal atom, *i.e.* Sm > Nd > Pr, Ce, La.

$$\mathrm{Ln(metal)} + C_8H_8 + 1/2I_2 \xrightarrow[\mathrm{THF}]{} \mathrm{LnI}(C_8H_8)(\mathrm{thf})_n \qquad (1)$$

1a: Ln = La, $n = 3$
1b: Ln = Ce, $n = 3$
1c: Ln = Pr, $n = 3$
1d: Ln = Nd, $n = 2$
1e: Ln = Sm, $n = 1$

When 1,2-dibromoethane was used instead of iodine, complex **2** was obtained in 45% yield. Similarly, chloro complex **3** was prepared in 44% yield by the reaction of samarium metal with Ph_3PCl_2. The reaction with 1,2-dichloroethane afforded **3** in low yields under the same conditions as used for **2**. The supernatant solution contains triphenylphosphine since the product does not form the phosphine adduct as is frequently observed for lanthanide halides. Such a direct reaction of R_3PI_2 with various kinds of transition metals has been reported to give some phosphine complexes such as $[MnI_2(PR_3)]_n$, $CoI_3(PMe_3)_2$ and so on [22].

$$2Sm + 2C_8H_8 + Ph_3PCl_2 \xrightarrow[\mathrm{THF}]{} \underset{\mathbf{3}}{[Sm(\mu\text{-}Cl)(C_8H_8)(\mathrm{thf})_2]_2} \qquad (2)$$

Diaryl disulfide can also be successfully employed as the oxidant [17b]. Reaction among Sm, COT, and diphenyl disulfide in THF in the presence of a catalytic amount of iodine afforded [Sm(μ-SPh)(cot)(thf)$_2$]$_2$ (**4a**) in 76% yield (eqn. 3). Similarly, [Sm(μ-SC$_6$H$_2$Me$_3$-2,4,6)(cot)(thf)$_2$]$_2$ (**4b**) and [Sm(μ-SC$_6$H$_2{}^i$Pr$_3$-2,4,6)(cot)(thf)]$_2$ (**4c**) were prepared in 34% and 25% yields, respectively. A benzeneselenolate complex [Sm(μ-SePh)(cot)(thf)$_2$]$_2$ (**5**) was also prepared in 46% yield by the same procedure. We have already reported the structures of **4a** and **4c** [17b]. The structure of **5** is determined by X-ray analysis (vide infra). Our synthetic method provides new chalcogenide complexes of samarium(III). Recently, chalcogenide complexes of lanthanide metals attracted much interest, since the chemical bond between soft donor ligand and hard metal ions is important and they are the molecular sources in material synthesis [23–29].

$$Sm + C_8H_8 + 1/2ArEEAr \xrightarrow[\mathrm{THF}]{I_2} 1/2[Sm(\mu\text{-}EAr)(C_8H_8)(\mathrm{thf})_n]_2 \qquad (3)$$

4a: EAr = SC_6H_5, $n = 2$
4b: EAr = $SC_6H_2Me_3$, $n = 2$
4c: EAr = $SC_6H_2{}^iPr_3$, $n = 1$
5: EAr = SeC_6H_5, $n = 2$

The plausible pathway for the formation of complexes **1e** and **4a** has been investigated by means of a careful search for possible intermediates. When a catalytic amount of iodine was used, the reaction of Sm with cyclooctatetraene resulted in the formation of [Sm(η^8-cot)(thf)]$_n$ (**6**) in modest yield. Complex **6** does not dissolve in common organic solvents, but dissolved rapidly in a THF solution of iodine to afford complex **1e** in good yield (eqn. 4). In the reaction course of **4a**, the brown compound **6** is precipitated initially and then gradually disappears by reaction with diphenyl disulfide (eqn. 5).

$$1/n\underset{\mathbf{6}}{[Sm(C_8H_8)(\mathrm{thf})]_n} + 1/2I_2 \xrightarrow[\mathrm{THF}]{} \underset{\mathbf{1e}}{SmI(C_8H_8)(\mathrm{thf})} \qquad (4)$$

$$2/n\underset{\mathbf{6}}{[Sm(C_8H_8)(\mathrm{thf})]_n} + PhS\text{-}SPh \xrightarrow[\mathrm{THF}]{} \underset{\mathbf{4a}}{[Sm(\mu\text{-}SPh)(C_8H_8)(\mathrm{thf})_2]_2} \qquad (5)$$

On the other hand, the addition of cyclooctatetraene to a deep blue THF solution of SmI_2, which was prepared by the reaction of Sm with iodine in THF [30], induced the rapid precipitation of SmI_3 and gave the violet solution of complex **1e** (eqn. 6). SmI_3 can be reduced by Sm metal to form SmI_2 [30]. Two moles of SmI_2 may be formally the source of one mole of "SmI" species through the disproportionation. Thiolate Sm^{II} complex, $[Sm(SC_6H_2{}^iPr_3\text{-}2,4,6)_2(THF)_3]_2$ [31], can be isolated and its reaction with cyclooctatetraene afforded complex **4a**. Such an oxidative reaction of Sm^{II} complexes with cyclooctatetraene has already been reported; *i.e.* two moles of $Sm^{II}Cp^*_2$ with COT give $Sm^{III}Cp^*_3$ and $Sm^{III}Cp^*(\eta^8\text{-cot})$ [32]. Thus, these two pathways are possible for the formation of Sm^{III} complexes.

$$2SmI_2 + C_8H_8 \xrightarrow[THF]{} \underset{\mathbf{1e}}{SmI(C_8H_8)(thf)} + SmI_3 \qquad (6)$$

2.2. *Crystal structure of [Sm(μ-SePh)(cot)(thf)$_2$]$_2$ (5)*

X-Ray quality crystals of **5** were obtained from the toluene solution and utilized for structure analysis. An ORTEP drawing of the resulting molecular structure is shown in Fig. 1 with pertinent bond distances and angles in Table 1. The dimeric structure of **5** is essentially the same as that of **4a** [17b]. Comparable data for **4a** and **5** are summarized in Table 2.

The samarium atom has a pseudo square pyramidal and four-legged piano-stool geometry coordinated by one planar $\eta^8\text{-}C_8H_8$ ring, two bridging selenium atoms, and two oxygen atoms of THF. Each unit of the dinuclear structure is related by the centrosymmetry.

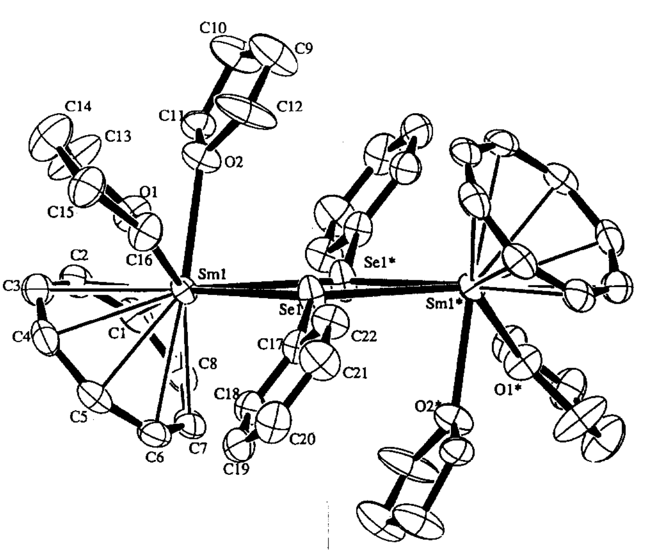

Fig. 1. ORTEP drawing of **5** with a numbering scheme; 30% probability ellipsoids.

TABLE 1. Selected bond distances (Å) and angles (°) of **5** [a]

Sm(1)–Se(1)	3.015(2)	Sm(1)–C(4)	2.70(1)
Sm(1)–Se(1*)	3.174(2)	Sm(1)–C(5)	2.68(1)
Sm(1)–O(1)	2.581(9)	Sm(1)–C(6)	2.69(1)
Sm(1)–O(2)	2.503(9)	Sm(1)–C(7)	2.66(1)
Sm(1)–C(1)	2.67(1)	Sm(1)–C(8)	2.66(1)
Sm(1)–C(2)	2.68(1)	Sm(1)–C_8H_8	1.94
Sm(1)–C(3)	2.70(1)	Se(1)–C(17)	1.92(1)
C_8H_8–Sm(1)–Se(1)	138.2	O(1)–Sm(1)–O(2)	70.2(3)
C_8H_8–Sm(1)–Se(1*)	118.2	O(1)–Sm(1)–Se(1*)	126.0(2)
C_8H_8–Sm(1)–O(1)	115.7	O(2)–Sm(1)–Se(1*)	75.7(2)
C_8H_8–Sm(1)–O(2)	128.4	Sm(1)–Se(1)–Sm(1*)	118.48(5)
Se(1)–Sm(1)–Se(1*)	61.52(5)	Sm(1)–Se(1)–C(17)	116.4(4)
Se(1)–Sm(1)–O(1)	79.7(2)	Sm(1*)–Se(1)–C(17)	119.1(4)
Se(1)–Sm(1)–O(2)	93.1(2)		

[a] C_8H_8 denotes the centre of gravity in the cyclooctatetraenyl ring.

The bond distances and angles of $Sm(\eta^8\text{-cot})(thf)_2$ fragment are quite normal and is similar to those found in **4a**.

The Sm_2Se_2 unit of **5** is exactly planar and two bridging selenium ligands are in a distorted trigonal-planar geometry; the angle sum for selenium atom is 354.0°, which is slightly deviated from the angle sum for sulfur atom (359.1°) of **4a** [17b]. Sm_2E_2 and phenyl planes are not parallel in **5**, while almost coplanar in **4a**. The Sm–Se bond distances of 3.015(2) and 3.174(2) Å in **5** are longer than that of monomeric selenolate complexes, $Cp^*_2Sm(SeC_6H_2(CF_3)_3)(thf)$ (2.919(1) Å) [15] and $L_2Yb(SePh)$ (L = *N,N'*-di-(trimethylsilyl)benzenamidinate) (2.805(1) Å) [16], taking into account the difference in ionic radii. The selenium bridges are distinctly asymmetric. The difference between two Sm–Se bonds is 0.159(2) Å and is in contrast to that (0.020(8) Å) found in **4a**.

Such a $Ln^{II}{}_2Se_2$ fragment has been found in the extended one-dimensional network of $[Eu(\mu\text{-}SePh)_2(THF)_3]_n$, in which the averaged Eu–Se distance is 3.14(1) Å [26]. This bond distance indicates

TABLE 2. Comparison of structural data of **4a** and **5**

	4a [31]	**5**
d(Sm–E) (Å)	2.914(8), 2.934(8)	3.015(2), 3.174(2)
av.	2.924(8)	3.095(2)
difference	0.020(8)	0.159(2)
∡(Sm–E–C) (°)	122.8(7), 119.9(7)	116.4(4), 119.1(4)
av.	121.4(7)	117.8(4)
difference	2.9(7)	2.7(4)
∡(Sm–E–Sm) (°)	116.4(1)	118.48(5)
sum of angle (°) around E	359.1	354.0
∡(E–Sm–E) (°)	63.6(1)	61.52(5)
dihedral angle (°) between Sm_2E_2 and Ph planes	8.5	50.6

that the bonding character is ionic. The complexes $Cp^*_2Lu(\mu\text{-}SePh)_2Li(THF)_2$ [23a] and $(py)_2Yb(SePh)_2(\mu\text{-}SePh)_2Li(Py)_2$ [28] have the bridging selenolate ligands. The Lu–Se bond distance is 2.80(1) Å and Yb–Se bond distances are 2.813(2) and 2.833(2) Å, which are rather shorter than that of **5**, even though taking account of the difference of metal radii. This difference is attributed to the bridging lithium atoms.

3. Experimental section

3.1. General

All manipulations involving air- and moisture-sensitive compounds were carried out by the standard Schlenk technique under argon. All solvents were purified by distillation under argon after drying over calcium hydride or sodium benzophenone ketyl.

Nuclear magnetic resonance (^1H, and ^{13}C NMR) spectra were measured on JEOL JNM-GX400 and EX-270 spectrometers. The chemical shifts of paramagnetic complexes depend on temperature and concentration. The measuring condition was set at 30°C and 5 mg/ml for the NMR measurement. Gas chromatographic (GLC) analyses were conducted on a Hitachi 263-30 equipped with a TCD detector. Elemental analyses were performed at the Elemental Analysis Centers of Osaka University and of Kyoto University. All melting points were measured in sealed tubes and were not corrected.

3.2. Synthesis of complexes 1–6

3.2.1. Synthesis of LaI(η^8-cot)(thf)$_3$ (1a)

The mixture of lanthanum metal (0.53 g, 3.82 mmol), COT (0.40 g, 3.82 mmol), and iodine (0.48 g, 3.82 mmol) in THF (70 ml) was stirred at 50°C for two days. The resulting pale yellow solution was filtered and then concentrated under reduced pressure. Off-white crystals (0.79 g) were obtained. On cooling the solution to −20°C, further crystals (0.60 g) were obtained. The solution was concentrated to give the third crop of 0.64 g, total yield 90%, m.p. 95–103°C. Anal. Calcd. C, 40.97; H, 5.50. Found. C, 40.75; H, 5.28%. ^1H NMR (270 MHz, THF-d_8, 30°C) δ 6.29 (s, C_8H_8). ^{13}C NMR (THF-d_8) δ 98.4 (J(C–H) = 156 Hz).

3.2.2. Synthesis of CeI(η^8-cot)(thf)$_3$ (1b)

To the cerium ingot (1.98 g, 14.13 mmol) and COT (1.47 g, 14.13 mmol) in THF (180 ml) was added iodine (1.79 g, 14.13 mmol). The reaction mixture was stirred at 50°C for three days. The excess of cerium metal (0.20 g) was recovered. The hot pale yellow solution was filtered through a pad of Celite. The bright yellow solid of **1b** (7.02 g, 94% yield) was thus obtained. M.p. 70–75°C (dec.). Anal. Calcd. C, 40.89; H, 5.49. Found. C, 40.61; H, 5.61%.

3.2.3. Synthesis of PrI(η^8-cot)(thf)$_3$ (1c)

Praseodymium metal (1.23 g, 8.72 mmol), and COT (1.11 g, 10.65 mmol) were placed in a Schlenk tube, and then THF (80 ml) and iodine (1.11 g, 8.74 mmol) were added. The reaction mixture was stirred at 50°C for four days. The hot pale yellow solution was filtered through a pad of Celite and the filtrate was concentrated to give a yellowish green solid **1c** (4.70 g, 92% yield), m.p. 77–85°C. Anal. Calcd. C, 40.83; H, 5.48. Found. C, 40.61; H, 5.61%.

3.2.4. Synthesis of NdI(η^8-cot)(thf)$_2$ (1d)

The mixture of metallic neodymium (0.88 g, 6.10 mmol), COT (0.64 g, 6.14 mmol), and iodine (0.78 g, 6.15 mmol) in THF (70 ml) was stirred at 50°C for four days. The brownish red solution was filtered through a pad of Celite. The filtrate was concentrated under reduced pressure to give **1d** as a powdery light green solid (3.37 g, 93% yield), m.p. > 320°C (dec.). Anal. Calcd. C, 36.99; H, 4.66. Found. C, 36.77; H, 4.76%.

3.2.5. Synthesis of SmI(η^8-cot)(thf) (1e)

The reaction mixture of samarium metal (0.35 g, 2.33 mmol), COT (0.26 ml, 2.33 mmol) and 1,2-diiodoethane (0.33 g, 1.16 mmol) in THF (60 ml) was stirred at 50°C. The colour of the solution changed from deep blue-green to deep violet after 24 h. Concentration under reduced pressure and then cooling the resulting solution afforded **1e** as violet crystals (0.86 g, 81% yield). The use of iodine instead of 1,2-diiodoethane gave the same product. M.p. 210–220°C (dec.). Anal. Calcd. C, 32.94; H,.3.69. Found. C, 32.87; H, 4.07%. ^1H NMR (270 MHz, THF-d_8, 30°C) δ 12.39 (s, 8H, C_8H_8).

3.2.6. Synthesis of [SmBr(η^8-cot)(thf)]$_2$ (2)

To the mixture of samarium metal (0.16 g, 1.04 mmol), COT (0.12 ml, 1.07 mmol) and 1,2-dibromoethane (0.05 ml, 0.58 mmol) in THF (40 ml) was added iodine (13 mg, 0.10 mmol). The reaction mixture was stirred at 50°C for 24 h. The solution changed to deep violet. Recrystallization from THF-hexane afforded **2** in 45% yield as purple crystals, m.p. > 220°C (dec). ^1H NMR (270 MHz, THF-d_8, 30°C) δ 11.80 (s, C_8H_8).

3.2.7. Synthesis of [SmCl(η^8-cot)(thf)]$_2$ (3)

To samarium metal (0.11 g, 0.78 mmol), COT (0.10 ml, 0.89 mmol) and dichlorotriphenylphosphorane (138 mg, 0.42 mmol) in THF (40 ml) was added iodine (8 mg, 0.06 mmol). The reaction mixture was stirred at 50°C for 2 h. Complex **3** was obtained by recrystallization from THF in 44% yield as purple crystals. ^{1}H NMR (270 MHz, THF-d_8, 30°C) δ 11.30 (s, C_8H_8).

3.2.8. *Synthesis of [Sm(μ-SPh)(η^8-cot)(thf)$_2$]$_2$ (4a)*

To the mixture of samarium metal (0.36 g, 2.43 mmol), COT (0.30 ml, 2.66 mmol) and diphenyl disulfide (0.28 g, 1.27 mmol) in THF (40 ml) was added a catalytic amount of iodine (19 mg, 0.15 mmol) and this mixture was then stirred at 50°C for 24 h. **4a** was obtained by recrystallization from THF in 76% yield as deep purple crystals. M.p. >300°C (dec.). ^{1}H NMR (270 MHz, THF-d_8, 30°C) δ 11.24 (s, 16H, C_8H_8), 10.41 (s, 4H, *o*-H), 7.99 (s, 4H, *m*-H), 7.83 (s, 2H, *p*-H).

3.2.9. *Synthesis of [Sm(SC$_6$H$_2$Me$_3$-2,4,6)(η^8-cot)(thf)$_2$]$_2$ (4b)*

The reaction mixture of samarium metal (0.50 g, 3.32 mmol), COT (0.40 ml, 3.55 mmol), bis(2,4,6-trimethylphenyl) disulfide (0.51 g, 1.70 mmol) and a catalytic amount of iodine in THF (40 ml) was stirred for a period of 48 h to give a deep violet THF solution and brown powder of [Sm(cot)(thf)]*n* as a by-product. The brown powder was filtered off, and then THF was removed from the filtrate *in vacuo*. The resulting residue was extracted with toluene. Cooling the saturated toluene solution gave **4b** in 34% yield as deep purple crystals. M.p. > 300°C (dec.). ^{1}H NMR (270 MHz, THF-d_8, 30°C) δ 11.19 (s, 16H, C_8H_8), 8.07 (s, 4H, *m*-H), 4.66 (s, 12H, *o*-Me), 2.65 (s, 6H, *p*-Me).

3.2.10. *Synthesis of [Sm(SC$_6$H$_2{}^i$Pr$_3$-2,4,6)(η^8-cot)(thf)]$_2$ (4c)*

To a mixture of samarium metal (0.24 g, 1.58 mmol), COT (0.20 ml, 1.77 mmol) and bis(2,4,6-triisopropylphenyl) disulfide (0.40 g, 0.86 mmol) in THF (40 ml) was added a catalytic amount of iodine. The colour of the solution changed to deep violet after five days and a brown powder [Sm(cot)(thf)]$_n$ was precipitated in 49% yield. The brown powder was filtered, and then THF was removed from the filtrate under reduced pressure. The residue was extracted with toluene, and cooling the saturated toluene solution gave **4c** in 32% yield as deep purple crystals. M.p. >300°C (dec.). ^{1}H NMR (270 MHz, THF-d_8, 30°C) δ 11.27 (s, 16H, C_8H_8), 7.95 (s, 4H, *m*-H), 7.08 (m, 4H, *o*-C*H*Me$_2$), 3.33 (m, 2H, *p*-C*H*Me$_2$), 2.25 (d, 24H, *o*-CH*Me$_2$*), 1.21 (d, 12H, *p*-CH*Me$_2$*).

3.2.11. *Synthesis of [Sm(SePh)(η^8-cot)(thf)$_2$]$_2$ (5)*

To a mixture of samarium metal (0.57 g, 3.78 mmol), COT (0.50 ml, 4.44 mmol) and diphenyl diselenide (0.61 g, 1.96 mmol) in THF (40 ml) was added a catalytic amount of iodine (21 mg, 0.16 mmol) and then the reaction mixture was stirred at 50°C for five days. Recrystallization from the deep violet THF solution afforded **5** in 46% yield as deep purple crystals. M.p. >300°C (dec.). ^{1}H NMR (270 MHz, THF-d_8, 30°C) δ 11.49 (s, 16H, C_8H_8), 9.74 (s, 4H, *o*-H), 7.71 (s, 6H, *m*- and *p*-H).

3.2.12. *Synthesis of Sm(η^8-cot)(thf) (6)*

The mixture of samarium metal (0.56 g, 3.72 mmol) and COT (0.39 g, 3.72 mmol) in THF (60 ml) was placed in a Schlenk tube and then iodine (10 mg) was added to activate the metal. After the reaction mixture was stirred at 50°C for three days to result in the formation of brown solid, the supernatant solution was decanted off and then the resulting solid (0.98 g, 81% yield) was dried *in vacuo*, m.p. > 400°C. Anal. Calcd. C, 44.13; H, 4.94. Found. C, 44.20; H, 5.03%.

3.2.13. *Reaction of 6 with iodine*

To the slurry of brown solid of Sm(cot)(thf) (0.10 g, 0.31 mmol) in THF (10 ml) was added iodine (39 mg, 0.31 mmol) at room temperature. Reaction immediately occurred to give a deep violet solution, from which crystalline **1e** was obtained in 65% yield on cooling the solution.

3.2.14. *Reaction of SmI$_2$ with COT*

To an intense green-blue solution of SmI$_2$ (0.45 g, 1.13 mmol) in THF (60 ml) was added COT (0.20 g,

TABLE 3. Crystal data and data collection parameters of **5**

formula	$C_{44}H_{58}O_4Se_2Sm_2$
formula weight	1109.66
crystal system	monoclinic
space group	$P2_1/n$
a, Å	8.500(5)
b, Å	21.805(6)
c, Å	12.042(5)
β, °	105.98(4)
Z	2
V, Å^3	2145(1)
D_{calcd}	1.717
radiation	Mo Kα
crystal size (mm)	0.25×0.30×0.50
abs. coeff (cm^{-1})	28.7
scan mode	$2\theta-\omega$
temperature (°C)	23
scan speed (deg min^{-1})	10
scan width (deg)	$1.73+0.35\tan\theta$
bkgd count (s)	5
$2\theta_{max}$ (deg)	55
unique data [$I > 3\sigma(I)$]	2061
no. of variables	235
R	0.055
R_w	0.062
GOF	2.29
largest peak (eÅ^{-3})	1.12

TABLE 4. Atomic coordinates of complex **5**

	x	y	z	B_{eq}
Sm(1)	0.11619(7)	0.11332(3)	0.04404(6)	3.32(1)
Se(1)	−0.1473(2)	0.02963(6)	−0.0952(1)	4.93(3)
O(1)	−0.139(1)	0.1799(5)	0.0304(8)	5.0(2)
O(2)	0.025(1)	0.1006(5)	0.2234(7)	4.9(2)
C(1)	0.429(1)	0.1234(7)	0.164(1)	4.8(3)
C(2)	0.359(2)	0.1799(8)	0.179(1)	5.1(4)
C(3)	0.258(2)	0.2237(8)	0.105(1)	5.5(4)
C(4)	0.187(2)	0.2273(7)	−0.016(2)	5.3(4)
C(5)	0.182(2)	0.1886(8)	−0.114(1)	4.9(4)
C(6)	0.253(2)	0.1320(7)	−0.129(1)	4.8(4)
C(7)	0.355(2)	0.0902(6)	−0.054(2)	5.1(4)
C(8)	0.429(1)	0.0875(7)	0.067(2)	5.0(4)
C(9)	−0.130(2)	0.049(1)	0.323(2)	8.8(6)
C(10)	0.034(2)	0.064(1)	0.408(1)	8.0(5)
C(11)	0.135(2)	0.0902(7)	0.337(1)	4.4(3)
C(12)	−0.138(2)	0.076(1)	0.217(2)	9.6(6)
C(13)	−0.151(2)	0.228(1)	0.113(2)	9.2(6)
C(14)	−0.294(3)	0.2617(9)	0.066(2)	8.3(6)
C(15)	−0.370(2)	0.2415(8)	−0.055(2)	6.4(5)
C(16)	−0.275(2)	0.1836(7)	−0.072(1)	5.2(4)
C(17)	−0.262(1)	0.0573(6)	−0.247(1)	3.8(3)
C(18)	−0.182(2)	0.0932(6)	−0.312(1)	4.6(3)
C(19)	−0.268(2)	0.1137(7)	−0.423(1)	5.3(4)
C(20)	−0.429(2)	0.0995(8)	−0.468(1)	6.0(4)
C(21)	−0.511(2)	0.0634(9)	−0.403(1)	6.7(5)
C(22)	−0.428(2)	0.0433(7)	−0.290(1)	5.1(3)

1.92 mmol) via syringe. After a few minutes, the purple solution was obtained and pale yellow crystalline solids of SmI_3 deposited. The supernatant solution was concentrated to give the purple solid of **1e** in 95% yield.

3.3. Crystal structure of 5

A single crystal was sealed in a glass capillary under argon atmosphere, and then transferred to a goniostat on a Rigaku AFC-5R diffractometer. A systematic search of a limited hemisphere of reciprocal space located a set of diffraction maxima revealed that the monoclinic symmetry of the crystal and systematic absence corresponded to the unique space group $P2_1/n$. Details of data collection and the final cell dimensions are given in Table 3.

The 2061 unique raw intensity data with $I > 3\sigma(I)$ were converted to values of the structure factor by correction for Lorentz and polarization effects. Inspection of the standard three reflections measured after every 100 reflections showed no systematic variation in intensity. An empirical absorption correction on azimuthal scans of several reflections was applied.

The location of the samarium atom was determined by the direct method (TEXSAN software package). A series of standard full matrix least-squares refinement and Fourier synthesis revealed the locations of the other nonhydrogen atoms. All hydrogen atoms were placed at the calculated positions as normal bond distances and angles. All nonhydrogen atoms of the complex **5** were refined anisotropically to $R = 0.055$ and $R_w = 0.062$. Final difference Fourier maps indicated no significant peak greater than 1.12 e Å^{-3}. Selected bond distances and angles are summarized in Table 1 and atomic coordinates are listed in Table 4.

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