# Samarium(III) Pentalene Sandwich Compounds [Sm($\eta^8$-C$_8$H$_4${Si$^i$Pr$_3$-1,4}$_2$)(Cp*)] and [Sm($\eta^8$-C$_8$H$_4${Si$^i$Pr$_3$-1,4}$_2$)($\eta^5$-C$_8$H$_5${Si$^i$Pr$_3$-1,4}$_2$)] and a Mixed-Valence Hexasamarium Cluster Derived from Sm(II)-Based Solvent Activation

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The reaction of the pentalene salt C$_8$H$_4${Si$^i$Pr$_3$-1,4}$_2$[K]$_2$ with [SmCp*($\mu$-I)(THF)$_2$]$_2$ yields not the expected Sm(II) pentalene-bridged dimer but the Sm(III) sandwich complexes [Sm($\eta^8$-C$_8$H$_4${Si$^i$Pr$_3$-1,4}$_2$)($\eta^5$-Cp*)] (**1**) and [Sm($\eta^8$-C$_8$H$_4${Si$^i$Pr$_3$-1,4}$_2$)($\eta^5$-C$_8$H$_5${Si$^i$Pr$_3$-1,4}$_2$)] (**2**) and the mixed-valence cluster [Cp*$_6$Sm$_6$(OMe)$_8$O][K(THF)$_6$] (**3**) via solvent activation of THF. The samarium(III) sandwich compound **2** incorporates an $\eta^8$-pentalene ligand and an $\eta^5$-hydropentalenyl ligand. X-ray crystallography shows the Sm(II)/Sm(III) mixed-valence cluster compound **3** to contain a centrosymmetric hexanuclear array of Cp*Sm units, bridged by face-centered $\mu_3$-methoxy groups, with a central oxo unit.

## Introduction

The organometallic chemistry of pentalene, an eight-membered bicyclic carbocycle, has gained interest largely due to its unique variety of multihaptic bonding modes and its highly effective capability of delocalizing charge between opposing metal centers in anti-bimetallics.[1] This has been demonstrated for the transition metals by Manriquez et al. in the cations of [MCp*]$_2$($\eta^5$:$\eta^5$-C$_8$H$_6$) (M = Fe, Co, Ni, Ru; see Chart 1a)[2,3] and O'Hare et al. in the anion [{Mn(CO)$_3$}$_2$($\eta^5$:$\eta^5$-C$_8$H$_6$)]$^-$-[counterion]$^+$.[4] The latter is particularly noteworthy, as it appears to have the strongest metal–metal coupling for any hydrocarbon-bridged mixed-valence bimetallic in the literature.

It was our intention to synthesize a samarium(II) analogue of the transition metal triple-decker pentalene complexes, capped with Cp* ligands, in order to investigate whether f-electrons could be delocalized to enable intermetallic communication. Evans and co-workers have previously prepared the COT analogue [Sm($\eta$-Cp*)(THF)]$_2$($\mu$-COT) from [Sm($\eta$-Cp*)($\mu$-I)-(THF)$_2$]$_2$ and COT[K]$_2$ in toluene (Chart 1b).[5] Therefore we investigated the corresponding reaction with the tri-isopropylsilyl pentalene salt C$_8$H$_4${Si$^i$Pr$_3$-1,4}$_2$[K]$_2$, as a route to [Sm(Cp*)(THF)]$_2$($\mu$-C$_8$H$_4${Si$^i$Pr$_3$-1,4}$_2$).

## Results

Addition of 1 equiv of C$_8$H$_4${Si$^i$Pr$_3$-1,4}$_2$[K]$_2$ to a toluene solution of [SmCp*($\mu$-I)(THF)$_2$]$_2$ initially yielded a green

**Chart 1**



(a)　　　　(b)
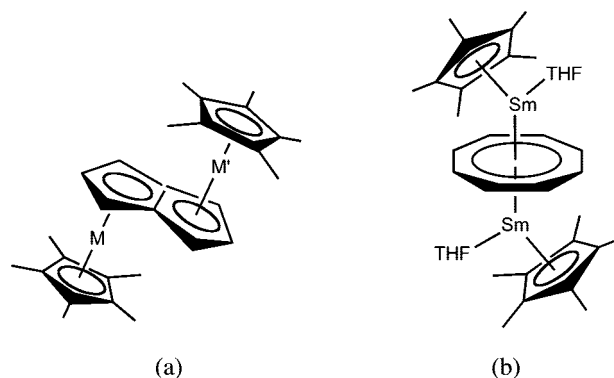
solution with red and white precipitates. Heating to reflux (90 °C) for 2 days was found to be necessary for the reaction to proceed to completion (i.e., the complete disappearance of starting material [SmCp*($\mu$-I)(THF)$_2$]$_2$ as evidenced by $^1$H NMR spectroscopy in $d_8$-toluene).

Attempts to recrystallize the crude green (toluene-soluble) reaction product(s) were unsuccessful; however, further heating *in vacuo* at 100 °C/10$^{-6}$ mbar to remove traces of volatiles and subsequent cooling (to −50 °C for 4 days) of a saturated toluene solution of the resultant green solids gave an unexpected mixture of cocrystallized samarium(III) products as green crystalline solids. The major fraction of these solids was identified by $^1$H NMR and single crystal diffraction methods as being the new pentalene/cyclopentadienyl mixed-sandwich compound [Sm($\eta^8$-C$_8$H$_4${Si$^i$Pr$_3$-1,4}$_2$)($\eta^5$-Cp*)] (**1**, see Scheme 1). A full discussion of the characterizing data is presented later. Although other paramagnetic impurities in samples of **1** were not detected in the $^1$H NMR spectra, examination of the mass spectra (EI) revealed clear peaks corresponding to both the parent ion of **1** (a complex mass envelope in the region $m/z$ = 693−705 amu) and another, heavier component with a set of closely spaced peaks at $m/z$ = 973−988, inconsistent with a fragmentation product (and with an isotopic distribution typical of a samarium-

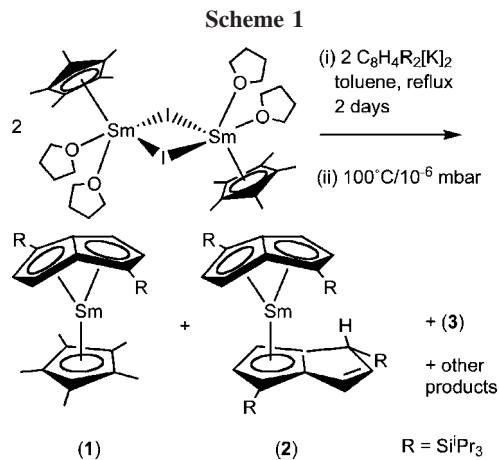* Corresponding author. E-mail: f.g.cloke@sussex.ac.uk.

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**Scheme 1**

(i) 2 $C_8H_4R_2[K]_2$
toluene, reflux
2 days

(ii) 100°C/10$^{-6}$ mbar

(1)      (2)      R = Si$^i$Pr$_3$

+ (3)
+ other products

**Figure 1.** ORTEP view of **1** (thermal ellipsoids at 50%, H atoms omitted for clarity).

**Figure 2.** ORTEP view of **2** (thermal ellipsoids at 50%; H atoms omitted for clarity, apart from H on C34).

containing compound). Careful analysis of the crystals under a microscope failed to reveal any discernible geometric and/or chromatic variations in the solids; however, repeated mounting of crystals from the same sample allowed us to identify a single crystal with a different unit cell from **1**. Structural data were refined and accordant with the new bis(pentalene) complex [Sm($\eta^8$-C$_8$H$_4${Si$^i$Pr$_3$-1,4}$_2$)($\eta^5$-C$_8$H$_5${Si$^i$Pr$_3$-1,4}$_2$)] (**2**, see Scheme 1), which corresponds with the anomalous peaks in the mass spectrum at $m/z = 973-988$. Simulation of a mass isotope pattern for a molecule with this formula (SmC$_{52}$H$_{93}$Si$_4$) gave a result in excellent agreement with the distribution of peaks obtained in the mass spectrum. Despite repeated attempts, a method of separating these products could not be found, and **2** thus lacks full supporting characterization data. Nonetheless, repeated preparations of **1** following this method always gave peaks for both **1** and **2** in the mass spectra. Although yet to be fully characterized, we believe that the inclusion of **2** in our discussions is warranted, since it is an important component of this complex reaction mixture.

The red, toluene-insoluble side-product was found to be soluble only in strong donor solvents (THF and DME) and was recrystallized from THF/pentane (1:5 ratio) to afford the mixed-valence cluster compound [Cp*$_6$Sm$_6$(OMe)$_{7.5}$(I)$_{0.5}$O][K(THF)$_6$] (**3**, see Scheme 1 and Figure 4), isolated in 20% yield (with respect to [SmCp*($\mu$-I)(THF)$_2$]$_2$). The fractional quantity of iodide was included to best refine the structural data and can be considered as incorporation of KI into the cluster (*vide infra*).

The compounds **1**−**3** are the products of a complex reaction in which the lanthanide centers are oxidized, the ligand is protonated in an aprotic medium, and solvent molecules are reduced and ring-opened. We now present a detailed examination of the experimental data.

Cocrystallized samples of [Sm($\eta^8$-C$_8$H$_4${Si$^i$Pr$_3$-1,4}$_2$)(Cp*)] (**1**) and [Sm($\eta^8$-C$_8$H$_4${Si$^i$Pr$_3$-1,4}$_2$)($\eta^5$-C$_8$H$_5${Si$^i$Pr$_3$-1,4}$_2$)] (**2**) were found to be moderately air-sensitive and highly soluble in arenes, aliphatic hydrocarbons, and ethers. $^1$H NMR (C$_6$D$_6$) spectroscopy revealed a full set of resonances for **1** consistent with a symmetrically bound pentalene ligand with diastereotopic silyl substituents (indicative of $\eta^8$ ligation to a single metal center) and a single peak corresponding to a set of equivalent Cp*-Me resonances; a single resonance was observed in the $^{29}$Si{$^1$H} spectrum at 20.54 ppm. These data are in accord with the formulation of **1** as [Sm(C$_8$H$_4${Si$^i$Pr$_3$-1,4}$_2$)(Cp*)]. However, the expected NMR resonances for **2** (four different $^{29}$Si signals and a set of both pentalenyl and hydropentalenyl $^1$H resonances) in this mixture were not observed, even with very concentrated samples and multiple scans. Elemental analysis (CH) obtained for these solids was also in good agreement for **1**, but not **2**
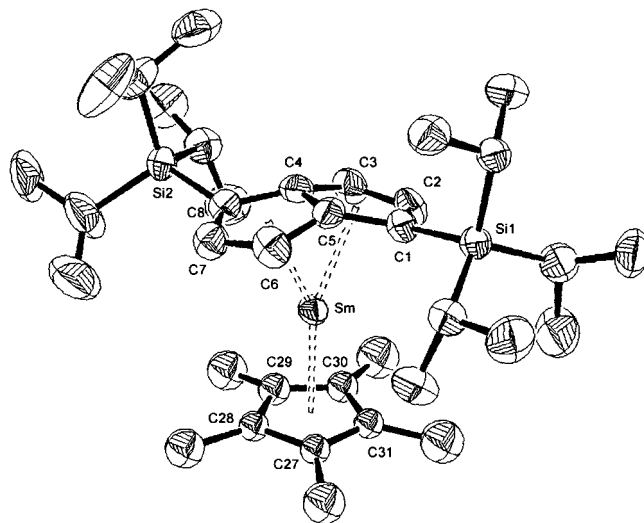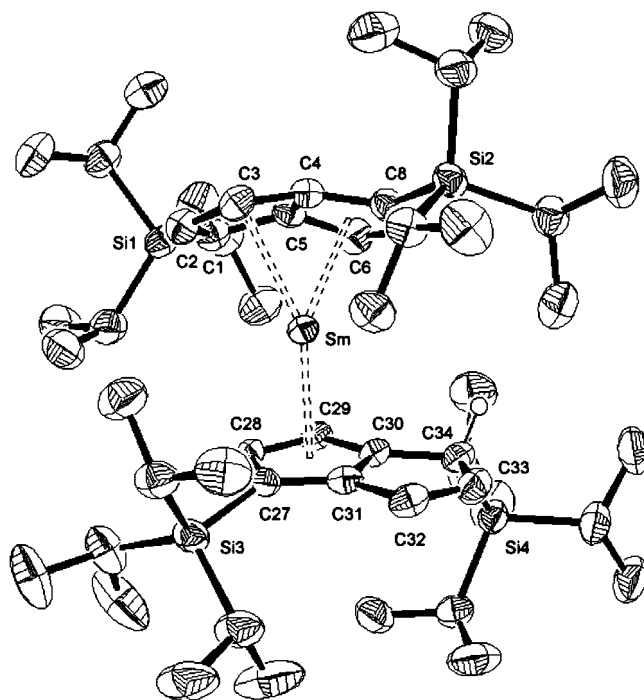
(which contains a higher percentage of carbon and hydrogen). Presumably this is because **2** is a very small (<5%) fraction of the cocrystallized sample.

Single crystals of **1** and **2** were obtained from slow cooling a saturated toluene solution to −50 °C over 4 days; the X-ray structures are shown in Figures 1 and 2, with selected bond lengths and angles in Tables 1 and 2.

The structure of the mixed-sandwich complex **1** reveals an $\eta^5$-bound Cp* ligand and an $\eta^8$-coordinated pentalene moiety, which folds to accommodate the large electropositive center, as is typical for the structures of f-element pentalene compounds. The arrangement of ligands is essentially linear through the midpoint of the bridgehead pentalene carbons and the centroid of the Cp* ring. The geometry of **1** is otherwise unexceptional; details of bond and angles are discussed in relation to **2** and other f-element compounds below.

**Table 1. Selected Bond Lengths (Å) and Angles (deg) for 1[a]**

| | | | |
|---|---|---|---|
| Sm–M(1) | 2.298(5) | Sm–C(4) | 2.414(4) |
| Sm–M(2) | 2.305(5) | Sm–C(5) | 2.424(4) |
| Sm–M(3) | 2.451(9) | Sm–C(3) | 2.644(5) |
| Sm–C(29) | 2.716(9) | Sm–C(6) | 2.674(5) |
| Sm–C(31) | 2.732(7) | Sm–C(8) | 2.686(5) |
| Sm–C(28) | 2.747(9) | Sm–C(30) | 2.690(8) |
| Sm–C(27) | 2.764(8) | Sm–C(1) | 2.690(4) |
| Sm–C(2) | 2.788(5) | Sm–C(7) | 2.799(5) |
| M(1)–Sm–M(2) | 48.9(2) | | |
| M(1)–Sm–M(3) | 154.2(3) | M(2)–Sm–M(3) | 155.9(3) |

[a] M(1), M(2), and M(3) are the centroids of the C(1) to C(5) ring, the C(4) to C(8) ring, and the C(27) to C(31) ring, respectively.

**Table 2. Selected Bond Lengths (Å) and Angles (deg) for 2[a]**

| | | | |
|---|---|---|---|
| Sm–M(1) | 2.305(5) | Sm–M(1b) | 2.289(5) |
| Sm–M(1a) | 2.299(5) | Sm–M(2) | 1.853(5) |
| Sm–C(4) | 2.414(5) | Sm–C(30) | 2.730(5) |
| Sm–C(5) | 2.418(5) | Sm–C(31) | 2.760(5) |
| Sm–C(6) | 2.645(5) | C(27)–C(31) | 1.435(7) |
| Sm–C(3) | 2.668(5) | C(27)–C(28) | 1.436(7) |
| Sm–C(8) | 2.680(5) | C(28)–C(29) | 1.412(6) |
| Sm–C(1) | 2.683(5) | C(29)–C(30) | 1.425(7) |
| Sm–C(7) | 2.775(5) | C(30)–C(31) | 1.412(6) |
| Sm–C(2) | 2.805(5) | C(30)–C(34) | 1.504(7) |
| Sm–C(27) | 2.778(5) | C(31)–C(32) | 1.458(7) |
| Sm–C(29) | 2.692(5) | C(32)–C(33) | 1.354(7) |
| Sm–C(28) | 2.706(5) | C(33)–C(34) | 1.508(7) |
| | | C(27)–C(31) | 1.435(7) |
| C(2)–C(1)–C(5) | 104.5(4) | C(7)–C(8)–C(4) | 103.8(4) |
| C(2)–C(1)–Si(1) | 126.8(4) | C(8)–C(4)–C(5) | 110.3(4) |
| C(5)–C(1)–Si(1) | 126.1(4) | C(8)–C(4)–C(3) | 135.4(5) |
| C(3)–C(2)–C(1) | 112.2(5) | C(5)–C(4)–C(3) | 106.4(4) |
| C(2)–C(3)–C(4) | 107.4(4) | C(6)–C(5)–C(1) | 135.7(5) |
| C(1)–C(5)–C(4) | 109.5(4) | C(6)–C(5)–C(4) | 106.3(4) |
| C(7)–C(6)–C(5) | 107.5(5) | C(6)–C(7)–C(8) | 112.2(5) |

[a] M(1) is the midpoint of the C(4)–C(5) bond, M(1a) is the centroid of the C(1)–C(5) ring, M(1b) is the centroid of the C(4)–C(8) ring, and M(2) is the centroid of the C(27) to C(31) ring.

The structure of **2** shows a mononuclear bis(pentalene) complex; however, unlike other compounds of this type, the rings are ligated in an asymmetric manner: one pentalene unit is bound in an $\eta^8$-fashion, whereas the other, effectively planar ligand (4° fold angle) is coordinated through only one ring in an $\eta^5$-fashion. The crystal was of sufficient quality to locate electron density consistent with a hydrogen atom bound to the carbon (C34) bearing a silyl substituent and pointing away from the bulky silyl group toward the $\eta^8$-ring; the bond angles around C34 are also consistent with $sp^3$ hybridization. Therefore, this ring has been protonated to form a bis(silyl)monohydropentalenyl ligand. Additionally, the C32–C33 distance is found to be shorter at 1.354(7) Å than the other C–C distances in the pentalene skeleton (av 1.449(7) Å), which is consistent with a localized double bond and is similar to that found in the Mn(II) complex [$Mn_2(C_8H_4\{Si^iPr_3-1,4\}_2)_2$] (1.383(7) Å)[6] and hydropentalenyl compounds [$Fe(\eta^5:\eta^5-C_8H_7)_2$] and [$Re(CO)_3$ $(\eta^5-C_8H_7)$] (C=C 1.329(8)–1.377(9) Å).[7–9] Although hydropentalenyl compounds are known to be formed from hydropentalenyl starting materials, it is rare that one is derived from the pentalenyl dianion.

Although the Sm–Pent(centroid) distances are similar in both compounds for the $\eta^8$-bound ligands (cf. 2.298(5) and 2.305(5)

Å in **1**, 2.299(5) and 2.289(5) Å in **2**), there is a significant disparity between the related distances of the centroids of the $\eta^5$- bound carbocycles: the Sm–Cp*(centroid) distance is 2.451(9) Å in **1**, while the Sm–PentH(centroid) distance is much closer at 1.853(5) Å in **2**, despite the apparent greater steric congestion in the latter. For comparison, the closest analogue of this type of mixed-sandwich complex is the U(III) complex [$U(C_8H_4\{Si^iPr_3-1,4\}_2)(Cp^*)$].[10] In spite of the difference in size of the 4f versus 5f element, the M–C(Cp*) bond lengths in **1** (2.690(8)–2.764(8) Å) and the uranium compound (2.734(8)–2.766(7) Å) are comparable, within esd's.[10]

To place these compounds in context within currently known pentalene complexes, **2** represents an unusual variant on the full-sandwich bis(pentalene) structure found for tetravalent metals Ti(IV), Zr(IV), Ce(IV), Th(IV), and U(IV).[11,12] In both **1** and **2** the trivalent samarium center is bound to three aromatic faces and as such are related to the pentalene/cyclopentadienyl mixed-sandwich structures known for Ti(III), V(III), and U(III).[10,13] The fold angle of the $\eta^8$-pentalene ligand in *both* **1** and **2** is found to be 25.5° and correlates well with that in other f-element pentalene sandwich compounds [$M(\eta^8-C_8H_4\{Si^iPr_3-1,4\}_2)_2$] (M = Ce (26°), Th (24°), U (25°)) and [$U(\eta^8-C_8H_4-\{Si^iPr_3-1,4\}_2)(\eta^5-Cp^*)$] (26°).[1,11,13]

Dark red crystalline samples of the cluster side-product **3** were found to be extremely air- and moisture-sensitive and highly paramagnetic, to the extent that no signals could be detected by $^1H$ with extended acquisition times and at variable temperatures. This is unsurprising given the formulation of the complex as a hexanuclear mixed-valance cluster, revealed by the single-crystal study (*vide infra*), which leads to each molecular unit containing three Sm(II) $f^6$ and three Sm(III) $f^5$ centers. Although the single-crystal X-ray data provided primary characterizing data, the formulation was verified by an elemental analysis of a crystalline sample of **3**. The parent ion could not be observed in electron-impact or electrospray (THF) mass spectrometry, unsurprising given the relatively large molecular weight of this cluster salt.

Single crystals of **3** were obtained by slow cooling a saturated THF/pentane (1:5 ratio) solution to −50 °C; the X-ray structure is shown in Figure 3, with selected bond lengths and angles in Table 3.

The structure of **3** shows a complex, hexanuclear samarium cluster anion and a [$K(THF)_6$]$^+$ counterion. The geometry of the cluster is a highly symmetrical octahedral arrangement of Sm centers around a central oxo unit (O1), with $\eta^5$-bound Cp* ligands capping each vertex of the octahedron. Across each face of the octahedron is a triply bridging methoxy group, in a cubic array (Figure 3). The structure was fully resolved by replacement, in one-half of the structures, of a single iodide in place of one methoxy group; these are found to be disordered mostly across two opposing faces, but also slightly over the remaining six faces; the data are best resolved with a one-half equivalent of iodide per cluster. This can be considered as a partial incorporation of KI; in total, the crystal is resolved as [($\eta^5$-Cp*)$_6$Sm$_6(\mu:\eta^3$-OMe)$_{7.5}(\mu:\eta^3$-I)$_{0.5}(\mu:\eta^6$-O)][$K(THF)_6$].

The cluster is remarkably similar to the hydroxide/Cp* samarium cluster, obtained by Evans et al. via controlled

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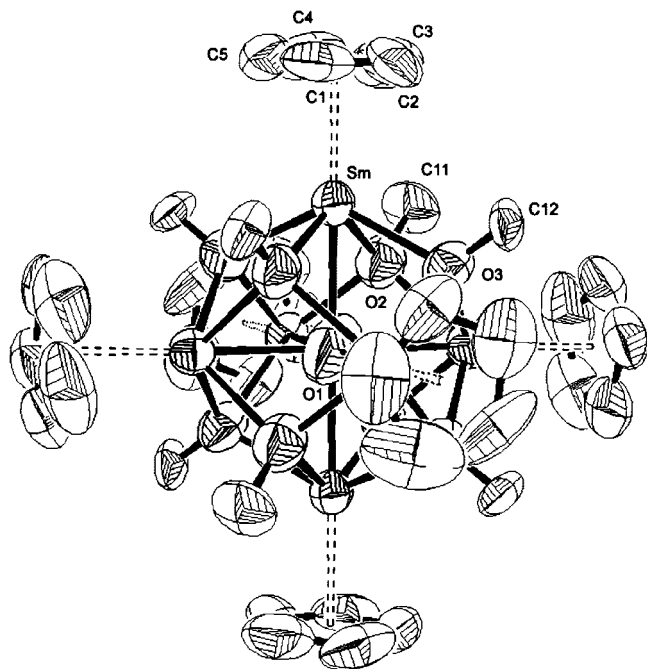(12) Cloke, F. G. N.; Hitchcock, P. B. *J. Am. Chem. Soc.* **1997**, 119, 7899–7900.

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**Figure 3.** ORTEP view of $[Sm_6(Cp^*)_6(OMe)_{7.5}(I)_{0.5}(O)]^-$ anion in **3** (H atoms and Cp*-Me omitted for clarity; half-equivalent disordered iodide not included; thermal ellipsoids at 50%).

**Table 3. Selected Bond Lengths (Å) and Angles (deg) for $[(Cp^*)_6Sm_6(OMe)_{7.5}(I)_{0.5}(O)][K(THF)_6]^a$**

| | | | |
|---|---|---|---|
| Sm−M(1) | 2.465(12) | Sm−C(2) | 2.686(15) |
| Sm−O(3) | 2.298(8) | Sm−C(1) | 2.720(12) |
| Sm−O(2)′ | 2.373(7) | Sm−C(3) | 2.747(13) |
| Sm−O(2) | 2.378(8) | Sm−C(5) | 2.762(12) |
| Sm−O(1) | 2.5369(5) | Sm−C(4) | 2.773(12) |
| O(2)−Sm′ | 2.373(7) | K−O(4) | 2.580(12) |
| O(2)−C(11) | 1.299(10) | | |
| O(3)−Sm−O(2)′ | 77.0(2) | O(3)−Sm−M(1) | 121.7(4) |
| O(3)−Sm−O(2)″ | 77.0(2) | O(2)′−Sm−M(1) | 114.4(2) |
| O(2)′−Sm−O(2)″ | 129.9(3) | O(2)″−Sm−M(1) | 115.7(2) |
| O(3)−Sm−O(2) | 124.5(5) | O(2)−Sm−M(1) | 113.7(2) |
| O(2)′−Sm−O(2) | 80.3(2) | O(3)−Sm−O(1) | 59.7(4) |
| O(2)″−Sm−O(2) | 80.3(2) | O(2)′−Sm−O(1) | 64.9(2) |
| Sm‴−O(1)−Sm | 90.730(17) | Sm−O(1)−Sm′ | 89.270(17) |
| Sm‴−O(1)−Sm′ | 180.00(3) | Sm−O(1)−Sm″ | 89.270(17) |

$^a$ M(1) is the centroid of the Cp* ring.

hydrolysis of $Sm(Cp^*)_2(THF)_2$ (Figure 4).[14] This has been formulated as a neutral compound $[Cp^*Sm]_6(OH)_6(O)_3$, and although the H atoms could not be located by crystallographic methods, the six OH⁻ anions give a fully trivalent complex. Other hexanuclear f-element clusters are known: $[SmCp^*]_6$-$Se_{11}$,[15] $\{[Yb(C_5Me_4SiMe_2{}^tBu)]_6I_8\}\{Li(THF)_4\}_2$,[16] $[Ln_6OH)_8(O)$-$((H_2O)_{24}]I_8(H_2O)_8$ (Ln = Nd, Eu, Tb, Dy),[17] $\{[CpYb)_6Cl_{13}\}^-$,[18] $\{[Nd(C_5H_4{}^tBu)]_6Se_{13}\}^-$,[19] and $[U_6(\mu_3\text{-}O)_8(\mu_2\text{-}OTf)_8(py)_8]$.[20] Of these, the ytterbium iodide cluster most closely resembles **3**, as



**Figure 4.** Synthetic routes to hexanuclear samarium cluster compounds from samarium diiodide (partial iodides omitted from **3**).

the iodides are found to be face-bridging, as with the methoxy and small iodide impurities in **3**, and the cluster is isolated as an alkali metal salt. Recently, Arnold and co-workers characterized a neutral oxygen-centered tetradecaimido hexatantalum cluster $(NPh)_6Ta_6(\mu:\eta^3\text{-}NPh)_8(\mu:\eta^6\text{-}O)$ with a centrosymmetric structure identical to the anion in **3**.[21]

Comparison of structural distances in **3** versus $[Cp^*Sm]_6$-$(OH)_6(O)_3$ show a similarly sized cluster: the Sm−O1 (central oxo) distance is 2.5369(5) Å in **3**, while it is an average 2.524(4) Å in the fully trivalent cluster. The average Sm−C(Cp*) distances are also similar: 2.738(13) Å in **3**, 2.741(4) Å in $[SmCp^*]_6(OH)_6(O)_3$, and slightly shorter at 2.679(4) Å in $[SmCp^*]_6Se_{11}$. The hydroxide cluster is found to be asymmetrical, which presumably reflects the mixture of facially bridging oxo dianions and hydroxide monoanions within the molecule, as opposed to the highly symmetrical cluster found in **3**, in which the samarium centers are facially bridged solely by monoanions. All samarium atoms are necessarily symmetry-related in the $I_{a3}$ space group; thus, an averaged structure is observed and any change in local coordination geometry due to instantaneous Sm(II) or Sm(III) valencies is not detected by the (slow) X-ray technique. Therefore while **3** is formulated as mixed-valence (an equal mixture of three Sm(II) and three Sm(III) centers), this assumption is based on charge balance factors alone.

## Discussion

The mechanism for the formation of these compounds is intriguing. Disproportionation of the starting materials may lead to product **1**; however, in **2** X-ray studies show that two pentalene rings are bound: one is coordinated $\eta^8$- and the other in an $\eta^5$-mode. Formally, the latter arises from protonation of the silyl-bound carbon on half of the bicyclic ring, giving a monoanionic hydropentalenyl species. Clearly, two processes have taken place: the oxidation of the samarium center (with concomitant reduction of another compound) and protonation of a pentalene ring in an aprotic solvent. The solvents were

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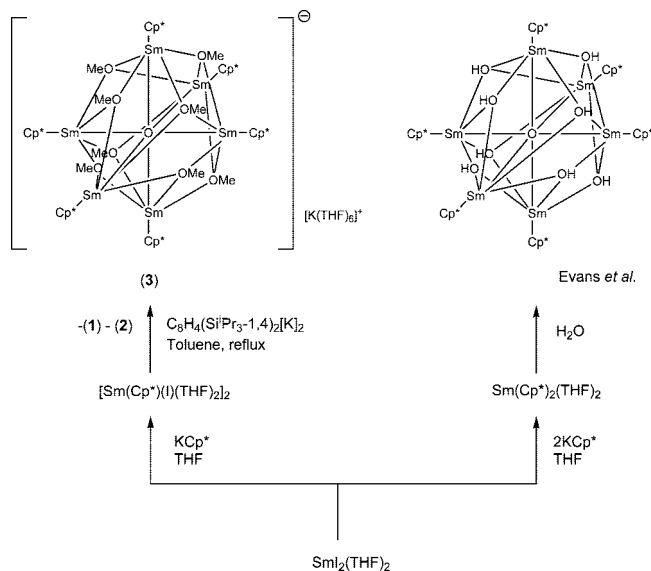
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rigorously dried, and extreme care was taken not to introduce any other possible sources of $H_2O$ or $O_2$; the experiment was also repeated many times (>10 times) and gave the same mixture of products each time.

The characterization of a side-product **3** revealed a mixed-valent cluster with eight methoxy anions and one oxo dianion, indicating that the THF solvent has been activated. Deprotonation of THF is commonly known to give ring-opened products such as the enolate ion plus ethylene.[22] Therefore the presence of both **2** and **3** in this reaction mixture is self-consistent: **2** contains an otherwise unexpected proton, and **3** contains the deprotonated THF fragments. Further reduction of enolate by Sm(II) to give $(O)^{2-}$ plus a coupled ethylenyl radical would give a samarium(III) center and the oxo product, but does not account for the formation of methoxy groups. The reaction mechanism is thus complex and not easily elucidated, giving ultimately a mixture of Sm(II) and oxidized Sm(III) centers and various fragments of reduced THF molecules. There are likely to be other samarium side-products than the cluster complex, as it is not possible to write a balanced chemical equation for the isolated products **1**−**3**. The presence of a samarium oxide side-product as a component of the white hydrocarbon-insoluble products seems, however, unlikely on the basis that these solids, once isolated, were found to be totally soluble in $H_2O$, as expected for KI and not for a lanthanide oxide.

Given that cluster **3** is extracted from the reaction mixture with THF, a question remains over the origin of the ring-opened THF products in the cluster: whether they are formed in the original reaction from the coordinated solvent present in the starting material $[SmICp*(THF)_2]_2$ or at the later stage, after products **1** and **2** have been filtered off. The red solids in the immediate reaction mixture did not appear to change in color between their initial appearance in the reaction in toluene and their later extraction into THF; furthermore, compounds **1** and **2** are obtained following a protonation and oxidation process, and this occurs *before* THF is added to extract **3**. Although the red solids from which **3** is crystallized are also soluble in DME, we have not been able to obtain single crystals from the DME solutions, so cannot provide a comparison with **3**. Although we cannot conclude with complete certainty the exact origin of the methoxy and oxo groups in **3**, it is most likely that they derive from the original reaction and not the subsequent extraction.

Although deprotonation of THF appears the most likely explanation for the samarium products obtained, we wished to investigate the possibility that the proton source may have also been the Cp* ligands or the toluene solvent. Volatiles from the reaction were isolated, for which GC-MS data showed the expected THF and toluene components, and additionally a smaller, less volatile fraction. The heaviest peak in this fraction occurred at $m/z = 136.1$, corresponding with free, protonated Cp*H. The fragmentation pattern correlated very well with that of a pure sample of Cp*H (peaks at $m/z = 77.0$, 91.0, 105.0, 121.0, and 136.1 amu), and the $^1H$ NMR spectrum of these volatiles gave the expected peaks for THF, toluene, and Cp*H. Additionally, there was no GC-MS evidence for the presence of fulvenes such as $C_5Me_4(CH_2)$, the expected products of a Cp* deprotonation.

Although the GC-MS and $^1H$ NMR evidence strongly supports the presence of Cp*H, the GC-MS fragmentation pattern may also be explained by the occurrence of xylenes $C_6H_4(Me)_2$ (RMM 106.2), methylanisole $C_6H_4(Me)(OMe)$ (RMM 123.1), and methylphenetole $C_6H_4(Me)(OEt)$ (RMM 137.2)

components, especially given the presence of peaks at $m/z = 77.0$ and 91.0, which may indicate phenyl and tolyl fragments. Such byproducts could be formed from radical-based combinations of ring-opened THF and deprotonated toluene. To conclusively rule out the possibility of toluene activation, a simple deuteration experiment was carried out with the same starting materials, but using $d_8$-toluene as the main solvent; any organic products formed by activation of toluene would naturally be expected to give a heavier set of ions in the mass spectrum. No change in the peaks for the GC-MS of the less volatile fraction was observed, and therefore it is concluded that this fraction reflects a Cp*H product, with the additional proton having been derived from activation of THF, not toluene.

Therefore it appears that the Cp* ligand is acting as a proton sink, not a proton source, and that *both* the pentalene and Cp* ligands have been partially protonated in this reaction. This perhaps explains why heating *in vacuo* was required in the workup of **1** and **2**: to remove the traces of this higher boiling Cp*H organic fraction and thus facilitate crystallization of the organometallic species.

It should be noted that radical abstraction of the THF α-hydrogen is a known complication in the reaction chemistry of $SmI_2(THF)_2$,[23] and it is not uncommon for low-valent f-element compounds to activate oxygen-containing solvents.[24] Identical reactions using base-free $SmI_2$ with KCp* in toluene gave a material assumed to be $[SmCp*I]_n$ (which has very low solubility), to which was added $C_8H_4\{Si^iPr_3-1,4\}_2[K]_2$. This resulted in the same cocrystallized mixture of products **1** and **2**, following a similar workup with toluene, and in similar yield to that obtained using $[SmCp*I(THF)_2]_2$; Cp*H was also detected in the reaction mixture. In this case, presumably the additional hydrogen required to form **2** (and Cp*H) arises from C−H activation of toluene; the latter has recently been observed for a bis(formamidinato) Sm(II) complex.[25]

Rational synthesis of **1** directly from $SmCl_3$, with stepwise addition of KCp* and $C_8H_4\{Si^iPr_3-1,4\}_2[K]_2$ in THF, failed for reasons unknown. Similar rational attempts to obtain the pentalenyl/hydropentalenyl Sm(III) complex **2** in a pure form were made by using the divalent starting material $SmI_2(THF)_2$ and the monopotassium salt of the silylated pentalene ligand $C_8H_5\{Si^iPr_3-1,4\}_2[K]$. Evans et al. have previously demonstrated that $Sm(Cp*)_2$ is capable of reducing CpH with concomitant evolution of $H_2$;[26] therefore it was hoped that 1 equiv of hydropentalenyl ligand would be reduced by the Sm(II) center to give the desired Sm(III) product, as outlined in Figure 5.

After workup, the reaction yielded a dark green oil, the mass spectrum (EI) of which was essentially identical to that previously obtained for **2**. The oil could not be crystallized however, probably due to the presence of isomers; use of asymmetrically substituted pentalene ligands such as $(C_8H_4\{SiMe_3-1,4\}_2)^{2-}$ and $(C_8H_5Me)^{2-}$ has caused similar difficulties

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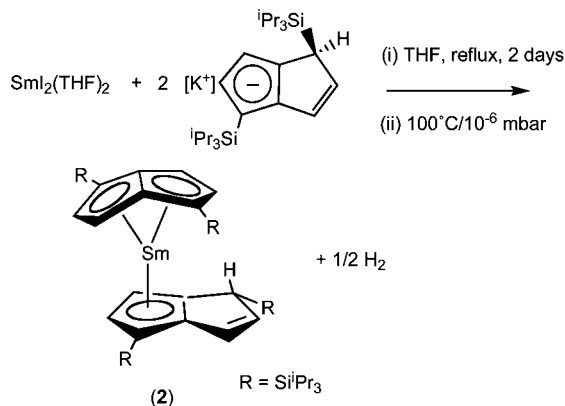
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**Figure 5.** Theoretical route for the synthesis of **2**; only one possible isomer illustrated.

in the synthesis of other organometallic species, e.g., iron(II) multidecker species.[27]

## Conclusion

In conclusion, the attempted synthesis of [SmCp*(THF)]$_2$($\mu$-$\eta^5$:$\eta^5$-C$_8$H$_4${Si$^i$Pr$_3$-1,4}$_2$) has been complicated by Sm(II)-based THF activation. The reaction gave instead novel trivalent species [Sm(C$_8$H$_4${Si$^i$Pr$_3$-1,4}$_2$)(Cp*)] (**1**) and Sm(C$_8$H$_4${Si$^i$Pr$_3$-1,4}$_2$)-(C$_8$H$_5${Si$^i$Pr$_3$-1,4}$_2$) (**2**), along with a methoxide-bridged, hexa-nuclear, mixed-valence oxo-centered cluster [Cp*$_6$Sm$_6$(OMe)$_{7.5}$-(I)$_{0.5}$O][K(THF)$_6$] (**3**). A pentalene ligand is presumably protonated by a THF molecule, resulting in the formation of **2**; the oxo and methoxy groups in **3** are most probably also derived from ring opening of THF. Furthermore, a fraction of the Cp* ligand from the original starting material is protonated and lost as free Cp*H; deuteration experiments using $d_8$-toluene indicate that the proton does not derive from the toluene and therefore presumably originates from the THF in the [SmCp*I(THF)$_2$]$_2$ starting material. However, use of base-free SmI$_2$ as the starting material and toluene solvent still results in the formation of **1** and **2** (but not **3**), so toluene activation occurs in the absence of THF.

We have presented here a full investigation into this unexpected reaction and provided another example of the unpredictable chemistry exhibited by compounds of the low-valent f-elements.

## Experimental Section

The reactions described below were conducted under purified argon using standard Schlenk double-manifold, high-vacuum, or glovebox techniques. Solvents were predried over activated 5 Å molecular sieves or sodium wire and then distilled over potassium (tetrahydrofuran) or sodium (toluene and DME) under a slow passage of nitrogen. Deuterated solvents were dried over molten potassium and distilled. Elemental analyses were carried out at the University of North London. Mass spectra were recorded by Dr. Ali Abdul-Sada at University of Sussex, on a VG autospec Fisons instrument (electron impact ionization at 70 eV). NMR spectra were recorded using a Varian VNMR spectrometer operating at 399.495 MHz for $^1$H measurements. The chemical shifts ($\delta$) in parts per million are given relative to the residual proton chemical shift of

the deuterated solvent. The starting materials [SmICp*(THF)$_2$]$_2$ and C$_8$H$_4${Si$^i$Pr$_3$-1,4}$_2$[K]$_2$ were prepared according to literature procedures.[28,29] Base-free SmI$_2$ was prepared by desolvation of SmI$_2$(THF)$_2$ at 150 °C/10$^{-6}$ mbar for 2 h. The monoydropentalenyl salt C$_8$H$_5${Si$^i$Pr$_3$-1,4}$_2$[K] was obtained by single deprotonation of the dihydropentalene C$_8$H$_6${Si$^i$Pr$_3$-1,4}$_2$ using potassium benzyl in $^t$BuOMe.[1] Celite filter aid was stored in an oven at 200 °C and flame dried under vacuum before use. Reactions were carried out in glass ampules equipped with high-vacuum, greaseless stopcocks.

**[Sm(C$_8$H$_4${Si$^i$Pr$_3$-1,4}$_2$)(Cp*)] (1), [Sm(C$_8$H$_4${Si$^i$Pr$_3$-1,4}$_2$)(C$_8$-H$_5${Si$^i$Pr$_3$-1,4}$_2$)] (2), and [Cp*$_6$Sm$_6$(OMe)$_8$O][K(THF)$_6$] (3) from [SmICp*(THF)$_2$]$_2$.** To an ampule containing a suspension of [SmICp*(THF)$_2$]$_2$ (200 mg, 0.180 mmol) in toluene (20 mL) was added dropwise with stirring a solution of C$_8$H$_4${Si$^i$Pr$_3$-1,4}$_2$[K]$_2$ (88 mg, 0.180 mmol) in toluene (15 mL). A green solution with a dark precipitate was observed. After 48 h of stirring at 80 °C under partial, static vacuum the solution was filtered from red and white solids using Celite and the solvent removed *in vacuo*. A pale olive green, oily solid was obtained and heated at 100 °C/10$^{-6}$ mbar for 5 h, after which time the solids were observed to change to a lighter green color. The Sm(III) product **1** cocrystallizes with small quantities of **2** as a dark green solid by cooling a very concentrated toluene solution (∼1 mL) at −50 °C over 4 days. Yield: 70 mg (0.1 mmol), 56% yield of **1** based on 1 equiv of C$_8$H$_4${Si$^i$Pr$_3$-1,4}$_2$[K]$_2$ (or 27% yield based on 0.5 equiv of [SmICp*(THF)$_2$]$_2$) and ignoring the impurity of **2**. Anal. Calc (found) for SmC$_{36}$H$_{61}$Si$_2$ (**1**): C 61.81 (61.88), H 8.57 (8.64). MS (EI): $m/z$ = 693−705 (**1** M$^+$, 2%, principal peak 701), 973−988 (**2** M$^+$, 1%, principal peak 983). $^1$H NMR (C$_6$D$_6$, 293 K): $\delta$ 16.9 (d, 2H, pent-H), 10.3 (d, 2H, pent-H), 1.5 (s, 15H, Cp*-Me), 0.4 (m, 18H, $^i$Pr-Me), −0.6 (m, 6H, $^i$Pr-CH), −2.7 (m, 18H, $^i$Pr-Me). $^{29}$Si{$^1$H} NMR (C$_6$D$_6$, 293 K): $\delta$ 20.54 (s).

The red and white solids collected on Celite after filtration (*vide supra*) were extracted with THF to give a dark blue/red dichroic, severely moisture-sensitive solution. The solvent was removed *in vacuo*, and recrystallization of the resultant solid from THF/hexane (1:5 ratio) yielded **3** as an extremely air-sensitive dark red crystalline solid after cooling at −50 °C for 3 days. Yield: 30 mg (0.0123 mmol), 20% based on 3 equiv of [SmICp*(THF)$_2$]$_2$. Anal. Calc (found) for Sm$_6$C$_{92}$H$_{162}$O$_{15}$K: C 45.11 (44.93), H 6.62 (6.43).

**[Sm(C$_8$H$_4${Si$^i$Pr$_3$-1,4}$_2$)(Cp*)] (1) and [Sm(C$_8$H$_4${Si$^i$Pr$_3$-1,4}$_2$)-(C$_8$H$_5${Si$^i$Pr$_3$-1,4}$_2$)] (2) from "Base-Free" SmI$_2$.** To an ampule containing SmI$_2$ (200 mg, 0.5 mmol) and KCp* (87 mg, 0.5 mmol) was added toluene (30 mL). After 48 h of stirring at 80 °C under partial, static vacuum a suspension of insoluble solids was visible, assumed to be a mixture of [SmICp*]$_n$ and KI, to which was added (at room temperature) a solution of C$_8$H$_4${Si$^i$Pr$_3$-1,4}$_2$[K]$_2$ (122 mg, 0.25 mmol) in toluene (15 mL) dropwise with stirring. After a further 48 h of stirring at 80 °C under partial, static vacuum the solution was filtered from white solids (dry Celite) and the solvent removed *in vacuo*, as previously described above. A pale olive green, oily solid was obtained and heated at 100 °C/10$^{-6}$ mbar for 5 h, after which cocrystallized samples of **1** and **2** may be obtained following recrystallization from toluene (∼1 mL) at −50 °C after 4 days. Yield: 80 mg (0.114 mmol), 46% yield of **1** based on C$_8$H$_4${Si$^i$Pr$_3$-1,4}$_2$[K]$_2$.

**Reaction of SmI$_2$(THF)$_2$ with C$_8$H$_5${Si$^i$Pr$_3$-1,4}$_2$[K].** To a mixture of SmI$_2$(THF)$_2$ (0.5 g, 0.91 mmol) and 2 equiv of C$_8$H$_5${Si$^i$Pr$_3$-1,4}$_2$[K] (898 mg, 1.82 mmol) in an ampule was added with stirring THF (70 mL). A very dark green solution with a white precipitate was observed. After 48 h of stirring at 80 °C reflux under partial, static vacuum, the solution was filtered (dry Celite) and the solvent removed *in vacuo*. The product was obtained as a dark

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green oil following sublimation at 240 °C/10$^{-5}$ mbar/6 h. MS (EI): $m/z$ = 973−988 (M$^+$ for **2** and isomers thereof, 5%).

**Crystal Structure Determination of 1.** Data were collected at 173 K on a Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo Kα radiation ($\eta$ = 0.71073 Å). Crystal data: SmC$_{36}$H$_{61}$Si$_2$, $M$ = 700.38, monoclinic space group $P2_1/n$ (No. 14), $a$ = 16.4072(5) Å, $b$ = 11.7609(4) Å, $c$ = 18.7910(5) Å, $V$ = 3625.84(19) Å$^3$, $Z$ = 4, $D_{calcd}$ = 1.28 Mg/m$^3$, abs coeff = 1.71 mm$^{-1}$, $R$ ($F$; $F^2 > 2\sigma$) = 0.042, $R_w$ ($F^2$; all data) = 0.066, theta range for data collection 3.46−26.05°, largest diff peak and hole 0.97 and −0.55 e Å$^{-3}$, reflections collected 29 669, independent reflections 7112 [$R$(int) = 0.051], reflections with $I > 2\sigma(I)$ 5389. Data collection KappaCCD, program package WinGX, abs correction MULTISCAN, refinement using SHELXL-97, drawing using ORTEP-3 for Windows. The Cp* ligand is disordered over two orientations, which were included with isotropic C atoms and restrained to have equivalent geometries using the SAME instruction.

**Crystal Structure Determination of 2.** Data were collected at 173 K on a Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo Kα radiation ($\eta$ = 0.71073 Å). Crystal data: SmC$_{52}$H$_{93}$Si$_4$, $M$ = 1073.11, triclinic space group $P\bar{1}$ (No. 2), $a$ = 12.3431(4) Å, $b$ = 14.8321(6) Å, $c$ = 17.3332(7) Å, $V$ = 3000.3(2) Å$^3$, $Z$ = 2, $D_{calcd}$ = 1.19 Mg/m$^3$, abs coeff = 1.09 mm$^{-1}$, $R$ ($F$; $F^2 2\sigma$) = 0.056, $R_w$ ($F^2$; all data) = 0.083, theta range for data collection 3.76 to 25.08°, largest diff. peak and hole 1.16 and −0.61 e Å$^{-3}$ (near Sm), reflections collected 41 967, independent reflections 10 561 [$R$(int) = 0.072], reflections with $I > 2\sigma(I)$ 8238. Data collection KappaCCD, program package WinGX, abs correction MULTISCAN, refinement using SHELXL-97, drawing using ORTEP-3 for Windows.

**Crystal Structure Determination of 3.** Data were collected at 173 K on a Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo Kα radiation ($\eta$ = 0. 71073 Å). Crystal data: C$_{91.5}$H$_{160.5}$I$_{0.5}$KO$_{14.5}$Sm$_6$, $M$ = 2497.35, cubic space group $I_{a3}$ (No. 206), $a$ = 26.6451(9) Å, $b$ = 26.6451(9) Å, $c$ = 26.6451(9) Å, $V$ = 18917.0(11) Å$^3$, $Z$ = 8, $D_{calcd}$ = 1.75 Mg/m$^3$, abs coeff = 3.93 mm$^{-1}$, $R$ ($F$; $F^2 > 2\sigma$) = 0.059, $R_w$ ($F^2$; all data) = 0.105, theta range for data collection 3.42−26.02°, largest diff peak and hole 1.24 and −0.83 e Å$^{-3}$ (near I), reflections collected 11 862, independent reflections 3095 [$R$(int) = 0.053], reflections with $I > 2\sigma(I)$ 1938. Data collection KappaCCD, program package WinGX, abs correction MULTISCAN, refinement using SHELXL-97, drawing using ORTEP-3 for Windows. The anion is basically [Sm$_6$-(Cp*)$_6$(O)(OMe)$_8$] but with a half of an iodide anion replacing half of an OMe anion and disordered mainly over the two unique faces lying on the $\bar{3}$ axis but possibly also slightly over the other six faces of the Sm$_6$ octahedron. These I atom positions essentially coincide with the methyl C atom positions and were not fully resolved.

**Supporting Information Available:** Complete X-ray data for **1**, **2**, and **3**. This material is available free of charge via the Internet at http:pubs.acs.org.

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