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Formation of a THF adduct of the organometallic samarium oxide $[(C_5Me_5)_2Sm]_2(\mu\text{-}O)$

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Abstract

$(C_5Me_5)_2Sm(THF)_2$ reacts with 1,2-epoxybutane in toluene to form, in addition to the toluene soluble $[(C_5Me_5)_2Sm]_2(\mu\text{-}O)$, **1**, the hexane soluble $[(C_5Me_5)_2Sm(THF)]_2(\mu\text{-}O)$, **2**. In hexane, **2** loses THF to form **1** as a precipitate, but **1** cannot be converted to **2** by addition of THF at room temperature. Compound **1** does convert to **2** in low yield in THF at reflux. The reaction of $(C_5Me_5)_2Sm(phthalan)$ with 1,2-epoxybutane generates **1** and a phthalan analog of **2**, $[(C_5Me_5)_2Sm(phthalan)]_2(\mu\text{-}O)$, **3**. Compound **2** reacts with Me_3CCN to form $[(C_5Me_5)_2Sm(NCCMe_3)]_2(\mu\text{-}O)$, **4**, by displacement of THF.

Key words: Samarium; Oxide; Pentamethylcyclopentadienyl; Epoxybutane; Lanthanide; Metallocenes

1. Introduction

Extensive studies of the reactivity of di- and trivalent organosamarium complexes containing the $(C_5Me_5)_2Sm$ unit [1] have shown that $[(C_5Me_5)_2Sm]_2(\mu\text{-}O)$, **1**, [2], is one of the most frequently formed byproducts obtained in the presence of a source containing oxygen. Despite the frequent occurrence of **1**, it is not readily prepared directly. The best synthesis of this complex from $(C_5Me_5)_2Sm(THF)_2$ and 1,2-epoxybutane gave **1** in only 55% yield [2]. We have now investigated the byproducts of this reaction and find that the other main organosamarium product in this reaction is another oxide complex namely the THF adduct of **1**, $[(C_5Me_5)_2Sm(THF)]_2(\mu\text{-}O)$, **2**. The identification of a THF solvate of **1** is surprising since the X-ray crystal structure of **1** suggested that it was too sterically crowded to coordinate an additional ligand as large as THF. Since the formation of **1** functions as a gauge of how well an organosamarium reaction occurs, it is important to identify other related oxide complexes which can provide similar information. The synthesis and characterization of **2** are described as well as the implications of this solvated complex in bis(pentamethylcyclopentadienyl)samarium chemistry in general.

2. Experimental details

The chemistry described below was performed under nitrogen with rigorous exclusion of air and water using Schlenk, vacuum line, and glovebox (Vacuum/Atmospheres HE-553 Dri-Lab) techniques. Physical measurements were obtained, solvents were purified [3], and $(C_5Me_5)_2Sm(THF)_2$ [4] was prepared as previously described. 1,2-Epoxybutane, phthalan, and Me_3CCN were obtained from Aldrich, dried over 4A molecular sieves, and degassed before use.

2.1. $[(C_5Me_5)_2Sm(THF)]_2(\mu\text{-}O)$, 2

Addition of 1,2-epoxybutane (76.0 μL, 0.882 mmol) by microliter syringe to $(C_5Me_5)_2Sm(THF)_2$ (0.951 g, 1.68 mmol) in toluene (100 mL), caused an immediate color change from purple to brownish-yellow. After the reaction mixture was stirred for 2 h, the volume was reduced by half and the mixture was centrifuged to remove **1** as a finely divided yellow solid (0.320 g, 0.373 mmol). The volatiles were removed in vacuo from the supernatant to yield a yellow-brown solid. The solid was extracted with hexanes and additional **1** (0.148 g, 0.173 mmol) was removed by centrifugation (overall yield of **1**: 65%). The volatiles were removed from the supernatant *in vacuo* to yield **2** as a brownish-yellow oily solid (0.357 g). ^1H NMR (C_6D_6, 250 MHz, 25°C) δ 1.41 (s, C_5Me_5), -2.6 (br $\Delta\nu_{1/2} = 15$ Hz, THF), -4.1

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(br $\Delta\nu_{1/2} = 20$ Hz, THF) ppm. ^1H NMR (C_4D_8O, 250 MHz, 25°C) δ 1.34 (s, C_5Me_5). ^{13}C NMR (C_6D_6, 300 MHz, 25°C) δ 113.7 (C_5Me_5), 60.7 (THF), 18.3 (THF), 17.9 ($C_5\mathit{Me}_5$) ppm. Attempts to convert the oily product to a solid suitable for elemental analysis by repeated hexane washing, drying under high vacuum, or by recrystallization caused conversion of **2** to **1** by loss of THF. Complexometric analysis of the oily material was consistent with the proposed formula: Anal. Calcd for $Sm_2C_{48}H_{76}O_s3$: Sm, 30.02%. Found: Sm, 28.0%.

2.2. $[(C_5Me_5)_2Sm(phthalan)]_2(\mu\text{-}O)$, 3

Phthalan, C_8H_8O (11.5 μL, 0.105 mmol), was added to a toluene (10 mL) solution of the green $(C_5Me_5)_2Sm(THF)$, which was obtained by removing solvent from a solution of $(C_5Me_5)_2Sm(THF)_2$ (0.059 g, 0.10 mmol) in toluene (10 mL) by rotary evaporation (1.5 h) [5]. The mixture was stirred for 15 min and the volatiles were removed under vacuum leaving a purple solid which was dissolved in toluene (10 mL). Addition of 1,2-epoxybutane (4.7 μL, 0.055 mmol) to the solution caused an immediate color change to brownish-yellow. After the reaction mixture was stirred for 1 h, the volatiles were removed in vacuo leaving an oily yellow solid. Extraction with hexanes, followed by centrifugation yielded **1** (0.032 g, 0.037 mmol, 71%) as a yellow solid. The volatiles were removed from the supernatant *in vacuo* leaving **3** as a brownish-yellow solid (0.025 g, 0.023 mmol). ^1H NMR (C_6D_6, 250 MHz, 25°C) δ 6.0 (br $\Delta\nu_{1/2} = 20$ Hz, phthalan), 5.2 (br $\Delta\nu_{1/2} = 25$ Hz, phthalan), 3.1 (br $\Delta\nu_{1/2} = 15$ Hz, phthalan), 1.37 (s, C_5Me_5) ppm. As with **2**, attempts to convert the oily product to a solid suitable for elemental analysis caused conversion of **3** to **1** by loss of phthalan. Complexometric analysis of the oily material was consistent with the proposed formula: Anal. Calcd for $Sm_2C_{56}H_{76}O_3$: Sm, 27.39%. Found: Sm, 27.3%.

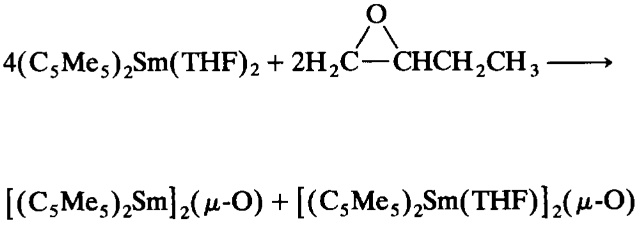
2.3. $[(C_5Me_5)_2Sm(NCCMe_3)]_2(\mu\text{-}O)$, 4

tert-Butylnitrile (9.7 μL, 0.088 mmol) was added to a solution of $[(C_5Me_5)_2Sm(THF)]_2(\mu\text{-}O)$ (0.044 g, 0.044 mmol) in toluene (5 mL). After the mixture was stirred for 0.5 h, the volatiles were removed *in vacuo* to leave **4** as an orange-yellow oil which by NMR spectroscopy was primarily the crystallographically characterized **4** [6]. ^1H NMR (C_6D_6, 250 MHz, 25°C) δ 1.45 (s, 30 H, C_5Me_5), −0.87 (s, 9H, Me_3CCN) ppm. This reaction was also monitored by NMR to observe the displacement of THF. A ^1H NMR sample of $[(C_5Me_5)_2Sm(THF)]_2(\mu\text{-}O)$ (0.036 g, 0.036 mmol) was prepared in C_6D_6 (0.5 mL). tert-Butylnitrile (8 μL, 0.07 mmol) was added by microliter syringe and the NMR spectrum was obtained. The spectrum of **4** plus THF at δ 3.0 and 1.2 ppm was observed. Removal of the volatiles and reexamination of the sample showed resonances only for **4**.

3. Results and discussion

The reaction of $(C_5Me_5)_2Sm(THF)_2$ with 1,2-epoxybutane in toluene had previously been found to form toluene soluble $[(C_5Me_5)_2Sm]_2(\mu\text{-}O)$, **1**, in 55% yield [2]. Attempts to characterize the hexane soluble byproduct of this reaction, **2**, were hindered by the fact that **2** readily decomposed to **1** when isolation was attempted. The C_5Me_5 ^1H NMR resonance of **2** in C_6H_6, δ 1.41 ppm, was significantly different from that of **1**, δ 0.06 ppm. However, it was closer to the 1.45 and 1.53 ppm shifts of the crystallographically characterized oxides $[(C_5Me_5)_2Sm(NCCMe_3)]_2(\mu\text{-}O)$, **4** (obtained as a byproduct of the reaction of $(C_5Me_5)_2Sm(THF)_2$ and Me_3CCN [6] and by addition of Me_3CCN to **1**), and $[(C_5Me_5)_2Sm(CNCMe_3)]_2(\mu\text{-}O)$, **5** (obtained from the reaction of **1** and tert-butylisonitrile [7]). Although these two examples indicated that adducts of **1**, *i.e.* $[(C_5Me_5)_2SmL]_2(\mu\text{-}O)$, could form, in both of these cases the adduct ligands have small cylindrical donor atom environments which make adduct formation more likely than with a ligand such as THF. Further evidence suggesting that the hexane soluble product could be $[(C_5Me_5)_2Sm(THF)]_2(\mu\text{-}O)$ was the recently reported existence of the cerium analog, $[(C_5Me_5)_2Ce(THF)]_2(\mu\text{-}O)$, which was characterized by X-ray crystallography [8]. However, since samarium is smaller than cerium [9], it was not certain if the more sterically crowded coordination environment in **1** could accommodate two additional THF ligands.

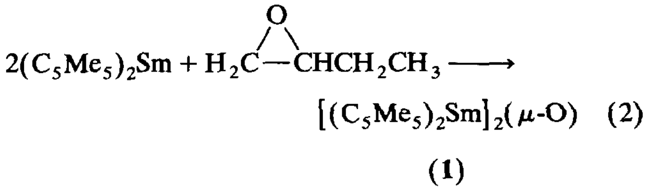
Complexometric analysis of **2** was consistent with its formulation as $[(C_5Me_5)_2Sm(THF)]_2(\mu\text{-}O)$ (eqn. (1)), but attempts to characterize it by crystallographic analysis were complicated by its oily nature and facile conversion to **1**. Confirmation of its identity was obtained by the following series of experiments.



$$4(C_5Me_5)_2Sm(THF)_2 + 2H_2\overset{O}{C\!-\!C}HCH_2CH_3 \longrightarrow [(C_5Me_5)_2Sm]_2(\mu\text{-}O) + [(C_5Me_5)_2Sm(THF)]_2(\mu\text{-}O) \qquad (1)$$

(1) (2)

The fact that **2** readily converts to **1** indicated that these complexes were closely related. Since it was unlikely that the short Sm–O bond would be cleaved or that a C_5Me_5 ring would be lost in this **2** to **1** conversion, THF loss seemed most likely for this room temperature process. However, since many organosamarium complexes decompose to **1** in solution this alone was not definitive. The formulation of **2** as a THF adduct of **1** was further supported by the observations that (a) crude $(C_5Me_5)_2Sm(THF)_2$/epoxybutane reaction mixtures contained more **2** than samples which had been washed with hexanes, (b) the reaction of $(C_5Me_5)_2Sm(THF)_2$ with epoxybutane *in THF* generated more **2** than the reaction in toluene, and (c), the reaction of unsolvated $(C_5Me_5)_2Sm$ [10] with 1,2-epoxybutane in toluene generates a quantitative yield of only **1** according to eqn. (2).

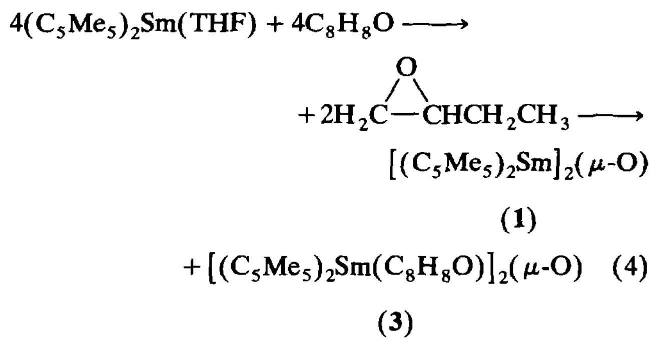


$$2(C_5Me_5)_2Sm + H_2\overset{O}{C{-}}CHCH_2CH_3 \longrightarrow \underset{(1)}{[(C_5Me_5)_2Sm]_2(\mu\text{-}O)} \quad (2)$$

Attempts to convert of **1** to **2** by addition of THF were not successful at room temperature. However, **1** does have a significantly different C_5Me_5 NMR shift in THF-d_8, 1.19 ppm (*cf.* 1.34 ppm for **2** in THF-d_8) and heating **1** in THF at reflux, forms a variety of products among which is **2**. The best evidence for the presence of coordinated THF in **2** was the fact that THF could be displaced by Me_3CCN in toluene to form the crystallographically characterized $[(C_5Me_5)_2Sm(NCCMe_3)]_2(\mu\text{-}O)$, **4** [6], according to eqn. (3).

$$\underset{(2)}{[(C_5Me_5)_2Sm(THF)]_2(\mu\text{-}O)} + 2Me_3CCN \longrightarrow 2THF + \underset{(4)}{[(C_5Me_5)_2Sm(Me_3CCN)]_2(\mu\text{-}O)} \quad (3)$$

Attempts to make a crystallographically characterizable analog of **2** were pursued with phthalan [11], eqn. (4). This reaction paralleled reaction (1) in that a



$$4(C_5Me_5)_2Sm(THF) + 4C_8H_8O + 2H_2\overset{O}{C{-}}CHCH_2CH_3 \longrightarrow \underset{(1)}{[(C_5Me_5)_2Sm]_2(\mu\text{-}O)} + \underset{(3)}{[(C_5Me_5)_2Sm(C_8H_8O)]_2(\mu\text{-}O)} \quad (4)$$

mixture of unsolvated **1** and a hexane soluble byproduct, **3**, which readily converted to **1**, was obtained. **3** had a C_5Me_5 ^1H NMR signal at δ 1.37 ppm similar to that of the other Lewis base adducts of **1** discussed above. Complexometric analysis was consistent with formation of a phthalan derivative, but single crystals suitable for X-ray crystallography have not been obtained.

The formation of THF and phthalan adducts of **1** suggested that other basic reagents should coordinate or react with **1**. Indeed, reactivity with PhNCO, Ph_3PO, C_5H_5NO, Et_4NCN, NO, CO_2, and NaC≡CPh was observed, but pure samples of characterizable products were not obtained.

4. Conclusion

The identification of **2** and **3** has important implications for the chemistry of organosamarium complexes. First, the formation of such oxide complex adducts could be more widespread than previously anticipated. Typically, observation of a C_5Me_5 shift at δ 0.06 ppm in a reaction involving a $(C_5Me_5)_2Sm$ unit indicates that some oxide formation has occurred, *i.e.* that **1** is present. The magnitude of this resonance indicates how much decomposition to this oxide has occurred. The present results show that this may be an underestimate of how much Sm–O–Sm formation has occurred, since the ^1H NMR shifts of base adducts **2** and **3** are significantly different from that of **1**. Hence, C_5Me_5 resonances in the 1.3–1.5 ppm range could also indicate the presence of a Sm–O–Sm unit existing as base adducts formed *in situ*. Second, this chemistry provides another example of how the four C_5Me_5 rings in a bimetallic $[(C_5Me_5)_2Sm]_2$(substrate) complex sterically control the reaction chemistry [11–13]. Base adducts of **1** can be much more readily formed in situ during assembly of the Sm–O–Sm unit in the presence of a coordinating ligand. Once the tetrahedral array of four C_5Me_5 rings is in place, it is much more difficult to form the base adducts. Finally, despite the compact nature of **1**, this complex appears to have latent reactivity with small basic substrates. The opportunity to do size selective reactions with this molecule is under investigation [14].

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