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## Preparation and crystal structures of silyl-substituted potassium cyclooctatetraenides

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Dedicated to Professor William J. Evans on the occasion of his 70th birthday.

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## ABSTRACT

Cyclooctatetraenyl complexes of potassium are readily available by the reaction of silyl-substituted cyclooctatrienes  $C_8H_8-1,4-(SiR_3)_2$  ( $SiR_3 = SiMe_3, SiMe_2Bu, SiPh_3$ ) with potassium hydride or potassium metal. While  $C_8H_8-1,4-(SiMe_3)_2$  gave a mixture of  $K_2\{C_8H_6-1,3-(SiMe_3)_2\}$  (**1a**) and  $K_2\{C_8H_7-SiMe_3\}$  (**1b**), the substitution pattern on the COT ring remained unchanged in the case of  $C_8H_8-1,4-(SiMe_2Bu)_2$  and  $C_8H_8-1,4-(SiPh_3)_2$ .  $[K_2\{C_8H_6-1,4-(SiMe_2Bu)_2\}(PhMe)]_\infty$  (**2**) crystallizes in the absence of DME, featuring a  $\mu_4$ -bridging COT ring, while in  $[K_2(C_8H_6-1,4-(SiPh_3)_2)(DME)_4]$  (**3**) the substituted COT ligand adopts a highly symmetric  $\mu-\eta^8:\eta^8$ -coordination, resulting in an “inverse sandwich” architecture. Compound **3** could be oxidized by treatment with iodine to give the corresponding neutral cyclooctatetraene derivative  $C_8H_6-1,4-(SiPh_3)_2$  (**4**).

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## 1. Introduction

The planar,  $10\pi$ -aromatic cyclooctatetraenide dianion,  $C_8H_8^{2-}$  (commonly abbreviated as COT), plays an indispensable role in the organometallic chemistry of *f*-elements since the discovery of iconic uranocene by Streitwieser and Müller-Westerhoff in 1968 [1]. Since then, numerous sandwich and half-sandwich COT complexes of lanthanides [2] and actinides [3] have been studied. Central precursor in most of their preparations is the di-potassium salt  $K_2C_8H_8$  or  $K_2COT$ .  $K_2C_8H_8$  was first mentioned in the literature by Katz in 1960 [4]. Crystalline  $K_2C_8H_8 \cdot THF$  was first made by Fritz and Keller in 1961 by direct reaction of 1,3,5,7-cyclooctatetraene with 2 equiv. of potassium metal in THF [5].  $K_2C_8H_8 \cdot THF$  forms yellow crystals which upon drying easily disintegrate to give a white powder of the unsolvated  $K_2C_8H_8$ . A remarkable property of  $K_2COT$  is its explosive decomposition in contact with air [5a]. The synthetic route to this important reagent was later improved by using inexpensive 1,5-cyclooctadiene as starting material [6]. Structurally characterized solvates of  $K_2C_8H_8$  include

$K_2C_8H_8(\text{diglyme})$  (diglyme =  $(MeOCH_2CH_2)_2O$ ) [7] and  $K_2C_8H_8(THF)_3$  [8]. More recently, bulky silyl-substituted COT ligands have entered the focus of attention. This remarkable recent development was possible mainly through the pioneering work of Cloke et al., who introduced silylated COT ligands of the type  $\{C_8H_6-1,4-(SiR_3)_2\}^{2-}$  (e.g.  $R = Me, iPr$ ) in organolanthanide and -actinide chemistry [9,10]. It has been demonstrated that the  $\{C_8H_6-1,4-(SiMe_3)_2\}^{2-}$  ligand (= COT<sup>''</sup>) imparts improved solubility and crystallinity over the parent  $C_8H_8^{2-}$  and enables e.g. the synthesis of anionic sandwich complexes  $[Ln\{C_8H_6-1,4-(SiMe_3)_2\}_2]^-$  for the entire lanthanide series [11]. Moreover, the use of silyl-substituted COT ligands led to the discovery of unusual molecular architectures (e.g. triple- and tetradecakers) [12], novel Ln(COT)-based organometallic sandwich molecular wires (OSMWs) [13] and single-molecule magnets (SMMs) [14] as well as unprecedented reactions of uranium COT complexes (e.g. carbon monoxide oligomerization) [15]. A new dimension in steric bulk was added to this chemistry by the introduction of the “superbulky” ligand COT<sup>big</sup> (= 1,4-bis(triphenylsilyl)-cyclooctatetraenyl dianion) by us and the Evans group in 2011 [16]. The use of COT<sup>big</sup> in organolanthanide and -actinide chemistry has led to interesting structural effects such as the formation of the significantly bent anionic Ce<sup>III</sup> sandwich

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complex  $[\text{Ce}\{\text{C}_8\text{H}_6\text{-}1,4\text{-(SiPh}_3)_2\}_2]^-$ , the novel neutral cerocene  $[\text{Ce}\{\text{C}_8\text{H}_6\text{-}1,3\text{-(SiPh}_3)_2\}_2]$  formed by  $\text{SiPh}_3$  group migration, as well as the first example of a bent uranocene,  $[\text{U}\{\text{C}_8\text{H}_6\text{-}1,4\text{-(SiPh}_3)_2\}_2]$ , which exhibits no additional ligands [16].

Key starting material in COT<sup>''</sup> chemistry is the lithium derivative  $\text{Li}_2\{\text{C}_8\text{H}_6\text{-}1,4\text{-(SiMe}_3)_2\}$ , which was first prepared by Cloke and co-workers [9]. Since then,  $\text{Li}_2\{\text{C}_8\text{H}_6\text{-}1,4\text{-(SiMe}_3)_2\}$  has been utilized as precursor for numerous early transition metal, lanthanide and actinide COT<sup>''</sup> complexes [9,12,14]. Structural studies have been carried out on the DME adduct  $[\text{Li}(\text{DME})_2]\{\text{C}_8\text{H}_6\text{-}1,4\text{-(SiMe}_3)_2\}$  and the dimeric THF adduct  $[\text{Li}(\text{THF})_2]_2[\text{Li}_2\{\text{C}_8\text{H}_6\text{-}1,4\text{-(SiMe}_3)_2\}]$  [17]. The molecular structure of  $[\text{Li}(\text{DME})_2]\{\text{C}_8\text{H}_6\text{-}1,4\text{-(SiMe}_3)_2\}$  consists of a  $\{\text{C}_8\text{H}_6\text{-}1,4\text{-(SiMe}_3)_2\}^{2-}$  dianion with the two lithium atoms coordinated to the ring in an  $\eta^3$ -allyl-like fashion [17a]. In  $[\text{Li}(\text{THF})_2]_2[\text{Li}_2\{\text{C}_8\text{H}_6\text{-}1,4\text{-(SiMe}_3)_2\}]$  two  $\text{Li}^+$  ions are sandwiched between two COT rings, while two  $\text{Li}(\text{THF})_2^+$  units are bonded to the outsides of the sandwich [17b]. The same authors reported the polymeric crystal structure of  $[\text{Na}_2\{\text{C}_8\text{H}_6\text{-}1,4\text{-(SiMe}_3)_2\}(\mu\text{-THF})_2]_n$ , which was prepared by treatment of  $[\text{Li}(\text{THF})_2]_2[\text{Li}_2\{\text{C}_8\text{H}_6\text{-}1,4\text{-(SiMe}_3)_2\}]$  with  $\text{NaCl}$  [17b]. The formation of  $\text{K}_2\{\text{C}_8\text{H}_6\text{-}1,4\text{-(SiMe}_3)_2\}$  was briefly mentioned in an early report [17a]. Alkali metal derivatives of COT<sup>big</sup> have not yet been isolated nor structurally characterized. We report here the first thorough preparative and structural investigation of a series of bis(silylated) potassium cyclooctatetraenides.

## 2. Results and discussion

### 2.1. Preparation of the compounds

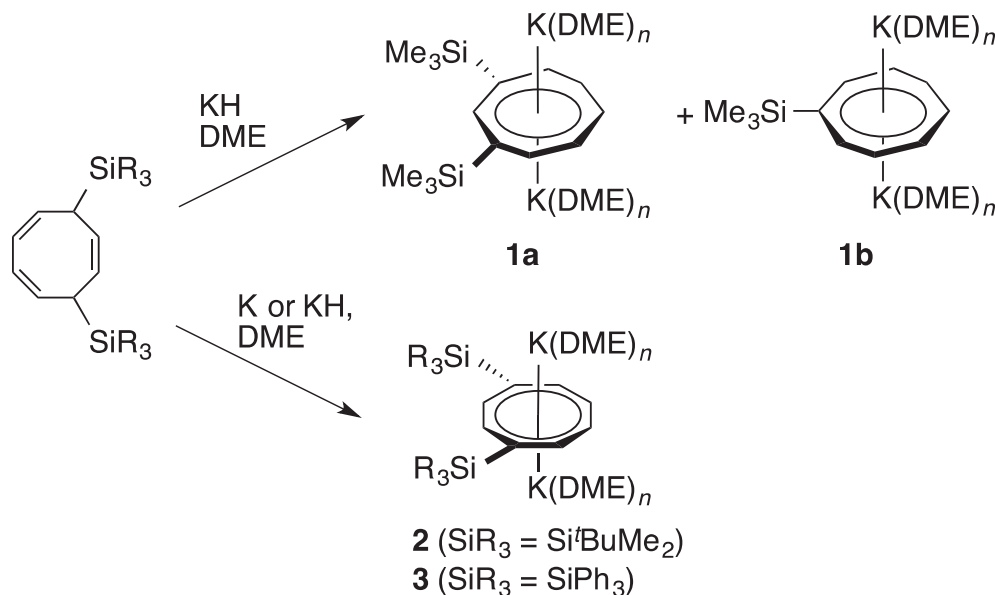
1,4-Disilylated cycloocta-2,5,7-trienes  $\text{C}_8\text{H}_8\text{-}1,4\text{-(SiR}_3)_2$  are readily deprotonated in the 1,4-positions upon treatment with <sup>n</sup>BuLi to yield the corresponding aromatic  $\{\text{C}_8\text{H}_6\text{-}1,4\text{-(SiR}_3)_2\}^{2-}$  anions ( $\text{SiR}_3 = \text{SiMe}_3, \text{Si}^t\text{BuMe}_2, \text{SiPh}_3$ ) [9,10,17]. We now found that similar reactions with potassium hydride or potassium metal can take a different course. For example, reaction of  $\text{C}_8\text{H}_8\text{-}1,4\text{-(SiMe}_3)_2$  with KH surprisingly afforded a mixture of  $\text{K}_2\{\text{C}_8\text{H}_6\text{-}1,3\text{-(SiMe}_3)_2\}(\text{DME})_2$  (**1a**) and the monosilylated species  $\text{K}_2\{\text{C}_8\text{H}_7\text{(SiMe}_3)\}(\text{DME})_2$  (**1b**; Scheme 1). The product ratio, determined by NMR spectroscopy, was always around 1:1, independent of the

reaction conditions (r.t. or reflux temperature, stoichiometric amount or excess KH). Due to very similar solubility properties, the two species could not be separated. Single-crystals of **1a** and **1b** could only be distinguished by their cell parameters as determined by X-ray diffraction because both species outwardly appeared as colorless, plate-like crystals. The actual target product,  $\text{K}_2\{\text{C}_8\text{H}_6\text{-}1,4\text{-(SiMe}_3)_2\}$  has never been found in the reaction mixture. In this context it is worth mentioning that in the reaction of the tetrasilylated cyclooctatriene  $\text{C}_8\text{H}_6\text{-}1,3,6,6\text{-(SiMe}_3)_4$  with KH, one equiv. of  $\text{Me}_3\text{SiH}$  is selectively released and the trisilylated potassium derivative  $\text{K}_2\{\text{C}_8\text{H}_5\text{-}1,3,6\text{-(SiMe}_3)_3\}$  (**1c**) has been isolated as the only product [18]. Similar treatment of  $\text{C}_8\text{H}_8\text{-}1,4\text{-(SiR}_3)_2$  ( $\text{R} = \text{Si}^t\text{BuMe}_2, \text{SiPh}_3$ ) with potassium metal or potassium hydride in DME led to formation of the metal derivatives  $\text{K}_2\{\text{C}_8\text{H}_6\text{-}1,4\text{-(SiR}_3)_2\}$ . The isolation of DME-solvated  $\text{K}_2\{\text{C}_8\text{H}_6\text{-}1,4\text{-(Si}^t\text{BuMe}_2)_2\}$  (**2**) has been reported earlier [19]. A DME-free form of **2** has now been obtained by recrystallization of the crude product from toluene in 70% yield. In the case of the  $\text{SiPh}_3$ -substituted ligand, the DME solvate  $[\text{K}_2\{\text{C}_8\text{H}_6\text{-}1,4\text{-(SiPh}_3)_2\}(\text{DME})_4]$  (**3**) was the only product obtained in 76% isolated yield. In both cases the silyl substitution pattern of the COT ligand remained unchanged upon metalation with KH or potassium metal, respectively.

Like the parent  $\text{K}_2\text{COT}$ , the new potassium COT complexes are highly oxidation sensitive, as it was illustrated at the example of compound **3**. Addition of iodine to a THF solution led to formation of the hitherto unknown cyclooctatetraene derivative  $\text{C}_8\text{H}_6\text{-}1,4\text{-(SiPh}_3)_2$  (**4**) which was obtained in the form of colorless, air-stable, high-melting crystals in 72% isolated yield (Scheme 2).

### 2.2. Crystal structures

Relevant interatomic distances in **1a**, **1b** and **2–4** are represented in Table 1, while experimental details on the structure analyses are summarized in Table 2. Both  $\text{SiMe}_3$ -substituted complexes **1a** and **1b** crystallize in the orthorhombic space group *Pnma*, featuring very similar molecular structures. The COT rings each adopt a highly symmetric  $\mu\text{-}\eta^8\text{:}\eta^8$ -bridging coordination mode (Figs. 1 and 2). The so-formed “inverse sandwich”-like [17b,20]  $\text{K}_2(\text{COT})$  moieties are interconnected by two  $\mu\text{-}\kappa\text{O},\text{O}':\kappa\text{O},\text{O}'$ -coordinated DME ligands, leading to a one-dimensional polymeric



Scheme 1. Preparation of the potassium complexes **1a–3**.

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