Preparation and Structural Characterization of the Dilithium 1,4-Bis(trimethylsilyl)cyclooctatetraenide Bis(dimethoxyethane) Adduct[†,1]

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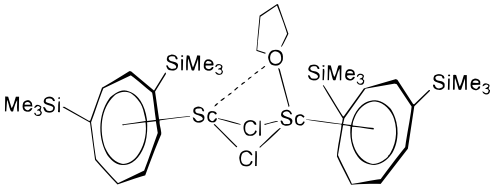
Summary: The organolithium compound $[Li(DME)]_2[C_8H_6(SiMe_3)_2\text{-}1,4]$ *(**2**) was prepared and characterized by a single-crystal X-ray structural analysis. The structure consists of a 1,4-bis(trimethylsilyl)cyclooctatetraene dianion with the two lithium atoms coordinated to the ring in an* η^3*-allyl-like fashion. The corresponding potassium derivative* $K_2[C_8H_6(SiMe_3)_2\text{-}1,4]$ *(**3**) has been prepared by deprotonation of 1,4-bis(trimethylsilyl)-2,5,7-cyclooctatriene with potassium hydride.*

Trimethylsilyl substituents attached to various organic ligands are generally considered to impose favorable effects on metal complexes containing these ligands. These effects include, for example, lower degrees of aggregation, better crystallinity, and higher solubility of the products as compared to the unsubstituted ligand systems. A typical example is the 1,3-bis(trimethylsilyl)cyclopentadienyl anion (=Cp″), which has been demonstrated to be a highly useful ligand in organotransition-metal and f-element chemistry.[2] In several cases, the properties of cyclooctatetraenyl metal complexes have also been shown to benefit from silyl substitution. Complexes containing the 1,4-bis(trimethylsilyl)cyclooctatetraenyl ligand, $[C_8H_6(SiMe_3)_2\text{-}1,4]^{2-}$ (=COT″, in analogy to Cp″) were first studied by Cloke et al.[3] Marked differences between certain COT″ complexes and their counterparts containing the unsubstituted cyclooctatetraenyl ligand (=COT) have been uncovered, including different stoichiometries and significantly higher solubilities. For example, the unusual scandium derivative $(\mu\text{-THF})(\mu\text{-Cl})_2[Sc(COT'')]_2$[3a] with a bridging THF ligand has no parent COT analogue:[4,5]



The most important starting material in this chemistry is the lithium derivative $Li_2[C_8H_6(SiMe_3)_2\text{-}1,4]$ (=Li_2COT″), which is generally prepared in situ by deprotonation of 1,4-bis(trimethylsilyl)-2,5,7-cyclooctatriene (**1**). The precursor **1** is readily available in one step from 1,5-cyclooctadiene.[3] Although Li_2COT″ has been frequently used as a precursor, its structure remains elusive. We report here the structural characterization of the dimethoxyethane adduct $[Li(DME)]_2[C_8H_6(SiMe_3)_2\text{-}1,4]$ (**2**) as well as the preparation of the hitherto unknown potassium derivative K_2COT″ (**3**).

The title compound **2** was first obtained serendipitously in our laboratory during an attempted recrystallization of polymeric $[Yb(COT'')]_n$ from DME/hexane (DME = 1,2-dimethoxyethane). This insoluble ytterbium(II) species had previously been prepared by reacting ytterbium diiodide with an equimolar amount of

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[†] Dedicated to Prof. Hartmut Bärnighausen on the occasion of his 65th birthday.

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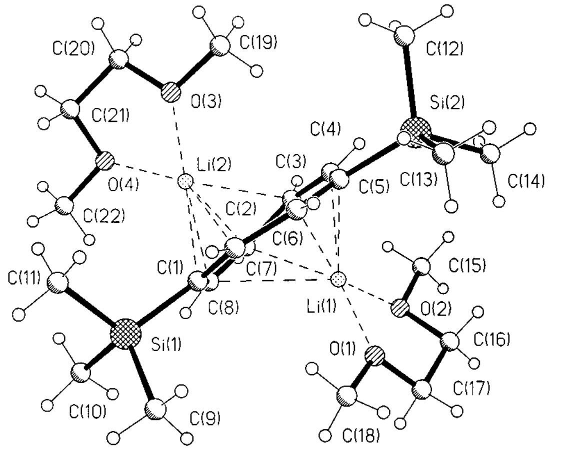


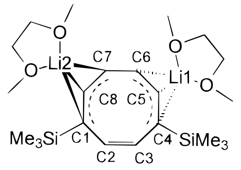
Figure 1. Molecular structure of **2**. Selected bond lengths (Å) and angles (deg): Li(1)−O(1) = 1.966(8), Li(1)−O(2) = 2.042(9), Li(1)−C(4) = 2.427(9), Li(1)−C(5) = 2.237(9), Li(1)−C(6) = 2.246(9), Li(2)−O(3) = 1.955(8), Li(2)−O(4) = 2.023(8), Li(2)−C(1) = 2.298(9), Li(2)−C(7) = 2.267(9), Li(2)−C(8) = 2.180(0), C(1)−C(2) = 1.429(6), C(2)−C(3) = 1.415(6), C(3)−C(4) = 1.417(6), C(4)−C(5) = 1.420(7), C(5)−C(6) = 1.407(7), C(6)−C(7) = 1.432(7), C(7)−C(8) = 1.405(7), C(1)−C(8) = 1.413(7); O(1)−Li(1)-O(2) = 81.7(3), C(4)−Li(1)-C(6) = 67.8(3), O(3)−Li(2)-C(4) = 81.3(3), C(1)−Li(2)-C(7) = 69.5(3).

Li_2COT″.[6] During the recrystallization process well-formed colorless crystals were observed which proved to be suitable for an X-ray diffraction study. Analytical and spectroscopic data of these crystals showed the material to be [Li(DME)]$_2$[$C_8H_6(SiMe_3)_2$-1,4] (**2**). Subsequently it was found that this compound is readily accessible by direct deprotonation of 1,4-bis(trimethylsilyl)-2,5,7-cyclooctatriene (**1**) with 2 equiv of *n*-butyllithium in hexane solution in the presence of DME (eq 1). The lithium derivative crystallizes directly from the

$$\underset{\mathbf{1}}{C_8H_8(SiMe_3)_2\text{-}1,4} + 2\ n\text{-BuLi} \xrightarrow[-2C_4H_{10}]{\text{DME}} \underset{\mathbf{2}}{[Li(DME)]_2[C_8H_6(SiMe_3)_2\text{-}1,4]} \quad (1)$$

concentrated reaction mixture. Elemental analysis and spectroscopic data reveal the identity of the product with the original crystals obtained from the [Yb(COT″)]$_n$ crystallization experiment. These were subsequently used for an X-ray structural determination of **2**. The molecular structure is shown in Figure 1.

The molecular structure consists of a [$C_8H_6(SiMe_3)_2$-1,4]$^{2-}$ dianion bridging two [Li(DME)]$^+$ units in a type of inverse sandwich complex. It might be anticipated that the lithium ions respond sensitively to electronic differences within the ring, as the ionic radius of Li^+ is too small for η^8 coordination. The shortest Li−C distances in **2** are Li(1)−C(5) (2.237 Å) and Li(2)−C(8) (2.180 Å). Thus, the Li^+ ions show a preference for the β positions with respect to the trimethylsilyl substituents. The overall coordination mode between lithium and the ring atoms can be described as distorted allyl-like (η^3). Together with the two oxygen atoms of the coordinated DME ligands each lithium atom adopts a formal coordination number of 5. The polymeric allyllithium derivative [Li(Et_2O)][1,3-$Ph_2C_3H_3$] has been reported to contain formally seven-coordinated lithium.[7] The C−C distances within the Li(η^3-allyl) units in both compounds agree favorably when the different coordination numbers around lithium are taken into account. The C−C distances in the eight-membered ring vary between 1.405 and 1.432 Å. A suitable description of the coordination mode in **2** is



Apparently no lithium derivative of the parent cyclooctatetraenyl dianion has been characterized by X-ray crystallography. In the structurally characterized potassium derivatives $K_2(C_8H_8)\cdot 3THF$[8a] and $K_2(C_8H_8)\cdot(MeOCH_2CH_2)_2O$[8b] the potassium ions are bridged by planar cyclooctatetraenyl rings in a μ-η:$^8\eta^8$ fashion to form polymeric chains.

In many cases potassium salts offer preparative advantages as ligand transfer reagents over the corresponding lithium derivatives.[9] This is in part due to the fact that in reactions with metal halides the resulting potassium halide byproducts are more readily separated from the reaction mixture than lithium halides due to their lower solubility in organic solvents. Thus, the hitherto unknown potassium salt of the [$C_8H_6(SiMe_3)_2$-1,4]$^{2-}$ dianion was prepared as a possible alternative starting material. Deprotonation of **1** was achieved by treatment with potassium hydride in boiling diethyl ether according to eq 2. The organopotassium

$$\underset{\mathbf{1}}{C_8H_8(SiMe_3)_2\text{-}1,4} + 2KH \xrightarrow[-2H_2]{Et_2O} \underset{\mathbf{3}}{K_2[C_8H_6(SiMe_3)_2\text{-}1,4]} \quad (2)$$

compound **3** was isolated as a white solid in only 27% yield by precipitation with hexane. Spectroscopic data are in agreement with the formulation of unsolvated K_2[$C_8H_6(SiMe_3)_2$-1,4]. However, the low product yield and the pyrophoric nature of **3** significantly diminish its synthetic value and make this compound a less attractive starting material than **2**. In fact, **2** is readily isolated as a stable crystalline solid which can be stored indefinitely under nitrogen. It is thus an easily handled, well-defined source of the COT″ ligand which can be used for stoichiometric reactions.

Experimental Section

General Procedures. All reactions were carried out under an atmosphere of purified nitrogen using standard Schlenk

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or glovebox techniques. A Braun MB 150-GI glovebox was used for storage of the compounds and to prepare samples for spectroscopic studies. Solvents were dried over sodium−benzophenone and freshly distilled under N_2 prior to use. 1,4-Bis(trimethylsilyl)-2,5,7-cyclooctatriene (**1**) was prepared as described elsewhere.[3a,b]

Elemental analyses were performed by the Analytisches Labor des Instituts für Anorganische Chemie der Universität Göttingen. NMR spectra were recorded on a Bruker AM 250 spectrometer and were externally referenced to TMS. FT-IR spectra were measured on a Bio-Rad FTS-7 as Nujol mulls between KBr plates in the range of 4000−380 cm^{-1}.

Preparation of $[Li(DME)]_2[C_8H_6(SiMe_3)_2\text{-}1,4]$ (2). To a stirred solution of 4.00 g (16.0 mmol) of 1,4-bis(trimethylsilyl)-2,5,7-cyclooctatriene in 100 mL of hexane/DME (10:1) was added at −78 °C 13.9 mL (32 mmol) of *n*-butyllithium (2.3 M in hexanes). The mixture was slowly warmed to room temperature and stirred at 25 °C for 15 h. The resulting brownish yellow solution was concentrated in vacuo to a total volume of ca. 50 mL. Crystallization at −20 °C (48 h) afforded 5.10 g (72%) of **2** as colorless, air-sensitive crystals. Mp: 163−165 °C dec. ^1H NMR (250 MHz, C_6D_6): δ 7.25 (m, 4 H, ring H), 7.13−7.04 (m, 2 H, m, 2 H, ring H), 3.78−3.66 (m, 8 H, OCH_2), 3.30 (s, 12 H, OCH_3), 0.18 (s, 18 H, $SiMe_3$) ppm. ^{13}C NMR (62.89 MHz, C_6D_6): δ 98.2, 96.9, 94.8, 88.2 (ring C), 93.4 (OCH_2), 55.6 (OCH_3), 1.1 ($SiMe_3$) ppm. ^{29}Si NMR (79.46 MHz, THF/C_6D_6): δ −0.5 (s) ppm. IR (Nujol mull): 1407 (w), 1308 (w), 1261 (s), 1244 (vs), 1160 (w), 1157 (m), 1089 (s br), 1050 (vs br), 1025 (w sh), 977 (m), 936 (s), 903 (m), 835 (vs), 810 (s), 803 (m sh), 785 (m), 746 (s), 720 (s), 688 (m), 636 (m), 557 (m), 522 (m), 391 (s) cm^{-1}. Anal. Calcd for $C_{22}H_{44}Li_2O_4Si_2$: C, 59.70; H, 10.02. Found: C, 59.48; H, 9.90.

Preparation of $K_2[C_8H_6(SiMe_3)_2\text{-}1,4]$ (3). A stirred suspension containing 6.35 g (25.4 mmol) of **1** and 2.01 g (50.0 mmol) of potassium hydride in 200 mL of diethyl ether was heated under reflux for 7 days, during which time the suspension turned greenish brown. The reaction mixture was filtered through a thin layer of Celite filter aid, and the clear filtrate was evaporated to dryness. Trituration of the brown, oily residue with hexane (50 mL) produced a microcrystalline, colorless precipitate, which was isolated by filtration and dried in vacuo: yield 1.77 g of **3** (27%); white, pyrophoric solid; mp ca. 330 °C dec. ^1H NMR (250 MHz, CD_3CN): δ 6.32−5.58 (m br, 6 H, ring H), 0.06 (s, 18 H, $SiMe_3$) ppm. ^{13}C NMR (62.89 MHz, CD_3CN): δ 97.1, 96.6, 93.1, 90.0 (ring C), 2.4 ($SiMe_3$) ppm. ^{29}Si NMR (79.46 MHz, THF/C_6D_6): δ −3.3 (s) ppm. IR (Nujol mull): 1651 (w br), 1560 (w), 1423 (w), 1304 (w), 1260 (s), 1247 (vs), 1197 (s), 1170 (w sh), 1151 (w sh), 1089 (vs br), 1058 (vs), 1030 (vs br), 1024 (s sh), 973 (m), 933 (s), 858 (s sh), 838 (vs), 823 (s), 802 (s), 775 (w sh), 751 (m), 724 (s), 679 (m), 639 (w), 514 (w), 450 (w), 409 (m) cm^{-1}.

Table 1. Crystallographic Data for 2

compd	$[Li(DME)]_2[C_8H_6(SiMe_3)_2\text{-}1,4]$ (**2**)
empirical formula	$C_{22}H_{44}Li_2O_4Si_2$
fw	442.63
temp (K)	153(2)
cryst size (mm)	0.7 × 0.7 × 0.6
cryst syst	triclinic
space group	$P\bar{1}$
a (Å)	7.85(1)
b (Å)	12.13(1)
c (Å)	16.35(1)
α (deg)	108.25(9)
β (deg)	94.76(3)
γ (deg)	108.09(4)
cell volume, V (nm^3)	1.377(2)
Z	2
ρ_c (g mm^{-3})	1.067
μ (mm^{-1})	0.150
F(000)	484
2θ range (deg)	7−45
no. of measd, unique data	3489, 3489 (R_{int} = 0.0000)
R,[a] wR2[b] ($I > 2\sigma(I)$)	0.0909, 0.2336
R, wR2 (all data)	0.1056, 0.2606
goodness of fit, S[c]	1.023
no. of refined params	281
largest diff peak, hole (e nm^{-3})	+651/−622

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum w(F_o^2 - F_c^2)^2]/[\sum w(F_o^2)^2]^{1/2}$. [c] $S = [\sum w(F_o^2 - F_c^2)^2]/[\sum(n - p)]^{1/2}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$; $P = [F_o^2 + 2F_c^2]/3$.

X-ray Structure Determination of 2. Crystallographic data for **2** are given in Table 1. The crystal of **2** was mounted on a Siemens-Stoe AED2 diffractometer with monochromated Mo Kα radiation (λ = 0.710 73 Å), and the data were collected at −120 °C. The structure was solved by direct methods using SHELXS-90.[10] The structure was refined against F^2 with a weighting scheme of $w^{-1} = \sigma^2(F_o^2) + (g_1P)^2 + g_2P$ with $P = (F_o^2 + 2F_c^2)/3$. The R values are defined as $R1 = \sum||F_o| - |F_c||/|F_o|$ and $wR2 = [\sum w(F_o^2 - F_c^2)^2]/[\sum w(F_o^2)^2]^{1/2}$. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were geometrically positioned and treated as riding.

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Supporting Information Available: Tables of crystal data, fractional coordinates, anisotropic displacement parameters, and bond lengths and angles for **2** (6 pages). Ordering information is given on any current masthead page.

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