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$_8$H$_6$(SiMe$_3$)$_2$-1,4] (**2**) was prepared and characterized
by a single-crystal X-ray structural analysis. The struc-
ture 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$_8$H$_6$(SiMe$_3$)$_2$-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 or-
ganic ligands are generally considered to impose favor-
able 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(trimethylsi-
lyl)cyclopentadienyl anion (=Cp″), which has been
demonstrated to be a highly useful ligand in organo-
transition-metal and f-element chemistry.[2] In several
cases, the properties of cyclooctatetraenyl metal com-
plexes have also been shown to benefit from silyl sub-
stitution. Complexes containing the 1,4-bis(trimethyl-
silyl)cyclooctatetraenyl ligand, [C$_8$H$_6$(SiMe$_3$)$_2$-1,4]$^{2-}$
(=COT″, in analogy to Cp″) were first studied by Cloke
et al.[3] Marked differences between certain COT″ com-
plexes and their counterparts containing the unsubsti-
tuted cyclooctatetraenyl ligand (=COT) have been un-
covered, including different stoichiometries and sig-

nificantly higher solubilities. For example, the unusual
scandium derivative (μ-THF)(μ-Cl)$_2$[Sc(COT″)]$_2$[3a] with
a bridging THF ligand has no parent COT analogue:[4,5]
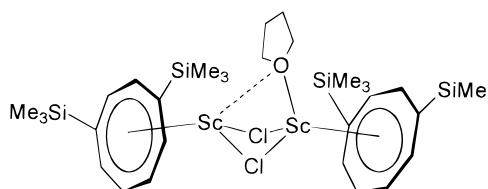
The most important starting material in this chem-
istry is the lithium derivative Li$_2$[C$_8$H$_6$(SiMe$_3$)$_2$-1,4]
(=Li$_2$COT″), which is generally prepared in situ by
deprotonation of 1,4-bis(trimethylsilyl)-2,5,7-cyclooc-
tatriene (**1**). The precursor **1** is readily available in one
step from 1,5-cyclooctadiene.[3] Although Li$_2$COT″ has
been frequently used as a precursor, its structure
remains elusive. We report here the structural char-
acterization of the dimethoxyethane adduct [Li(DME)]$_2$-
[C$_8$H$_6$(SiMe$_3$)$_2$-1,4] (**2**) as well as the preparation of the
hitherto unknown potassium derivative K$_2$COT″ (**3**).

The title compound **2** was first obtained serendipi-
tously in our laboratory during an attempted recrystal-
lization of polymeric [Yb(COT″)]$_n$ from DME/hexane
(DME = 1,2-dimethoxyethane). This insoluble ytter-
bium(II) species had previously been prepared by react-
ing ytterbium diiodide with an equimolar amount of

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6718327. E-mail: Frank.Edelmann@Chemie.Uni-Magdeburg.DE.
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65th birthday.
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(1) Cyclooctatetraenyl Complexes of the Early Transition Metals and
Lanthanides. 11. Part 10: Poremba, P.; Edelmann, F. T. *J. Organomet.
Chem.*, in press.
(2) For leading references on this subject see: (a) Tolstikov, G. A.;
Miftakhov, M. S.; Monakov, Y. B. *Zh. Obshch. Khim.* **1976**, *46*, 1778.
(b) Okuda, J.; Herdtweck, E. *J. Organomet. Chem.* **1989**, *373*, 99. (c)
Winter, C. H.; Dobbs, D. A.; Heeg, M. J. *Organometallics* **1991**, *10*,
210. (d) Jutzi, P.; Seufert, A. *J. Organomet. Chem.* **1979**, *169*, 373. (e)
Okuda, J. *J. Organomet. Chem.* **1988**, *356*, C43. (f) Lappert, M. F.;
Leung, W. P.; Bartlett, R. A.; Power, P. P. *Polyhedron* **1989**, *8*, 1883.
(g) Lappert, M. F.; Singh, A.; Atwood, J. L.; Hunter, W. E. *J. Chem.
Soc., Chem. Commun.* **1981**, 1190. (h) Lappert, M. F.; Singh, A.;
Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Chem. Commun.* **1981**,
1191.
(3) (a) Burton, N. C.; Cloke, F. G. N.; Hitchcock, P. B.; de Lemos, H.
C.; Sameh, A. A. *J. Chem. Soc., Chem. Commun.* **1989**, 1462. (b)
Burton, N. C.; Cloke, F. G. N.; Joseph, S. C. P.; Karamallakis, H.;
Sameh, A. A. *J. Organomet. Chem.* **1993**, *462*, 39. (c) Kilimann, U.;
Herbst-Irmer, R.; Stalke, D.; Edelmann, F. T. *Angew. Chem.* **1994**, *106*,
1684; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1618.

(4) For recent reviews on organolanthanide chemistry, see: (a)
Schaverien, C. J. *Adv. Organomet. Chem.* **1994**, *36*, 283. (b) Köhn, R.
D.; Kociok-Köhn, G.; Schumann, H. In *Encyclopedia of Inorganic
Chemistry*; King, R. B., Ed.; Wiley: New York, 1994. (c) Schumann,
H.; Meese-Marktscheffel, J. A.; Esser, L. *Chem. Rev.* **1995**, *95*, 865.
(d) Edelmann, F. T. In *Comprehensive Organometallic Chemistry II*;
Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford,
U.K., 1995; Vol. 4, Chapter 2.
(5) For recent advances in organolanthanide cyclooctatetraenyl
chemistry, see: (a) Edelmann, F. T. *New J. Chem.* **1995**, *19*, 535
(review). (b) Schumann, H.; Winterfeld, J.; Köhn, R. D.; Esser, L.; Sun,
J.; Dietrich, A. *Chem. Ber.* **1993**, *126*, 907. (c) Schumann, H.; Winter-
feld, J.; Görlitz, F. H.; Pickardt, J. *J. Chem. Soc., Chem. Commun.*
1993, 623. (d) Schumann, H.; Winterfeld, J.; Esser, L.; Kociok-Köhn,
G. *Angew. Chem.* **1993**, *105*, 1212; *Angew. Chem., Int. Ed. Engl.* **1993**,
32, 1202. (e) Kilimann, U.; Edelmann, F. T. *J. Organomet. Chem.* **1993**,
444, C15. (f) Kilimann, U.; Edelmann, F. T. *J. Organomet. Chem.* **1994**,
469, C5. (g) Kilimann, U.; Schäfer, M.; Herbst-Irmer, R.; Edelmann,
F. T. *J. Organomet. Chem.* **1994**, *469*, C10. (h) Mashima, K.; Na-
kayama, Y.; Nakamura, A.; Kanehisa, N.; Kai, Y.; Takaya, H. *J.
Organomet. Chem.* **1994**, *473*, 85. (i) Amberger, H. D.; Edelmann, F.
T. *J. Organomet. Chem.* **1996**, *508*, 275. (j) Xia, J.; Jin, S.; Chen, W.
Polyhedron **1996**, *15*, 809. (k) Schumann, H.; Rosenthal, E. C. E.;
Winterfeld, J.; Weimann, R.; Demtschuk, J. *J. Organomet. Chem.* **1996**,
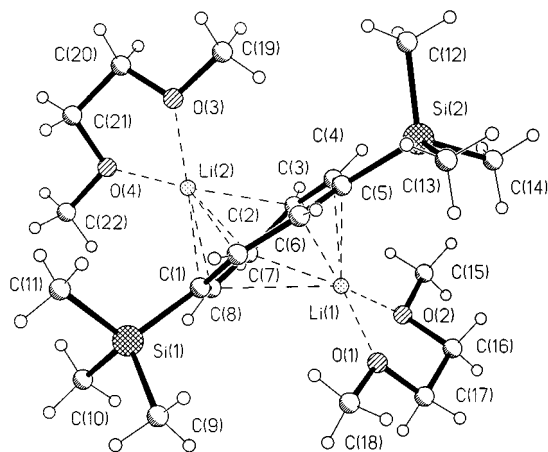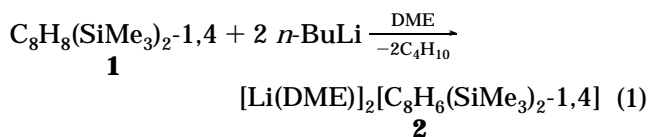*507*, 287.

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$_2$COT''.[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$_8$H$_6$(SiMe$_3$)$_2$-1,4] (**2**). Subsequently it was found that this compound is readily accessible by direct deprotonation of 1,4-bis(trimethyl-silyl)-2,5,7-cyclooctatriene (**1**) with 2 equiv of *n*-butyl-lithium in hexane solution in the presence of DME (eq 1). The lithium derivative crystallizes directly from the

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

$$[Li(DME)]_2[C_8H_6(SiMe_3)_2\text{-}1,4] \quad (1)$$
$$\mathbf{2}$$

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$_8$H$_6$(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 allyl-lithium derivative [Li(Et$_2$O)][1,3-Ph$_2$C$_3$H$_3$] 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
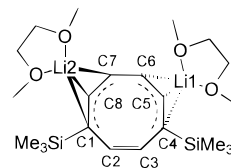
Apparently no lithium derivative of the parent cy-clooctatetraenyl dianion has been characterized by X-ray crystallography. In the structurally characterized po-tassium derivatives K$_2$(C$_8$H$_8$)·3THF[8a] and K$_2$(C$_8$H$_8$)·(MeOCH$_2$CH$_2$)$_2$O[8b] the potassium ions are bridged by planar cyclooctatetraenyl 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 corre-sponding lithium derivatives.[9] This is in part due to the fact that in reactions with metal halides the result-ing 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$_8$H$_6$-(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

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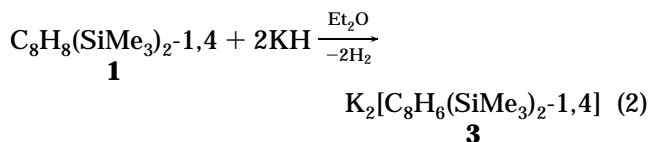
$$K_2[C_8H_6(SiMe_3)_2\text{-}1,4] \quad (2)$$
$$\mathbf{3}$$

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$_8$H$_6$(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 attrac-tive 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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(6) Poremba, P. Ph.D. Thesis, Universität Göttingen, Göttingen, Germany, 1995.

(7) Boche, G.; Etzrodt, H.; Marsch, M.; Massa, W.; Baum, G.; Dietrich, H.; Mashdi, W. *Angew. Chem.* **1986**, *98*, 84; *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 104.

(8) (a) Noordik, J. H.; van den Hark, Th. E. M.; Mooij, J. J.; Klaassen, A. A. K. *Acta Crystallogr.* **1974**, *B30*, 833. (b) Hu, N.; Gong, L.; Jin, Z.; Chen, W. *J. Organomet. Chem.* **1988**, *352*, 61.

(9) See, for example: (a) Evans, W. J.; Grate, J. W.; Choi, H. W.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 941. (b) Schaverien, C. J. *Organometallics* **1994**, *13*, 69. (c) Girardello, M. A.; Conticello, V. P.; Brard, L.; Sabat, M.; Rheingold, A. L.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 10212.

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$_8$H$_6$(SiMe$_3$)$_2$-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. ^{1}H NMR (250 MHz, C$_6$D$_6$): 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$_6$D$_6$): 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$_6$D$_6$): 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$_2$O$_4$Si$_2$: C, 59.70; H, 10.02. Found: C, 59.48; H, 9.90.

Preparation of K$_2$[C$_8$H$_6$(SiMe$_3$)$_2$-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. ^{1}H NMR (250 MHz, CD$_3$CN): 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$_3$CN): δ 97.1, 96.6, 93.1, 90.0 (ring C), 2.4 (SiMe$_3$) ppm. ^{29}Si NMR (79.46 MHz, THF/C$_6$D$_6$): 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}.

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

Table 1. Crystallographic Data for 2

compd	[Li(DME)]$_2$[C$_8$H$_6$(SiMe$_3$)$_2$-1,4] (**2**)
empirical formula	C$_{22}$H$_{44}$Li$_2$O$_4$Si$_2$
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] $S = [\sum w(F_o{}^2 - F_c{}^2)^2]/[\sum(n - p)]^{1/2}$; $w^{-1} = \sigma^2(F_o{}^2) + (aP)^2 + bP$; $P = [F_o{}^2 + 2F_c{}^2]/3$.

Mo Kα radiation ($\lambda = 0.710\ 73$ 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 $w^{-1} = \sigma^2(F_o{}^2) + (g_1 P)^2 + g_2 P$ 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.

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.

(10) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *46*, 467.