

**Unprecedented Examples of Heterobimetallic  
Cerium(IV) Disiloxanediolates**

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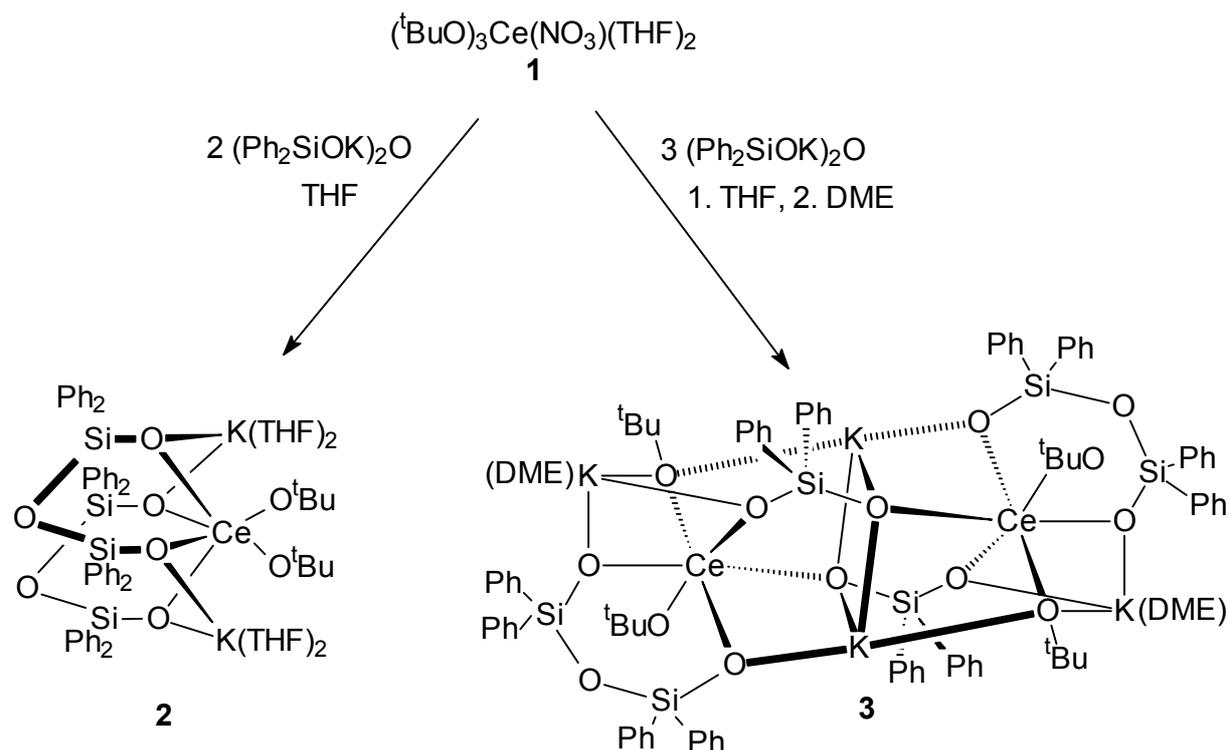
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**Supporting Information**

## Experimental Details

**General Comments.** All reactions were conducted in oven-dried or flame-dried glassware under an inert atmosphere of dry argon employing standard Schlenk and glovebox techniques. THF and DME were distilled from sodium/benzophenone under nitrogen atmosphere. All glassware was oven-dried at 140 °C for at least 24 h, assembled while hot, and cooled under high vacuum prior to use. The starting materials  $(t\text{BuO})_3\text{Ce}^{\text{IV}}(\text{NO}_3)(\text{THF})_2$  (**1**)<sup>1</sup>, 1,1,3,3-tetraphenyl-1,3-disiloxanediol,  $(\text{Ph}_2\text{SiOH})_2\text{O}$ ,<sup>2</sup> and  $\text{KN}(\text{SiMe}_3)_2$ <sup>3</sup> were prepared according to literature procedures. <sup>1</sup>H (400 MHz), <sup>13</sup>C NMR (101 MHz) and <sup>29</sup>Si (79.5 MHz) were recorded in THF-*d*<sub>8</sub> solutions on a Bruker DPX 400 spectrometer at 25 °C. Chemical shifts were referenced to TMS. IR spectra were recorded using KBr pellets on a Perkin Elmer FT-IR spectrometer system 2000 between 4000 cm<sup>-1</sup> and 400 cm<sup>-1</sup>. Microanalyses of the compounds were performed using a Leco CHNS 923 apparatus.

- (1) Evans, W. J.; Deming, T. J.; Olofson, J. M.; Ziller, J. W. *Inorg. Chem.* **1989**, *28*, 4027.
- (2) Harris, G. I. *J. Chem. Soc.* **1963**, 5978.
- (3) U. Wannagat, H. Niederprüm, *Chem. Ber.* **1961**, *94*, 1540.



**$[\{(\text{Ph}_2\text{SiO})_2\text{O}\}_2\{\text{K}(\text{THF})_2\}]_2\text{Ce}(\text{O}^t\text{Bu})_2$  (2):** A mixture of 2.23 g (5.38 mmol) of  $(\text{Ph}_2\text{SiOH})_2\text{O}$  and 2.15 g (10.78 mmol) of  $\text{KN}(\text{SiMe}_3)_2$  was dissolved in 100 ml of THF to form a light brown solution, which was stirred for 18 h at room temperature. The solvent was completely evaporated in vacuum in order to remove any traces of  $\text{HN}(\text{SiMe}_3)_2$ . 1.50 g (2.65 mmol) of  $(^t\text{BuO})_3\text{Ce}(\text{NO}_3)(\text{THF})_2$  were dissolved in 100 ml of THF. The resulting clear yellow solution was added to the solid residue of the first solution. Upon stirring at room temperature a colorless precipitate began to form. After 48 h of continued stirring the resulting yellow solution was separated from a small amount of colorless precipitate by filtration through a P4 glass sinter frit. Slow evaporation of the solvent afforded yellow, block-shaped crystals suitable for X-ray diffraction. Continued evaporation to dryness afforded a second crop of crystals. Combined yield: 3.18 g (81%). Anal. Calcd for  $\text{C}_{72}\text{H}_{90}\text{CeK}_2\text{O}_{12}\text{Si}_4$  ( $M_r = 1478.12$ ): C, 58.51; H, 6.14. Found: C, 58.82; H 5.69.  $^1\text{H}$  NMR (400.1 MHz,  $\text{THF}-d_8$ , 20 °C):  $\delta = 7.67$  (m br, 16H, Ph), 7.11 (m br, 24 H, Ph), 3.62 (16 H, THF), 1.77 (16H, THF), 1.04 (18 H, Bu).  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{THF}-d_8$ , 20 °C):  $\delta = 142.6$  (*ipso*-C, Ph), 135.6, 128.7, 127.6 (Ph), 78.4

(OC(CH<sub>3</sub>)<sub>3</sub>), 68.13 (THF), 34.3 (OC(CH<sub>3</sub>)<sub>3</sub>), 26.3 (THF). <sup>29</sup>Si NMR (79.5 MHz, THF-*d*<sub>8</sub>, 20 °C): δ = -48.6. IR (KBr): 3067, 3047, 1589, 1484, 1428, 1308, 1244, 1185, 1120, 1032, 1006, 990, 937, 744, 712, 524 cm<sup>-1</sup>. Mp: 178 °C (dec).

**[{(Ph<sub>2</sub>SiO)<sub>2</sub>O}<sub>2</sub>]{(DME)KO<sup>t</sup>Bu}{(Ph<sub>2</sub>SiO)<sub>2</sub>K}Ce]<sub>2</sub> (3):** A mixture of 2.18 g (5.26 mmol) of (Ph<sub>2</sub>SiOH)<sub>2</sub>O and 2.08 g (10.43 mmol) KN(SiMe<sub>3</sub>)<sub>2</sub> was dissolved in 100 ml of THF and stirred for 18 h at room temperature. The solvent was completely evaporated in vacuum in order to remove any traces of HN(SiMe<sub>3</sub>)<sub>2</sub>. 1.00 g (1.77 mmol) of (<sup>t</sup>BuO)<sub>3</sub>Ce(NO<sub>3</sub>)(THF)<sub>2</sub> was dissolved in 100 ml of THF. The resulting clear yellow-colored solution was added to the solid residue of the first solution. Upon stirring at room temperature a colorless precipitate immediately began to form. After 70 h of continued stirring the resulting clear yellow solution could be separated from a small amount of colorless precipitate by filtration through a P4 glass sinter frit. Evaporation to dryness and recrystallization of the residue from DME (ca. 120 ml) afforded light yellow, rod-shaped crystals in ca. 70% yield. Anal. Calcd for C<sub>100</sub>H<sub>126</sub>Ce<sub>2</sub>K<sub>4</sub>O<sub>20</sub>Si<sub>6</sub> (*M<sub>r</sub>* = 2253.19): C, 53.31; H, 5.64. Found: C, 52.04; H, 5.16. <sup>1</sup>H NMR (400.1 MHz, THF-*d*<sub>8</sub>, 20 °C): δ = 8.20 – 7.68 (m, Ph), 7.55 – 6.73 (m, Ph), 6.62 (m br, Ph), 6.29 (s br, Ph), 3.42 (s, DME), 3.26 (s, DME), 1.29 (s, <sup>t</sup>BuO bridging), 1.14 (s, <sup>t</sup>BuO terminal). <sup>13</sup>C NMR (100.6 MHz, THF-*d*<sub>8</sub>, 20 °C): δ = 136.1 – 135.4 (m, Ph), 134.4 (Ph), 128.7 – 127.6 (m, Ph), 72.7 (CH<sub>2</sub>, DME), 58.9 (CH<sub>3</sub>, DME), 31.7, 30.6 (CH<sub>3</sub>, <sup>t</sup>BuO). Interpretable <sup>29</sup>Si NMR data could not be obtained due to solubility problems. IR (KBr): 3469, 2926, 2861, 1494, 1452, 1428, 1403, 1113, 1050, 1011, 993, 946, 904, 825, 745, 706, 606, 525 cm<sup>-1</sup>. Mp: 160 °C (dec). The IR and <sup>1</sup>H NMR spectra of the single-crystals used for X-ray diffraction were identical with that of the bulk sample.

# Crystallographic Data

## Crystal Data Collection, Structure Solution, and Refinement

The intensity data of **2** and **3** were collected on a Stoe IPDS 2T diffractometer with MoK $\alpha$  radiation. The data were collected with the Stoe XAREA program using  $\omega$ -scans. Numeric absorption correction was applied. The space groups were determined with XPREP program, and the structures were solved by direct methods (SHELXS-97) and refined with all data by fullmatrix least-squares methods on  $F^2$  using SHELXL-97.<sup>1</sup> CCDC-652558 (**2**) and CCDC-652557 (**3**) contain the detailed crystallographic data for the compounds reported here. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre at [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). Data collection parameters are given in Table 1.

- (1) (a) G. M. Sheldrick, *SHELXL-97 Program for Crystal Structure Refinement*, Universität Göttingen (Germany) **1997**; (b) G. M. Sheldrick, *SHELXS-97 Program for Crystal Structure Solution*, Universität Göttingen (Germany) **1997**.

**Table 1.** Crystallographic Data of  $((\text{Ph}_2\text{SiO})_2\text{O})_2(\text{K}(\text{THF})_2)\{\text{Ce}(\text{O}^t\text{Bu})_2\}$  (**2**) and  $[\{(\text{Ph}_2\text{SiO})_2\text{O}\}_2\{(\text{DME})\text{KO}^t\text{Bu}\}\{(\text{Ph}_2\text{SiO}_2)\text{K}\}\text{Ce}]_2$  (**3**)

	<b>2</b>	<b>3</b>
Formula	$\text{C}_{72}\text{H}_{90}\text{CeK}_2\text{O}_{12}\text{Si}_4$	$\text{C}_{100}\text{H}_{126}\text{Ce}_2\text{K}_4\text{O}_{20}\text{Si}_6$
Fw	1478.12	2253.19
temperature (K)	293(2)	180(2)
crystal system, space group	monoclinic C2/c	triclinic P-1
unit cell dimensions ( $\text{\AA}$ , deg)	$a = 24.961(5)$ $b = 13.628(3)$ $c = 24.371(5)$ $\alpha = 90$ $\beta = 113.39(3)$ $\gamma = 90$	$a = 13.5372(7)$ $b = 14.1050(7)$ $c = 17.7666(9)$ $\alpha = 87.960(4)$ $\beta = 72.411(4)$ $\gamma = 61.666(4)$
volume ( $\text{\AA}^3$ )	7609(3)	2822.8(2)
Z, calculated density ( $\text{g}\cdot\text{cm}^{-3}$ )	4, 1.290	1, 1.325
absorp. coeff. ( $\text{mm}^{-1}$ )	0.826	1.068
F(000)	3080	1162
$\theta$ -range for data collection (deg)	2.12 to 29.29	1.91 to 29.32
limiting indices	$-34 \leq h \leq 32,$ $-18 \leq k \leq 18,$ $-33 \leq l \leq 33$	$-18 \leq h \leq 17,$ $-19 \leq k \leq 19,$ $-24 \leq l \leq 0$
reflections collected / unique	34951 / 10305 [R(int) = 0.0416]	15155 / 15155 [R(int) = 0.0719]
completeness to	$\theta = 29.29$ 99.0 %	$\theta = 29.32$ 97.9 %
absorp. corr.	None	None
max. and min. Transmission	0.7335 and 0.6828	0.6747 and 0.6173
refinement method	Full-matrix least-squares on $F^2$	Full-matrix least-squares on $F^2$
data / restraints / parameters	10305 / 0 / 439	15155 / 0 / 635
goodness-of-fit on $F^2$	0.955	1.026
final R indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0365,$ $wR_2 = 0.0826$	$R_1 = 0.0486,$ $wR_2 = 0.1222$
R indices (all data)	$R_1 = 0.0500,$ $wR_2 = 0.0865$	$R_1 = 0.0634,$ $wR_2 = 0.1285$
largest diff. peak and hole $e\cdot\text{\AA}^{-3}$	0.700 and -1.025	2.045 and -1.842

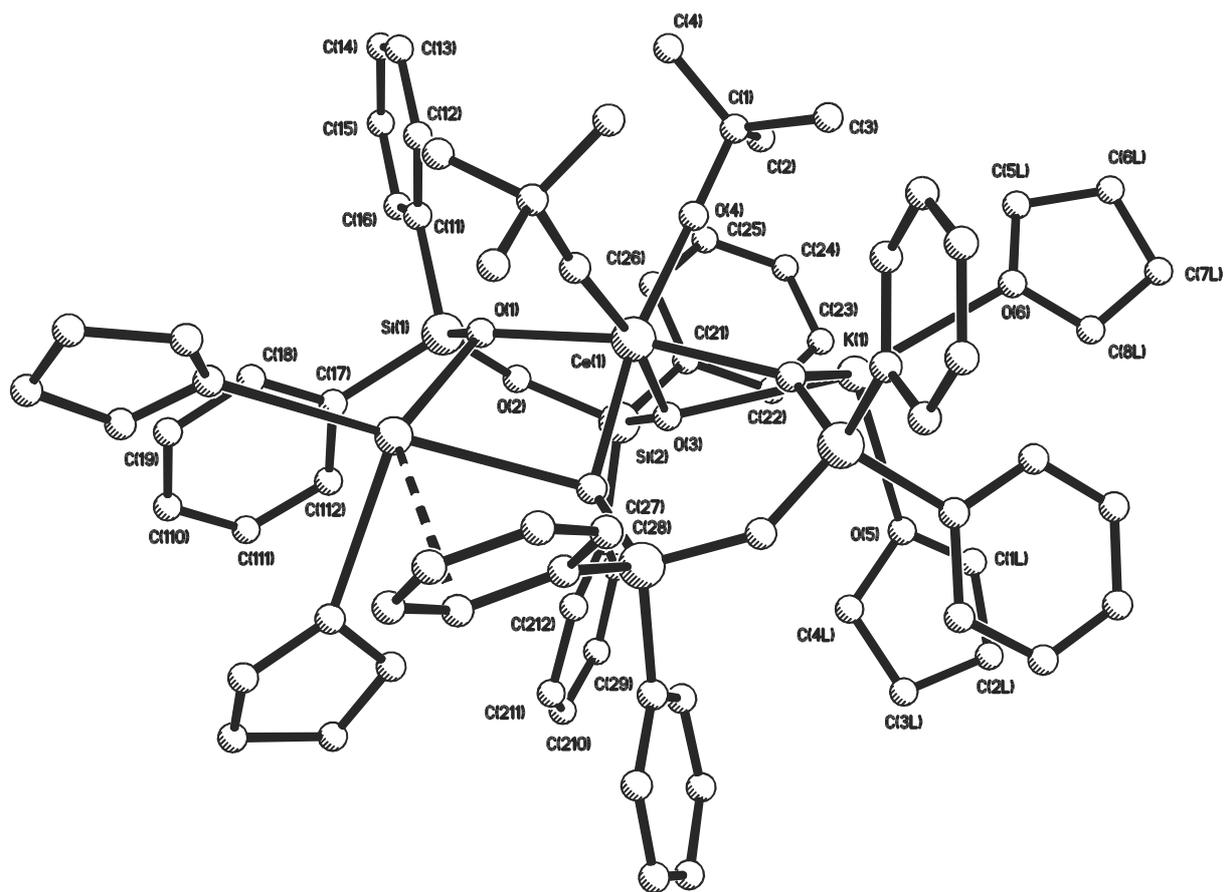
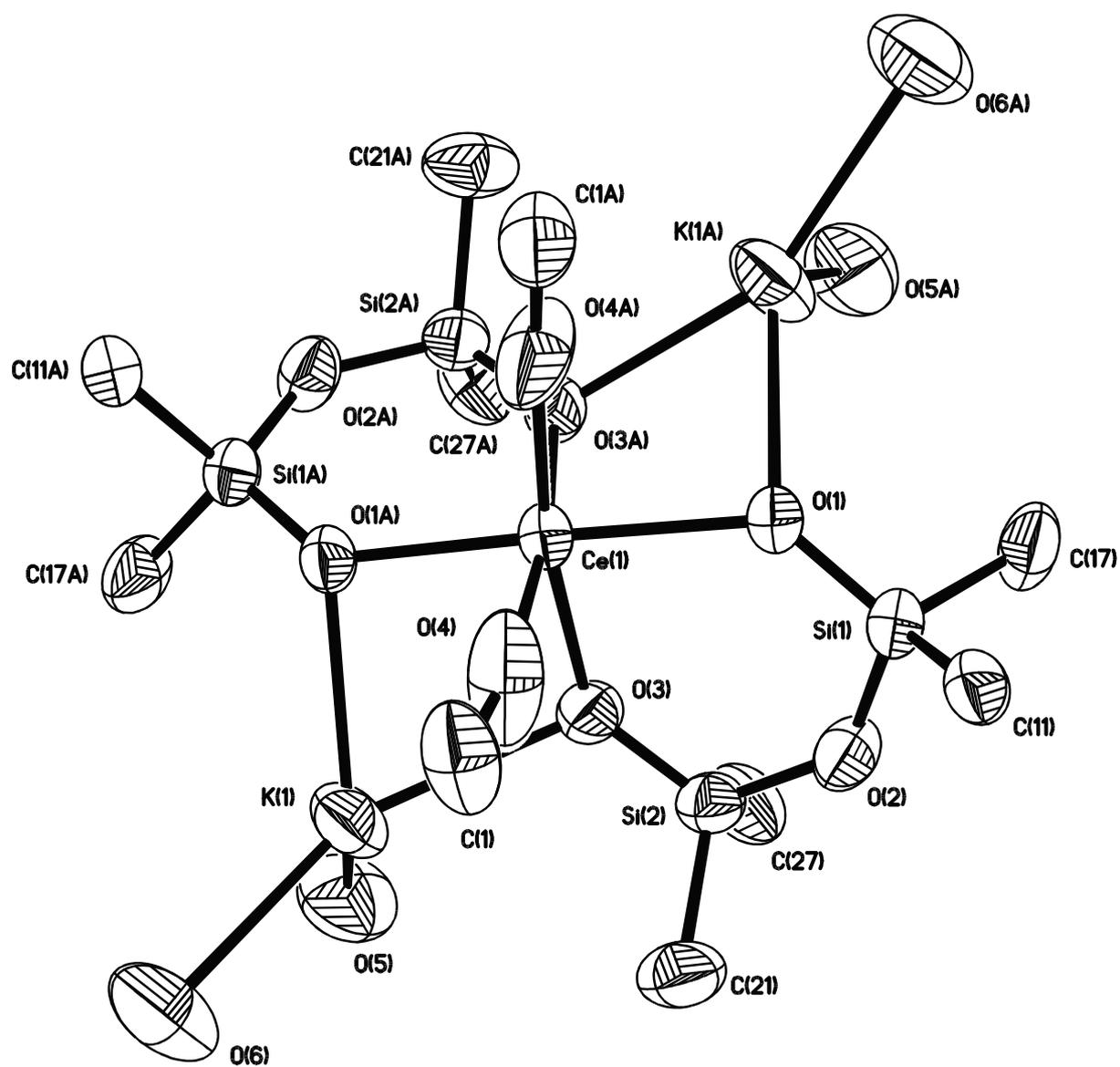


Figure 1a. Molecular structure of 2.



**Figure 1b.** ORTEP drawing of **2** (for clarity, only the *ipso*-carbon atoms of the phenyl substituents are shown)

