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In situ crystallization of 2,2-dimethoxypropane and dimethyldimethoxysilane: hunting for Group 14 isomorphism

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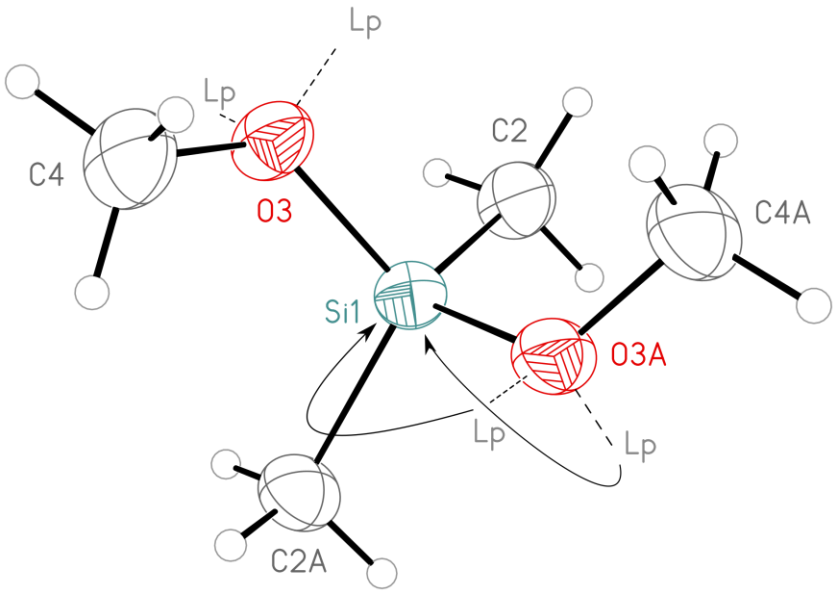

Figure S1 Numbering scheme and stereoelectronic interactions of lone pairs of electrons of oxygen atoms (Lp), drawn in idealized directions, and antibonding NBO orbitals of Si1−C1 and Si1−O1 bonds in **1Si**.

Table S1 Bond lengths and angles in **1Si** and **1C**, compared to average values from CSD.

	Experimental		CSD		DFT (exp.cell)	
	Si	C	Si	C	Si	C
X1-C2	1.8468(16)	1.521(2)	1.85 ±0.02	1.52±0.02	1.850 1.850	1.513 1.511
X1-O3	1.6391(9)	1.424(2)	1.646±0.012	1.43±0.02	1.665 1.659	1.423 1.420
C2−X1−C2A	113.98(10)	112.1(2)	115±3	114±3	114.5 115.1	112.0 112.0
O3−X1−O3A	110.92(7)	110.3(2)	110±3	110±2	109.6 108.9	110.2 110.2
C2−X1−O3	104.25(5)	104.83(9)	105±2	106±2	105.4 105.1	105.4 105.4
C2A−X1−O3	111.81(6)	112.47(10)	110±2	111±2	111.1 111.3	112.0 112.2

Notes:

Mean values and associated standard deviations were calculated using data from Cambridge Structural Database (CSD v. 5.40, with updates up to November 2018; search restrictions: only organic structures, no ions, no disorder, no powder structures).

The CSD means were calculated for 203 (X=Si) and 3032 (X=C) structures containing the $XC_2(OC)_2$ fragment, where X was not the part of a cycle with a ring size ≤ 5. Standard deviations for the CSD data are given in ± notation to distinguish them from refined s.u. values.

DFT results correspond to PBE0-D3/POB-TZVP calculations, the values in crystal structure with experimental unit cell are shown in black, and in optimized isolated molecules are shown in blue

Table S2 Experimental and DFT-optimized unit cell parameters (Å and degrees). ΔV_{exp} is the difference (%) to the experimental value at 120K.

	a	b	c	β	V	ΔV_{exp}
			1Si			
x-ray	11.788(7)	10.0768(6)	8.3937(9)	131.6270(10)	745.3(5)	
DFT	12.035	9.177	8.389	135.72	647	-13.2
			1C			
x-ray	10.7198(16)	6.3871(10)	9.6730(14)	105.873(5)	637.04(17)	
DFT	10.331	6.190	9.377	104.54	580	-12.0
			1Si[1C]			
DFT	10.679	6.638	9.750	105.41	666	
			1C[1Si]			
DFT	10.599	9.034	7.775	125.98	602	

***Ab initio* calculations** of crystals and isolated molecules were performed with CRYSTAL17 package with PBE0-D3 method and POB-TZVP basis set optimized for calculations of periodic structures. Atomic coordinates were first optimized using experimental unit cell parameters and symmetry. Shrinking factors of 4 4 4 was used for the Monkhorst–Pack grid for periodic calculations, yielding in total 24 k-points for both compounds. In full structure optimization, unit cell parameters were optimized together with atomic coordinates. To calculate the structures using packing patterns of heteroanalogues (**1Si**[1C] and **1C**[1Si]) the type of the central atom was simply changed, and full geometry optimization was performed. For calculation of the Basis Set Superposition Error, a method implemented in CYRYSTAL17 was used (MOLEBSSE keyword). Isolated molecules were optimized in C_2 symmetry, that correspond to the energy minimum. Harmonic frequencies were calculated for all optimized structures by a numerical algorithm using two displacements in each Cartesian direction.

X-ray diffraction experiments were performed on a Bruker APEX II diffractometer equipped with CCD detector (graphite-monochromated MoKα radiation, λ = 0.71073 Å). Frames were integrated using the Bruker SAINT software package[S1] by a narrow-frame algorithm. A semiempirical absorption correction was applied with the SADABS[S2] program using the intensity data of the equivalent reflections.

It should be noted that after the zone melting the capillaries still contained multiple crystals. In the case of **1Si** the diffraction spots from different crystals almost did not overlap. In the case of **1C**, the diffraction from **2** and **3** crystals was considered (for 120 and 218 K), and the algorithms routinely used in SAINT and SADABS programs for twinned crystals were applied for frame integration, data reduction and absorption correction to achieve acceptable data completeness and redundancy.

The structures were solved with dual-space methods with SHELXT[S3] and refined by the full-matrix least-squares technique against F^2_{hkl} in the anisotropic approximation with SHELXL[S4] software packages. Hydrogen atoms were placed in calculated positions and refined in the riding model with $U_{iso}(H)= 1.5U_{eq}(C)$. The structure **1C** was determined at two temperatures, since it was supposed that the diffraction pattern deteriorated after cooling to 120 K.

Detailed crystallographic information is provided in Table TS3. Structures were deposited to Cambridge Structural Database, CCDC 1903036-1903038 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via https://www.ccdc.cam.ac.uk/structures/.

[S1] *Bruker, SAINT v8.34A*, Bruker AXS Inc., Madison, Wisconsin, USA, 2014.

[S2] SADABS 2016/2: L. Krause, R. Herbst-Irmer, G.M. Sheldrick and D. J. Stalke, *J. Appl. Crystallogr.*, 2015, **48**, 3.

[S3] SHELXT 2012/2: G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 2005, **71**, 3.

[S4] SHELXL 2018/3: G. M. Sheldrick, *Acta Crystallogr., Sect. C*, 2005, **71**, 3.

Table S3 Crystallographic data for **1Si** and **1C**.

Compound ID	**1Si**	**1C**	
CCDC number	1903038	1903036	1903037
Formula	$C_4H_{12}O_2Si$	$C_5H_{12}O_2$	
Formula weight	120.23	104.15	
Crystal system	monoclinic	monoclinic	
Space group	*C*2/*c*	*C*2/*c*	
Z / Z'	4 / 0.5	4 / 0.5	
T, K	120	120	218
a, Å	11.788(7)	10.7198(16)	10.8012(16)
b, Å	10.0768(6)	6.3871(10)	6.4347(10)
c, Å	8.3937(9)	9.6730(14)	9.7496(14)
α, °	90	90	90
β, °	131.6270(10)	105.873(5)	106.103(6)
γ, °	90	90	90
V, Å^3	745.3(5)	637.04(17)	651.03(17)
d_{calc}, g cm^{-3}	1.071	1.086	1.063
μ, cm^{-1}	2.3	0.82	0.8
$2\theta_{max}$, °	60	60	60
Completeness to $2\theta_{max}$	0.885	0.939	0.958
Reflections collected /independent	3675 / 966	4827 / 874	4921 / 907
Observed reflections [I>2σ(I)]	913	627	525
Number of refined parameters	35	35	35
R_1	0.0297	0.0709	0.0616
wR_2	0.0877	0.1876	0.1606
GOF	1.044	1.021	1.025
Residual density, e Å^{-3} (d_{max}/d_{min})	0.286/-0.216	0.326/-0.406	0.310/-0.303