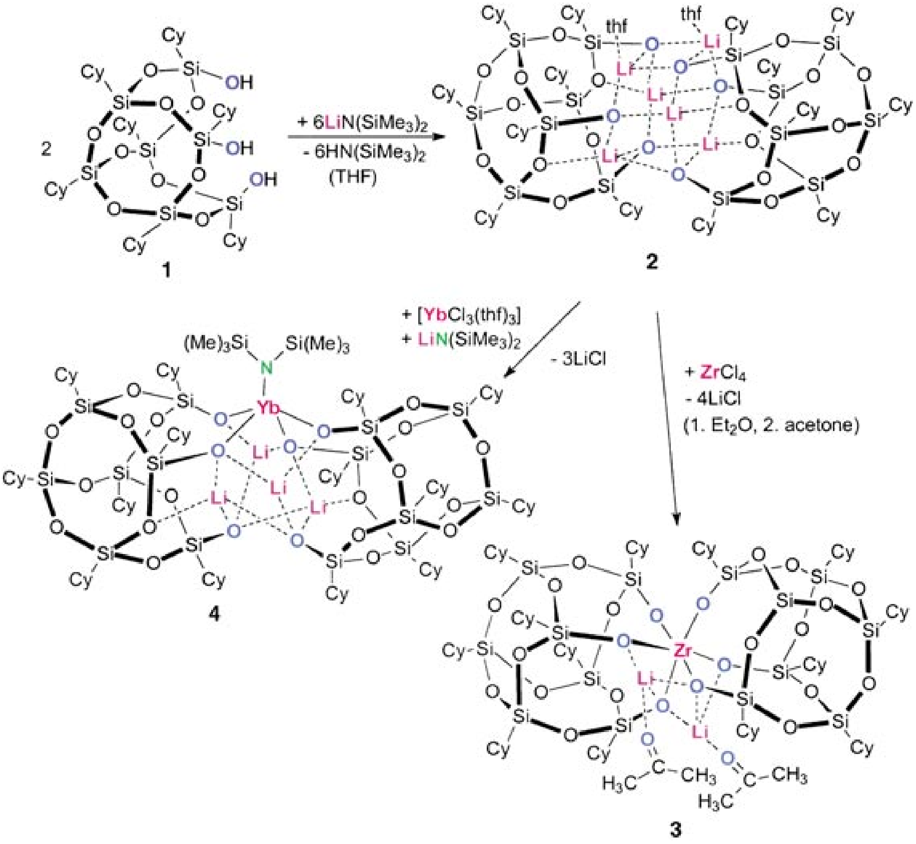
Catalyst Models

Fully Metalated Silsesquioxanes: Building Blocks for the Construction of Catalyst Models**

*Volker Lorenz, Stephan Gießmann, Yurii K. Gun'ko, Axel K. Fischer, John W. Gilje, and Frank T. Edelmann**

Dedicated to Professor Gerd-Volker Röschenthaler on the occasion on his 60th birthday

Numerous industrially and commercially important processes such as the production of polyolefins are catalyzed by transition-metal complexes immobilized on silica surfaces.[1] However, due to the heterogeneous nature of these catalysts, full characterization of the catalytically active species is often difficult, and little is known about the reaction mechanisms and the nature of the metal–silica interactions. Surface organometallic chemistry (SOMC), developed by Basset and co-workers, is one suitable approach towards a better understanding of heterogeneous catalytic processes.[2] A different approach uses suitable well-defined homogeneous model systems that provide a coordination environment similar to that of silica surfaces. In recent years, polyhedral metallasilsesquioxanes have been promoted as molecular model compounds which to some extent can provide insight into the scenarios occurring on metal-modified silica surfaces.[3] Feher et al. have established that the incompletely condensed silsesquioxane derivative $Cy_7Si_7O_9(OH)_3$ (**1**, Cy = cyclohexyl, Scheme 1) shares structural similarities with crystalline forms of silica such as β-cristobalite and β-tridymite.[4] Fully metalated silsesquioxane derivatives of the type $Cy_7Si_7O_9(OM)_3$ (M = Li, Na, K) would constitute highly desirable precursors for the construction of catalyst model compounds, including novel heterobimetallic species. However, such alkali metal derivatives of **1** were unknown until recently, and structural information on such materials is still lacking.



Scheme 1. Synthesis of the metalated silsesquioxanes **2**–**4** (Cy = cyclohexyl).

There have been contrasting reports in the literature concerning the metalation of **1** by alkali metal reagents. It was reported by Feher et al. that treatment of **1** with three equivalents of NaO*t*Bu resulted in complete breakdown of the silsesquioxane cage.[3a] In contrast, Aspinall and co-workers more recently succeeded in synthesizing $Cy_7Si_7O_9(OLi)_3$ by the reaction of **1** with *n*-butyllithium.[5] $Cy_7Si_7O_9(OLi)_3$ was isolated in virtually quantitative yield as an amorphous, air-stable (!) solid of unknown structure. We report here that with the proper choice of deprotonating agents well-defined, crystalline alkali metal silsesquioxanes are readily available. These represent excellent precursors for the preparation of unprecedented catalyst model compounds.

We found that alkali metal bis(trimethylsilyl)amides are the reagents of choice for achieving smooth and high-yield deprotonation of the incompletely condensed silsesquioxane **1**. Treatment of **1** with $LiN(SiMe_3)_2$ in diethyl ether/THF afforded the crystalline lithium silsesquioxane dimer $[\{(c\text{-}C_6H_{11})_7Si_7O_{12}\}_2Li_6(C_4H_8O)_2]\cdot C_4H_{10}O$ (**2**) in 93% yield

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(Scheme 1). This reaction is not limited to the THF-adduct **2**. The corresponding acetone solvate $[\{(c\text{-}C_6H_{11})_7Si_7O_{12}\}_2Li_6(Me_2CO)_3]$ as well as the dimeric potassium derivative $[\{(c\text{-}C_6H_{11})_7Si_7O_{12}\}_2K_6(dme)_4]$ (dme = dimethoxyethane) have been isolated in a similar manner.[3d,6]

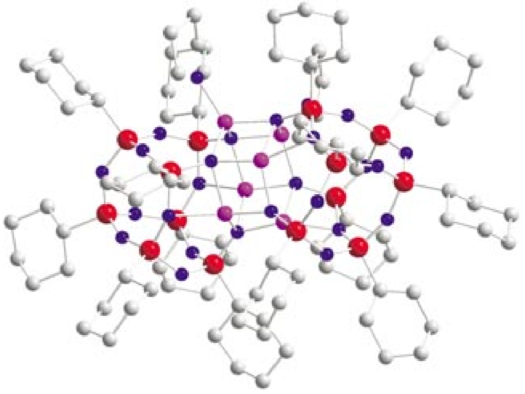

Figure 1. Molecular structure of **2** (● = C, ● = O, ● = Si, ● = Li). Selected bond lengths [Å] and angles [°]: Si-O 1.613(4)–1.662(4), Si-$\mathrm{O_{(Li)}}$ 1.584(4)–1.596(4), Li-O 1.889(10)–2.327(10), O-Si-O 105.9(2)–114.0(2), Si-O-Si 131.2(2)–158.4(3), Si-O-Li 85.7(3)–152.9(3).

An X-ray diffraction study revealed the dimeric molecular structure of **2** (Figure 1).[7] The central structural unit of **2** consists of a box-shaped Li_6O_6 polyhedron. Two lithium ions coordinate to thf ligands, while the other four interact with framework oxygen atoms of the silsesquioxane cages. This bonding situation results in tetracoordination around each lithium center. Structurally related box-shaped Li_6O_6 or Li_6S_6 polyhedra have previously been reported for some hexameric lithium phenoxides or arenethiolates,[8] but are unprecedented in silsesquioxane chemistry. The same structural motif has been established for the closely related molecular structures of $[\{(c\text{-}C_6H_{11})_7Si_7O_{12}\}_2Li_6(Me_2CO)_3]$ and $[\{(c\text{-}C_6H_{11})_7Si_7O_{12}\}_2K_6(dme)_4]$.[3d,6]

With the lithiated silsesquioxane **2** now being readily available in large quantities, we began exploring its derivative chemistry with the aim of synthesizing novel molecular model systems for silica-supported heterogeneous catalysts. For this purpose **2** can be employed as the starting material, but it has been found that the more convenient use of $Cy_7Si_7O_9(OLi)_3$, prepared in situ, in further reactions also gives excellent results. For example, the reaction of $Cy_7Si_7O_9(OLi)_3$ with $ZrCl_4$ in THF/acetone followed by crystallization from acetone afforded the novel heterobimetallic metallasilsesquioxane $[\{[(c\text{-}C_6H_{11})_7Si_7O_{12}]Li(OCMe_2)\}_2Zr]$ (**3**) as a colorless, crystalline material (Scheme 1). The molecular structure of **3** was established by single-crystal X-ray diffraction (Figure 2). The central zirconium atom is encapsulated by two silsesquioxanes cages resulting in an approximate octahedral coordination environment. Two $Li(OCMe_2)$ units are attached to this formally dianionic $\{(c\text{-}C_6H_{11})_7Si_7O_{12}\}_2Zr^{2-}$ moiety. Tetracoordination around each Li ion is achieved through coordinative interaction with three cage oxygen atoms.

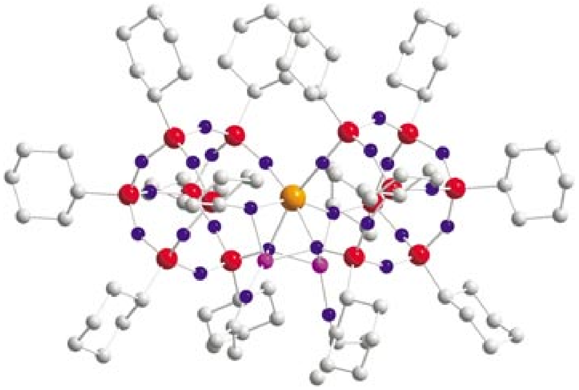

Figure 2. Molecular structure of **3** (● = C, ● = O, ● = Si, ● = Li, ● = Zr). Selected bond lengths [Å] and angles [°]: Zr-O 1.978(3)–2.080(3), Zr-$\mathrm{O_{Li}}$ 2.44(4), Si-O 1.607(3)–1.646(3), Li-O 1.895(8)–2.066(9); $\mathrm{O_{Li}}$-Zr-$\mathrm{O_{Li}}$ 70.75(11)–79.45(11), $\mathrm{O_{Si}}$-Zr-$\mathrm{O_{Si}}$ 96.40(13)–99.64(11), Si-O-Si 107.74(16)–112.12(17).

The most unusual heterometallasilsesquioxane made from **2** thus far is the ytterbium bis(trimethylsilylamide) derivative $[\{[(c\text{-}C_6H_{11})_7Si_7O_{12}]_2Li_4\}YbN(SiMe_3)_2]$ (**4**) which was prepared by reacting **2** (prepared in situ) with anhydrous $YbCl_3$ according to Scheme 1 (51 % yield). The structurally characterized ytterbium(III) complex **4** represents a novel type of heterobimetallic metallasilsesquioxane, as it contains an additional functional group at the metal center.[9] Ytterbium is coordinated through oxygen atoms to a lithium silsesquioxane framework made up of two $(c\text{-}C_6H_{11})_7Si_7O_{12}Li_2$ units. Owing to the involvement of cage oxygen atoms in the coordination to the Li ions, there are no additional ligands such as Et_2O or THF present in this molecule. The overall structure with a reactive $[YbN(SiMe_3)_2]$ unit residing on a model silica surface resembles that of typical catalytically active lanthanide metallocenes such as $[(C_5Me_5)_2LnN(SiMe_3)_2]$.[10] In **4** two bulky silsesquioxane cages play the role of the pentamethylcyclopentadienyl ligands in the bent metallocene unit (Figure 3). Most notably, however, the molecular compound

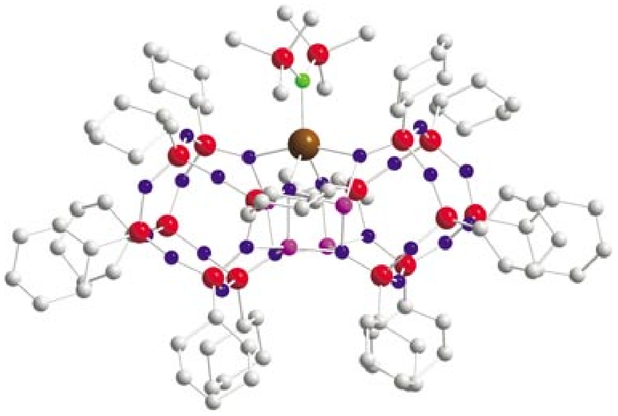

Figure 3. Molecular structure of **4** (● = C, ● = O, ● = Si, ● = N, ● = Li, ● = Yb). Selected bond lengths [Å] and angles [°]: Yb-O 2.194(8)–2.256(9), Yb-N 2.236(3), Si-O 1.606(9)–1.657(10), Li-O 1.96(2)–2.19(2); $\mathrm{O_{Li}}$-Yb-$\mathrm{O_{Li}}$ 77.8(3), N-Yb-O 99.9(5)–132.9(6), Si-O-Si 102.5(5)–112.0(5).

4 represents the first “realistic” model for a reactive lanthanide silylamide species bound to a silica surface. Such lanthanide silylamides grafted on silica or the mesoporous silicate MCM-41 are interesting catalysts which have been investigated in detail by Anwander et al.[11]

In summary, we have demonstrated that fully metalated silsesquioxane derivatives such as dimeric **2** are readily available in high yields by using alkali metal silylamides as deprotonating agents. These fully metalated silsesquioxane derivatives are versatile building blocks for the construction of molecular models for heterogeneous catalysts, including bimetallic species and complexes containing functional groups. As the reactions reported here appear to be quite general, the results are expected to stimulate further research in this area.

Experimental Section

All reactions were carried out under nitrogen and in carefully dried and degassed solvents.

2: Compound **1** (2.0 g, 2.054 mmol) was added to a solution of $LiN(SiMe_3)_2$ (prepared in situ by reaction of *n*-butyllithium (4.13 mL of a 1.6 M solution in diethyl ether) with $HN(SiMe_3)_2$ (1.06 g, 1.40 mL, 6.574 mmol)) in THF (100 mL) at room temperature. The reaction mixture was stirred for 10 h. Compound **2** precipitated almost quantitatively as a white microcrystalline solid after partial removal of solvents. The crude product was isolated by filtration. Colorless crystals of **2** (2.1 g; 93 %) were separated after recrystallization from a mixture of diethyl ether and THF. Correct elemental analysis for $[\{(c\text{-}C_6H_{11})_7Si_7O_{12}\}_2Li_6(C_4H_8O)_2]\cdot C_4H_{10}O$, $C_{96}H_{180}Si_{14}O_{27}Li_6$. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 3.77$ (br s, 8H; OCH_2CH_2, thf), 3.34 (q, $^3J(H,H) = 7.0$ Hz 4H; OCH_2CH_3, Et_2O), 1.85 (br s, 8H; OCH_2CH_2, thf), 1.73 (br m, 70H; CH_2, $c\text{-}C_6H_{11}$), 1.23 (br m, 70H; CH_2, $c\text{-}C_6H_{11}$), 1.08 (t, $^3J(H,H) = 7.0$ Hz 6H; OCH_2CH_3, Et_2O), 0.88 ppm (br m, 14H; SiCH, $c\text{-}C_6H_{11}$); ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): $\delta = 68.06$ (OCH_2CH_2, THF), 65.84 (OCH_2CH_3, Et_2O), 28.44, 27.83, 27.75, 27.61, 27.10, 26.97, 26.89, 26.73, 26.65 (CH_2, $c\text{-}C_6H_{11}$), 25.59 (OCH_2CH_2, THF), 25.31, 24.83, 23.96, 23.82, 23.23 (SiCH, $c\text{-}C_6H_{11}$), 15.27 ppm (OCH_2CH_3, Et_2O); ^{29}Si NMR (79.5 MHz, $CDCl_3$, 25 °C): $\delta = -58.22$, -66.98, -67.14 ppm; IR (KBr disc): $\tilde{\nu} = 2925$ (vs, ν_{C-H}), 2848 (vs, ν_{C-H}), 1447 (s, δ_{CH_2}), 1268 (m), 1195 (s), 1130 (vs, $\nu_{as(Si\text{-}O\text{-}Si)}$), 1110 (vs, $\nu_{as(Si\text{-}O\text{-}Si)}$), 1083 (vs), 1057 (vs), 1025 (vs), 1010 (vs), 894 (s), 847 (s), 823 (m), 750 (m), 739 (m), 635 (m), 524 (vs, $\nu_{s(Si\text{-}O\text{-}Si)}$), 410 cm^{-1} (m, $\delta_{(O\text{-}Si\text{-}O)}$).

3: Compound **1** (3.00 g, 3.081 mmol) was added to a THF solution of $LiN(SiMe_3)_2$ (prepared in situ by reaction of *n*-butyllithium (5.80 mL of a 1.6 M solution in diethyl ether) with $HN(SiMe_3)_2$ (1.50 g, 1.94 mL, 9.243 mmol)). The white slurry was stirred overnight at room temperature. Then $ZrCl_4$ (0.37 g, 1.588 mmol) and acetone (30 mL) were added, followed by stirring for another 48 h. The solvents were evaporated in vacuum. The solid residue was extracted with boiling acetone/diethyl ether for two days, after which **3** was isolated (1.10 g) in 33 % yield. Compound **3** is very poorly soluble in hexane, THF, diethyl ether, and acetone. Crystals suitable for X-ray crystallography were obtained from a saturated acetone/diethyl ether solution at 25 °C after 14 days. Correct elemental analysis for $[\{[(c\text{-}C_6H_{11})_7Si_7O_{12}]Li(OCMe_2)\}_2Zr]$, $C_{90}H_{166}Si_{14}O_{26}Li_2Zr$. ^1H NMR (600.1 MHz, $[D_8]$THF, 25 °C): $\delta = 2.02$ (s, 12H; CH_3, acetone), 2.00–1.70 (br m, 70H; CH_2, $c\text{-}C_6H_{11}$), 1.55–1.25 (br m, 70H; CH_2, $c\text{-}C_6H_{11}$) 0.81–0.74 ppm (br m, 14H; SiCH, $c\text{-}C_6H_{11}$); ^{13}C NMR (150.9 MHz, $[D_8]$THF, 25 °C): $\delta = 205.68$ (C=O), 30.46 (CH_3), 28.69, 28.63, 28.51, 28.42, 28.37, 28.29, 28.05, 28.00, 27.96, 27.93, 27.88, 27.88, 27.81, 27.76, 27.66, 27.45 (CH_2, $c\text{-}C_6H_{11}$), 25.69, 25.55, 25.45, 25.29, 24.73, 24.63, 24.47 ppm (SiCH, $c\text{-}C_6H_{11}$); ^{29}Si NMR (119.2 MHz, $[D_8]$THF, 25 °C): $\delta = -70.89$, -70.90, -71.03, -71.10, -71.63, -71.83, -71.92, -72.75, -72.78, -72.82, -73.04 ppm; IR (KBr disc): $\tilde{\nu} = 2917$ (vs, ν_{C-H}), 2850 (vs, ν_{C-H}), 1637 (w, $\nu_{C=O}$), 1448 (vs, δ_{CH_2}), 1380 (m), 1355 (m), 1346 (m), 1326 (m), 1292 (m), 1268 (s), 1252 (m), 1196 (vs), 1119 (vs, $\nu_{as(Si\text{-}O\text{-}Si)}$), 942 (vs), 894 (s), 846 (s), 824 (s), 757 (vs), 688 (m), 647 (m), 619 (m), 575 (m), 556 (m), 516 (vs, $\nu_{s(Si\text{-}O\text{-}Si)}$), 455 (vs), 415 cm^{-1} (m, $\delta_{(O\text{-}Si\text{-}O)}$).

4: Compound **1** (2.00 g, 2.054 mmol) was added to a THF solution of $LiN(SiMe_3)_2$ (prepared in situ by reaction of *n*-butyllithium (4.50 mL of a 1.6 M solution in diethyl ether) with $HN(SiMe_3)_2$ (1.16 g, 1.50 mL, 7.200 mmol)). The white slurry was stirred overnight at room temperature. Then $[YbCl_3(thf)_3]$ (0.51 g, 1.030 mmol) was added, followed by stirring for another 24 h. The solvents were evaporated in vacuum. The solid residue was extracted with boiling diethyl ether for two days, after which compound **4** was isolated (1.20 g; 51 %) as a white crystalline solid. Crystals suitable for X-ray crystallography were obtained from a saturated diethyl ether solution at 5 °C after seven days. Correct elemental analysis for $[\{[(c\text{-}C_6H_{11})_7Si_7O_{12}]_2Li_4\}YbN(SiMe_3)_2]$, $C_{90}H_{172}Si_{16}NO_{24}Li_4Yb$. NMR: Because of the paramagnetic properties of **4**, it was impossible to obtain NMR data. IR (KBr disc): $\tilde{\nu} = 2922$ (vs, ν_{C-H}), 2850 (vs, ν_{C-H}), 1448 (s, $\delta_{(-CH_2-, -CH_3)}$), 1268 (m), 1252 (m), 1196 (s), 1110 (vs, $\tilde{\nu}_{as(Si\text{-}O\text{-}Si)}$), 1039(vs), 1027(vs), 1009(vs), 942(m), 895 (s), 846 (s), 824 (m), 757 (s), 647 (m), 619 (m), 516 (s, $\nu_{s(Si\text{-}O\text{-}Si)}$), 492 (m), 456 (s), 418 cm^{-1} (m, $\delta_{(O\text{-}Si\text{-}O)}$).

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[7] X-ray data collection and structure refinement: The measurements on **2–4** were performed on a Siemens SMART CCD

system with $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) and graphite monochromator. Selected crystals of **2**–**4** were coated with mineral oil, mounted on a glass fiber, and transferred to the cold nitrogen steam (Siemens LT-2 attachment). Full hemispheres of the reciprocal space were scanned by ω in three sets of frames of 0.3°. The SADABS routine was applied as an absorption correction. For structure solution and refinement the programs SHELXS86 and SHELXL97 were used.[12] CCDC-182421 (**2**), CCDC-182423 (**3**), CCDC-182420 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk). **2**: $C_{96}H_{180}Li_6O_{27}Si_{14}$, $M_w = 2201.30\,\mathrm{g\,mol^{-1}}$, $T = 173(2)$ K, triclinic, space group $P\bar{1}$, $a = 14.3986(6)$, $b = 18.4236(8)$, $c = 25.6539(4)$ Å, $\alpha = 103.852(3)$, $\beta = 93.379(4)$, $\gamma = 108.523(3)°$, $V = 6197.4(4)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.180\,\mathrm{g\,cm^{-3}}$, $\mu = 0.208\,\mathrm{mm^{-1}}$, reflections collected: 41313, independent reflections: 29171 ($R_{int} = 0.0523$), final R indices [$I > 2\sigma I$]: $R1 = 0.0912$, $wR2 = 0.2232$, R indices (all data): $R1 = 0.1889$, $wR2 = 0.2861$. **3**: $C_{90}H_{166}Li_2O_{26}Si_{14}Zr$, $M_w = 2162.59\,\mathrm{g\,mol^{-1}}$, $T = 143(2)$ K, orthorhombic, space group $Pca2(1)$, $a = 22.1136(10)$, $b = 26.2423(10)$, $c = 19.5055(10)$ Å, $V = 11319.3(9)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.269\,\mathrm{g\,cm^{-3}}$, $\mu = 0.311\,\mathrm{mm^{-1}}$, reflections collected: 58115, independent reflections: 17109 ($R_{int} = 0.0611$), final R indices [$I > 2\sigma I$]: $R1 = 0.0410$, $wR2 = 0.0989$, R indices (all data): $R1 = 0.0598$, $wR2 = 0.1153$. **4**: $C_{90}H_{172}Li_4NO_{24}Si_{16}Yb$, $M_w = 2302.53\,\mathrm{g\,mol^{-1}}$, $T = 173(2)$ K, monoclinic, space group Cc, $a = 27.1505(3)$, $b = 15.5354(9)$, $c = 30.0056(15)$ Å, $\beta = 111.077°$, $V = 11809.5(9)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.295\,\mathrm{g\,cm^{-3}}$, $\mu = 1.017\,\mathrm{mm^{-1}}$, reflections collected: 39125, independent reflections: 19390 ($R_{int} = 0.0293$), final R indices [$I > 2\sigma I$]: $R1 = 0.0338$, $wR2 = 0.0699$, R indices (all data): $R1 = 0.0457$, $wR2 = 0.0774$.

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