

Supplementary Material: Cu₄₂Ge₂₄Na₄—A Giant Trimetallic Sesquioxane Cage: Synthesis, Structure, and Catalytic Activity

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1. Experimental

PhGeCl₃ was purchased from ABCR and was used as received. Toluene (≥ 99.0 %), *n*-butanol (≥ 99.5 %), ethanol (≥ 99.5 %), DMF (≥ 99.5 %) and CHCl₃ (≥ 99.8 %) were purchased from Merck and used without further purification. Elemental analyses was carried out with a XRF spectrometer VRA-30. IR spectra were recorded on Shimadzu IR Prestige21 FTIR spectrometer in KBr pellets in the 600 – 1200 cm⁻¹ range. Experimental values of IR-active bands:^{7a} νOH^{bond} 1100 cm⁻¹; ν_{as} Ge-O 840-820 cm⁻¹; ν_s Ge-O 950 cm⁻¹; σ_{C-H} of mono-substituted phenyl groups 680-670 cm⁻¹, δ_{Ge-O} 459 cm⁻¹

A solution of 2 g (7.89 mmol) of PhGeCl₃ in 40 ml of toluene was added dropwise (at room temperature, during 1 hour) into the beaker equipped with a magnetic stirrer and filled with 60 ml of mixture of *n*-butanol/water (v/v, 2/1). Resulted mixture was left under stirring for 12 hours, then the hydrolysate of PhGeCl₃, as the organic phase, was separated. Thereafter, the hydrolysate was washed with deionized water till neutral pH and dried *in vacuo*. Anal. Calcd for [C₆H₅GeO_{1.5}] C, 41.48; H, 2.90; Ge, 41.81. Found (for vacuum-dried sample): C, 41.39; H, 3.01; Ge, 41.78%. Yield 1.23 g (91%).

1 g of [PhGeO_{1.5}]_n (6.78 mmol referenced to a [PhGeO_{1.5}] unit) were placed in a 100 mL round-bottomed flask, equipped with a magnetic stirrer and condenser, and mixed with 75 ml of ethanol. 0.62 g (9.23 mmol) of NaOH were added to the same flask. After 1.5 hour of intense stirring under reflux, the mixture became homogeneous and 0.26 g (4.11 mmol) of CuCl₂ were added to the mixture. Resulted solution was left under reflux for 1 hour and, after cooling to room temperature, was filtered from insoluble fraction. The resulted solution was dried *in vacuo* and dissolved in 50 ml the mixture of DMF/CHCl₃ (v/v, 2/1). A slow spontaneous evaporation of solvates gave crystalline material within 3 weeks. Several single crystals were manually selected to be studied by X-ray diffraction (see below for details). The rest of crystalline phase was dried *in vacuo*. Anal. Calcd for

[Na₄Cu₄₂(Ph₂Ge₂O₅)₁₂(OH)₄₀] Cu, 33.38; Na, 1.15; Ge, 21.80. Found (for vacuum-dried sample): Cu, 33.01; Na, 1.08; Ge, 21.66%. Yield 0.27 g (43%).

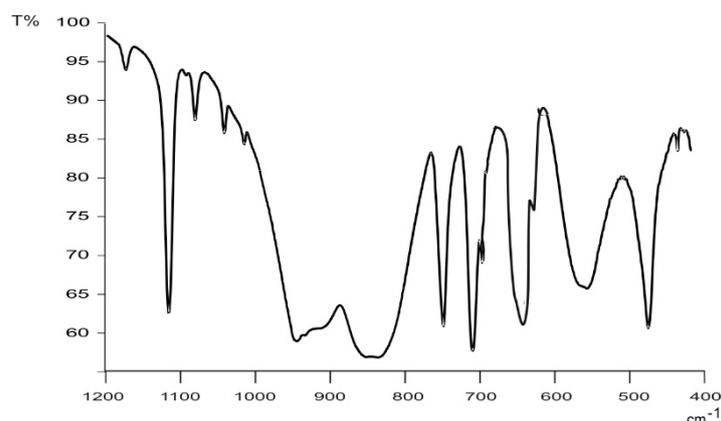


Figure S1. IR spectrum of oligomeric [C₆H₅GeO_{1.5}]_n.

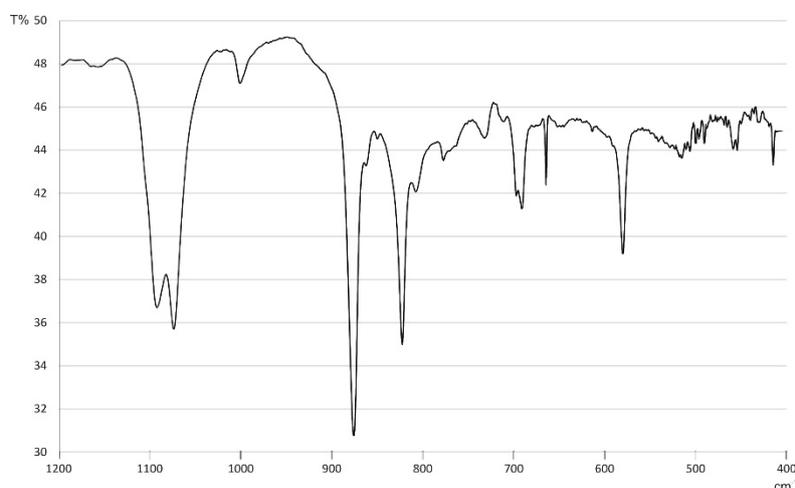


Figure S2. IR spectrum of **1**.

1.1 X-ray Diffraction Study

The single-crystal X-ray diffraction data for **1** were collected on the ‘Belok’ beamline of the Kurchatov Synchrotron Radiation Source (National Research Center ‘Kurchatov Institute’, Moscow, Russian Federation) using a Rayonix SX165 CCD detector at $\lambda = 0.96990 \text{ \AA}$. A total of 720 images for two different orientations of the crystal were collected using an oscillation range of 1.0° and φ scanning mode. The data were indexed and integrated using the utility iMOSFLM from the CCP4 program suite^{S1} and then scaled and corrected for absorption using the Scala^{S2} program. For details, see Table 1. The structure was determined by direct methods and refined by full-matrix least square technique on F^2 in anisotropic approximation for non-hydrogen atoms. The intracage chloroform molecules were strongly disordered. The crystal of **1** contained the dimethylformamide and water solvate molecules, most of which were strongly disordered as well. All attempts to model and refine their positions were unsuccessful. Therefore, the contribution to the scattering by the disordered solvate molecules was removed by the use of the utility SQUEEZE in PLATON06^{S3}. The hydrogen atoms of the OH-groups and the water molecules were localized in the difference-Fourier maps and included into the refinement within the riding model with fixed isotropic displacement parameters [$U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$]. The other hydrogen atoms were placed in calculated positions and refined within the riding model with fixed isotropic displacement parameters [$U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for the methyl groups and $1.2U_{\text{eq}}(\text{C})$ for the other groups]. All calculations were carried out using the SHELXTL^{S4} program suite. Crystallographic data for **1** have been deposited with the Cambridge Crystallographic Data Center, CCDC 1857969. The supplementary crystallographic data can be

obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 1. Crystal data and structure refinement.

Compound	1•2DMF•H ₂ O
Empirical formula	C ₁₆₃ H ₂₀₇ N ₆ O ₁₀₈ Na ₄ Cl ₃ Cu ₄₂ Ge ₂₄
Formula weight	8587.48
Temperature, K	100.0(2)
Crystal system	Monoclinic
Space group	C2/m
<i>a</i> , Å	40.682(8)
<i>b</i> , Å	26.453(5)
<i>c</i> , Å	18.950(4)
α , deg.	90
β , deg.	116.35(3)
γ , deg.	90
<i>V</i> , Å ³	18274(8)
<i>Z</i>	2
<i>D</i> _{calc} , g·cm ⁻³	1.561
Absorption coefficient, μ , mm ⁻³	10.013
<i>F</i> (000)	8344
Crystal size, mm	0.06×0.09×0.12
Theta range for data collection	1.64 – 38.49
	-48 < <i>h</i> < 48
Index ranges	-33 < <i>k</i> < 33
	-21 < <i>l</i> < 23
Reflections collected	136079
Independent reflections, <i>R</i> _{int}	19585, 0.097
Reflections observed with <i>I</i> > 2σ(<i>I</i>)	7209
Absorption correction	semi-empirical
Data / restraints/ parameters	19585 / 214 / 693
Goodness-of-fit on <i>F</i> ²	1.034
<i>R</i> ₁ [<i>I</i> > 2σ(<i>I</i>)]	0.104
<i>wR</i> ₂ [all data]	0.240
Extinction coefficient	0.000078(6)
<i>T</i> _{min} / <i>T</i> _{max}	0.363 / 0.535

2. General Procedure for the Formation of Amides

2.1. General Considerations

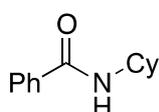
All reagents were purchased from Aldrich Chemical Co., Fluka and Alfa Aesar and used without further purification. Analyses were performed at the 'Plateforme Technologique Laboratoire de Mesures Physiques' (IBMM, Université de Montpellier). ¹H NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer. Chemical shifts are reported in ppm and referenced to the solvent peak (CDCl₃ at 7.26 ppm). Data are reported as s = singlet, d = doublet, t = triplet, q = quadruplet, qt = quintuplet, sept = septuplet, m = multiplet; coupling constants in Hz; integration. ¹³C NMR spectra were recorded on a Bruker Avance III HD 100 MHz spectrometer. Chemical shifts are reported in ppm and referenced to the solvent peak (CDCl₃ at 77.16 ppm).

2.2. General Procedure

Amine hydrochloride (0.5 mmol), CaCO₃ (25.0 mg, 0.25 mmol), CH₃CN (1 mL), **1** (40 μL of a solution of 1.9 mg of **1** in 2 mL of CH₃CN), benzylic alcohol (105 μL, 1.0 mmol) and TBHP (5.5M in nonane, 225 μL, 1.25mmol) were successively added to a sealed tube. The mixture was stirred at 80 °C for 2 h and TBHP (5.5M in nonane, 225 μL, 1.25 mmol) were again added to the mixture. After 22 h at 80 °C, the mixture was cooled to room temperature and 1N HCl and EtOAc were added. The mixture was extracted twice with AcOEt, and the combined organic phases were washed with a saturated solution of NaHCO₃ and brine, and concentrated under reduced pressure. To remove the excess of benzylic alcohol, 80 mL of H₂O were added and evaporated under reduced pressure. Crude product was then purified using silica gel chromatography using gradients of cyclohexane/AcOEt to yield the pure compounds.

2.3. Description of Amides

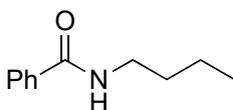
N-Cyclohexylbenzamide^{S5}



¹H NMR (300 MHz, CDCl₃) δ 7.79 – 7.70 (m, 2H), 7.47 – 7.31 (m, 3H), 6.30 (d, *J* = 6.0 Hz, 1H), 4.01 – 3.85 (m, 1H), 2.03 – 1.93 (m, 2H), 1.77 – 1.66 (m, 2H), 1.66 – 1.54 (m, 1H), 1.44 – 1.06 (m, 5H).

¹³C NMR (126 MHz, CDCl₃) δ 166.7, 135.1, 131.2, 128.4, 127.0, 48.8, 33.2, 25.6, 25.0.

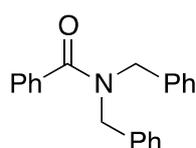
N-*n*-butylbenzamide^{S5}



¹H NMR (300 MHz, CDCl₃) δ 7.80 – 7.71 (m, 2H), 7.49 – 7.32 (m, 3H), 6.56 (s, 1H), 3.46 – 3.34 (m, 2H), 1.62 – 1.50 (m, 2H), 1.44 – 1.29 (m, 2H), 0.91 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 167.7, 134.9, 131.3, 128.5, 127.0, 39.9, 31.8, 20.2, 13.8.

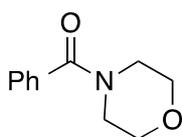
N,N-Dibenzylbenzamide^{S5}



¹H NMR (300 MHz, CDCl₃) δ 7.57 – 7.50 (m, 2H), 7.44 – 7.28 (m, 11H), 7.21 – 7.14 (m, 2H), 4.60 (s, 2H), 4.44 (s, 2H).

¹³C NMR (75 MHz, CDCl₃) δ 172.3, 137.0, 136.5, 136.2, 129.7, 128.8, 128.6, 128.4, 127.6, 127.0, 126.8, 51.6, 46.9.

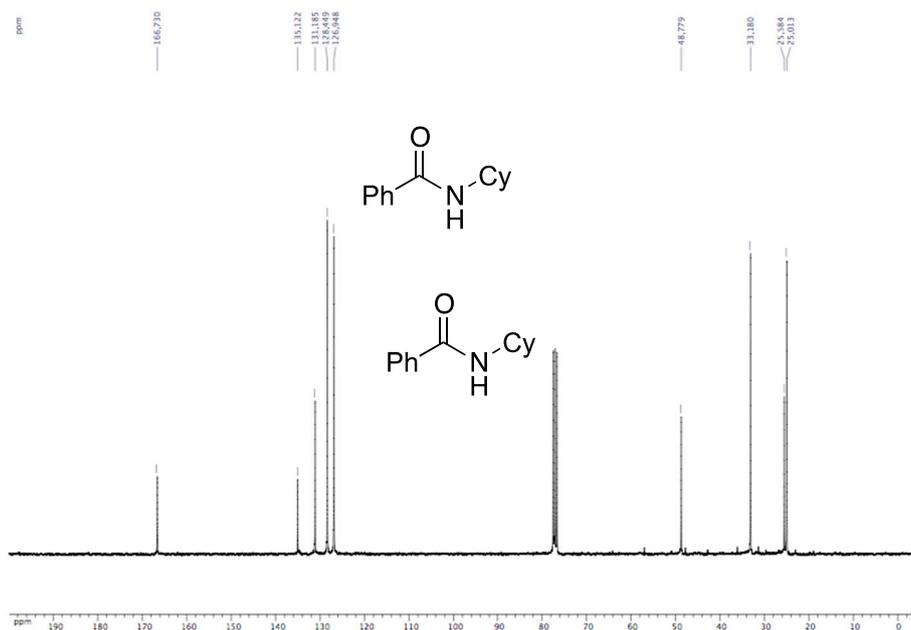
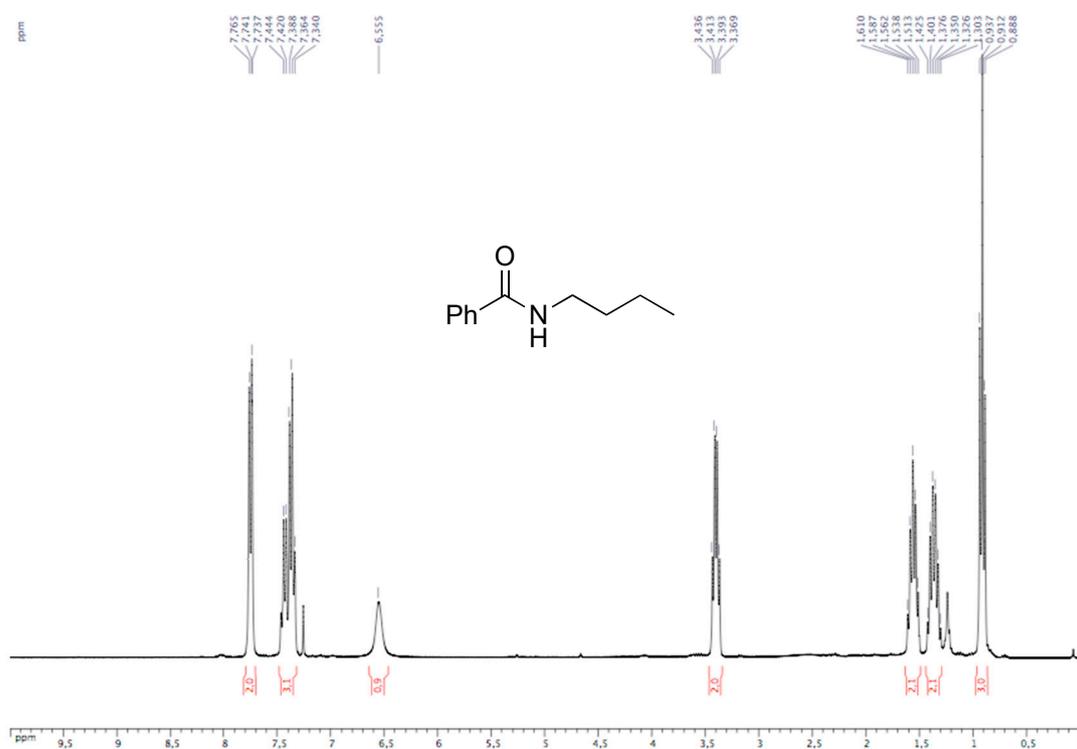
N-Benzoylmorpholine^{S5}

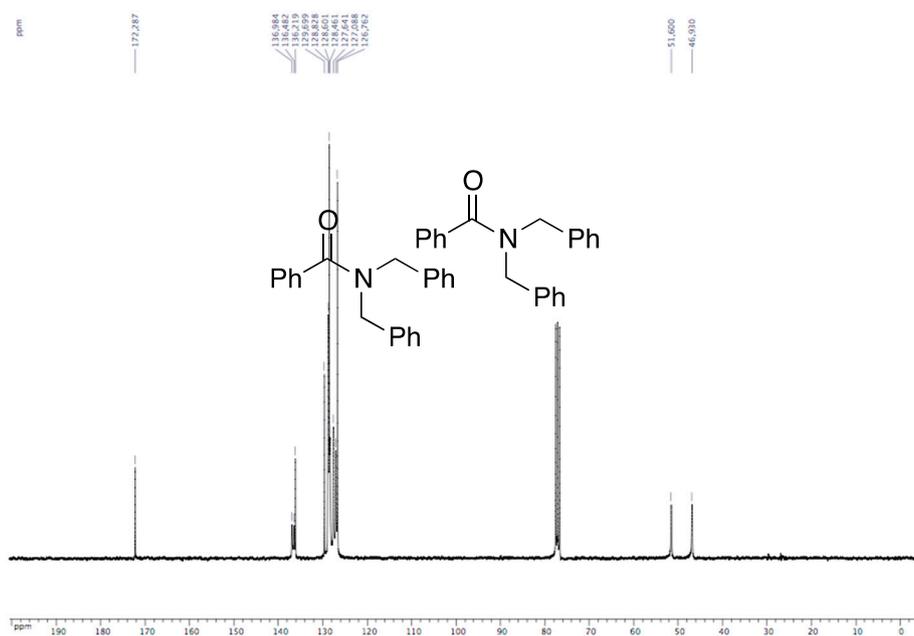
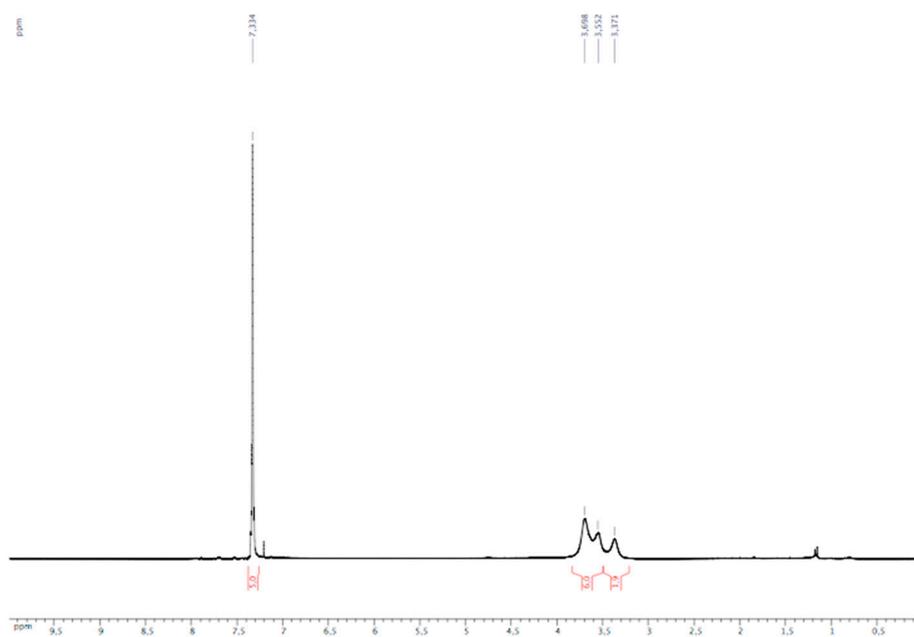


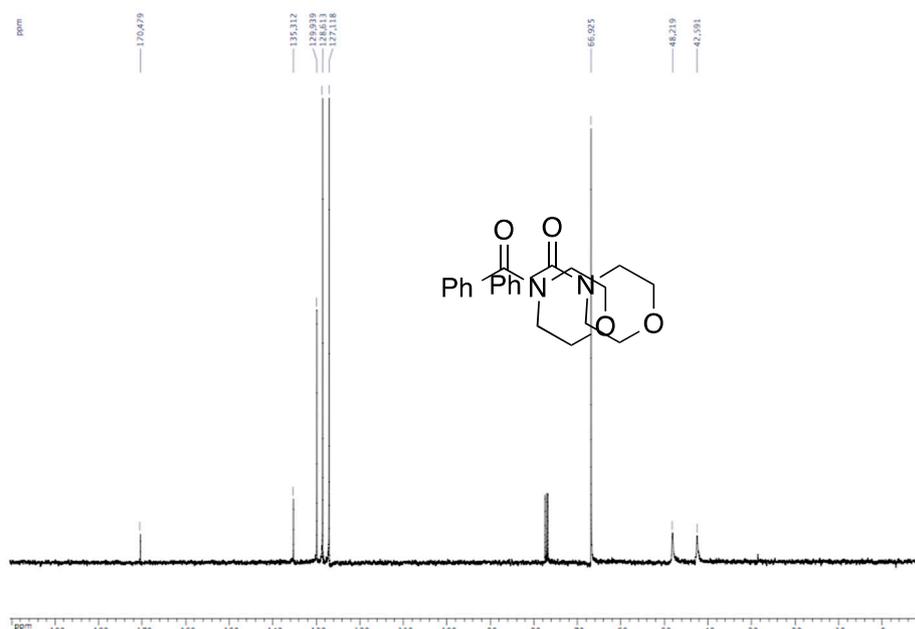
¹H NMR (300 MHz, CDCl₃) δ 7.37 – 7.29 (m, 5H), 3.97 (s, 4H), 3.55 (s, 2H), 3.37 (s, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 170.5, 135.3, 130.0, 128.6, 127.1, 66.9, 48.2, 42.6.

2.4. Calculation of TON and TOF

^{13}C NMR (126 MHz, CDCl_3) of *N*-Cyclohexylbenzamide ^1H NMR (300 MHz, CDCl_3) of *N*-*n*-butylbenzamide

^{13}C NMR (75 MHz, CDCl_3) of *N,N*-Dibenzylbenzamide ^1H NMR (300 MHz, CDCl_3) of *N*-Benzoylmorpholine

^{13}C NMR (75 MHz, CDCl_3) of *N*-Benzoylmorpholine

2.6. Alkane and Alcohol Oxidations

CAUTION. The combination of air or molecular oxygen and H_2O_2 with organic compounds at elevated temperatures may be explosive! Compound **1** was introduced into the reaction mixture in the form of solid powder. The alkane was added to compound **1** and acetonitrile and the reaction started when hydrogen peroxide was introduced in one portion. The reactions after addition of nitromethane as a standard compound were analyzed by GC. As we made previously, the samples obtained in the alkane oxidation were typically analyzed twice (before and after their treatment with PPh_3) by GC (LKhM-80-6 instrument, columns 2 m with 5% Carbowax 1500 on 0.25–0.315 mm Inerton AW-HMDS; carrier gas argon). This method (the comparison of chromatograms of the same sample obtained before and after addition of PPh_3) which was proposed by G. B. Shul'pin earlier¹⁴ allows us to estimate real concentration of alkyl hydroperoxide, ketone (aldehyde) and alcohol present in the reaction solution. In our kinetic studies described here, we measured concentrations of cyclohexanone and cyclohexanol only after reduction of the reaction mixture with PPh_3 .

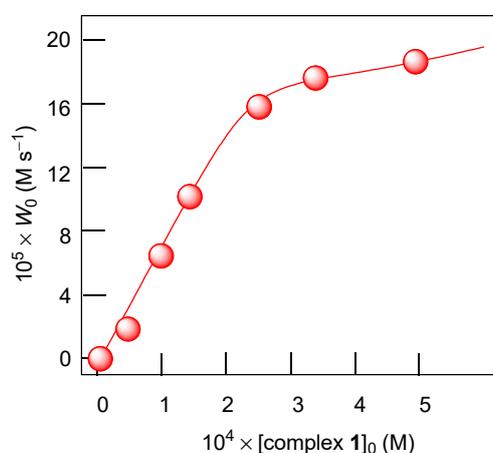


Figure S3. Cyclohexane oxygenation in acetonitrile. Dependence of the initial oxidation rate W_0 on initial concentration of catalyst **1**. Conditions: $[\text{cyclohexane}]_0 = 0.46$ M; $[\text{H}_2\text{O}_2]_0 = 2.0$ M; $[\text{HNO}_3] = 0.05$ M; 40 °C.

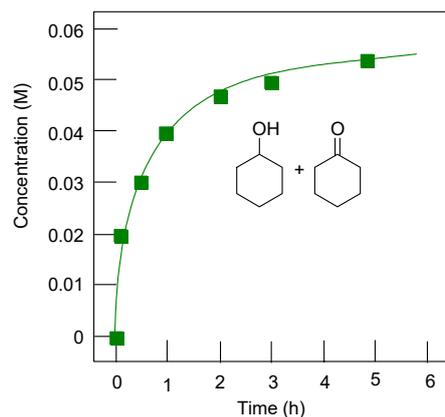


Figure S4. Accumulation of cyclohexanol and cyclohexanone in the oxidation of cyclohexane (0.46 M) with H_2O_2 (0.5 M containing 0.94 M H_2O) catalyzed by complex **1** (4.0×10^{-4} M) in the presence of HNO_3 (0.05 M) at 20 °C. Concentrations of products were measured by GC after reduction of the reaction sample with solid PPh_3 .

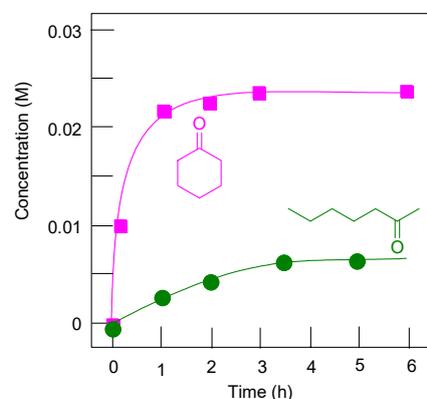


Figure S5. Accumulation of cyclohexanone and heptanone-2 in the oxidation of cyclohexanol (0.46 M) and heptanol-2 (0.5 M), respectively, with *tert*-butyl hydroperoxide (1.2 M) catalyzed by complex **1** (2.5×10^{-4} M) in the presence of HNO_3 (0.05 M) at 50 °C. Concentrations of products were measured by GC after reduction of the reaction samples with solid PPh_3 .

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