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High nuclear Cu14 ionic complex featuring 1,3-bis(diphenylphosphino)propane and methylsilsesquioxane ligands: high efficient catalysis of mild peroxidative alkane fuctionalizations

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General Experimental Considerations

All reagents were purchased from the usual suppliers (Sigma, Fluka) and used without further purification. Elemental analysis was carried out with an XRF spectrometer VRA-30. IR spectrum of the compound **1** (KBr pellets) was measured on a IRSpirit Shimadzu FTIR spectrophotometer with a diamond crystal (range 4000 – 400 cm^{-1}). UV-Vis spectrum for polycrystalline powder of **1** was measured with a VARIAN CARY 50 spectrophotometer (range 200 – 1000 nm) using nujol suspensions spread over two quartz plates. The aliquots of the catalyzed reaction solution were analyzed by chromatograph mass spectrometer (Shimadzu, Japan). The ion registration mode was Scan (33-500), the ion source temperature was 280°C. The injector temperature was 280°C. The capillary column was Restek Rxi-5ms, 30 m×0.25 mm×0.25 μm and helium as a carrier gas. The temperature program for chromatographic separation was as follows: 30°C (5 min), the temperature increase rate was 20°C/min, and the final temperature was 300°C.

Synthesis of **1**

0.272 g (2 mmol) of $MeSi(OMe_3)_3$ and 0.14 g (3.5 mmol) of NaOH were dissolved in 30 ml of EtOH under ultrasonic conditions (Stegler 3DT, 25° C, 120 W). Then 0.236 g (1.75 mmol) of $CuCl_2$ 10 ml of EtOH was added at once. The resulting blue mixture was stirred without heating for 24 h, followed by the addition of dppp (0.206 g, 0.5 mmol) in 10 ml of $CHCl_3$. This mixture was stirred without heating for a week followed by the centrifugation of precipitate. Crystallization of filtrate gave in a 3-4 days a crystalline material, including single crystals that were used for X-ray diffraction analysis. The remaining part of the crystalline material was dried in vacuum to calculate yield.

Anal. Calcd for $[(Me_4Si_4O_8)_2(Me_2Si_2O_5)_4(Cu)_{12}(Cl)_{0.9}(OH)_{0.9}(CO_3)_{0.1}][(Ph_2P(CH_2)_3PPh_2)_2(Cu)]_2$
Cu, 23.06; P, 6.42; Si, 11.65

Found: Cu, 22.95; P, 6.38; Si, 11.58. Yield: 0.324 г (65%).

X-ray diffraction studies

The single-crystal X-ray diffraction data for **1** were collected on a four-circle XtaLAB Rigaku Synergy-S diffractometer equipped with a HyPix-6000HE area-detector (T = 100 K, $\lambda(\mathrm{Cu}K\alpha)$-radiation, graphite monochromator, shutterless ω-scan mode). The data were integrated and corrected for absorption by the *CrysAlisPro* program.[S1]

The structures were solved by intrinsic phasing modification of direct methods[S2] and refined by a full-matrix least squares technique on F^2 with anisotropic displacement parameters for non-hydrogen atoms. Some solvate chloroform molecules were strongly disordered. All attempts to model and refine positions of these molecules were unsuccessful. Therefore, their contribution to the total scattering pattern was removed by use of the utility SQUEEZE in PLATON15.[S3] The hydrogen atom of the OH-group was objectively localized in the difference-Fourier maps and refined within riding model with fixed isotropic displacement parameters [$U_{\mathrm{iso}}(\mathrm{H}) = 1.5U_{\mathrm{eq}}(\mathrm{O})$]. The other hydrogen atoms were placed in calculated positions and refined within riding model with fixed isotropic displacement parameters [$U_{\mathrm{iso}}(\mathrm{H}) = 1.5U_{\mathrm{eq}}(\mathrm{C})$ for the CH_3-groups and $1.2U_{\mathrm{eq}}(\mathrm{C})$ for the other groups]. All calculations were carried out using the SHELXTL program.[S4]

Crystallographic data for **1** have been deposited with the Cambridge Crystallographic Data Center, CCDC 2494574. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk).

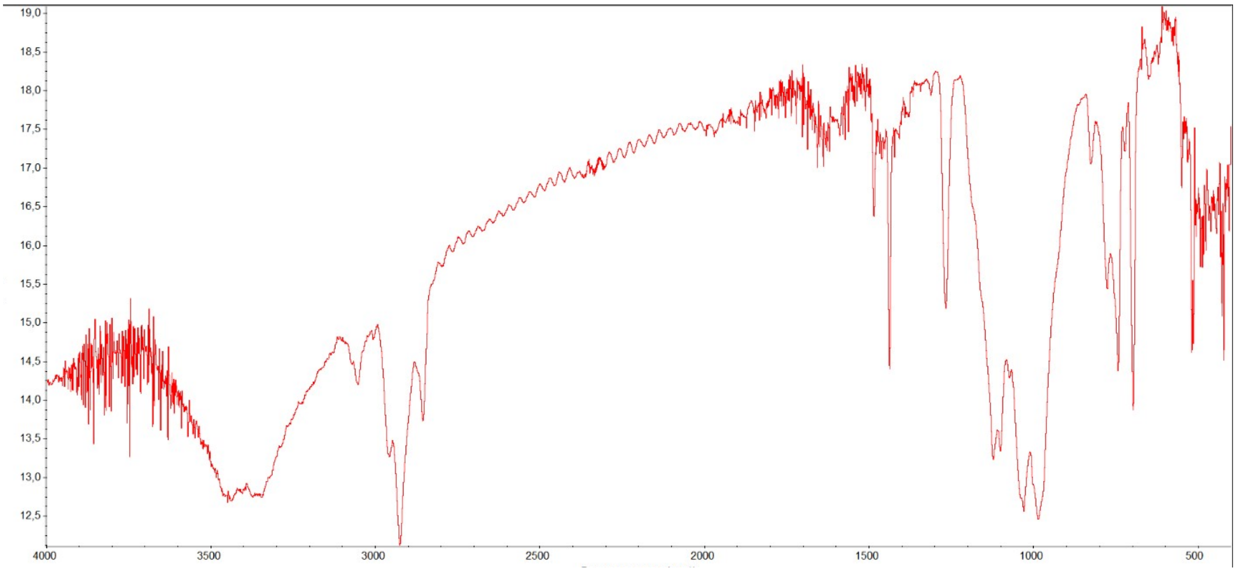

Fig. S1. IR spectra of **1**.

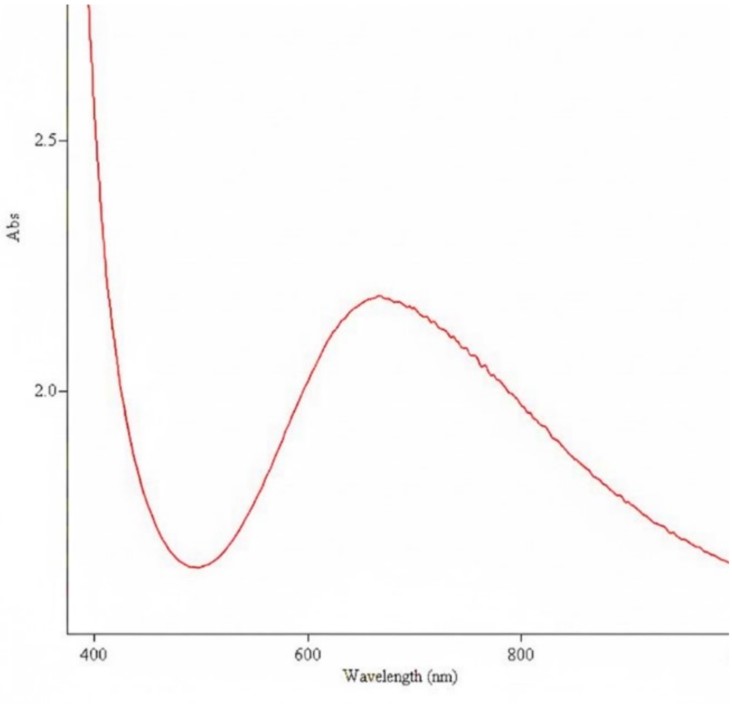

Fig. S2. UV-vis spectra of **1**.

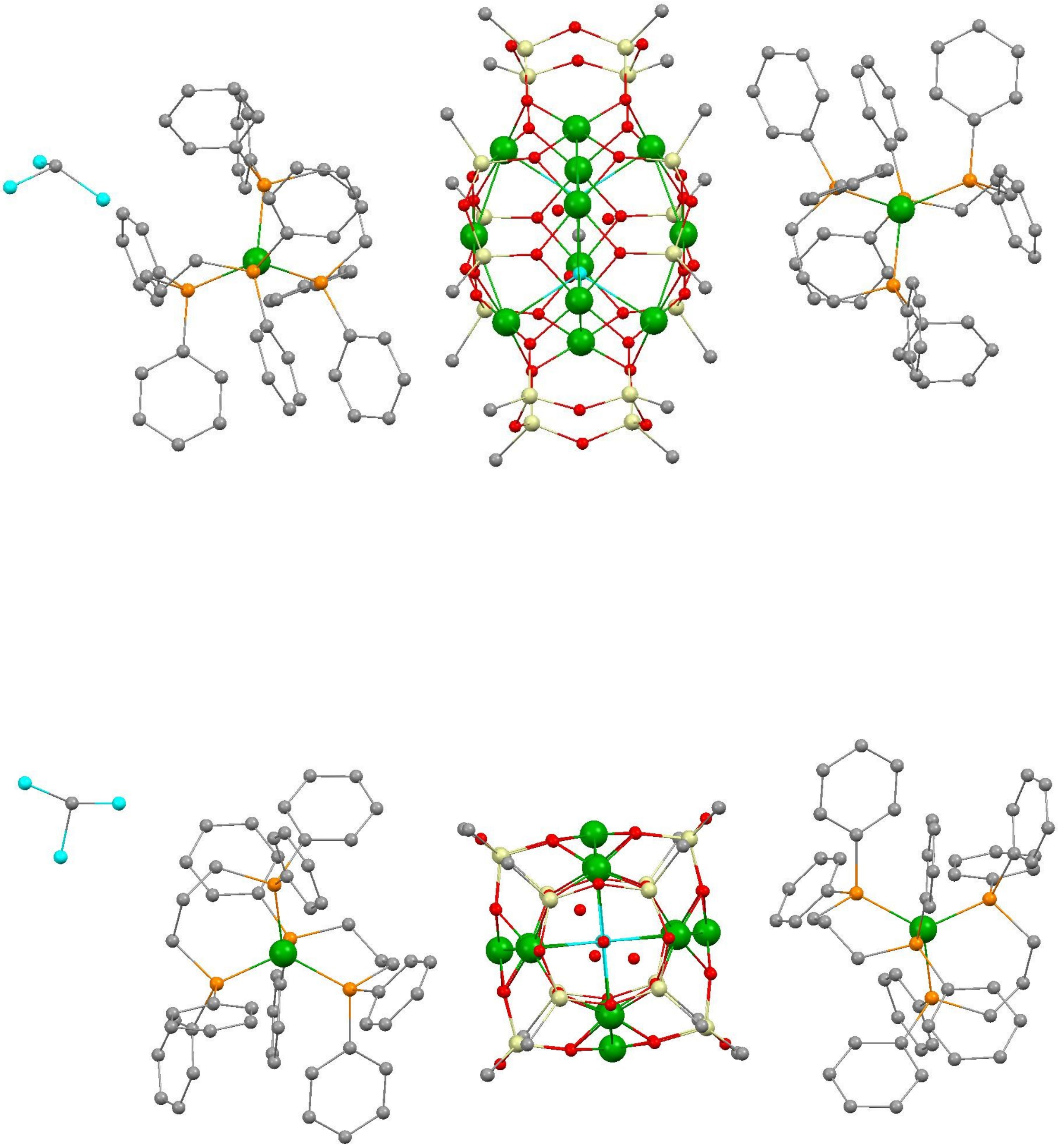

Fig. S3. Two projection of molecular structure of **1**

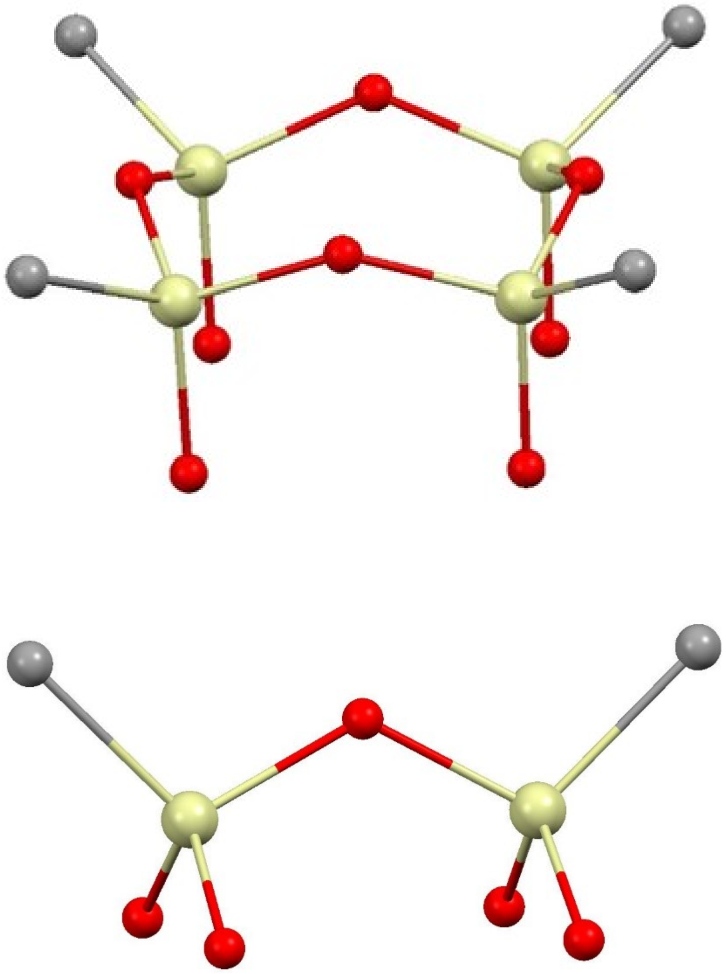

Fig. S4. Top. Cyclic silsesquioxane ligand in **1**. Bottom. Acyclic silsesquioxane ligand in **1**

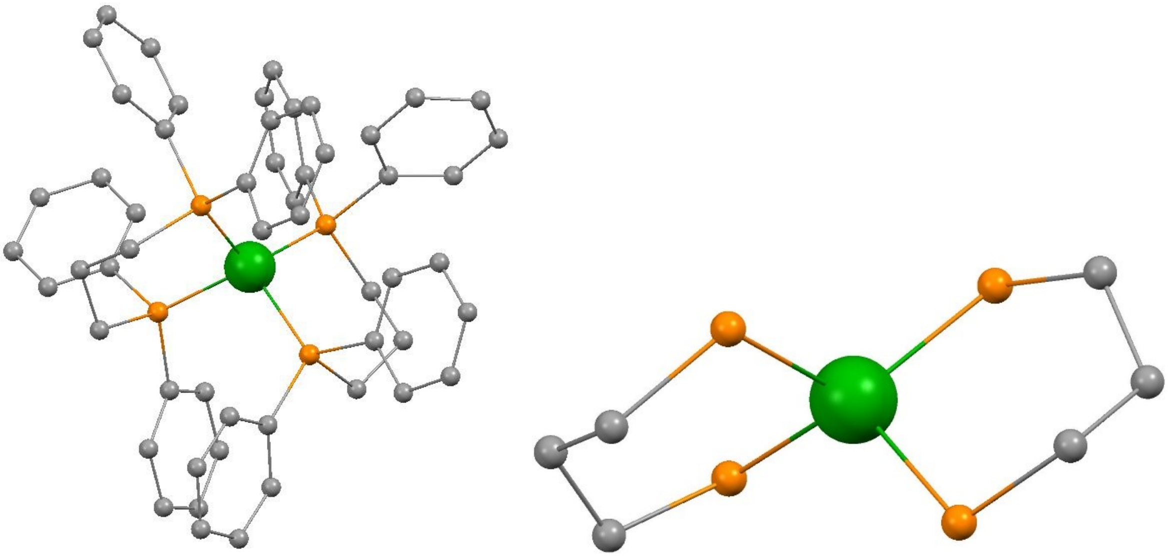

Fig. S5. Left. Structure of Cu(dppp)$_2$ cation in **1**. Right. Structure of the same cation. Phenyl groups are not shown for clarity

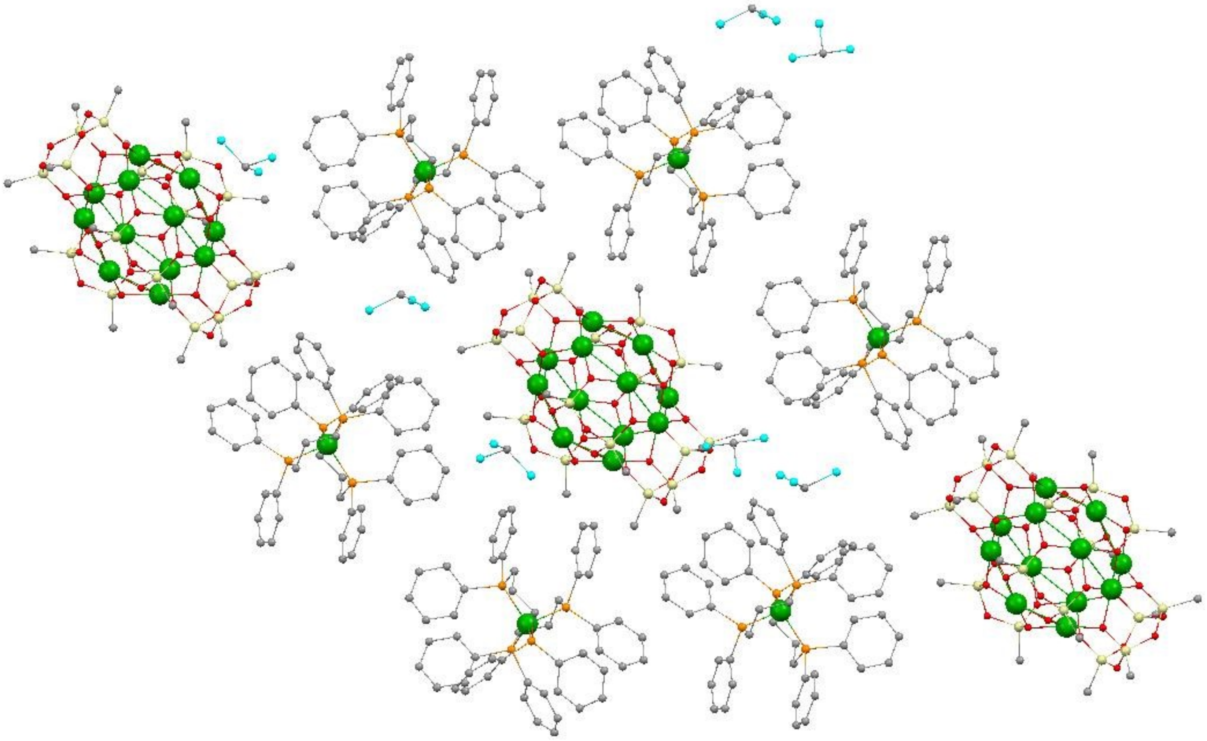

Fig. S6. “Tic tac toe” packing of **1**

Catalytic Considerations

Oxidation of alkanes:

Cylindrical vessels with vigorous stirring of the reaction mixute were used for the oxidation of alkanes with hydrogen peroxide were typically carried out in air in thermostated solution. Total volume of the reaction solution was 2.5 mL (**CAUTION**: the combination of air or molecular oxygen and H_2O_2 with organic compounds at elevated temperatures may be explosive!). Initially, a portion of 50% aqueous solution of hydrogen peroxide was added to the solution of the catalyst, co-catalyst and substrate in acetonitrile.

Attribution of peaks was made by comparison with chromatograms of authentic samples. Usually samples were analysed twice, i.e. before and after the addition of the excess of solid PPh_3. This method was developed and used previously[28]

The effect of adding triphenylphosphine to a sample of the reaction mixture can be explained by the fact that the main product of the oxidation reaction is alkyl hydroperoxide. In the absence of phosphine, it decomposes to form a ketone and alcohol in comparable amounts in an injector of GC. Triphenylphosphine reduces an alkyl hydroperoxide to alcohol, so we see a sharp increase in the amount of alcohol on the chromatogram. In many cases, the sum of alcohol and ketone before the addition of triphenylphosphine is approximately equal the sum of products after the addition of PPh_3 (for example, in 60 minutes the sum of the ketone and alcohol is 0.1M before the addition of PPh_3 and 0.09M after the addition PPh_3). This method allows us to calculate the real concentrations not only of the hydroperoxide but of the alcohols and ketones present in the solution at a given moment.

Oxidation of alkanes:

The oxidation of alcohols was carried out similarly to the method of oxidation of liquid alkanes at 50°C with the addition of triphenylphosphine to each sample for chromatography.

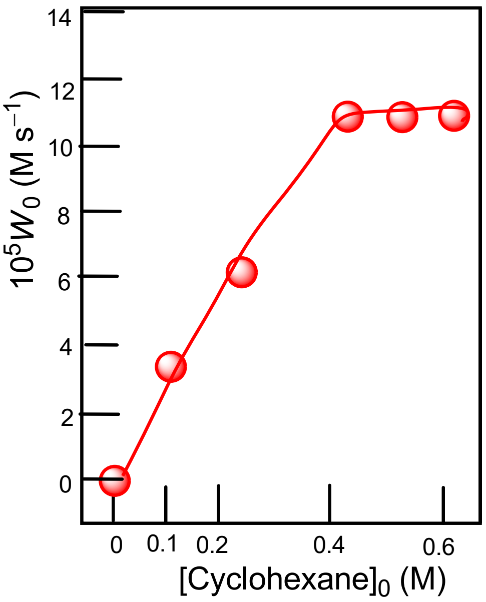

Fig. S7. Dependence of the initial rate of oxygenate (sum cyclohexanol+cyclohexanone) formation W_0 for complex **1** (5×10^{-4} M) on the initial concentration of cyclohexane in the oxidation of cyclohexane with hydrogen peroxide (2.0 M, 50 % aqueous) in the presence of HNO_3 (0.02 M) in MeCN at 40 °C.

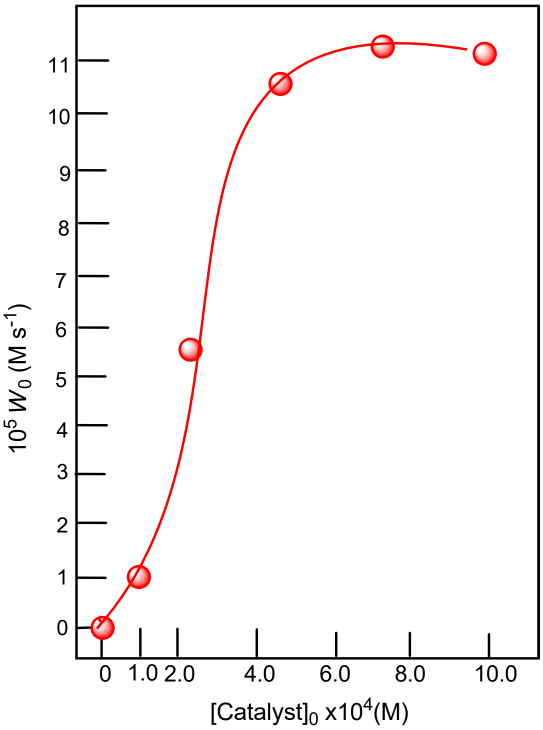

Fig. S8. Dependence of the initial rate of oxygenate (sum cyclohexanol+cyclohexanone) formation W_0 for complex **1** on the initial concentration of catalyst in the oxidation of cyclohexane (0.46 M) with hydrogen peroxide (2.0 M, 50 % aqueous) in the presence of HNO_3 (0.02 M) in MeCN at 40 °C.

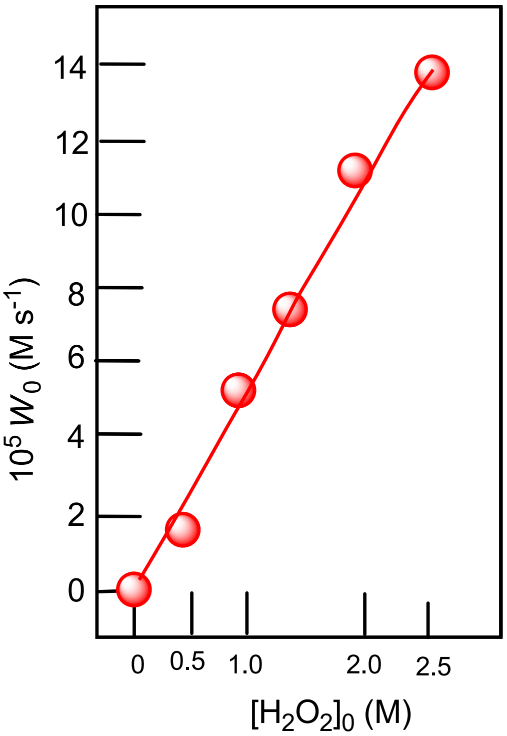

Fig. S9. Dependence of the initial rate of oxygenate (sum cyclohexanol+cyclohexanone) formation W_0 for complex **1** (5×10^{-4} M) on the initial concentration of H_2O_2 in the oxidation of cyclohexane (0.46 M) with HNO_3 (0.02 M) in MeCN at 40 °C.

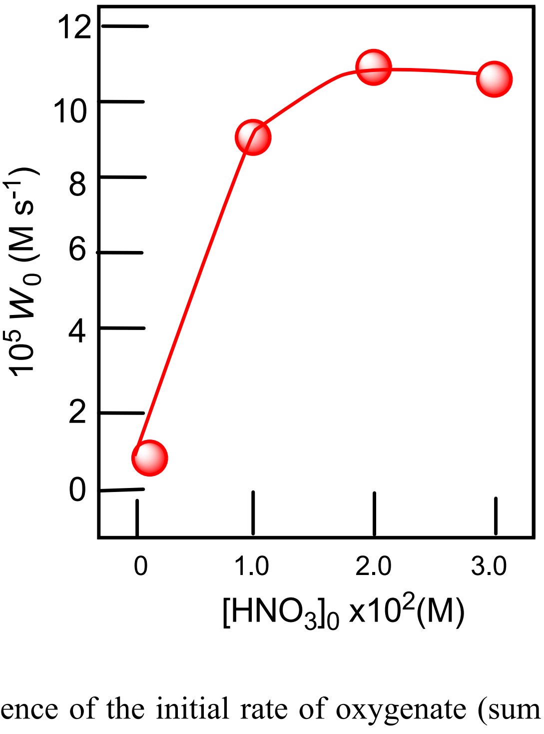

Fig. S10. Dependence of the initial rate of oxygenate (sum cyclohexanol+cyclohexanone) formation W_0 for complex **1** (5×10^{-4} M) on the initial concentration of HNO_3 in the oxidation of cyclohexane (0.46 M) with hydrogen peroxide (2.0 M, 50 % aqueous) in MeCN at 40 °C.

References

[S1] Rigaku, *CrysAlisPro Software System, v. 1.171.41.106a*, Rigaku Oxford Diffraction, **2021**.

[S2] Sheldrick, G. M. *Acta Crystallogr.* **2015**, *A71*, 3–8.

[S3] Spek, A. L. *PLATON*, A Multipurpose Crystallographic Tool, Utrecht University, the Netherlands, **2015**.

[S4] Sheldrick, G. M. *Acta Cryst.* **2015**, *C71*, 3-8.