Supplementary Information

Oxidation of Cycloalkanes by H_2O_2 Using a Copper-Hemicryptophane Complex as a Catalyst

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Experimental section

The reactions were carried out under argon by means of an inert gas/vacuum double manifold and standard Schlenk techniques. Dichloromethane was dried and degassed on a solvent station by passage through an activated alumina column followed by an argon flush. Other solvents were dried prior to use over molecular sieves. Mass spectra were recorded by the Centre de Spectrométrie de Masse, Institut de Chimie, Lyon. The UV-Vis/NIR spectra were recorded with a Jasco V-570 spectrophotometer.

Compound **2** was prepared according to the published procedure.[1]

SAFETY NOTE: Caution! perchlorate salts of metal complexes with organic ligands are potentially explosive and should be handled only in small quantities with appropriate precautions.

Synthesis of compound 1.[2]

Hemicyptophane ligand[3] (41 mg, 44 µmol) and $Cu(ClO_4)_2(H_2O)_6$ (19.4 mg, 52 µmol) dissolved in dry CH_2Cl_2 (3 mL), MeOH (200 µL) and triethylamine (7 µL, 50 µmol), were stirred at room temperature under argon for 90 min. The solvents were then evaporated and the residue was dissolved in CH_2Cl_2 (20 mL), washed with water (3 x 5 mL), dried over Na_2SO_4, filtered and concentrated under vacuum. Precipitation from pentane afforded **1** as a pale green powder (44 mg, 82%): near-IR/vis (CH_2Cl_2, 298 K) λ_{max} = 870 nm, ε = 181 cm^{-1} M^{-1} (shoulder at 700 nm). Anal. Calcd. For $[C_{57}H_{66}Cl_2CuN_4O_{17}\cdot H_2O]\cdot 2CH_2Cl_2\cdot C_5H_{12}$ (1471.63): C, 52.23; H, 5.62; N, 3,81. Found: C, 52.31; H, 6.08; N, 3.67. ESI-MS m/z: 506.7081 $[M–H_2O]^{2+}$ (calcd. for $C_{57}H_{66}CuN_4O_9$: 506.7057). IR (KBr) $\bar{\upsilon}$ = 3259, 2931, 2869, 1610, 1511, 1261, 1087, 622 (ClO_4^-) cm^{-1}.

Catalytic oxidation

Catalytic oxidation of cyclohexane

Typical procedure for oxidation of cyclohexane: To 0.3-2.4 µmol of metal complex contained in a reaction flask were successively added 250 µL of CH_3CN, 3.2 µL of cyclohexane and 300-1000 µL of H_2O_2. The reaction mixture was stirred at room temperature for 6 h, or at 35°C for 2 h. Then, a 0.1 M solution of chlorobenzene was added and the resulting mixture was analyzed by GC using a HP 6890 instrument with a 50 m DB 5MS capillary column.

Procedure for scale-up

To 0.01 mmol of metal complex contained in a reaction flask were successively added 8.3 mL of CH_3CN, 105.6 µL (1.0 mmol) of cyclohexane and 10 mL (10 mmol) of H_2O_2. The reaction mixture was stirred at 35°C for 2 h. Then, a 0.1 M solution of chlorobenzene was added and the resulting mixture was analyzed by GC using a HP 6890 instrument with a 50 m DB 5MS capillary column.

Competitive experiments

Procedure for cyclohexane/cyclooctane competition

To 0.3 µmol of metal complex contained in a reaction flask was added succesfully a 1:1 mixture of cyclohexane (1.6 µL, 15 µmol), and cyclooctane (1.6 µL, 15 µmol), in CH_3CN (250 µL) and 300 µmol of H_2O_2. The reaction mixture was stirred at 35°C for 4h. Then, a 0.1

M solution of chlorobenzene (250 µL) was added and the resulting mixture was analyzed by GC using a HP 6890 instrument with a 50 m DB 5MS capillary column.

Procedure for cyclohexane/adamantane competition

To 0.3 µmol of metal complex contained in a reaction flask was added succesfully a 1:1 mixture of cyclohexane (1.6 µL, 15 µmol), and adamantane (2.0 mg, 15 µmol), in CH_3CN (500 µL), and 300 µmol of H_2O_2. The reaction mixture was stirred at 35°C for 4h. Then, a 0.1 M solution of chlorobenzene (250 µL) was added and the resulting mixture was analyzed by GC using a HP 6890 instrument with a 50 m DB 5MS capillary column.

Catalytic oxidation of 1,3-d_2-adamantane

1,3-d_2-Adamantane (Ad-d_2) was prepared as previously described.[4] Ad-d_2 (1.1 mg) and copper catalyst (0.42 mg of **1** or 0.13 mg of **2**) were dissolved in acetonitrile (300 µL) and H_2O_2 (30 %; 35 µL) was added. The resulting mixture was stirred at 35°C for 1 h. The reaction products were analyzed at 15, 30, 45 and 60 min by GC-MS method [Hewlett Packard 5973/6890 system; electron impact ionization at 70 eV, He carrier gas, 30 m x 0.25 mm cross-linked 5% PHME (0.25 µm coating) capillary column, HP-5MS]. The exact isotopic composition of 1-adamantanol was calculated by integration of all scans of the 1-adamantanol peak since AdOH-d_1 and AdOH-d_2 were partially separated on the GC column. Kinetic isotope effects (KIE) were obtained from the intensities of the molecular peaks at $m/z = 154$ (for AdOH-d_2) and $m/z = 153$ (for AdOH-d_1) after correction for natural ^{13}C abundance (1.08% x 10 carbon atoms = 10.8 %).[3] The same KIE values were obtained at different reaction times.

References

1. M. Ciampolini and N. Nardi, *Inorg. Chem.*, 1966, **5**, 41.
2. For more details on the characterization of **1**, see: O. Perraud, J.-B. Tommasino, V. Robert, B. Albela, L. Khrouz, L. Bonneviot, J.-P. Dutasta and A. Martinez, *Dalton Trans.*, DOI: 10.1039/C2DT31530K.
3. B. Chatelet, E. Payet, O. Perraud, P. Dimitrov-Raytchev, L.-L. Chapellet, V. Dufaud, A. Martinez and J.-P. Dutasta, *Org. Lett.*, 2011, **13**, 3706.
4. A. Sorokin, A. Robert and B. Meunier, *J. Am. Chem. Soc.*, 1993, **115**, 7293.