

# Organometallics, communication

## ESI

### Mild and regioselective hydroxylation of methyl group in neocuproine: approach to N,O-ligated Cu<sub>6</sub> cage phenylsilsesquioxane

Alexey N. Bilyachenko,<sup>\*,†,‡</sup> Mikhail M. Levitsky,<sup>†</sup> Victor N. Khrustalev,<sup>‡</sup> Yan V. Zubavichus,<sup>†</sup>

Lidia S. Shul'pina,<sup>†</sup> Elena S. Shubina,<sup>†</sup> and Georgiy B. Shul'pin<sup>\*,§,Ψ</sup>

<sup>†</sup>Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Vavilov Str., 28, Moscow, Russia

<sup>‡</sup>Peoples' Friendship University of Russia (RUDN University), Miklukho-Maklay Str., 6, Moscow, Russia

<sup>†</sup>National Research Center "Kurchatov Institute", Akademika Kurchatova pl., 1, Moscow, Russia

<sup>§</sup>Semenov Institute of Chemical Physics, Russian Academy of Sciences, ulitsa Kosygina, dom 4, Moscow, Russia

<sup>Ψ</sup>Plekhanov Russian University of Economics, Stremyannyi pereulok, dom 36, Moscow, Russia

Corresponding Authors

\*E-mails: bilyachenko@ineos.ac.ru (ANB), shulpin@chph.ras.ru (GBS)

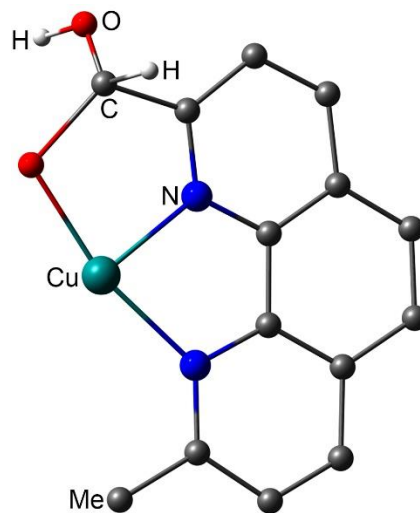
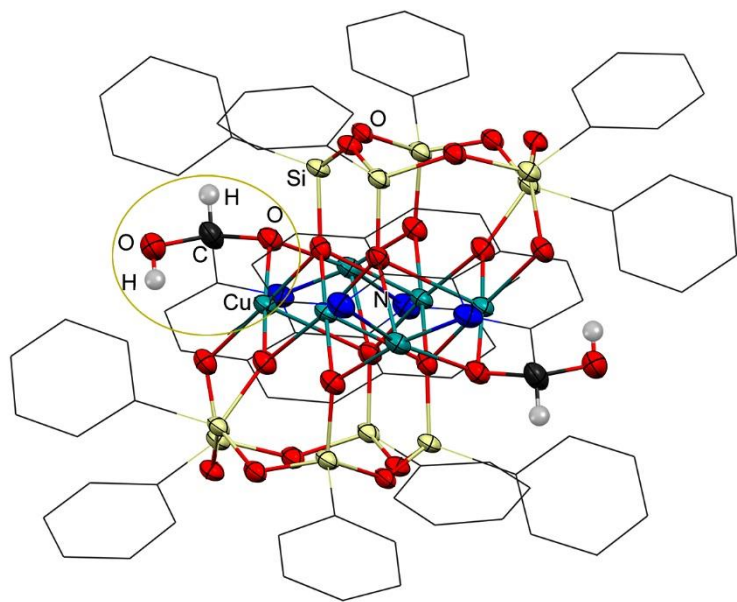
#### X-ray crystal structure determination.

X-ray diffraction data for **1** were collected on the 'Belok' beamline<sup>S1a</sup> of the National Research Center 'Kurchatov Institute' (Moscow, Russian Federation) using a Rayonix SX165 CCD detector. A total of 720 images were collected using an oscillation range of 1.0° and  $\varphi$  scan mode, and corrected for absorption using the *Scala* program.<sup>S1b</sup> The data were indexed, integrated and scaled using the utility *iMOSFLM* in CCP4 program.<sup>S1c</sup> The structure was determined by direct methods and refined by full-matrix least squares technique on  $F^2$  with anisotropic displacement parameters for non-hydrogen atoms. The hydrogen atoms of the OH-groups were localized in the difference-Fourier map and included in 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 riding model with fixed isotropic displacement parameters [ $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$  for the CH<sub>3</sub>-groups and  $1.2U_{\text{eq}}(\text{C})$  for the other groups]. All calculations were carried out using the SHELXTL<sup>S1d</sup> and Olex2<sup>S1e</sup> programs.

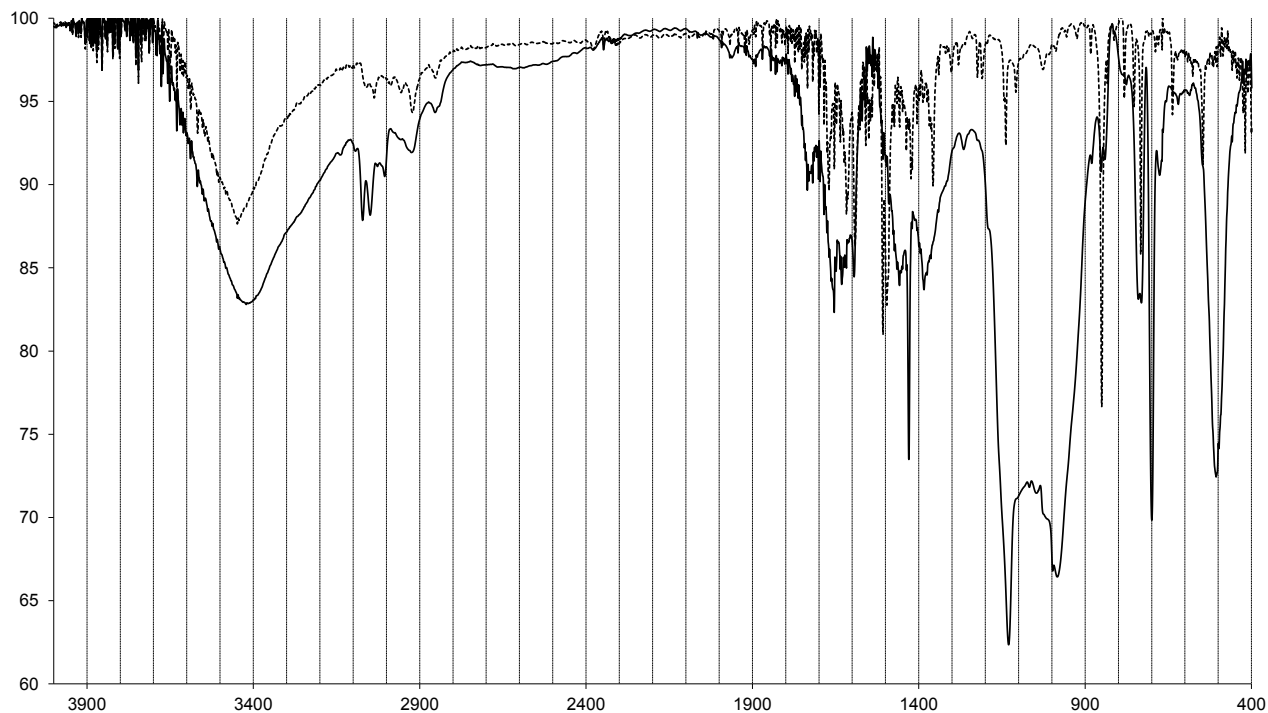
Crystallographic data for **1** have been deposited with the Cambridge Crystallographic Data Center, CCDC 1565125. Copy of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336033; e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk) or [www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk)).

**Table S1.** Crystal data and structure2 refinement for **1**.

Identification code	<b>1•0.5C<sub>4</sub>H<sub>8</sub>O<sub>2</sub>•C<sub>3</sub>H<sub>7</sub>NO</b>
Empirical formula	C <sub>93</sub> H <sub>83</sub> Cu <sub>6</sub> N <sub>5</sub> O <sub>26</sub> Si <sub>10</sub>
Formula weight	2348.78
Temperature, K	100(2)
Crystal size, mm	0.06 × 0.08 × 0.12
Wavelength, Å	0.96990
Crystal system	Triclinic
Space group	<i>P</i> -1
<i>a</i> , Å	15.283(3)
<i>b</i> , Å	15.580(3)
<i>c</i> , Å	21.790(4)
$\alpha$ , deg.	85.37(3)
$\beta$ , deg.	72.21(3)
$\gamma$ , deg.	86.33(3)
<i>V</i> , Å <sup>3</sup>	4920.0(18)
<i>Z</i>	2
Density (calc.), g/cm <sup>3</sup>	1.586
$\mu$ , mm <sup>-1</sup>	3.414
<i>F</i> (000)	2396
Theta range, deg.	3.32 – 38.45
Index ranges	-19 ≤ <i>h</i> ≤ 19, -19 ≤ <i>k</i> ≤ 19, -27 ≤ <i>l</i> ≤ 25
Reflections collected	66565
Independent reflections	18506 ( <i>R</i> <sub>int</sub> = 0.0767)
Reflections observed	11527
<i>R</i> <sub>1</sub> / <i>wR</i> <sub>2</sub> ( <i>I</i> > 2σ( <i>I</i> ))	0.0927 / 0.2014
<i>R</i> <sub>1</sub> / <i>wR</i> <sub>2</sub> (all data)	0.1443 / 0.2390
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.059
Extinction coefficient	0.00368(12)
<i>T</i> <sub>min</sub> / <i>T</i> <sub>max</sub>	0.680 / 0.800
Δρ <sub>max</sub> / Δρ <sub>min</sub> , e <sup>-</sup> Å <sup>-3</sup>	1.424 / -1.408



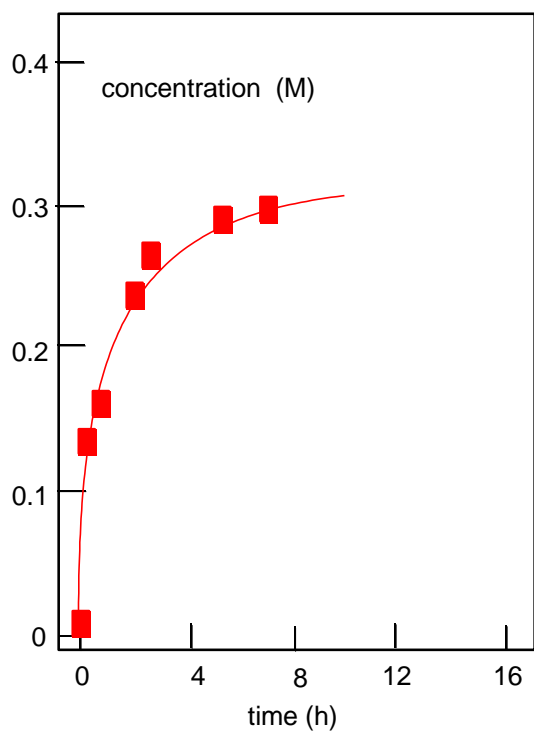
**Figure S1.** Structure of compound **1** (left). The yellow oval highlights the hydroxylated methyl group of the neocuproine ligand coordinated to the copper ion. Color code: Si, yellow; O, red; Cu, green; N, blue; C, black; H, gray. The essential fragment of the coordinated neocuproine is shown on the right for clarity



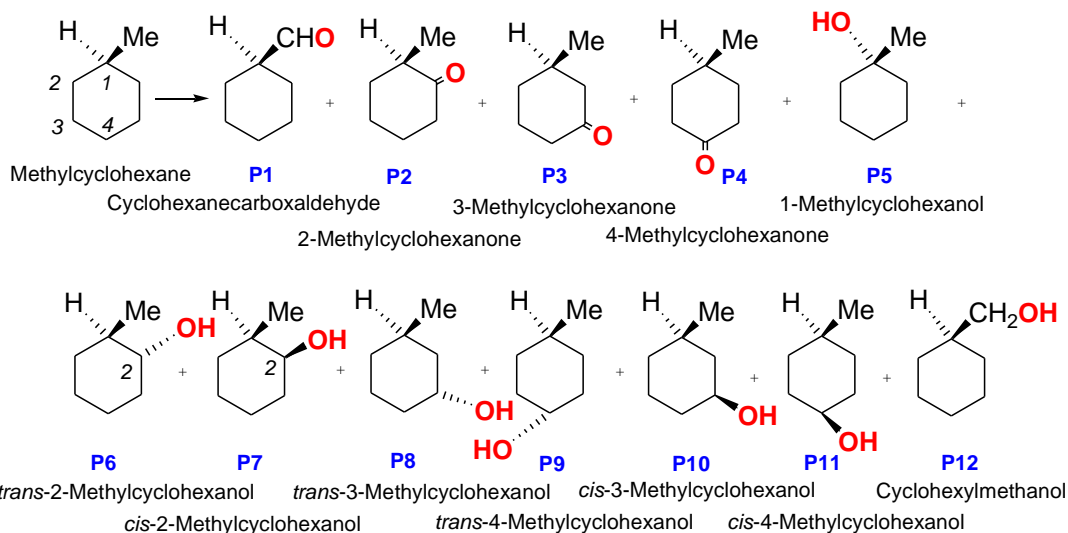
**Figure S2.** IR spectra of **1** (solid line) and neocuproine ligand (dotted line)

### Details of the catalytic experiments

Catalyst **1** was introduced into the reaction mixture in the form of solid powder. The alkane was then added and the reaction started when hydrogen peroxide was introduced in one portion. (**CAUTION.** The combination of air or molecular oxygen and H<sub>2</sub>O<sub>2</sub> with organic compounds at elevated temperatures may be explosive!). The reactions after addition of nitromethane as a standard compound were analyzed by GC (the Instrument LKhM-80-6 was used; columns 2 m with 5% Carbowax 1500 on 0.25–0.315 mm Inerton AW-HMDS; carrier gas argon). Attribution of peaks was made by comparison with chromatograms of authentic samples and by GC–MS.



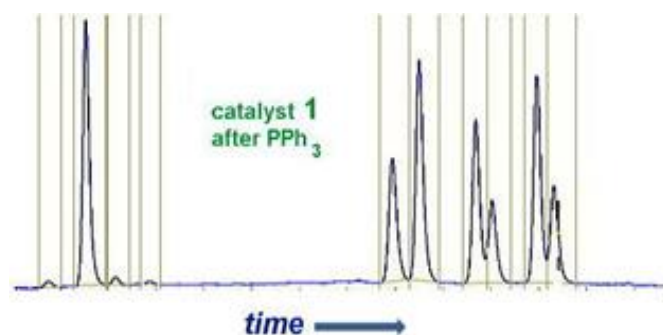
**Figure S3.** Accumulation of cyclohexanone with time in the oxidation of cyclohexanol (initial concentration was 0.4 M) with TBHP (70% aqueous; initial concentration 1.2 M) catalyzed by compound **1** ( $5 \times 10^{-4}$  M). Solvent was acetonitrile (total volume of the reaction solution was 5 mL); 60 °C.



**Figure S4.** Products obtained in the methylcyclohexane oxidation with TBHP catalyzed by complex **1**.

**Table S2.** Oxidation of methylcyclohexane (CyMe) with  $\text{H}_2\text{O}_2$  catalyzed by complex **1**.

entry	time (min)		P2	P3	P4	P5	P6	P7	P8	P9	P10	P11	sum
1	10	before $\text{PPh}_3$	0.07	0.06	0.03	0.06	0.02	0.04	0.05	0.007	0.03	0.01	0.38
2	10	after $\text{PPh}_3$	0.01	0.01	0.005	0.15	0.05	0.10	0.07	0.04	0.11	0.005	0.55
3	20	before $\text{PPh}_3$	0.10	0.09	0.04	0.06	0.02	0.05	0.05	0.01	0.06	0.03	0.51
4	20	after $\text{PPh}_3$	0.01	0.01	0.007	0.33	0.18	0.31	0.23	0.12	0.30	0.14	1.64
5	60	before $\text{PPh}_3$	0.20	0.18	0.08	0.14	0.05	0.15	0.10	0.05	0.18	0.09	1.22
6	60	after $\text{PPh}_3$	0.02	0.02	0.01	0.78	0.44	0.73	0.56	0.27	0.67	0.34	3.84
7	120	before $\text{PPh}_3$	0.50	0.50	0.20	0.20	0.05	0.15	0.13	0.06	0.27	0.14	2.20
8	120	after $\text{PPh}_3$	0.07	0.08	0.04	1.30	0.70	1.11	0.87	0.46	1.10	0.50	6.23
9	180	before $\text{PPh}_3$	0.30	0.30	0.10	0.30	0.10	0.20	0.20	0.10	0.40	0.20	2.20
10	180	after $\text{PPh}_3$	0.14	0.19	0.08	1.25	0.63	1.09	0.09	0.45	1.17	0.59	6.49



**Figure S5.** Chromatogram of products of methylcyclohexane oxidation with hydrogen peroxide catalyzed by complex **1**.

(S1) a) Lazarenko, V.A.; Dorovatovskii, P.V.; Zubavichus, Y.V.; Burlov, A.S.; Koshchienko, Y.V.; Vlasenko, V.G.; Khrustalev, V.N. *Crystals*. 2017, 7, 325-1-19; b) Evans, P. R. *Acta Cryst.* 2006, D62, 72-82; c) Battye, T. G. G.; Kontogiannis, L.; Johnson, O.; Powell, H. R.; Leslie, A. G. W. *Acta Cryst.* 2011, D67, 271-281; d) Sheldrick, G. M. *Acta Cryst.* 2015, C71, 3-8; e) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. J. *Appl. Cryst.* 2009, 42, 339-341.