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Mild and Regioselective Hydroxylation of Methyl Group in Neocuproine: Approach to an N,O-Ligated Cu_6 Cage Phenylsilsesquioxane

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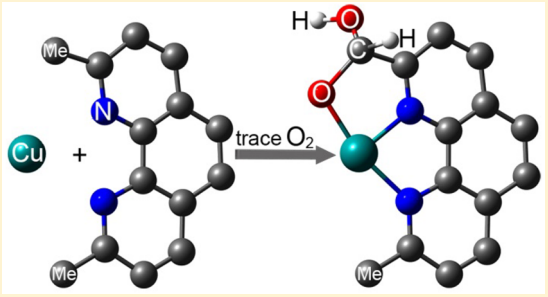
Supporting Information

ABSTRACT: The self-assembly synthesis of Cu(II)-silsesquioxane involving 2,9-dimethyl-1,10-phenanthroline (neocuproine) as an additional N ligand at copper atoms was performed. The reaction revealed an unprecedented aerobic hydroxylation of only one of the two methyl groups in neocuproine to afford the corresponding geminal diol. The produced derivative of oxidized neocuproine acts as a two-centered N,O ligand in the assembly of the hexacopper cage product $[Cu_6(Ph_5Si_5O_{10})_2{\cdot}(C_{14}H_{11}N_2O_2)_2]$ (**1**), coordinating two of the six copper centers in the product. Two siloxanolate ligands $[PhSi(O)O]_5$ in the cis configuration coordinate to the rest of the copper(II) ions. Compound **1** is a highly efficient homogeneous precatalyst in the oxidation of alkanes and alcohols with peroxides.



In the ever-expanding field of C−H functionalization, significant attention has been paid to the use of complexes of inexpensive metals. The most intriguing feature is that the catalytic activity of metal complexes can be dramatically enhanced by selecting an appropriate ligand environment of the metal site in such systems. In the context of these works, some of us presented the first results concerning an application of polynuclear complexes of non-noble metals in sesquioxane ($REO_{1.5}$, E stands for silicon (Si) or germanium (Ge)) matrixes.[1−3] Very recently, it has been shown that both the structural and catalytic features of such metalla compounds may be tailored due to the involvement of additional organic (nitrogen-[4] or phosphorus-containing[5]) ligands. Thus, further exploration of the chemistry of sesquioxane metallacomplexes seemed to be of significant profit. According to known literature data, there are three strategies for the "ligand assisted" synthesis of metallasilsesquioxanes. First, the ligand could enter into the composition of the metallasilsesquioxane along with a metal ion in the case of using a metallacomplex as a reactant for the synthesis (e.g., Cp^*TaCl_4,[6] $(dcpe)FeCl_2$,[7] $[(PPh_3)_2PtI(Ph)]$,[8] $Fe[N(SiMe_3)_2]_2$[9]). In the second method, a postsynthesis treatment of a metallasilsesquioxane with the ligand was suggested (e.g., by tmeda,[10] PMe_3,[11] NO,[12] NEt_3[13]). Finally, the simplest and most convenient approach, developed by our team, involves self-assembly of a metallasilsesquioxane in the presence of an additional ligand (e.g., phenanthroline[4] or dppe[5]). Herewith, we present an unexpected reactivity of 2,9-dimethyl-1,10-phenanthroline (neocuproine) exhibited by this heterocyclic ligand in the course of such a reaction.

Interaction of $PhSi(OMe)_3$ (1 g; 5.04 mmol) in 20 mL of an ethanol/methanol (1/1) mixture with solid NaOH (0.20 g; 5 mmol) was carried out by heating under reflux for 1.5 h. Afterward, the solution was cooled to room temperature and 0.226 g (1.68 mmol) of $CuCl_2$ was added at once. The solution was stirred for 3 h, and 0.175 g (0.840 mmol) of neocuproine (solution in 35 mL of a 1/1 1,4-dioxane/DMF mixture) was added (Figure 1). The reaction solution was intensely stirred for 2 h and then filtered to remove the insoluble precipitate. The filtrate was stored in a flask in air to admit a slow evaporation of the solvents for crystal growth. After roughly 2 weeks the formation of crystalline material **1** of the composition $[Cu_6(Ph_5Si_5O_{10})_2{\cdot}(C_{14}H_{11}N_2O_2)_2]{\cdot}0.5(dioxane){\cdot}DMF$ occurred; a few selected single crystals were used for the X-ray diffraction analysis. Anal. Calcd for $[Cu_6(Ph_5Si_5O_{10})_2{\cdot}(C_{14}H_{11}N_2O_2)_2]$: Cu, 17.08; N, 2.51; Si, 12.59. Found (for vacuum-dried sample): Cu, 16.89; N, 2.42; Si, 12.40 (elemental analysis was carried out with an XRF VRA-30 spectrometer). Yield: 0.27 g (43%).

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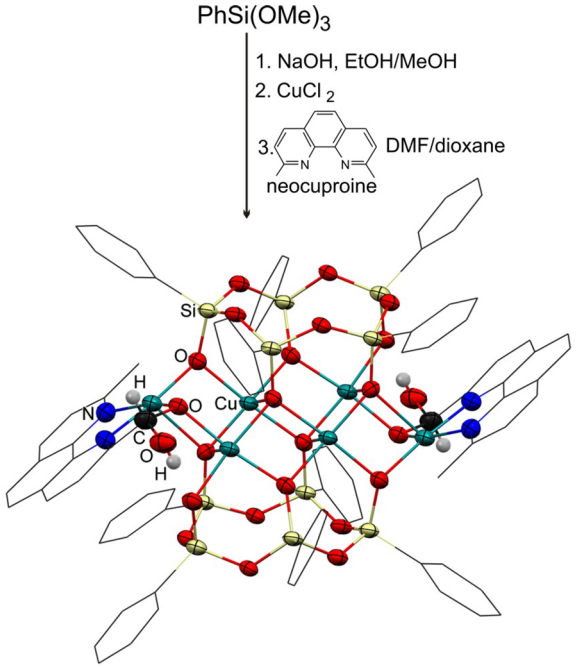

Figure 1. General scheme of synthesis of hexacopper silsesquioxane **1** containing hydroxylated neocuproine ligands. Color code: Si, yellow; O, red; Cu, green; N, blue; C, black; H, gray.

An X-ray diffraction study of **1** revealed a cage consisting of two Cu_3 linear trimers sandwiched between two cisoid $[PhSi(O)O]_5$ siloxanolate ligands. This is an unusual combination of complex components—while hexacopper compounds are in principle well-known in the chemistry of metallasilsesquioxanes,[14] the presence of five-membered siloxanolate rings is not so common.[15] Since five siloxanolate oxygen atoms from each side of such a sandwich are obviously insufficient to complete coordination of the six Cu(II) ions, the involvement of two additional (i.e., neocuproine) ligands is needed. The actual method of this involvement, to the best of our knowledge, turned out to be absolutely unexpected and unprecedented. Surprisingly, one methyl group of each neocuproine moiety was oxidized (or, more strictly speaking, hydroxylated) to produce a geminal diol fragment, −CH(OH)-(OH). One of the −OH fragments of this diol is then deprotonated to coordinate the Cu(II) ion, −CH(OH)(O···Cu^{II}). Simultaneously, N atoms of the neocuproine ligand also participate in the coordination with the same copper site (Figure S1, Supporting Information). Thus, such a transformation of neocuproine into the two-centered N,O ligand provides better coordination conditions for copper sites and therefore can be considered as a driving force of the whole product **1** assembly.

Several earlier works concerning metallasilsesquioxane synthesis pointed at the "oxidation prospective" conditions of such reaction systems. For example, Ce^{III} to Ce^{IV},[16] U^{IV} to U^{VI} [17] and Cr^{II} to Cr^{IV} [18] oxidations were observed in the course of synthesis of cerium-, uranium- and chromium-based silsesquioxanes, respectively. Moreover, tetrahydrofuran to γ-butyrolactone oxidation was reported for iron-silsesquioxane synthesis performed in THF as a reaction medium.[19] Thus, the oxidation of neocuproine's methyl groups under conditions of the synthesis of **1**′ is not inexplicable.[20,21] The most attractive feature in our report is the formation of a geminal diol as a product of the neocuproine methyl group oxidation, while the aforementioned synthetic protocols earlier gave rise to alcohol,[20] aldehyde, or carboxylic[21] fragments. We could only compare our results to works discussing "methyl to gem-diol" transformation as an intermediate step in enzyme-assisted oxidations.[22]

We assume that, in our neocuproine case, the molecular oxygen is coordinated to two copper ions to give species **B** (Figure 3), and then a peroxo dicopper intermediate is generated. Such complexes containing one or two copper ions surrounded with N-donor ligands have been reported earlier.[23−26] These compounds are capable of hydroxylating C−H bonds to afford phenols for the intramolecular reaction involving a benzene ring or THF oxygenated products in the intermolecular case.[25] A copper(II)−OOH complex has been isolated and characterized as a structural/functional model of dopamine β-hydroxylases hydroxylating sp^3-CH bonds.[23] Hydroxyl radicals have been produced from H_2O_2 under the action of Cu(II)-bridged peroxo species.[26] The oxygen atom from coordinated O_2 in species **B** abstracts a hydrogen atom to produce in species **C** a hydroperoxy ligand and alkyl radical fragment. A recombination of the two radicals −CuO$^{\bullet}$ and $^{\bullet}$CH(OH)− in **D** and then H atom abstraction in **E** gives finally structure **G** (isolated complex **1**) via a rebound mechanism in structure **F**.

Multicopper complexes are known to catalyze functionalization of alkanes and other C−H compounds under mild conditions.[27−31] These complexes are models of the reaction sites of certain enzymes.[32−34] It is worth mentioning that earlier work of Waymouth and colleagues[35] noted that oxidation of a methyl group at the neocuproine (to a carboxylate fragment) strongly inhibited the corresponding palladium complex toward the aerobic alcohol oxidation. In contrast to this, we have found that compound **1** is a highly efficient homogeneous catalyst in the oxidation of alkanes and alcohols with peroxides. As we indicated previously, the samples obtained in the alkane oxidation were typically analyzed twice (before and after their treatment with PPh_3) by GC. This method (the comparison of chromatograms of the same sample obtained before and after addition of PPh_3) which was proposed by Shul'pin earlier[1,36−42] allows us to estimate the real concentrations of alkyl hydroperoxide, ketone (aldehyde), and alcohol present in the reaction solution. The experiments on the methylcyclohexane oxidations catalyzed by **1** are described in the Supporting Information. All of the peculiarities of alkane oxidation indicate that the oxidation with H_2O_2 occurs with the participation of free hydroxyl radicals.[43−53] Complex **1** also efficiently catalyzes the oxidation of alcohols to ketones with TBHP in acetonitrile. The oxidation of alcohols apparently involves the generation of hydroxyl radicals (see the Supporting Information).

In summary, an unprecedented "methyl to diol" hydroxylation of one methyl group in a neocuproine ligand coordinated to copper was observed. This unusual reaction became possible, most likely, via peroxo dicopper intermediate formation. Importantly, this intermediate was formed during the metallasilsesquioxane assembly in the presence of ambient oxygen, without the use of any added oxidant reagent. The resulting neocuproine derivatives act as two-centered N,O ligands, essential for the assembly of the hexacopper cage product **1**. The rest of the coordination sites of copper ions are filled by oxygen centers of siloxanolate ligands $[PhSi(O)O]_5$. Compound **1** is a very efficient precatalyst in the homogeneous oxidation of alkanes and alcohols with peroxides.

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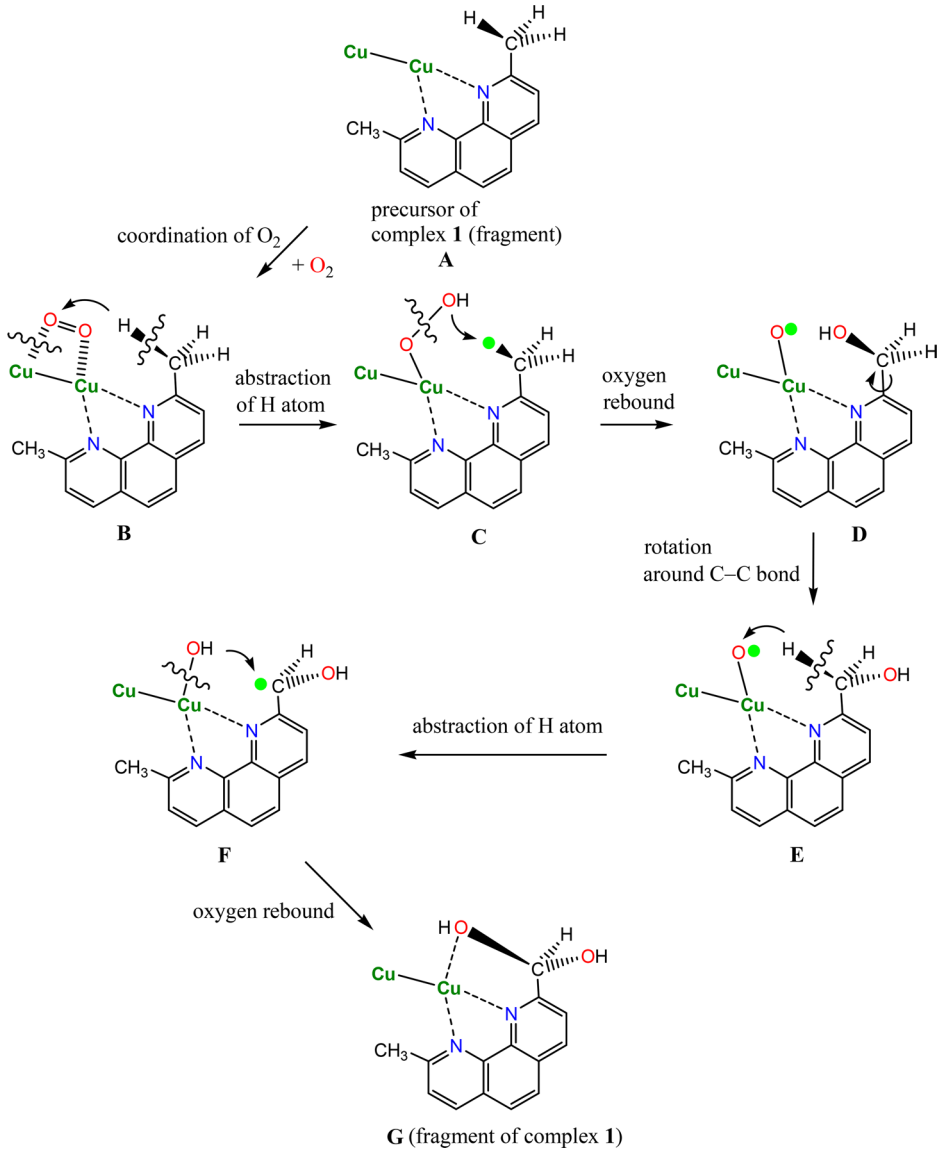

Figure 3. Mechanism proposed for the hydroxylation of neocuproine's methyl group to afford complex **1**.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.7b00845.

Details of X-ray experiments and catalytic oxidations (PDF)

Accession Codes

CCDC 1565125 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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The authors declare no competing financial interest.

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