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$Si_{10}Cu_6N_4$ Cage Hexacoppersilsesquioxanes Containing N Ligands: Synthesis, Structure, and High Catalytic Activity in Peroxide Oxidations

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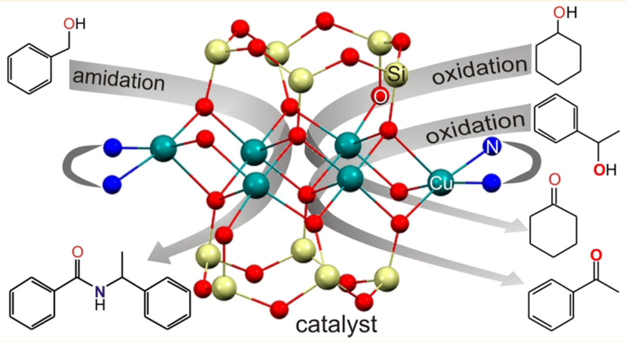
S Supporting Information

ABSTRACT: The synthesis, composition, and catalytic properties of a new family of hexanuclear Cu(II)-based phenylsilsesquioxanes are described here. Structural studies of 17 synthesized compounds revealed the general principle underlying their molecular topology: viz., a central metal oxide layer consisting of two Cu_3 trimers is coordinated by two cyclic $[PhSiO_{1.5}]_5$ siloxanolate ligands to form a skewed sandwich architecture with the composition $[(PhSiO_{1.5})_{10}(CuO)_6]^{2+}$. In addition to this O ligation by the siloxanolate rings, two opposite copper ions are additionally coordinated by the nitrogen atoms of corresponding N ligand(s), such as 2,2′-bipyridine (compounds **1**−**9**), 1,10-phenanthroline (compounds **10**−**13**), mixed 1,10-phenanthroline/2,2′-bipyridine (compound **14**), or bathophenanthroline (compounds **15**−**17**). Finally, the charge balance is maintained by two HO^- (compounds **1**−**7**, **10**−**13**, and **15**−**17**), two H_3CO^- (compound **8**), or two CH_3COO^- (compounds **9** and **14**) anions. Complexes **1** and **10** exhibited a high activity in the oxidative amidation oxidation of alcohols. Compounds **1**, **10**, and **15** are very efficient homogeneous catalysts in the oxidation of alkanes and alcohols with peroxides.



■ INTRODUCTION

In the past decades, metal-containing cagelike compounds (polycyclic 3D structures with well-defined geometry) have attracted enormous attention from scientific groups due to their striking molecular topology[1] as well as their huge potential for practical applications.[2] These latter applications include, for example, intriguing cases of development of polymer science[3] and medicine.[4] A diversity of self-assembly procedures was elaborated for the construction of cagelike compounds,[5] suggesting different ideas on structure control by means of, e.g., an appropriate choice of linkers[5b] or ligand shape.[5d]

Among the variety of metal-containing cage complexes, a family of $RSiO_{1.5}$-based metallacomplexes (cagelike metallasilsesquioxanes, CLMSs) has drawn special attention as attractive molecular architectures[6] exhibiting unusual magnetic (spin glass behavior) effects[7] and opportunities for the creation of inorganic materials[8] or nanoparticles.[9] In turn, great deal of attention has been devoted to the investigation of the catalytic activity of metallasilsesquioxanes.[10] For example, their high activity was reported for such reactions of high demand as olefin[11] or ring-opening polymerization,[12] olefin epoxidation,[13] polycarbonate synthesis,[14] and a Meerwein−Ponndorf reaction,[15] as well as for hydroformylation.[16] In turn, our team reported on the catalytic

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activity of cagelike metallasilsesquioxanes in oxidative hydrocarbon functionalization[17] and amidation[18] reactions. Very recently, some of us presented the first example of the successful testing of CLMSs, including additional organic (phosphorus-based[19]) ligands in such oxidative reactions. According to this, we were interested in further investigation of "organic ligand assisted" synthesis of metallasilsesquioxanes and the application of potential products of such an approach in catalysis. It should be emphasized that among publications describing synthetic approaches to CLMSs one could find some examples of CLMS formation in the presence of different organic ligands. Mostly, these ligands were used in the reaction of metallasilsesquioxane synthesis as reagents (being a part of a metal complex) and they were inherited in the composition of the product. These cases include the classical work on the very first cubane CLMS[20] (complex with Cp*) synthesis as well as numerous types of other complexes: with carborane,[21] acac,[22] tricyclohexylphosphine,[23] cyclooctenyl,[24] methyl,[25] or silylamide[26] ligands just to mention a few. Several examples of postsynthesis CLMS functionalization by the organic ligands *N*,*N*-dimethylhydroxylamine and acacH,[27] tris(2-pyridylmethyl)amine[28] and bipy[29] are also worth mentioning. Very recently, our group suggested a quite convenient method of CLMS self-assembly, assisted by the interaction of 2,2′-bipyridine or phenanthroline with the product of the interaction of methylalkoxysilane with NaOH and $CuCl_2$.[30] It should be mentioned that the nature of the silicon atom substituent could have great influence on the process of cage assembly (compare, for example, penta-[7b,d] or hexanuclear[18a,31] prismatic CLMSs, characteristic for phenyl-substituted reagent, to octa-[32] or nonanuclear[30] methyl-based prisms). This is why we were interested in the investigation of self-assembling reactions involving phenylalkoxysilane and different ligands of the 2,2′-bipy family. These ligands (with a transfer from 2,2′-bipyridine to bathophenanthroline) could give valuable information on the influence of steric factors (due to an increase in N-ligand bulkiness) for the process of cage product assembly. Of course, we were interested in the first study of catalytic properties of potential products of these reactions, CLMSs, bearing N ligands.

We present here an extended series of 17 complexes (with 2,2′-bipy, phenanthroline, or bathophenanthroline ligands) and the determination of their structures by single-crystal X-ray diffraction. A study of the catalytic activity of these complexes in peroxide oxidations of alcohols and alkanes as well as in amidation reactions under mild conditions is also described.

■ EXPERIMENTAL SECTION

Synthesis. $PhSi(OMe)_3$, solvents, and N ligands were purchased from Acros Organics and used as received. All manipulations required no inert atmosphere.

Complex 1. A 1 g portion (5.04 mmol) of $PhSi(OMe)_3$, 0.20 g (5 mmol) of NaOH, and 20 mL of an ethanol/methanol (1/1) mixture were placed in a three-neck round-bottom flask (equipped with magnetic stirrer and condenser). The resulting solution was heated under reflux for 1.5 h and then was cooled to room temperature, and 0.226 g (1.68 mmol) of $CuCl_2$ was added at once. The mixture was stirred for 3 h and filtered from NaCl. The filtrate was dried under vacuum, and then 0.131 g (0.839 mmol) of 2,2′-bipyridine in 35 mL of DMSO was placed in the same evaporation flask. The resulting solution was intensely stirred for 2.5 h with a magnetic stirrer and then filtered from the insoluble precipitate. The filtrate was stored in a vial equipped with a septum with a needle to allow the slow evaporation of solvents for crystallization. After 1 week the formation of crystalline material was observed; several single crystals were used for X-ray diffraction analysis (for details of the X-ray diffraction study see below). The rest of the crystalline fraction was separated from the solution, washed with *n*-heptane, and dried under vacuum. Anal. Calcd for $[(PhSiO_{1.5})_{10}(CuO)_6(HO_{0.5})_2(C_{10}H_8N_2)_2]$: Cu, 18.16; N, 2.67; Si, 13.38. Found (for vacuum-dried sample): Cu, 18.07; N, 2.59; Si, 13.29. Yield: 0.36 g (61%).

Complex 2. A 1 g portion (5.04 mmol) of $PhSi(OMe)_3$, 0.20 g (5 mmol) of NaOH, and 20 mL of an ethanol/methanol (1/1) mixture were placed in a three-neck round-bottom flask (equipped with a magnetic stirrer and condenser). The resulting solution was heated under reflux for 1.5 h and then was cooled to room temperature, and 0.226 g (1.68 mmol) of $CuCl_2$ was added at once. The mixture was stirred for 3 h and filtered from NaCl. The filtrate was dried under vacuum, and then 0.131 g (0.839 mmol) of 2,2′-bipyridine in 35 mL of MeCN was placed in the same evaporation flask. The resulting solution was intensely stirred for 2.5 h with a magnetic stirrer and then filtered from the insoluble precipitate. The filtrate was stored in a vial equipped with a septum with a needle to allow the slow evaporation of solvents for crystallization. After 1 week the formation of crystalline material was observed; several single crystals were used for X-ray diffraction analysis (for details of the X-ray diffraction study see below). The rest of the crystalline fraction was separated from the solution, washed with *n*-heptane, and dried under vacuum. Anal. Calcd for $[(PhSiO_{1.5})_{10}(CuO)_6(HO_{0.5})_2(C_{10}H_8N_2)_2]$: Cu, 18.16; N, 2.67; Si, 13.38. Found (for vacuum-dried sample): Cu, 18.05; N, 2.60; Si, 13.27. Yield: 0.24 g (40%).

Complex 3. A 1 g portion (5.04 mmol) of $PhSi(OMe)_3$, 0.20 g (5 mmol) of NaOH, and 20 mL of an ethanol/methanol (1/1) mixture were placed in a three-neck round-bottom flask (equipped with magnetic stirrer and condenser). The resulting solution was heated under reflux for 1.5 h and then was cooled to room temperature, and 0.226 g (1.68 mmol) of $CuCl_2$ was added at once. The mixture was stirred for 3 h and filtered from NaCl. The filtrate was dried under vacuum, and then 0.131 g (0.839 mmol) of 2,2′-bipyridine in 35 mL of a MeCN/PhCN mixture (2/1) was placed in the same evaporation flask. The resulting solution was intensely stirred for 2.5 h with a magnetic stirrer and then filtered from the insoluble precipitate. The filtrate was stored in a vial equipped with a septum with a needle to allow the slow evaporation of solvents for crystallization. After 1 week the formation of crystalline material was observed; several single crystals were used for X-ray diffraction analysis (for details of the X-ray diffraction study see below). The rest of the crystalline fraction was separated from the solution, washed with *n*-heptane, and dried under vacuum. Anal. Calcd for $[(PhSiO_{1.5})_{10}(CuO)_6(HO_{0.5})_2(C_{10}H_8N_2)_2]$: Cu, 18.16; N, 2.67; Si, 13.38. Found (for vacuum-dried sample): Cu, 18.07; N, 2.61; Si, 13.30. Yield: 0.12 g (20%).

Complex 4. A 1 g portion (5.04 mmol) of $PhSi(OMe)_3$, 0.20 g (5 mmol) of NaOH, and 20 mL of an ethanol/methanol (1/1) mixture were placed in a three-neck round-bottom flask (equipped with a magnetic stirrer and condenser). The resulting solution was heated under reflux for 1.5 h and then was cooled to room temperature, and 0.226 g (1.68 mmol) of $CuCl_2$ was added at once. The mixture was stirred for 3 h and filtered from NaCl. The filtrate was dried under vacuum, and then 0.131 g (0.839 mmol) of 2,2′-bipyridine in 35 mL of a MeCN/PhCN mixture (1/2) was placed in the same evaporation flask. The resulting solution was intensely stirred for 2.5 h with a magnetic stirrer and then filtered from the insoluble precipitate. The filtrate was stored in a vial equipped with a septum with a needle to allow the slow evaporation of solvents for crystallization. After 1 week the formation of crystalline material was observed; several single crystals were used for X-ray diffraction analysis (for details of the X-ray diffraction study see below). The rest of the crystalline fraction was separated from the solution, washed with *n*-heptane, and dried under vacuum. Anal. Calcd for $[(PhSiO_{1.5})_{10}(CuO)_6(HO_{0.5})_2(C_{10}H_8N_2)_2]$: Cu, 18.16; N, 2.67; Si, 13.38. Found (for vacuum-dried sample): Cu, 18.09; N, 2.60; Si, 13.29. Yield: 0.06 g (10%).

Complex 5. A 1 g portion (5.04 mmol) of $PhSi(OMe)_3$, 0.20 g (5 mmol) of NaOH, and 20 mL of an ethanol/methanol (1/1) mixture were placed in a three-neck round-bottom flask (equipped with a magnetic stirrer and condenser). The resulting solution was heated under reflux for 1.5 h and then was cooled to room temperature, and 0.226 g (1.68 mmol) of $CuCl_2$ was added at once. The mixture was stirred for 3 h and filtered from NaCl. The filtrate was dried under vacuum, and then 0.131 g (0.839 mmol) of 2,2′-bipyridine in 35 mL of

PhCN was placed in the same evaporation flask. The resulting solution was intensely stirred for 2.5 h with a magnetic stirrer and then filtered from the insoluble precipitate. The filtrate was stored in a vial equipped with a septum with a needle to allow the slow evaporation of solvents for crystallization. After 1 week the formation of crystalline material was observed; several single crystals were used for X-ray diffraction analysis (for details of the X-ray diffraction study see below). The rest of the crystalline fraction was separated from the solution, washed with *n*-heptane, and dried under vacuum. Anal. Calcd for $[(PhSiO_{1.5})_{10}(CuO)_6(HO_{0.5})_2(C_{10}H_8N_2)_2]$: Cu, 18.16; N, 2.67; Si, 13.38. Found (for vacuum-dried sample): Cu, 18.07; N, 2.58; Si, 13.26. Yield: 0.08 g (14%).

*Complex **6**.* A 1 g portion (5.04 mmol) of $PhSi(OMe)_3$, 0.20 g (5 mmol) of NaOH, and 20 mL of an ethanol/methanol (1/1) mixture were placed in a three-neck round-bottom flask (equipped with magnetic stirrer and condenser). The resulting solution was heated under reflux for 1.5 h and then was cooled to room temperature, and 0.226 g (1.68 mmol) of $CuCl_2$ was added at once. The mixture was stirred for 3 h and filtered from NaCl. The filtrate was dried under vacuum, and then 0.131 g (0.839 mmol) of 2,2′-bipyridine in 35 mL of THF was placed in the same evaporation flask. The resulting solution was intensely stirred for 2.5 h with a magnetic stirrer and then filtered from the insoluble precipitate. The filtrate was stored in a vial equipped with a septum with a needle to allow the slow evaporation of solvents for crystallization. After 1 week the formation of crystalline material was observed; several single crystals were used for X-ray diffraction analysis (for details of the X-ray diffraction study see below). The rest of the crystalline fraction was separated from the solution, washed with *n*-heptane, and dried under vacuum. Anal. Calcd for $[(PhSiO_{1.5})_{10}(CuO)_6(HO_{0.5})_2(C_{10}H_8N_2)_2]$: Cu, 18.16; N, 2.67; Si, 13.38. Found (for vacuum-dried sample): Cu, 18.10; N, 2.59; Si, 13.29. Yield: 0.28 g (48%).

*Complex **7**.* A 1 g portion (5.04 mmol) of $PhSi(OMe)_3$, 0.20 g (5 mmol) of NaOH, and 20 mL of an ethanol/methanol (1/1) mixture were placed in a three-neck round-bottom flask (equipped with magnetic stirrer and condenser). The resulting solution was heated under reflux for 1.5 h and then was cooled to room temperature, and 0.226 g (1.68 mmol) of $CuCl_2$ was added at once. The mixture was stirred for 3 h and filtered from NaCl. The filtrate was dried under vacuum, and then 0.131 g (0.839 mmol) of 2,2′-bipyridine in 35 mL of a toluene/DMSO mixture (3/1) was placed in the same evaporation flask. The resulting solution was intensely stirred for 2.5 h with a magnetic stirrer and then filtered from the insoluble precipitate. The filtrate was stored in a vial equipped with a septum with a needle to allow the slow evaporation of solvents for crystallization. After 1 week the formation of crystalline material was observed; several single crystals were used for X-ray diffraction analysis (for details of the X-ray diffraction study see below). The rest of the crystalline fraction was separated from the solution, washed with *n*-heptane, and dried under vacuum. Anal. Calcd for $[(PhSiO_{1.5})_{10}(CuO)_6(HO_{0.5})_2(C_{10}H_8N_2)_3]$: Cu, 16.90; N, 3.73; Si, 12.45. Found (for vacuum-dried sample): Cu, 16.81; N, 3.68; Si, 12.37. Yield: 0.08 g (12%).

*Complex **8**.* A 1 g portion (5.04 mmol) of $PhSi(OMe)_3$, 0.20 g (5 mmol) of NaOH, and 20 mL of an ethanol/methanol (1/1) mixture were placed in a three-neck round-bottom flask (equipped with magnetic stirrer and condenser). The resulting solution was heated under reflux for 1.5 h and then was cooled to room temperature, and 0.226 g (1.68 mmol) of $CuCl_2$ was added at once. The mixture was stirred for 3 h and then mixed with 0.131 g (0.839 mmol) of 2,2′-bipyridine (solution in 35 mL of THF). The resulting solution was intensely stirred for 2.5 h with a magnetic stirrer and then filtered from the insoluble precipitate. The filtrate was stored in a vial equipped with a septum with a needle to allow the slow evaporation of solvents for crystallization. After 1 week the formation of crystalline material was observed; several single crystals were used for X-ray diffraction analysis (for details of the X-ray diffraction study see below). The rest of the crystalline fraction was separated from the solution, washed with *n*-heptane, and dried under vacuum. Anal. Calcd for $[(PhSiO_{1.5})_{10}(CuO)_6(CH_3O_{0.5})_2(C_{10}H_8N_2)_2]$: Cu, 17.92; N, 2.63; Si, 13.20. Found (for vacuum-dried sample): Cu, 18.10; N, 2.59; Si, 13.29. Yield: 0.16 g (27%).

*Complex **9**.* A 1 g portion (5.04 mmol) of $PhSi(OMe)_3$, 0.20 g (5 mmol) of NaOH, and 20 mL of an ethanol/methanol (1/1) mixture were placed in a three-neck round-bottom flask (equipped with a magnetic stirrer and condenser). The resulting solution was heated under reflux for 1.5 h and then was cooled to room temperature, and 0.226 g (1.68 mmol) of $CuCl_2$ was added at once. The mixture was stirred for 3 h and then mixed with 0.131 g (0.839 mmol) of 2,2′-bipyridine (solution in 35 mL of MeCN). The resulting solution was intensely stirred for 2.5 h with a magnetic stirrer and then filtered from the insoluble precipitate. The filtrate was stored in a vial equipped with a septum with a needle to allow the slow evaporation of solvents for crystallization. After 1 week the formation of crystalline material was observed; several single crystals were used for X-ray diffraction analysis (for details of the X-ray diffraction study see below). The rest of the crystalline fraction was separated from the solution, washed with *n*-heptane, and dried under vacuum. Anal. Calcd for $[(PhSiO_{1.5})_{10}(CuO)_6(CH_3COO_{0.5})_2(C_{10}H_8N_2)_2]$: Cu, 17.46; N, 2.57; Si, 12.86. Found (for vacuum-dried sample): Cu, 17.37; N, 2.49; Si, 12.77. Yield: 0.15 g (25%).

*Complex **10**.* A 1 g portion (5.04 mmol) of $PhSi(OMe)_3$, 0.20 g (5 mmol) of NaOH, and 20 mL of an ethanol/methanol (1/1) mixture were placed in a three-neck round-bottom flask (equipped with a magnetic stirrer and condenser). The resulting solution was heated under reflux for 1.5 h and then was cooled to room temperature, and 0.226 g (1.68 mmol) of $CuCl_2$ was added at once. The mixture was stirred for 3 h and filtered from NaCl. The filtrate was dried under vacuum, and then 0.151 g (0.840 mmol) of 1,10-phenanthroline in 35 mL of DMSO was placed in the same evaporation flask. The resulting solution was intensely stirred for 2.5 h with a magnetic stirrer and then filtered from the insoluble precipitate. The filtrate was stored in a vial equipped with a septum with a needle to allow the slow evaporation of solvents for crystallization. After 1 week the formation of crystalline material was observed; several single crystals were used for X-ray diffraction analysis (for details of the X-ray diffraction study see below). The rest of the crystalline fraction was separated from the solution, washed with *n*-heptane, and dried under vacuum. Anal. Calcd for $[(PhSiO_{1.5})_{10}(CuO)_6(HO_{0.5})_2(C_{12}H_8N_2)_2]$: Cu, 17.75; N, 2.61; Si, 13.08. Found (for vacuum-dried sample): Cu, 17.64; N, 2.53; Si, 12.99. Yield: 0.39 g (65%).

*Complex **11**.* A 1 g portion (5.04 mmol) of $PhSi(OMe)_3$, 0.20 g (5 mmol) of NaOH, and 20 mL of an ethanol/methanol (1/1) mixture were placed in a three-neck round-bottom flask (equipped with a magnetic stirrer and condenser). The resulting solution was heated under reflux for 1.5 h and then was cooled to room temperature, and 0.226 g (1.68 mmol) of $CuCl_2$ was added at once. The mixture was stirred for 3 h and filtered from NaCl. The filtrate was dried under vacuum, and then 0.151 g (0.840 mmol) of 1,10-phenanthroline in 35 mL of toluene was placed in the same evaporation flask. The resulting solution was intensely stirred for 2.5 h with a magnetic stirrer and then filtered from the insoluble precipitate. The filtrate was stored in a vial equipped with a septum with a needle to allow the slow evaporation of solvents for crystallization. After 1 week the formation of crystalline material was observed; several single crystals were used for X-ray diffraction analysis (for details of the X-ray diffraction study see below). The rest of the crystalline fraction was separated from the solution, washed with *n*-heptane, and dried under vacuum. Anal. Calcd for $[(PhSiO_{1.5})_{10}(CuO)_6(HO_{0.5})_2(C_{12}H_8N_2)_2]$: Cu, 17.75; N, 2.61; Si, 13.08. Found (for vacuum-dried sample): Cu, 17.66; N, 2.54; Si, 12.99. Yield: 0.22 g (37%).

*Complex **12**.* A 1 g portion (5.04 mmol) of $PhSi(OMe)_3$, 0.20 g (5 mmol) of NaOH, and 20 mL of an ethanol/methanol (1/1) mixture were placed in a three-neck round-bottom flask (equipped with a magnetic stirrer and condenser). The resulting solution was heated under reflux for 1.5 h and then was cooled to room temperature, and 0.226 g (1.68 mmol) of $CuCl_2$ was added at once. The mixture was stirred for 3 h and filtered from NaCl. The filtrate was dried under vacuum, and then 0.151 g (0.840 mmol) of 1,10-phenanthroline in 35 mL of DMF was placed in the same evaporation flask. The resulting solution was intensely stirred for 2.5 h with a magnetic stirrer and then filtered from the insoluble precipitate. The filtrate was stored in a vial equipped with a septum with a needle to allow the slow evaporation of solvents for crystallization. After 1 week the formation of crystalline material was observed; several single crystals were used for X-ray

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diffraction analysis (for details of the X-ray diffraction study see below). The rest of the crystalline fraction was separated from the solution, washed with *n*-heptane, and dried under vacuum. Anal. Calcd for $[(PhSiO_{1.5})_{10}(CuO)_6(HO_{0.5})_2(C_{12}H_8N_2)_2]$: Cu, 17.75; N, 2.61; Si, 13.08. Found (for vacuum-dried sample): Cu, 17.68; N, 2.54; Si, 13.00. Yield: 0.28 g (47%).

Complex 13. A 1 g portion (5.04 mmol) of $PhSi(OMe)_3$, 0.20 g (5 mmol) of NaOH, and 20 mL of an ethanol/methanol (1/1) mixture were placed in a three-neck round-bottom flask (equipped with a magnetic stirrer and condenser). The resulting solution was heated under reflux for 1.5 h and then was cooled to room temperature ,and 0.226 g (1.68 mmol) of $CuCl_2$ was added at once. The mixture was stirred for 3 h and then mixed with 0.151 g (0.840 mmol) of 1,10-phenanthroline (solution in 35 mL of pyridine). The resulting solution was intensely stirred for 2.5 h with a magnetic stirrer and then filtered from the insoluble precipitate. The filtrate was stored in a vial equipped with a septum with a needle to allow the slow evaporation of solvents for crystallization. After 1 week the formation of crystalline material was observed; several single crystals were used for X-ray diffraction analysis (for details of the X-ray diffraction study see below). The rest of the crystalline fraction was separated from the solution, washed with *n*-heptane, and dried under vacuum. Anal. Calcd for $[(PhSiO_{1.5})_{10}(CuO)_6(HO_{0.5})_2(C_{12}H_8N_2)_2]$: Cu, 17.75; N, 2.61; Si, 13.08. Found (for vacuum-dried sample): Cu, 17.66; N, 2.52; Si, 12.99. Yield: 0.18 g (31%).

Complex 14. A 1 g portion (5.04 mmol) of $PhSi(OMe)_3$, 0.20 g (5 mmol) of NaOH, and 20 mL of an ethanol/methanol (1/1) mixture were placed in a three-neck round-bottom flask (equipped with a magnetic stirrer and condenser). The resulting solution was heated under reflux for 1.5 h and then was cooled to room temperature, and 0.226 g (1.68 mmol) of $CuCl_2$ was added at once. The mixture was stirred for 3 h and filtered from NaCl. The filtrate was dried under vacuum, and then 0.065 g (0.420 mmol) of 2,2′-bipyridine and 0.076 g (0.420 mmol) of 1,10-phenanthroline (solution in 35 mL of DMF) was placed in the same evaporation flask. The resulting solution was intensely stirred for 2.5 h with a magnetic stirrer and then filtered from the insoluble precipitate. The filtrate was stored in a vial equipped with a septum with a needle to allow the slow evaporation of solvents for crystallization. After 1 week the formation of crystalline material was observed; several single crystals were used for X-ray diffraction analysis (for details of the X-ray diffraction study see below). The rest of the crystalline fraction was separated from the solution, washed with *n*-heptane, and dried under vacuum. Anal. Calcd for $[(PhSiO_{1.5})_{10}(CuO)_6(CH_3COO_{0.5})_2(C_{12}H_8N_2)(C_{10}H_8N_2)]$: Cu, 17.27; N, 2.54; Si, 12.72. Found (for vacuum-dried sample): Cu, 17.20; N, 2.47; Si, 12.67. Yield: 0.19 g (31%).

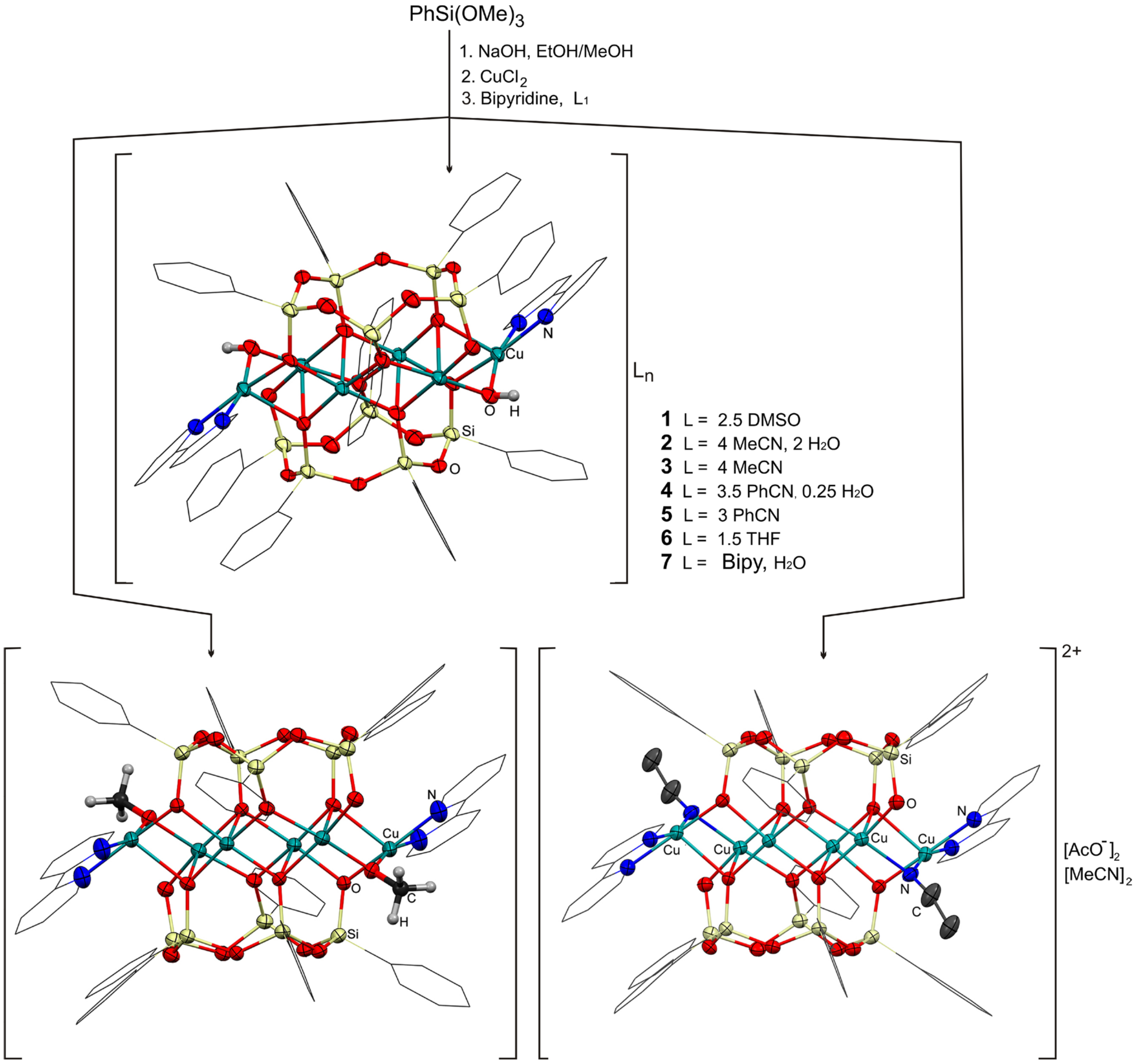
Complex 15. A 1 g portion (5.04 mmol) of $PhSi(OMe)_3$, 0.20 g (5 mmol) of NaOH, and 20 mL of an ethanol/methanol (1/1) mixture were placed in a three-neck round-bottom flask (equipped with a magnetic stirrer and condenser). The resulting solution was heated under reflux for 1.5 h and then was cooled to room temperature, and 0.226 g (1.68 mmol) of $CuCl_2$ was added at once. The mixture was stirred for 3 h and filtered from NaCl. The filtrate was dried under vacuum, and then 0.280 g (0.840 mmol) of bathophenanthroline (solution in 35 mL of MeCN) was placed in the same evaporation flask. The resulting solution was intensely stirred for 2.5 h with a magnetic stirrer and then filtered from the insoluble precipitate. The filtrate was stored in a vial equipped with a septum with a needle to allow the slow evaporation of solvents for crystallization. After 1 week the formation of crystalline material was observed; several single crystals were used for X-ray diffraction analysis (for details of the X-ray diffraction study see below). The rest of the crystalline fraction was separated from the solution, washed with *n*-heptane, and dried under vacuum. Anal. Calcd for $[(PhSiO_{1.5})_{10}(CuO)_6(HO_{0.5})_2(C_{24}H_{16}N_2)_2]$: Cu, 15.55; N, 2.28; Si, 11.45. Found (for vacuum-dried sample): Cu, 15.48; N, 2.20; Si, 11.36. Yield: 0.28 g (41%).

Complex 16. A 1 g portion (5.04 mmol) of $PhSi(OMe)_3$, 0.20 g (5 mmol) of NaOH, and 20 mL of an ethanol/methanol (1/1) mixture were placed in a three-neck round-bottom flask (equipped with a magnetic stirrer and condenser). The resulting solution was heated under reflux for 1.5 h and then was cooled to room temperature, and 0.226 g (1.68 mmol) of $CuCl_2$ was added at once. The mixture was stirred for 3 h and filtered from NaCl. The filtrate was dried under vacuum, and then 0.280 g (0.840 mmol) of bathophenanthroline (solution in 35 mL of toluene) was placed in the same evaporation flask. The resulting solution was intensely stirred for 2.5 h with a magnetic stirrer and then filtered from the insoluble precipitate. The filtrate was stored in a vial equipped with a septum with a needle to allow the slow evaporation of solvents for crystallization. After 1 week the formation of crystalline material was observed; several single crystals were used for X-ray diffraction analysis (for details of the X-ray diffraction study see below). The rest of the crystalline fraction was separated from the solution, washed with *n*-heptane, and dried under vacuum. Anal. Calcd for $[(PhSiO_{1.5})_{10}(CuO)_6(HO_{0.5})_2(C_{24}H_{16}N_2)_2]$: Cu, 15.55; N, 2.28; Si, 11.45. Found (for vacuum-dried sample): Cu, 15.47; N, 2.19; Si, 11.36. Yield: 0.21 g (30%).

Complex 17. A 1 g portion (5.04 mmol) of $PhSi(OMe)_3$, 0.20 g (5 mmol) of NaOH, and 20 mL of an ethanol/methanol (1/1) mixture were placed in a three-neck round-bottom flask (equipped with a magnetic stirrer and condenser). The resulting solution was heated under reflux for 1.5 h and then was cooled to room temperature, and 0.226 g (1.68 mmol) of $CuCl_2$ was added at once. The mixture was stirred for 3 h and then mixed with 0.280 g (0.840 mmol) of bathophenanthroline (solution in 35 mL of benzene). The resulting solution was intensely stirred for 2.5 h with a magnetic stirrer and then filtered from the insoluble precipitate. The filtrate was stored in a vial equipped with a septum with a needle to allow the slow evaporation of solvents for crystallization. After 1 week the formation of crystalline material was observed; several single crystals were used for X-ray diffraction analysis (for details of the X-ray diffraction study see below). The rest of the crystalline fraction was separated from the solution, washed with *n*-heptane, and dried under vacuum. Anal. Calcd for $[(PhSiO_{1.5})_{10}(CuO)_6(HO_{0.5})_2(C_{24}H_{16}N_2)_2]$: Cu, 15.55; N, 2.28; Si, 11.45. Found (for vacuum-dried sample): Cu, 15.48; N, 2.18; Si, 11.34. Yield: 0.15 g (22%).

IR spectra were recorded on a Shimadzu IR Prestige21 FTIR spectrometer in KBr pellets. UV−vis absorption spectra were recorded on a Varian Cary 50 spectrophotometer in a cell with 10 mm optical path length.

X-ray Crystal Structure Determination. X-ray diffraction data for **1**, **4**, **6**−**9**, **11**, **12**, **14**, **16**, and **17** were collected on the "Belok" beamline 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 φ scan mode and corrected for absorption using the Scala program.[33a] The data were indexed, integrated, and scaled using the utility iMOSFLM in the CCP4 program.[33b] X-ray diffraction data for **2**, **3**, **5**, **10**, **13**, and **15** were collected on a three-circle Bruker APEX-II CCD diffractometer (graphite monochromator, φ and ω scan mode) and corrected for absorption using the SADABS program.[33c] The data were indexed and integrated using the SAINT program.[33d] For details, see Table S1 in the Supporting Information. The structures were determined by direct methods and refined by full-matrix least-squares techniques on F^2 with anisotropic displacement parameters for non-hydrogen atoms. In the case of **7**, **8**, **10**, **11**, **16**, and **17**, all attempts to model and refine positions of the solvate molecules were unsuccessful. Therefore, their contribution to the total scattering pattern was removed by use of the utility SQUEEZE in PLATON06[33e] or the Solvent mask procedure in the Olex2 program. The hydrogen atoms of the OH groups as well as the water and acetonitrile solvate molecules were localized in the difference Fourier map and included in the refinement within the riding model with fixed isotropic displacement parameters. The other hydrogen atoms were placed in calculated positions and refined within the riding model with fixed isotropic displacement parameters ($U_{iso}(H) = 1.5U_{eq}(C)$ for the CH_3 groups and $1.2U_{eq}(C)$ for the other groups). All calculations were carried out using the SHELXTL[33f] and Olex2[33g] programs. Crystallographic data for **1**−**17** have been deposited with the Cambridge Crystallographic Data Center as files CCDC 1565028−1565032, 1565113−1565124.



8 **9**

Figure 1. General scheme of synthesis of hexacoppersilsesquioxanes **1**−**9** containing 2,2′-bipyridine ligands. Color code: Si, yellow; O, red; C, black; H, gray; Cu, green; N, blue.

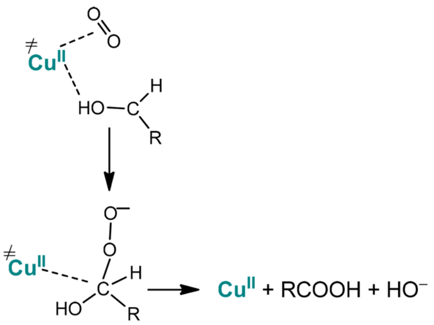


Figure 2. Presumable scheme of oxidation of a primary alcohol directly to the corresponding carboxylic acid.

Oxidation of Alcohols to Amides. 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 DPX 400 MHz spectrometer. Chemical shifts are reported in ppm and referenced to the solvent peak ($CDCl_3$ at 7.26 ppm). Data are reported as follows: s = singlet, d = doublet, t = triplet, q = quadruplet, qt = quintuplet, sept = septuplet, m = multiplet; coupling constant in Hz; integration. ^{13}C NMR spectra were recorded on a Bruker Avance AM 100 MHz spectrometer. Chemical shifts are reported in ppm and referenced to the solvent peak ($CDCl_3$ at 77.16 ppm).

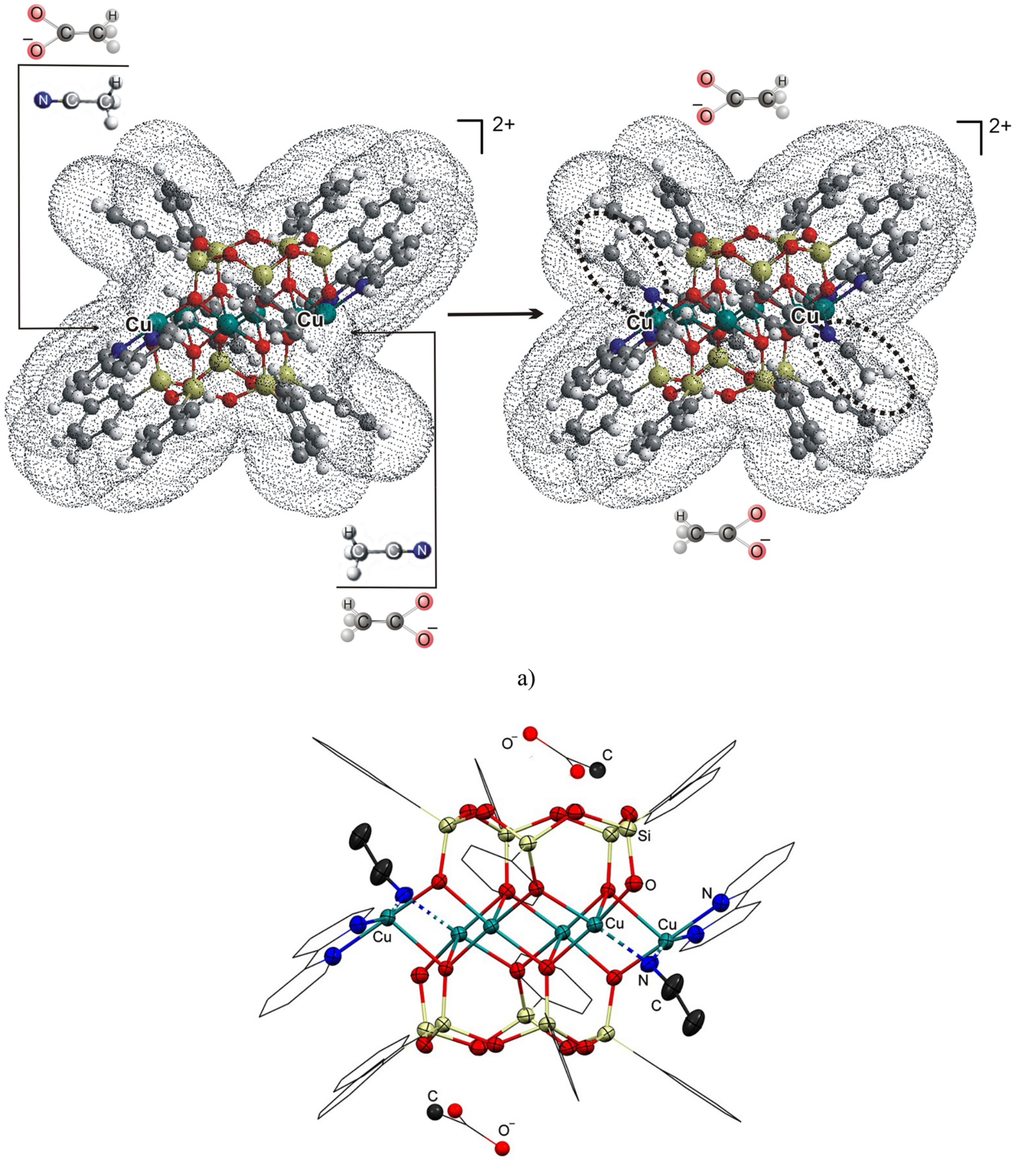
General Procedure for the Formation of Amides. In a sealed tube were added successively amine hydrochloride (0.5 mmol), $CaCO_3$ (50.1 mg, 0.5 mmol), CH_3CN (1 mL), **1** (20 μL of a solution of 1.8 mg of **1** in 2 mL of CH_2Cl_2) or **10** (40 μL of a solution of 1.7 mg of **10** in 4 mL of $CHCl_3$), benzylic alcohol (105 μL, 1.0 mmol), and TBHP (5.5 M in nonane, 225 μL, 1.25 mmol). The mixture was stirred at 80 °C for 2 h, and TBHP (5.5 M in nonane, 225 μL, 1.25 mmol) was again added to the mixture. After 16−22 h at 80 °C, the mixture was cooled to room temperature and 1 N HCl and EtOAc were added. The mixture was extracted twice with EtOAc, and the combined organic phases were washed with a saturated solution of $NaHCO_3$ and brine and concentrated under reduced pressure. To remove the excess of benzylic alcohol, 80 mL of H_2O was added and evaporated under reduced pressure. The crude product was then purified using silica gel chromatography with gradients of cyclohexane/EtOAc to yield the pure compounds.

Oxidation of Alcohols to Ketones. The substrate was added to the reaction solution, and the process was started when the oxidant was introduced in one portion. The reactions of alcohols were carried out in air in thermostated Pyrex cylindrical vessels with vigorous stirring and using MeCN as solvent. Concentrations of products obtained in the oxidation of 1-phenylethanol after certain time intervals were measured using ^{1}H NMR methods (solutions in acetone-d_6; Bruker AMX-400 instrument, 400 MHz). In the oxidation of cyclohexanol, concentrations of the substrate and products were measured by GC.

Oxidation of Alkanes. Catalysts **1**, **10**, and **15** were introduced into the reaction mixture in the form of solid powder. The alkane was then added, and the reaction was started when hydrogen peroxide was introduced in one portion. (*Caution*! The combination of air or molecular oxygen and H_2O_2 with organic compounds at elevated temperatures may be explosive!). The reactions after addition of nitromethane as a standard compound were analyzed by GC. As we had done previously, the samples obtained in the alkane oxidation were typically analyzed twice (before and after their treatment with PPh_3) by GC (Model 3700 chromatograph; fused silica capillary column FFAP/OV-101 20/80 w/w, 30 m × 0.2 μm × 0.3 μm; argon as a carrier gas). 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[34] allows us to estimate the real concentration of alkyl hydroperoxide, ketone (aldehyde) and alcohol present in the reaction solution. Attribution of peaks was made by comparison with chromatograms of authentic samples and by GC-MS. In our kinetic studies described below, we measured concentrations of cyclohexanone and cyclohexanol only after reduction of the reaction mixture with PPh_3 because in this case we measured the precise concentration of a sum of the oxygenates. Blank experiments with cyclohexane showed that in the absence of a catalyst products were formed in negligible concentrations.

■ RESULTS AND DISCUSSION

Synthesis and Structures of the Complexes. A two-stage scheme of synthesis of complexes of Cu(II) phenylsilsesquioxanes with bidentate N ligands was applied. In the first step of the reaction an interaction of the phenyltrialkoxysilane $PhSi(OMe)_3$ with sodium hydroxide (NaOH) in alcohol solution occurs. According to previous results,[6a,f] this reaction leads to the formation of highly reactive sodium siloxanolate species. No doubt, an investigation of such alkali-metal-based species is an interesting scientific topic by itself.[35] Nevertheless, in the context of cage



a)

b)

Figure 3. "Acetonitrile to copper" coordination in complex **9**: (a) van der Waals radii given to show the steric limitations; (b) molecular structure of complex **9**. Color code: Si, yellow; O, red; C, dark gray; H, light gray; Cu, green; N, blue.

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metallasilsesquioxane assembly, an elucidation of the sodium siloxanolate structure in this work seemed for us to be not very essential. In several works by us[35a,m] and others[35i,k,l,n,p,r] it has been established that such siloxanolates tend to form tri- or tetrameric cyclic structures in the crystal phase. In turn, the corresponding trimeric silsesquioxane cycles were never observed in the composition of arised CLMSs, while tetrameric cycles remain an extremely rare type of CLMS ligand.[6g] Thus, we focus on the second stage of the synthetic scheme—the in situ interaction of presumably formed sodium siloxanolate $[(PhSiO_{1.5})(NaO_{0.5})]_n$ with $CuCl_2$ in the presence of 2,2′-bipyridine in different solvent media. It was found that, despite changes in the reaction regime, the synthesis gives rise to a family of only hexacopper complexes **1**−**9** (Figure 1). These products are characterized by the presence of analogous central frameworks, with two cisoid silsesquioxane rings $[(PhSiO_{1.5})_5]$ forming a skewed sandwich cage.

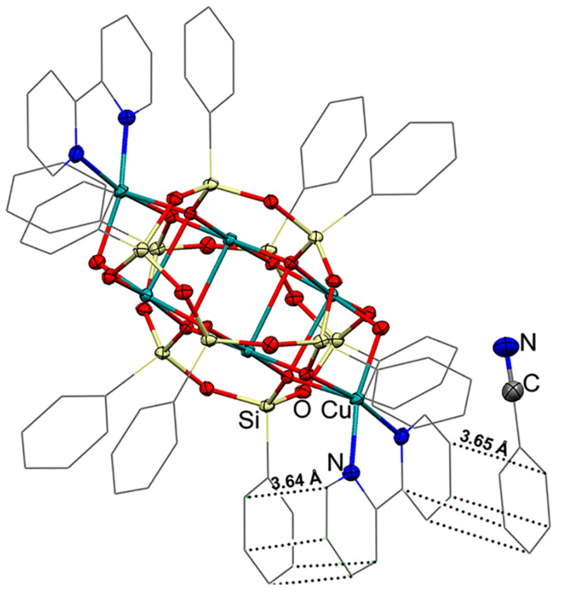


Figure 4. Triple π−π aromatic stacking (phenyl group−bipy−benzonitrile) interactions in complex **5**. Color code: Si, yellow; O, red; C, gray; Cu, green; N, blue.

Symptomatically, each of the complexes **1**−**9** contains six Cu^{2+} ions, giving 12 positive charges. Two pentameric silsesquioxane ligands donate 10 negative charges. Two extra negative charge carriers are hydroxide, methoxide, and acetate anions (for **1**−**7**, **8**, and **9**, respectively). The formation of some of these anions deserves to be discussed. The appearance of methoxy groups in **8** could be easily explained by the methanol-containing media of synthesis. The formation of acetate groups in **9** is not so evident. Similarly to copper methylsilsesquioxanes from ref 30, we could suggest the possible mechanism of homogeneous oxidation of ethanol (in the presence of copper ions), giving rise to the acetate groups (Figure 2). This transformation could be compared to the process mentioned earlier by Rudakov and co-workers[36a] as well as Sakharov and Skibida:[36b] namely, the oxidations of primary alcohols directly to the corresponding carboxylic acids in aqueous alkaline solutions catalyzed by copper phenanthroline complexes.

Another attractive feature of complex **9** in comparison to compounds **1**−**8** is "a flipping" of charged (HO^-, CH_3COO^-, CH_3O^-) and neutral (DMSO, MeCN, THF, PhCN, H_2O) ligands. Namely, in the case of compounds **1**−**8** the "charge balancing" groups (HO^- or CH_3O^-) directly coordinate Cu(II) ions (forming tight ion pairs). In case of compound **3** the positions next to Cu(II) are occupied by neutral acetonitrile molecules (Figure 3a). Anionic CH_3COO^- fragments are located in the outer sphere of the complex, forming solvent-separated ion pairs (Figure 3b). We may suggest as an explanation of this fact the coordinative strength of acetonitrile (ligation factor) acting along with the bulkiness of phenyl and acetate groups (steric factor). For the methyl-based hexacopper complexes from ref 30 such "flipping" was not detected.

In turn, we would like to mention several features of products **5**, **7**, and **8** in the context of their solvate surroundings. The presence of benzonitrile ligands in the composition of **5** allows us

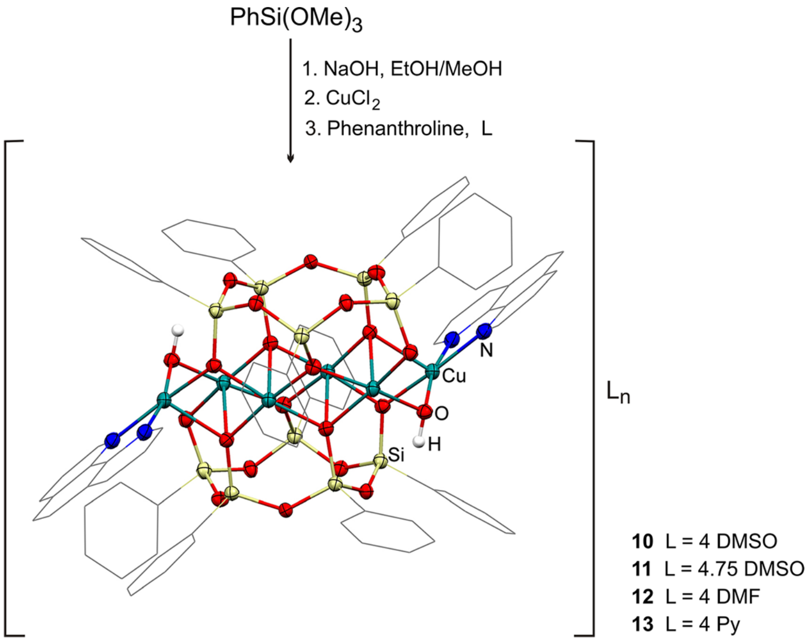


Figure 5. General scheme of synthesis of hexacoppersilsesquioxanes **10**-**13** containing 1,10-phenanthroline ligands. Color code: Si, yellow; O, red; H, white; Cu, green; N, blue.

to observe a specific “triple $\pi-\pi$ aromatic connection” including a phenyl group (at the silicon atom)—bipy—benzonitrile (Figure 4). It is of note that another benzonitrile-containing compound (benzonitrile/water complex **4**) does not reveal such a stacking.

In turn, features of CLMSs **8** and **9** are as follows. It is known that CLMSs often form solvates with different organic solvents. Surprisingly, compound **8** contains no solvate molecules at all, while water molecules are the only solvating ligands in compound **7**. This is also a quite rare feature among known CLMSs; we could cite only the Cu_2Na_2 CLMS reported very recently.[37] Note that compound **7** contains (in addition to two 2,2′-bipyridines at copper ions) one extra uncoordinated 2,2′-bipyridine.

At the second stage of the synthetic work similar self-assembly reactions but in the presence of phenanthroline have been studied. These yielded (Figure 5) the four hexacopper complexes **10−13** with a molecular architecture similar to that of the aforementioned compounds **1−9**.

For all compounds **10−13** the charge compensation is achieved by the presence of HO^- groups exclusively (unlike the “anion diversity” mentioned for products **1−9**). In addition, products

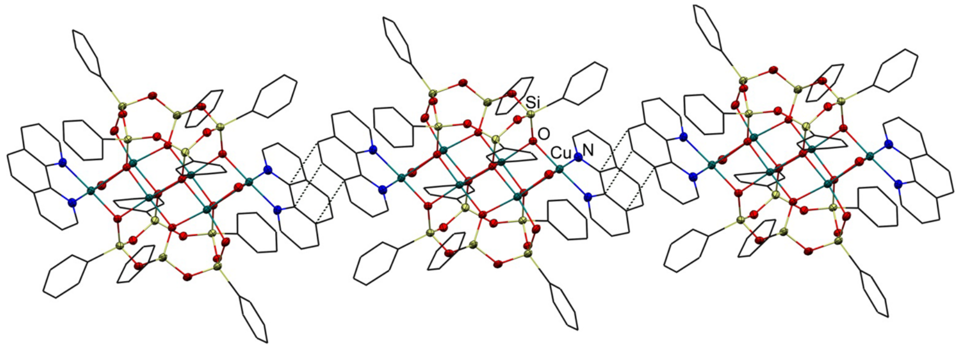
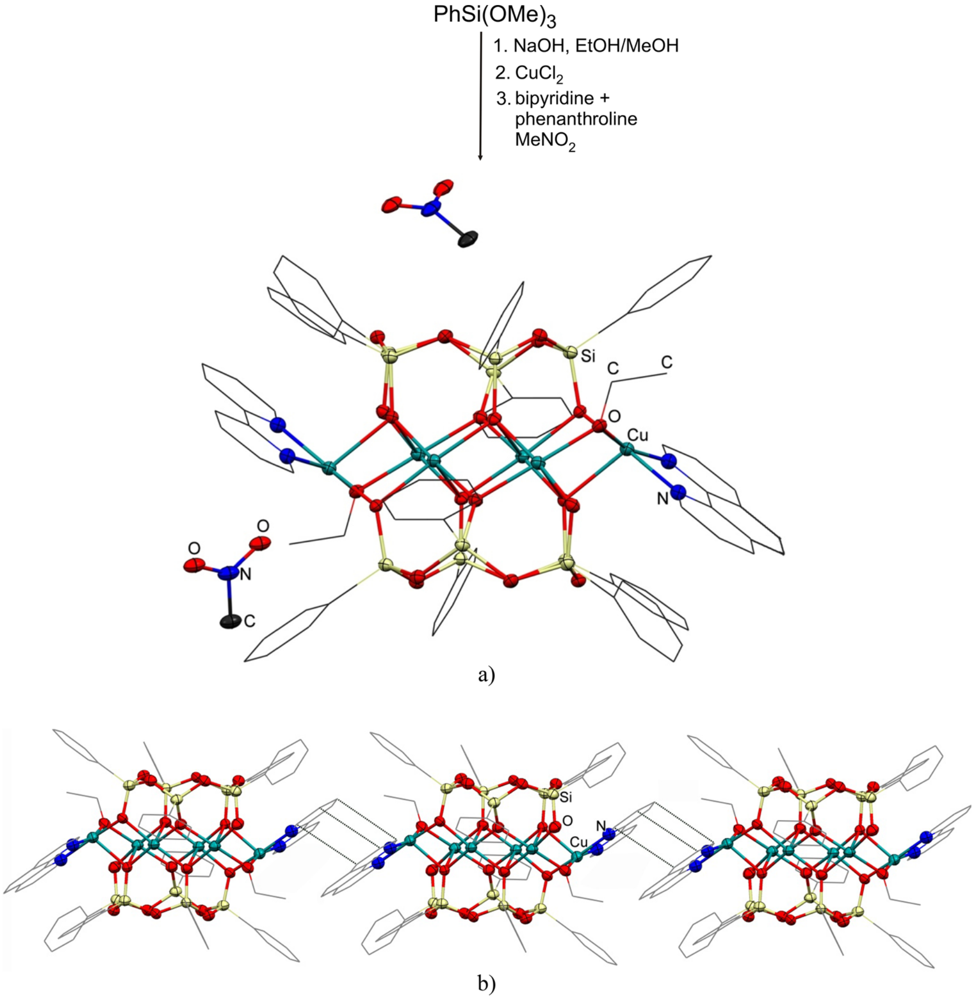


Figure 6. $\pi-\pi$ aromatic stacking (“phenanthroline to phenanthroline”) in complex **11**. Color code: Si, yellow; O, red; Cu, green; N, blue.



a)

b)

Figure 7. (a) General scheme of synthesis of hexacoppersilsesquioxane containing 1,10-phenanthroline and 2,2′-bipyridine ligands **14**. (b) $\pi-\pi$ aromatic stacking (“phenanthroline to bipyridine”) in complex **14**. Color code: Si, yellow; O, red; C, black; Cu, green; N, blue.

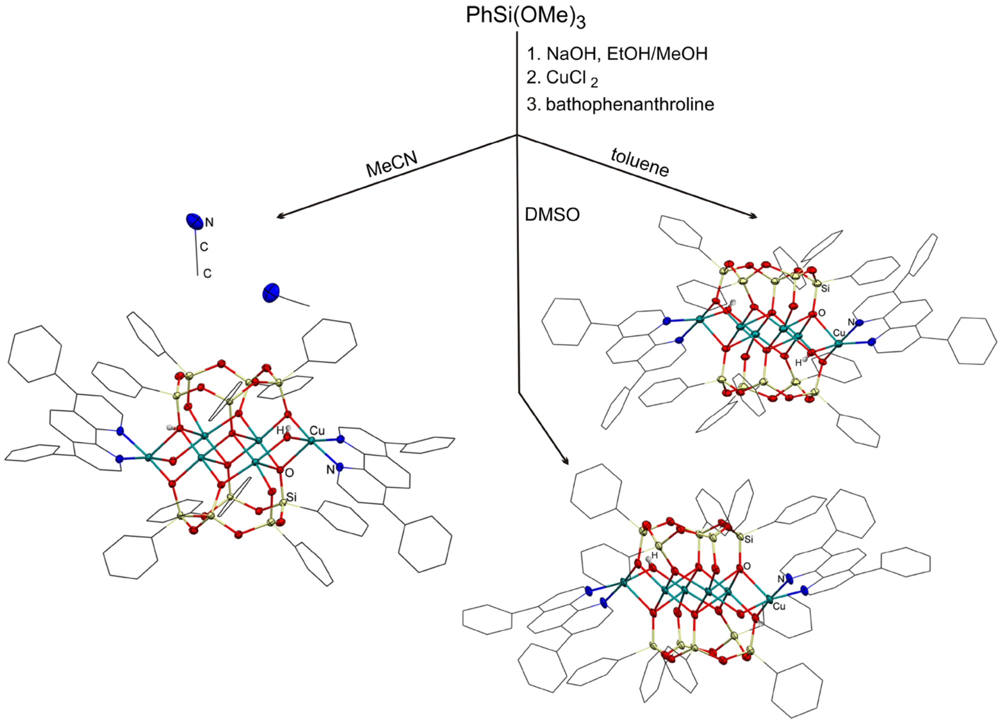


Figure 8. General scheme of synthesis of hexacoppersilsesquioxanes **15**−**17** containing bathophenanthroline ligands. Color code: Si, yellow; O, red; C, black; Cu, green; N, blue.

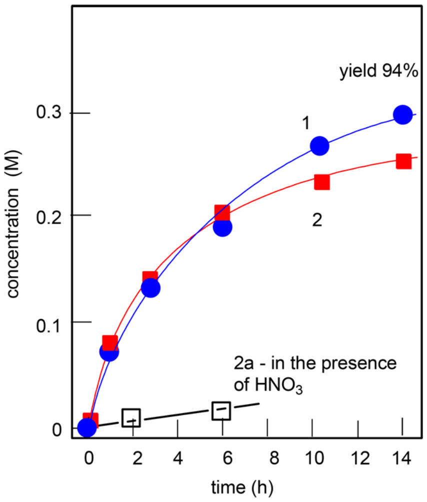


Figure 9. Accumulation of acetophenone with time in the oxidation of 1-phenylethanol (initial concentration was 0.33 M) with TBHP (70% aqueous; initial concentration 1.2 M) catalyzed by compounds **10** (5×10^{-4} M, curve 1) and **1** (5×10^{-4} M, curve 2; curve 2a, in the presence of 0.05 M of HNO_3). The solvent was acetonitrile (total volume of the reaction solution was 5 mL), and the temperature was 50 °C.

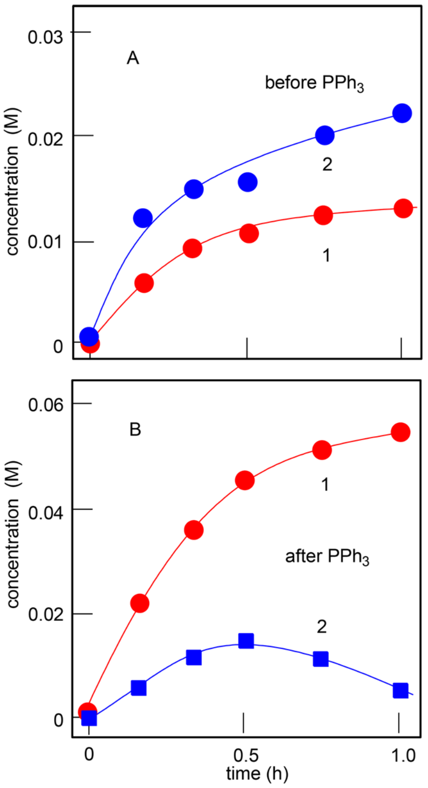


Figure 10. Oxidation of cyclohexane (0.46 M) with H_2O_2 (50%, 3 M) catalyzed by complex **10** (5×10^{-4} M) in the presence of HNO_3 (0.05 M) at 60 °C. Concentrations of cyclohexanol (curves 1) and cyclohexanone (curves 2) were measured both before and after reduction with PPh_3.

10−**13** could be easily distinguished from compounds **1**−**9** by their tendency toward π−π stacking interactions of aromatic systems of the phenanthroline ligands. While 2,2′-bipyridine-based compounds **1**−**9** show no affinity for the "ligand to ligand" packing, products **10** (solvated by DMSO) and **11** (containing no solvates) pack in the crystal to form a ladderlike motif (Figure 6). In turn, compounds **12** and **13** (DMF and pyridine solvates, correspondingly) crystallize in an islandlike structure. This points to a possible important role of solvate molecules for the formation/cleavage of the packing. We will try to shed some light on this intriguing situation in our future reports. Corresponding investigations on CLMS structure formation assisted by ligands of other types (not just of bipy family) are currently in progress iby our team.

It is interesting that our efforts in similar self-assembly reactions with both 2,2′-bipyridine and phenanthroline simultaneously present in the reaction mixture resulted in the formation of complex **14** (Figure 7a). One could expect the formation of a product with alternating 2,2′-bipyridine- and phenanthroline-containing CLMSs in the crystal. In reality, **14** includes both types of ligands statistically disordered over the same structural position. Both ligands coordinate the copper ion in the same fashion as was described for compounds **1**−**13**. It is worth noting that we succeeded in the isolation of single crystals of **14** only from a nitromethane solution. To the best of our knowledge, product **14** is the first example of a CLMS complex with nitromethane. Along with products **10** and **11**, compound **14** demonstrates the ability to pack into an infinite ladder structure (Figure 7b). It is important to emphasize the presence of two "charge compensating" CH_3COO^- moieties in the composition of this complex. Unlike the case for compound **9**, these groups in **14** form tight ion pairs with the copper ions. We suggest that this difference could be explained by the similarity in molecular geometries of nitromethane and acetate anion (∠ONO 125.9°, ∠OCO = 129.2°). Thus, the ionic interactions could play the principal role and, indeed, acetate anions coordinate copper centers.

The self-assembly reaction approach was efficiently applied yet another time by adding bathophenanthroline to the reaction mixture. The three complexes **15**−**17** with the same type of molecular topology as described for compounds **1**−**14** were obtained (with OH^- groups as charge balancers, Figure 8). To the best of our knowledge, complexes **15**−**17** are the first CLMSs containing bathophenanthroline ligands. Compounds **15**−**17** show no tendency to form supramolecular aggregates through packing.

As a short conclusion to the synthetic part of this work, it could be also stated that formation of one and the same type of central cage core (of $Si_{10}Cu_6$ composition) for 17 products no doubt witnesses to the high stability of such a structural unit under conditions of the CLMS synthesis assisted by bidentate chelating ligands of the 2,2′-bipy family. An opportunity of isolation of another core, $Me_8Si_8Cu_3$, in the case of using a methyl-substituted silane for the synthesis of the bipy derivative of Cu(II)-CLMS (ref 30) indicates the complicated character of such a type of self-assembly reaction. To some extent, such a difference could be due to steric and solubility differences for phenyl- and methyl-based silsesquioxane matrixes. Further investigations of this intriguing synthetic scheme deserve significant attention and are being studied now by our team.

Catalyzed Oxidation of Alcohols to Ketones and Benzene to Phenol. Alcohols are efficiently oxidized to the corresponding ketones with TBHP in MeCN when complex **1** or **10** is used as a catalyst (Figure 9). The oxidation of 1-phenylethanol with TBHP at 50 °C catalyzed by **10** gave acetophenone in 94% yield (TON = 600) after 14 h. Figure S1 in the Supporting Information shows that aliphatic cyclohexanol is oxidized to cyclohexanone. Complex **10** exhibited moderate activity in benzene oxidation with H_2O_2. Thus, the reaction of benzene (0.3 M) with H_2O_2 (50%, 3 M) in the presence of **10** (5×10^{-4} M) and HNO_3 (0.05 M) at 60 °C afforded phenol after 2 h in 15% yield. The efficiency of complex **1** turned out to be the same: the reaction at 60 °C gave after 2 h 0.41 M (14%) of phenol and 0.008 M of *p*-quinone.

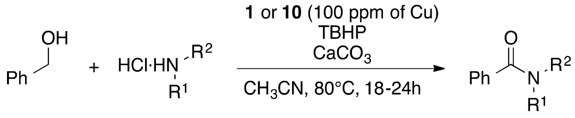
Catalyzed Oxidation of Alkanes with H_2O_2 to the Corresponding Alkyl Hydroperoxides. It is noteworthy that alkanes can be oxidized[38−40] in acetonitrile solution to the corresponding alkyl hydroperoxides by hydrogen peroxide in air in the presence of catalytic amounts of complex **1**, **10**, **15** and nitric acid. The alkyl hydroperoxide is relatively stable in solution and can be easily reduced by PPh_3 to the corresponding alcohol. The chromatogram obtained after reduction with PPh_3 is distinguished from the chromatogram obtained for an unreduced sample (compare graphs A and B in Figure 10), which indicates that cyclohexyl hydroperoxide is formed in the process.[34] The reaction proceeds not only at 60 °C (Figure 10) but also at 20 °C (Figure S2 in the Supporting Information). Regioselectivity parameters in the oxidation of *n*-heptane catalyzed by complex **1** are collected in Table 1. The oxidation of *cis*-1,2-dimethylcyclohexane with H_2O_2 occurs without retention of configuration (the trans/cis ratio was

Table 1. Regioselectivity Parameters in the *n*-Heptane (0.46 M) Oxidation with H_2O_2 (0.5 M) Catalyzed by Complex 10 at 60 °C[a]

entry	time, min	C(1):C(2):C(3):C(4)
1	60	1.0:5.2:5.2:4.7
2	180	1.0:5.6:5.2:6.3
3	360	1.0:6.0:5.9:7.0

[a] The selectivity parameter in the *n*-heptane oxidation C(1):C(2):C(3):C(4) denotes reactivities of the H atoms at carbons 1−4 (relative to the reactivity of hydrogens at carbon 1) of the *n*-heptane chain, which are normalized by taking into account the number of hydrogen atoms at each carbon.

Table 2. Oxidative Amidation at Low Catalyst Loading[a]



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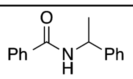
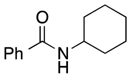
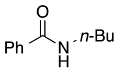
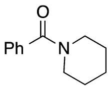
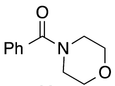
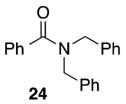
Entry	Amide	Cat.	Yield (%)	TON/TOF (h^{-1})[b,c]
1	 **19**	**1**	75	7500 / 313
2		**10**	84	8400 / 467
3	 **20**	**1**	78	7800 / 325
4		**10**	70	7000 / 389
5	 **21**	**1**	67	6700 / 279
6		**10**	68	6800 / 378
7	 **22**	**1**	60	6000 / 250
8		**10**	59	5900 / 328
9	 **23**	**1**	59	5900 / 246
10		**10**	61	6100 / 339
11	 **24**	**1**	86	8600 / 358
12		**10**	86	8600 / 478

[a] Reaction conditions: amine·HCl (0.5 mmol), benzyl alcohol (1.0 mmol), $CaCO_3$ (99.995% pure; 0.5 mmol), TBHP (5.5 M in nonane, 2.5 mmol), **1** or **10** (100 ppm of Cu), CH_3CN (1 mL), 80 °C, 24 h. Isolated yields are given. [b] TON = (mmol of product)/(mmol of Cu). [c] TOF = TON/(reaction time); given in h^{-1}.

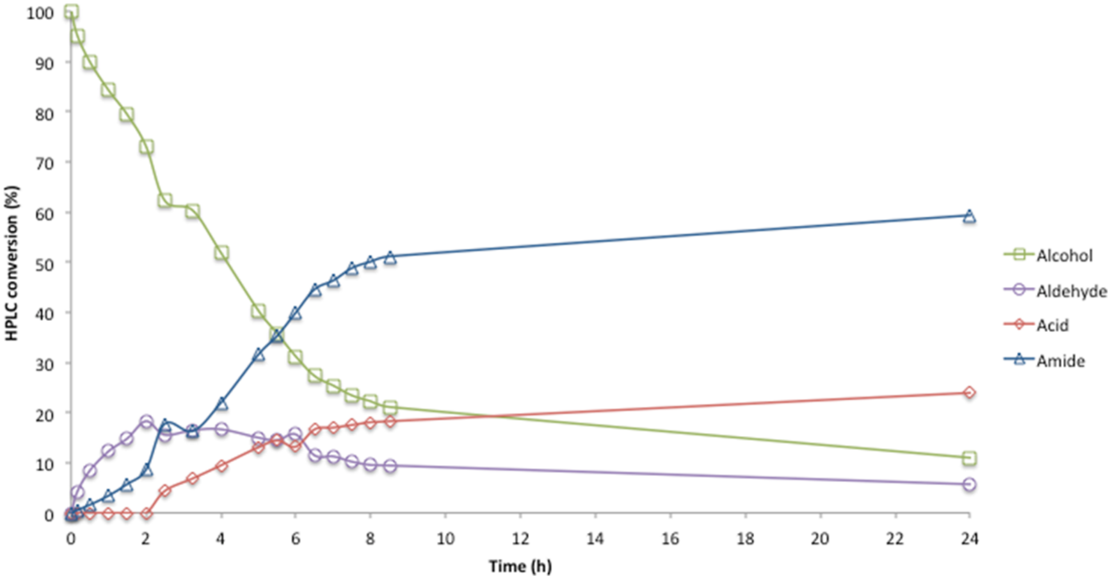
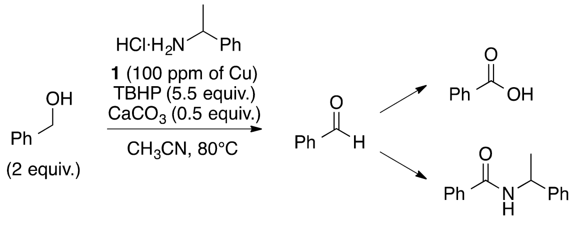


Figure 11. Conversion of benzylic alcohol in the oxidative amidation reaction.

0.7 for **1** and **10** and 0.8 for **15**, where trans/cis is the ratio of isomers of *tert*-alcohols with mutual trans and cis orientation of the methyl groups). The experiments on the methylcyclohexane oxidations are described in Figures S3 and S4 and Tables S1−S4 in the Supporting Information. All of these peculiarities indicate that the oxidation with H_2O_2 occurs with the participation of free hydroxyl radicals.[25]

Catalyzed Oxidation of Alcohols to Amides. Complexes **1** and **10** were also evaluated in the oxidative amidation of alcohols (Table 2). This reaction, initially developed using copper,[41] iron,[42] and zinc salts,[43] proved to be highly efficient when copper silsesquioxanes were used, with catalyst loadings down to 100 ppm of copper.[18a,19] This represents a good alternative to methodologies using expensive ruthenium[44] and rhodium catalysts.[45] Thus, benzyl alcohol was reacted with several amines, protected as their ammonium salts, in the presence of catalytic quantities of **1** or **10** and TBHP as oxidant. Calcium carbonate, with a high purity of 99.995% to avoid any metallic contamination, was also added to slowly deprotonate the ammonium. As demonstrated in Figure 11, oxidation of benzylic alcohol in the presence of α-methylbenzylamine and catalyst **1** produced, in addition to the expected benzamide **19**, benzaldehyde and benzoic acid as side products:



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Interestingly, the proportion of benzaldehyde reached a maximum after 2 h and then slowly decreased as the quantity of benzamide and benzoic acid increased. After 24 h of reaction, benzylic alcohol was converted at 60% into benzamide, 24% into acid, and 6% into benzaldehyde. This kinetic plot also shows that it is necessary to use an excess of alcohol in this reaction, since the formation of benzoic acid is difficult to avoid under the reaction conditions.

Even though compounds **1** and **10** have a unique structure, their catalytic activities in the oxidative amidation were found to be similar, giving secondary and tertiary amides **19**−**24** in 59−86% yields (Table 2). As observed previously with other cagelike compounds, it was found possible to work with as low as 100 ppm of copper in this reaction without affecting the yields. Moreover, turnover number (TON) and frequency (TOF) values up to 8600 and 478 h^{-1} could be obtained, respectively, which is significantly better than the 44 and 11 h^{-1} values obtained in the initial report with CuO as catalyst.[26]

Discussion on Precatalyst Transformations. In order to study the possible structural transformation of the catalyst under catalytic act conditions, we were interested in additional studies. To simulate the catalytic act of C−H compound oxidation, we performed the following experiments. Successive measurements of UV−vis spectra (for example of compound **1**) were made for (i) **1**′ acetonitrile solution, (ii) this solution with nitric acid additive, and finally (iii) the solution with hydrogen peroxide additive. These activities provoked no significant changes in spectra (see the Supporting Information), which is not surprising, bearing in mind the results of UV−vis experiments presented recently by some of us for Fe(III) silsesquioxane.[18b] Thus, we may conclude that compound **1** could undergo some structural modification during the catalytic reaction but total decomposition of cage structure did not occur.

■ CONCLUSION

An extended series of 17 new complexes were found to be easily available through the self-assembly reaction of in situ generated sodium phenylsiloxanolate and copper(II) chloride in the presence of four types of nitrogen-based ligands: 2,2′-bipyridine (compounds **1**−**9**), 1,10-phenanthroline (compounds **10**−**13**), 1,10-phenanthroline/2,2′-bipyridine (compound **14**), and bathophenanthroline (compounds **15**−**17**). As was established by single-crystal X-ray diffraction, compounds **1**−**17** all belong to the same type of molecular topology despite the difference in the N-ligand chemical nature. That no doubt points at the high stability of such “major” type ($Si_{10}Cu_6$) of cluster under conditions of copper(II) phenylsilsesquioxane synthesis, assisted by ligands of the bipy family. This fascinating molecular cage can be described as a metal oxide $(CuO)_6$ layer sandwiched by two pentagonal phenylsiloxanolate $[PhSiO_{1.5}]_5$ ligands. Two opposite copper ions are additionally coordinated by the nitrogen atoms of the corresponding ligand and oxygen atom of hydroxy (compounds **1**−**7**, **10**−**13**, **15**−**17**), methoxy (compound **8**), or acetoxy groups (compounds **9** and **14**). The formation of acetoxy fragments most likely may be explained by homogeneous oxidation of ethanol (reaction medium) in the presence of copper centers.

Complexes **1**, **10**, and **15** efficiently catalyze oxidation of alcohols to ketones with TBHP and of alkanes to alkyl hydroperoxides with H_2O_2 in acetonitrile. The oxidation of alcohols apparently involves the generation of hydroxyl radicals. Complexes **1** and **10** catalyzed the amidation of benzyl alcohols with low catalyst loading and high turnover.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.7b02320.

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

Accession Codes

CCDC 1565028−1565032 and 1565113−1565124 contain 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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